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Introduction

Since the very beginning of European Young Engineers Conference, since the first meeting of Students Scientific Club in 2011, we were wondering, how we can develop our work and how to provide a new, attractive and easy way to exchange knowledge and experience between young people. People who, like us, are passionate about creation, search for answers, create innovative solutions for current issues. In short – people of Science.

It may sound pompous, after all, there are many other conferences for young scientists, but we believe that thanks to EVEC's scope, friendly atmosphere and high level of presented research, it is the best way to start or continue your scientific career.

It is already the eighth edition of EVEC and we still have not materialized half of our ideas. Every year we try to give you something new: interesting guest speakers, additional workshops or exciting contests. It is also the sixth time we give you our EVEC Monograph. In this book, you can find the most promising, important and reviewed papers of European Young Scientists. We hope, that this book you are holding right now, will be the first step in a great career of each and every participant of our conference.

This year we are pleased to continue section of our monograph: "From expert's perspective". We encourage to read articles written by experienced scientists: Dr. Magda Barecka, Prof. Lorenz Ratke, and Prof. Jörg Vienken, as a great opportunity to get involved in a new field of interest. We hope you will find the papers within this book as interesting and important, as we do.

Here we would like to thank our Special Guests, the Scientific Commission, and all members of the Scientific Committee for your hard work in ensuring the highest level of contributed papers. Your invaluable help and advice is greatly appreciated by all of us, young researchers.

Organising Committee

Editorial Team of EYEC Monograph

1 Special Guests

1.1 Prof. Jörg Vienken – Honorary Guest

Institute for Bioengineering, Technical University of Applied Sciences Mittelhessen, Giessen, Germany

Jörg Vienken graduated in Chemical Engineering at the Technical University of Darmstadt and received a Doctoral Degree in Biophysics and Bioengineering from the Technical University of Aachen, both in Germany. He was then appointed the position of an Associate Professor at the Institute for Biotechnology of the University of Würzburg, Germany.

In 1985 he switched to the medical device industry and worked for 11 years at AKZO NOBEL Membrana in Wuppertal as a Director for Clinical Research and Science Services, followed by a position as a Vice President BioSciences in Fresenius Medical Care in Bad Homburg, Germany which he held until his retirement in 2013. Then he served



as one of the Nephro-Solutions AG Board Members in Hamburg. Since 2016 he works as a Freelance Advisor for the Medical Device Industry.

He has been awarded the Emil-Bücherl Award for the life-time achievement in the realm of Artificial Organs from the European Society for Artificial Organs (ESAO) and is a distinguished fellow of ERA-EDTA, the European Dialysis and Transplantation Association.

Jörg Vienken is a Past President of the International Federation of Artificial Organs (IFAO, representing the umbrella organisation of the continental societies from Europe (ESAO), the USA (ASAIO) and Japan (JSAO)). He was a long lasting Board member of the European Society for Artificial Organs (ESAO) and served as its secretary treasurer between 1998 and 2006. He is also a Past President of the Association of German Biotech Companies (VBU-DECHEMA).

Jörg Vienken still teaches Biomaterials and Artificial Organs at several German and European Universities. He has published more than 300 scientific publications and book chapters as well as 8 own books.

Abstract: Reliability, fraud and misunderstandings in Science. The four "Fs"

KEYWORDS: bad science, reproducibility, cost of misconduct, predatory journals.

Precision, reproducibility and honesty form the basis of public opinion about scientific investigations. The four "Fs", i.e. fraud, fiction, fake and falsifications depart from community norms, so scientists do not want to think about it. When "publish or perish" has become a familiar quotation and the provision of grants and budgets for research projects has been made in many cases dependent on the number and not the quality of published articles, predatory journals have emerged. Here scientific publications are made available to the public without editorial services, check for quality and – last but not least – the need for making payments. In this paper, bad or floppy science will be described and examples will be given for the four "Fs". In life sciences, non-reproducible results from published preclinical investigations further lead to high investment losses for industrial companies which may add to about 50 % of all cost. Finally, recommendations will be given in order to perform reliable experiments.

1.2 Magda H. Barecka, PhD

Lodz University of Technology/TU Dortmund University



Dr.-Ing. Magda H. Barecka is a chemical engineer with expertise in process intensification, process retrofitting and design. She was the first one to receive the PhD title from both TU Dortmund University and Lodz University of Technology as a joint Diploma.

She is an author of a systematic methodology supporting implementation of intensified technologies in the chemical industry. She is interested in the development and application of novel intensified operations that can overcome current limitations in chemical engineering.

Apart from research related to process simulations, modelling and photochemistry, she actively

contributed in several European grants in the field of energy efficiency, sustainability and environmental impact assessment (LCA).

Abstract: Process intensification: chances & barriers for process retrofitting

Keywords: process intensification, process retrofit, debottlenecking, ethylene oxide, ethylene glycol.

Retrofitting projects target overcoming key process bottlenecks, yet many of them such as heat and mass transfer or reaction equilibrium limitations cannot be tackled within classical chemical engineering approaches. While Process Intensification (PI) technologies have potential to drastically improve chemical production processes, their implementations on industrial scale are still rare. Realistic chances for overcoming current manufacturing limitations by means of PI as well as barriers for wide application of intensified technologies will be discussed in this talk. As one of the challenges for implementation of PI is diffculcy in integration of those into current manufacturing processes, a systhematic methodolgy for process retrofit including intensified options will be presented. The method was applied to two industrial case studies of bulk chemicals production, resulting in each case in possible savings in operational costs of over \$10 million annually.

1.3 Heinrich Eckhard Kolb, PhD

Institut für Mechanische Verfahrenstechnik und Mechanik, Karlsruhe Institute of Technology, 76131 Karlsruhe, Germany

Heinrich Eckhard Kolb became fascinated by the field of gas kinetics and filtration in his undergrad studies. This fascination continuously inspires him even after 8 years of academic and industrial experience.

He received his Diploma from the Karlsruhe Institute of Technology in 2014 with a student research project about the permeability of dust cakes and a thesis on the nucleation and coagulation of sulfuric acid aerosols.

Eckhard has recently graduated with a PhD degree at the Karlsruhe Institute of Technology in the group of Professor Gerhard Kasper. His research comprises many aspects of oil mist filters for the



filtration of compressed gases. Recent publications of him in this field deal with the re-entrainment of droplets from filters, the impact of operating conditions, influences and description of glass fiber media properties as well as the extension of the "Film-and-Channel-Model" towards the efficiency of oil mist filters.

Abstract: Transitional phenomena in oil mist filtration

KEYWORDS: filtration, oil mist, coalescence filter, efficiency, pressure drop.

Air-borne oil droplets (so-called "mist") can be found in a variety of technical applications such as the crankcase ventilation of engines, metal cutting, natural gas production and the operation of oil-flooded screw compressors. In order to remove submicron mist, multi-layered filters of highly efficient glass microfiber papers are typically used. Unlike in common air and liquid filters, which have to be replaced when fully loaded, the deposited liquid drains at the rear-side of a mist filter in direction of gravity. This results in an equilibrium between the oil mass flow entering and exiting the filter. Pressure drop and fractional efficiency are commonly assumed to be in steady state at this equilibrium.

The increase of pressure drop during the transitional loading prior to steady state, typically achieved within 10–20 h, can be attributed to the formation of liquid channels and films within the filter. This knowledge, as best described by the so-called "Film-and-Channel-Model" by Kampa et al., can be seen as a starting point for the present work. Dependencies of the channels' pressure drop, $\Delta p_{channel}$, and the film's Δp_{jump} are discussed on basis of experiments with wettable and non-wettable filters continuously operated at variable face velocities (v0 = 5-70 cm/s) and oil loading rates (R = 15-1100 mg/(m² s)).

Transitional effects of oil loading on the efficiency of mist filters can be described by means of a meso-scale model which takes into account the sectional efficiencies of the channels and the film. Experiments furthermore show that transitional "phenomena" are not limited to filter loading prior to steady state, but also to a slow increase of pressure drop several hundreds of hours beyond this point. Therefore, this work corrects the traditional definition of the "steady state" for continuous loading and provides estimations for experiments which are not feasible to conduct.

Acknowledgments

This work was in part supported by Atlas-Copco Airpower n.v.

1.4 Wiktor Lewandowski, PhD

Department of Chemistry, University of Warsaw, Warsaw, Poland

In 2008, he graduated from the Inter-faculty Studies in Mathematics and Natural Sciences at the University of Warsaw with the title of MA in chemistry and MA in biotechnology. In 2013, he obtained a PhD in international doctoral studies at the Faculty of Chemistry of the University of Warsaw under the supervision of prof. J. Mieczkowski. He is currently an Adjunct Professor at the Faculty.

During his work he has been internships abroad several times, including in the group of prof. Swager (MIT, USA) or prof. Liz-Marzan'a (CICbioma-GUNE, Spain). He was the head of several research grants – Preludium (NCN), Sonata (NCN), Mobility Plus (MNiSW), Inter (FNP) and First Team (FNP). His doctoral dissertation was awarded the Minister of Science and Higher Education Prize and the Aleksander Zamojski of the Polish Chemical Society. He is also a two-time winner of the start scholarship (FNP) and has received a scholarship for outstanding young scientists (MNiSW). In 2009–2010 vicechairman of the SSPTChem, co-organizer of the SSPTC meetings.



He has published 18 papers (including top journals such as Nature communications, Angewandte Chemie, Chemistry of materials) in the areas of material chemistry/nanotechnology, with particular emphasis on utilizing organic chemistry tools in development of nanomaterials. Lately, he focuses on dynamic selfassembly of nanomaterials with the perspective applications in metamaterial, optoelectronic and chiral plasmonic technologies.

Abstract: Switchable metamaterials working in the visible

Keywords: plasmonics, dynamic nanomaterials, self-assembly, liquid crystals.

Metamaterials working in the visible have the potential to revolutionize future photonic technologies, providing means to efficiently manipulate light, and opening the access to fantastic devices used e.g. for cloaking. One of the intriguing ways to build metamaterials is through the use of self-assembly of plasmonic nanoparticles (NPs). However, achieving nanoparticle assemblies with the required complexity and active tenability is a grand challenge.

To combat these challenges, metal nanoparticles can be combined with liquidcrystals. We have previously shown that such structures can exhibit non-closed packed symmetries as well as thermo-/light-responsive behavior (Angew. Chem., 2009, 48, 5167). Here, I will show how the observed structural reconfigurability can translate to functional switchability of epsilon near zero metamaterials (Nat. Commun., 2015, 6, 6590). Also, I will discuss practical aspects of durability of such materials (Chem. Mater, 2018, 30, 8201).

Finally, the possibility of achieving reconfigurable, chiral plasmonic metamaterials by combining LC-coated NPS (spherical and nanorods) with a LC-template will be discussed (Figure 1.4.1), together with the outlook on their potential applications.



Figure 1.4.1: Scheme showing helical assemblies of nanoparticle (spheres) grafted onto an organic template.

Acknowledgments The research was partially conducted under Reinforce project carried out within the First Team programme of the Foundation for Polish Science co-financed by the European Union under the European Regional Development Fund.

1.5 Prof. Dr. Dr. h.c. Lorenz Ratke

Institute of Materials Research, German Aerospace Center, DLR, Cologne, Germany



Professor in Materials Physics at the Technical University of Aachen and retired head of the Aerogels Department of the Institute of Materials Research at the German Aerospace Center (DLR) in Cologne, Germany.

He received his diploma in Physics from the University of Muenster and a PhD in Metal Physics from the University of Aachen. Professor Ratke held positions at the Vereinigte Aluminium Werke Bonn, the Technical University in Clausthal, the Max-Planck-Institute for Metals Research in Stuttgart and visiting positions at the Technical University of Miskolc (Hungary) and the University of Iowa (USA).

He has received the Georg Sachs Award of the German Society of Materials, Acta Metallurgica et Materialia Outstanding Paper Award, Senior Scientist Award of the German Aerospace Center (DLR) and the Silver Medal of the University of Miskolc. Moreover: a honoris causa doctorate degree of the University of Miskolc, the Innovation Award of the City of Cologne, the Bavarian State Innovation Award and the DLR Idea Award.

He has published over 300 papers in the areas of corrosion, powder metallurgy, in-situ composites, polyphase solidification, coarsening and aerogels. His current research activities are devoted to organic and biopolymeric aerogels, their nanostructure formation and properties.

Abstract: Aerogels – synthesis, properties and applications of an almost nothing

Keywords: aerogels, sol-gel processing, nanostructures, mechanical properties, thermal conductivity.

Aerogels are a fascinating material: they consist mainly of air entrapped into an open porous solid network of nanoparticles. They are in a certain sense an almost nothing. Their properties are outstanding: their density is low, typically around 100 kg/m³, their thermal conductivity can be as low as 0.01 W/mK, their specific surface area is typically between a few hundred to a few thousand m^2/g . The microstructures of aerogels are characterized by well accessible branched mesopores in the range of 10 to 100 nm and a solid network of nano-particles or fibrils spanning the whole volume. Aerogels can be made from inorganics, especially oxides like silica, corundum, zirconia, and many others, but also polymers, like phenolic or resorcinol resins, polyimides and polyurethanes and a few of them can be converted into carbon aerogels. Recently aerogels made from biopolymers came into focus of research like cellulose, alginates, chitosans and many other polysaccharides. A brief overview about aerogels, their synthesis, properties and applications as well as a perspective for their future is given.

2 Scientific Commission

2.1 Zoltán Kovács, PhD - Head of the Scientific Commission

Dr Kovács currently holds the position of associate professor at the Department of Food Engineering, Szent István University, Hungary. He received his MSc degree on Food Engineering in 2003 from the Szent István University. In 2008, he obtained his PhD degree on Chemical Engineering from the Institute of Process Engineering at the Johannes Kepler Universität Linz, Austria. Prior to his current position, he had worked as a senior scientist for 5 years at the Institute of Bioprocess Engineering and Pharmaceutical Technology of the University of Applied Sciences Mittelhessen, Giessen, Germany.



In 2013, he obtained the Marie Curie Career

Integration Grant that allowed him – after 10 years of international experience in abroad – to return in his home country and to establish his own research group. During his career, he has received distinctions from the European Membrane Society, the Association of German Engineers, and recently awarded the Bolyai Research Fellowship by the Hungarian Academy of Sciences. He has participated to and is responsible for many out-of-campus projects with industrial partners on bioprocess design and membrane technology development.

2.2 Oleksandr Ivashchuk, PhD

Associate Dean for Master's Studies for Educational and Organizational Work at Institute of Chemistry and Chemical Technologies, Associate Professor of the Department of Chemical Engineering at Lviv Polytechnic National University (Lviv, Ukraine). Oleksandr Ivashchuk received his PhD degree in 2008 for the research of the catalytic liquid-phase cyclohexane oxidation – he has developed effective catalytic systems for the process (binary system, catalytic complex solutions and individual catalysts).

For ten years Dr. Ivashchuk has been working on the implementation of 6 research themes of the technologies of organic products (researching of catalytic oxidization of liquid hydrocarbons, sonochemistry intensification of catalytic oxidization of cyclohexane, development of homogeneous catalysts, intensification of diesel fuel with organic compounds etc.) at Lviv Polytechnic National University (Lviv, Ukraine). In 2012 he has received an academic status of Senior Research Fellow. Now Oleksandr Ivashchuk works with computer simulation in different fields of the chemical technology and engineering.



He is a co-author of more than 100 scientific and educational works, including 3 patents and 5 electronic textbooks. Dr. Ivashchuk was the Head of Young Scientists' Council of the Institute of Chemistry and Chemical Technologies at Lviv Polytechnic National University till 2017. Now he is the Head of Comission for International Affairs of Scientific Society of Students, Doctoral Candidates and Young Researchers at the University.

Oleksandr Ivashchuk is a Secretary of the International Scientific Conference "Chemical Technology and Engineering" and the International Youth Science Forum "Litteris Et Artibus". Now Dr. Ivashchuk works as a Associate Dean for Master's Studies for Educational and Organizational

Work at Institute of Chemistry and Chemical Technologies at Lviv Polytechnic National University.

2.3 Andrzej Krasiński, PhD



Dr Andrzej Krasiński holds Ph.D. in chemical engineering obtained in 2005 at Faculty of Chemical and Process Engineering of Warsaw University of Technology, and in 2018 the D.Sc. (habilitation) for a comprehensive research on emulsion separation using the coalescence filtration method.

From 2006 he has been employed as Assistant Professor at afore mentioned faculty, currently in Chair of Integrated Processes Engineering (2006–2009 in Process Equipment Department). From 2007 to 2009 during his postdoctoral stay in the UK he was employed by the University of Reading in a KTP Programme on the position of Product Development Engineer. From 2012 he takes the po-

sition of Associate Dean for Student Affairs.

Dr Andrzej Krasiński is a co-author of more than 40 publications in peer reviewed journals, over 30 conference presentations, and 2 patents. He is an expert of National Center for Research and Development, and past member of IChemE, where in 2009 he achieved the Chartered Engineer (CEng) status. His research track is related to the separation processes, with focus on the droplets coalescence and separation of gas-liquid and liquid-liquid dispersions, pervaporation and gas cleaning techniques. He has also been involved in industrially oriented projects related to pyrolysis of wastes, development of filtration products for automotive industry and ammonia plant. Based on past experience his area of expertise covers also aggregation of particles in turbulent flows, precipitation, CFD modeling of reactive and multiphase flows, and rheology of dense suspensions.

2.4 Marcin Małek, PhD

Marcin Małek studied Materials Sciences and Engineering on Military University of Technology (Poland). He defended his PhD thesis "The ecological method of ceramic shell moulds fabrication for precision casting process of aircraft turbine blades using nickel superalloys" in 2017 on Warsaw University of Technology at the Faculty of Materials Science and Engineering (Poland). Since 2017 he is employed as an Assistant Professor at the Faculty of Civil Engineering and Geodesy at the Military University of Technology.



His topic area focuses on concrete technology and ecology in building processes. He is trying to modify the concrete structure using waste materi-

als and increase their mechanical and physical properties. His scientific area includes waste material with natural and artificial origin e.g. fibers from tires, waste fibers PE, PP, PET, ABS, every type of glass (from car crashes, bulbs, cans, bottles), fly ashes, and natural additives: zeolite, kaolinite, SiC, Al₂O₃ and more. Marcin Małek is a co-author of more than 40 original manuscripts, 6 patents and 3 patent applications. In 2018 he received an Outstanding Young Researchers Scholarship from the Minister of Science and Higher Education for 3 years.

2.5 Artur Małolepszy, PhD

Artur Małolepszy has defended his PhD thesis "Production and characterization of multiwalled carbon nanotubes and metal oxide functional composites for formic acid fuel cells applications" in 2015 at Faculty of Materials Science and Engineering Warsaw University of Technology. Since 2016 he is employed as Assistant Professor at Faculty of Chemical and Process Engineering Warsaw University of Technology.



He is focused on the carbon nanomaterials synthesis, characterization and looking for a new applications for these nanomaterials in the field of biomaterials, alternative energy sources, electromagnetic screens and against infrared radiation. He is a principal investigator of "Fluorescent carbon nanodots production" LIDER IX project financed by National Centre for Research and Development. Artur Małolepszy is the co-author of more than 30 publications in peerreviewed international journals. In 2013 he received team award of the 1st degree for scientific-research achievements founded by Rector of Warsaw University of Technology.

2.6 Piotr Mazurek, PhD



Piotr Mazurek studied chemical engineering at the West Pomeranian University of Technology (Szczecin, Poland) graduating with a Bachelor degree in 2011 (one semester spent at the German Aerospace Center, Braunschweig, Germany) and MSc degree in 2012. He received a PhD degree in polymer science from the Technical University of Denmark (DTU) in 2016 for the study on the development of functional materials used as dielectric elastomer transducers (DET). After the graduation he became an industrial postdoctoral researcher at Grundfos (Denmark) working on smart anti-corrosion materials. He was a visiting postdoc-

toral researcher at the McMaster University (Hamilton, Canada) where he investigated new strategies for preparation of silicone membranes with physically immobilized enzymes. Currently he is a researcher at the Danish Polymer Centre, DTU where he works on smart elastomeric silicone membranes and foams used in DET, biomedical drug delivery and magnetochromatic systems.

3 Scientific Committee

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4 Organizers of the 8th EYEC

The eighth edition of the European Young Engineers Conference has been organized by the following members of the Scientific Club of Chemical and Process Engineering and the Foundation of Young Science:

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Agnieszka Kaczmarek-Kacprzak, MSc – Member of the Board of the Foundation of Young Science

5 From expert's perspective

5.1 Process intensification: chances & barriers for process retrofitting

Magda H. Barecka^{*,1}

1 Lodz University of Technology/TU Dortmund University

KEYWORDS: process intensification, process retrofit, debottlenecking, ethylene oxide, ethylene glycol.

Process retrofitting is one of the most common and complex activities in the chemical industry. Process intensification (PI) technologies, attracting increasing attention due to their potential to drastically improve chemical processes, could tackle the most difficult process bottlenecks. Yet, the number of successful PI implementations in industry is limited. One of the reasons for this is difficulty in both selection of the most promising PI option for a given process and evaluation of the improvement through implementation of this novel technology. A detailed investigation of all existing PI options by experiments or rigorous modelling is not feasible since time and resources are constrained. Consequently, it is also complex to systematically benchmark performance of PI versus classical processes and decide when the implementation of PI is justified. As a result, approaches for process retrofit integrating PI technologies within the portfolio of retrofit options are missing.

To fill the gap in the existing knowledge, this talk presents a methodology for process retrofitting which enables step-wise screening and selection of the most promising PI options from a broad database of intensified technologies. Reduction of options to consider is achieved by application of a series of dedicated short-cut methods, which enable determination of the main chemical/physical phenomena limiting the process performance and resulting in the observed bottleneck. Further, process improvement by means of enhancement of these phenomena is quantified, what gives clear metrics for comparison of different strategies. Possibilities of intensification of determined phenomena are studied firstly by refitting of the existing equipment. If the improvement is not satisfactory, PI options are systematically generated. Final choice of the most promising option is based on shortcut modelling results. The selected technology is subsequently integrated within the process flowsheet, which is further rigorously simulated. As a result, this methodology enables to determine the most promising retrofit design and proposes the use of tailored PI technologies when their performance

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enables significant improvement and therefore it is justified to introduce PI on industrial level.

The approach is illustrated with two case studies: ethylene oxide and ethylene glycol production. For both case studies, proposed retrofit enabled savings of over 10 M\$ annually for medium-size processingplants and significant reduction of environmental impact (see Fig. 5.1.1). However, most promising process improvement was achieved by combining both classical chemical engineering and intensified methods. Benefit from application of intensified technologies as well as current barriers will be broadly discussed based on those examples.



Figure 5.1.1: Summary of results for retrofitting of ethylene glycol production process.

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5.2 Aerogels – synthesis, properties and applications of an almost nothing

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1 Institute of Materials Research, German Aerospace Center, DLR, Cologne, Germany

Keywords: *aerogels, sol-gel processing, nanostructures, mechanical properties, thermal conductivity.*

Abstract

Aerogels are a fascinating material: they consist mainly of air entrapped into an open porous solid network of nanoparticles. They are in a certain sense an almost nothing. Their properties are outstanding: their density is low, typically around 100 kg/m^3 , their thermal conductivity can be as low as 0.01 W/mK, their specific surface area is typically between a few hundred to a few thousand m^2/g . The microstructures of aerogels are characterized by well accessible branched mesopores in the range of 10 to 100 nm and a solid network of nano-particles or fibrils spanning the whole volume. Aerogels can be made from inorganics, especially oxides like silica, corundum, zirconia, and many others, but also polymers, like phenolic or resorcinol resins, polyimides and polyurethanes and a few of them can be converted into carbon aerogels. Recently aerogels made from biopolymers came into focus of research like cellulose, alginates, chitosans and many other polysaccharides. Here a brief overview about aerogels, their synthesis, properties and applications as well as a perspective for their future is given.

Introduction

Aerogels are a fascinating material: they consist mainly of air entrapped into an open porous solid network of nanoparticles. They are in a certain sense an almost nothing. Their properties are outstanding: their density is low, typically around 100 kg/m³, their thermal conductivity can be as low as 0.01 W/mK, their specific surface area is typically between a few hundred to a few thousand m²/g. The microstructures of aerogels are characterized by well accessible branched mesopores in the range of 10 to 100 nm and a solid network of nano-particles or fibrils spanning the whole volume, meaning any branch of the network can be reached from any point. Aerogels are produced principally in a simple way and were first synthesized by Kistler 1931 [1]: monomers are dissolved in a suitable solvent, these monomers react to form oligomers and nanoparticles, which by

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some mechanism aggregate and form a gel. Such a gel consists of solid particles forming a three dimensional random network and a fluid in the pore system. If the gel fluid is exchanged with air without changing the solid particle network, an aerogel is created.

Aerogels belong to the broader class of porous materials. Materials are porous if they contain cavities, channels, funnels, holes, bubbles filled with air or a blowing agent (pentane or carbon dioxide for instance). The pores may be regularly arranged as in honeycombs or zeolithes. However, the more common situation is an irregular pore structure, as obtained by cross-linking of polymer chains, aggregation or agglomeration of small particles, or selective removal of elements or phases of a multi-phase solid (e.g. by etching or pyrolysis, chemical bleaching of one phase of a two-phase material). And even expansion of a polymer solution by a blowing agents leads generally to a pore system with a certain pore size distribution. Porous solids can be further divided into closed-cell and open-cell porous ones. A typical foam as made for instance by blowing of polystyrene or polyurethane with a suitable gas consists of cell walls separating the pores. In an open porous foam all pores are interconnected. An excellent overview about structure and properties of porous materials is provided in the textbook of Lorna Gibson and Michael Ashby [2]. The physical properties of a porous solid and its reactivity are effectively influenced by the kind, shape, and size of the pores. Some technical terms are defined in Table 5.2.1.

Term	Explanation
porosity	ratio of the pore volume to the volume occupied by the particles or fibrils
pore shape	ink-bottle, cylindrical, funnel, or slit-shaped
pore accessibility	closed, blind or through pores
pore size and dominating transport mechanism	micropores: < 2 nm \rightarrow activated transport mesopores: 2–50 nm \rightarrow Knudsen diffusion, surface diffusion along the pore walls, capillary transport macropores: > 50 nm \rightarrow molecular diffusion
density	skeletal density: density of the solid network envelope density: mass per total volume (volume = solid phase + closed pores + open pores)

Table 5.2.1: Definition of terms used to characterize porous solids.

The term aerogel is by no means clearly defined in the literature. There are many definitions possible.
- 1. First, all materials prepared from wet gels by a special drying process, the supercritical drying technique, were called aerogels irrespective of their structural appearance and their properties. With the development of new drying techniques, this definition no longer appears appropriate.
- 2. According to an alternative definition, materials in which the typical structure of the pores and the network is largely maintained while the pore liquid of a gel is replaced by air are called aerogels. However, it is not always clear to what extent the structure was maintained even in the case of supercritical drying. Rearrangement and shrinkage in the gel body during drying are normal phenomena.
- 3. Another definition would be: aerogels are open porous nanostructured solids obtained from a sol-gel process, irrespective of the way, a wet gel is dried, if the majority of pores is in the meso-porous range, meaning the pores are typically below 50 nm.

The unique materials properties of aerogels result from the special arrangement of their solid network, which is schematically shown in Figure 5.2.1 for a SiO_2 aerogel.



Figure 5.2.1: A picture of a silica aerogel block with a schematic depiction of the particles building the solid skeleton and the amorphous SiO₂ structure of the nanoparticles building the slightly bigger aggregated particle network. Note, that silica aerogels are typically transparent to translucent, depending on their density and that they scatter light, such that they appear blue (Rayleigh scattering).

How aerogels are made

The classical example illustrating the process of making an aerogel is based on the famous and best investigated material in this respect, silica. The first silica aerogels were made by Kistler starting with water glass, which is a colloidal solution of sodium silicate in water. Such a so-called *sol* can be prepared from quartz sand mixed with caustic soda and water in a hot steam reactor leading to $(Na_2O)_xSiO_2$ nanosized particles dispersed in water. Adding to such a water glass sol an acid destabilizes the sol and leads to gelation: The nanosized particles form a 3D network. Washing the sodium salt out of the pores and heating then the pure pore fluid to a temperature above its critical point in a high pressure vessel (autoclave) transforms the fluid into a supercritical one, such that the supercritical fluid can leave the pore space by diffusion on simply depressurizing the autoclave at constant temperature. This process was already invented, patented and used industrially by Kistler and the company he founded in the forties of the last century. Today this process is not used anymore. Excellent reviews on aerogels, their synthesis and properties can be found in [14, 15, 16, 19].

Silica aerogels The modern technique to prepare a silica aerogels starts with a so-called alkoxide, like tetramethoxy- or tetraethoxysilane, тмоs or теоs. These molecules react in water to form silicic acid, Si(OH)₄, a process called hydrolysis. The byproduct is an alcohol. Silicic acid molecules react with each other and form amorphous silica by a polycondensation reaction, leaving water or alcohol. TEOS is not really miscible with water. A suitable amount of amorphous silica can be dissolved in a mixture of water and ethanol (or methanol). In reality the hydrolysis is never complete, but there always will be species in solution with only one ethoxy group replaced by an OH-group, or two or three. A partially hydrolyzed ethoxysilane can react with another TEOS leaving then an alcohol. Hydrolysis can be accelerated by the pH-value of the solution. The rate of hydrolysis decreases with increasing pH, such that it formally comes to zero at pH 7. The polycondensation reaction between partially hydrolyzed silanes instead increases with increasing pH value. It increases until pH 14. There are many factors having influence on the hydrolysis and polycondensation reaction which always run concurrently.

These factors are: the pH-value, the type of molecular precursor (TMOS, TEOS, ...), ratio of precursor to alcohol, ratio of precursor to water and of course temperature. All affect not only the time to gelation, but essentially the microstructure. Whereas under acidic conditions the polycondensation reaction occurs mainly at the terminal Si atoms having no other -Si-O- bond, but only silanol bonds, under basic conditions the polycondensation reaction occurs at the central Si atom, having already -O-Si- bonds. This is due to the fact that the character of the Si- atoms changes with the number of -O-Si- bonds be-

ing there. The more -O-Si- bonds exist the less basic is the residual OH-Si bond. Therefore one obtains under acidic conditions a loose fractal network of very small amorphous silica particles and under base conditions bigger particles and a more dense network. This is best illustrated with a picture going back to Iler and is shown in fig. 5.2.2.

The typical procedure preparing a silica aerogel, however, is today a so-called two-step routine. First the alkoxide is mixed with acidic water such that colloidal silica particles are formed and might start to aggregate to branched networks, but not making a spanning clusters and then the pH-value is turned to base condition (larger 7) inducing rapid polycondensation and gelation by adding all monomers and oligomers in solution to the already existing clusters of silica. The sol of silica particles under acidic conditions is stable for a prolonged time, especially at lower temperature (storage in a fridge). The whole process is schematically shown in fig. 5.2.3. One should mention that typically after gelation the wet gel is aged, meaning it is left in the solution, which still contains some monomers, oligomers which have time to add to the existing spanning cluster and stiffen the solid network.



Figure 5.2.2: Influence of pH-value on the formation of colloidal silica networks after [3].





Figure 5.2.3: General scheme for preparing aerogels by sol-gel processing.

Having prepared a wet gel, the essential process is to dry it. Drying can lead to two types of dry gels: aerogels and xerogels. The latter one are obtained by evaporation of the pore fluid for instance under ambient conditions or at elevated temperature. A huge shrinkage is then observed, typically about 40 to 60%. This is due to capillary forces: on drying the pore fluid evaporates at the liquid-gas interface inside the pores. This interface is concave and therefore the pore liquid is sucked to the surface of the wet gel. The gas-liquid interface tension pulls on the solid network and thereby reduces during evaporation the pore size until the pore walls come into touch (the smaller ones first, the bigger ones later or never) and then the silanol groups at the wall surface can make a polycondensation reaction leaving a water molecule. Such Si – O – Si bonds are irreversible. They keep the body into the shrunken shape.

In order to avoid capillary driven shrinkage of the wet gel, the most elegant processing is, as mentioned above, supercritical drying. Today this is mostly achieved by first exchanging the pore fluid in the wet gel with liquid carbon dioxide being already in an autoclave and then heating the autoclave above the critical point of CO_2 . At the critical point the difference between fluid and gas disappears and as such, no meniscus separating fluid and gas appears anymore. After that transformation into the supercritical state, the supercritical fluid can be released from the autoclave at constant temperature and a dry gel results. Depending on details of the solvent exchange and the supercritical processing a material can be achieved with almost no shrinkage.

Silica aerogels processed in this way have, however, for some applications an

essential drawback: they are hydrophilic. Although they are stable under normal humidity conditions for years, they never should get really wet again. Once water is sucked into the nano-network upon drying they would shrink to xerogels. For applications as superisolation of pipelines or houses this would not be acceptable. The material has to be hydrophobic. Fortunately this can easily be achieved. If the wet gel is treated with trimethlychlorosilane (TMCS), the OH-groups at the surface of the solid network are exchanged by an $O - Si - (CH_3)_3$ group which repels water. This exchange also leads to an interesting property: Although during evaporative drying menisci are inside the gel and the solid network shrinks, the methyl groups repel each other and after complete drying the solid network elastically goes almost back into its original shape before drying (spring-back effect). This effect can be used at least for granulate silica gels, to avoid the process of supercritical drying.

Silica aerogels processed as sketched above and supercritically dried have a typical particulate microstructure. Fig. 5.2.4 shows a scanning electron micrograph (SEM) of such a silica aerogel. Looking at the scale bar of 100 nm shows, that the three dimensional network of silica particles exists, which looks like strings of pearls. The pores have a diameter below 100 nm, most of them are below 50 nm.



Figure 5.2.4: The left picture shows a SEM micrograph of a silica aerogel dried supercritically. The right picture a transmission electron micrograph of a silica aerogel exhibiting the nano-network of colloidal silica particles having an amorphous structure itself and thick bridges connecting them.

The microstructure can be resolved in more detail using transmission electron microscopy (TEM). A picture taken with a TEM is shown in the right picture of fig. 5.2.4. In this picture the scale bar at the lower left corner shows that the silica particles are less than 20 nm in size and that the particles are connected by thick bridges. This is important for the thermal conductivity. One can imagine, that

the contribution of the solid network to the total thermal conductivity increases the thicker the bridges between the nano-sized particles.

RF aerogels

Another classical example of an aerogel is a so-called RF-aerogel first synthesized by Pekala and co-workers using resorcinol (R) and formaldehyde (F) diluted in water with sodium carbonate as a catalyst adjusting the pH-value of the solution into the slight base regime of around 7 [4, 5]. Resorcinol is a 1,3-dihydroxybenzene, meaning on the benzene ring at positions 1 and 3 OH-groups exist. This changes the charge distribution in the benzene ring, making positions 2, 4 and 6 more reactive especially more positive. In a water solution at pH values above 5 especially position 2 is activated and formaldehyde is attached there leading to a so-called hydroxymethylresorcinol (HMR). The activated resorcinols make a polycondensation reaction leading to chain, ring or branched structures of a polymer. Such structures aggregate in the solution and can make a gel network. A scheme, going back to Pekala, is shown in fig. 5.2.5.



Figure 5.2.5: Scheme for the reaction between resorcinol and formaldehyde in base solutions leading to a gel network [4].

Many parameters affect the gelation and the properties of RF-aerogel. Most important is the pH value. RF-aerogels can be prepared not only under base

conditions, but also under acidic conditions, using for instance citric or hydrochloric acid [18]. Under acidic conditions the polycondensation reaction is extremely fast such that gel can be prepared within seconds, whereas under base conditions gelation typically takes hours to days. Another important parameter is the ratio of R to F. For a complete reaction 2 molecules of formaldehyde should be used per molecule of resorcinol. An excess of either R or F changes the structure in that the bridges between the R-rings can be pure methylene or dimethylenether groups and a more chain-like or branched structure can be attained. Very important for the final density of an RF-aerogel is, however, the dilution, i.e. the ratio of R to water (R/w). As usual in a chemical reaction, temperature is of utmost importance as shown in fig. 5.2.6. This figure shows an RF-solution catalyzed with a small amount of catalyst (ratio R/C = 1500). The kinematic viscosity changes first approximately linear with time, but after a certain time the viscosity increases drastically by a few orders of magnitude, signaling that the system changed from liquid to a more solid like behaviour: a wet gel is formed.



Figure 5.2.6: Temperature and time dependence of the viscosity of an RF solution.

Typical parameters to prepare RF-aerogels after the recipes given by Pekala and co-workers are R/w ratios between 0.003 and 0.02, R/C ratios between 100 and 500 and R/F is close to 1/2. As a catalyst sodium carbonate is used with a pH value around 7 ± 0.5 . The material produced has a brown or dark violet color and consist of necklace like string of particles with sizes very well below 100 nm. A SEM picture of such an RF aerogel is shown in fig. 5.2.7 and a picture of a sample is shown in the right panel of fig. 5.2.7, showing the typical dark-brown color.

5.2. Aerogels – synthesis, properties and applications of an almost nothing



Figure 5.2.7: The left picture shows a SEM micrograph of an RF-aerogel prepared after the recipe of Pekala dried supercritically. The right picture shows a sample of such a RF aerogel.

If one changes the chemistry a bit, one can prepare RF-aerogels without supercritical drying, as discovered by Fricke and coworkers [6, 7, 9]. If one uses an R/w ratio around 0.03, R/F is also around R/F= 1/2 and essential is, to use much larger R/c ratios, namely greater than 1000, such that the pH value is around 6 ± 0.5 . The samples look different, they have a color of light ochre to brown and the microstructure is different, meaning there is a 3D network of particles with a size of around 100 nm to 1 µm. Figures 5.2.8 show a fracture surface of such an aerogel and a SEM picture of the microstructure. The microstructure consists of small particles having a size of around 100 nm connected in 3D and highly branched. Pores of the same size are visible.



Figure 5.2.8: The left picture shows a sample of such an ambient dried RF aerogel prepared after the recipe of Fricke. The right picture shows a SEM micrograph of such an RF-aerogel.

A very interesting property of RF-aerogels is, that they can be converted to carbon aerogels. Pyrolysis under oxygen free atmosphere (nitrogen, argon) at around 1000 °C yields a glassy carbon aerogel. If the pyrolysis is done at higher temperatures graphitization takes place. Although during such a heat treatment around 50% of the material is lost, the conversion to a carbon aerogel with a very high surface area allows to apply such aerogels in supercapacitors or batteries. This is especially true, if the pyrolysis is done under a suitable carbon dioxide atmosphere, which yields not only carbon aerogels, but introduces at the surface of the particles micropores of around 2 nm in size and thus increasing the specific surface area to values of around 3000 m²/g.

Cellulose aerogels

In contrast to many inorganic aerogels, biopolymeric aerogels do not start from monomers which somehow polymerize in a highly diluted environment and then build a gel, but they start directly with polymers, which are dissolved in a suitable solvent and are then brought to gel either by changing the temperature or the charge distribution on the polymer strands. An example of such biopolymers is cellulose.

Cellulose is a the most abundant natural polymer found in any plant. It consists of repeating cellobiose units. The cellulose molecule is stiffened by intramolecular hydrogen bonds and polymer strands arranged parallel or antiparallel together can form crystals of cellulose. These polymer strands are bonded together by intermolecular hydrogen bonds. All native cellulose is organized into fringes and fibrils [10, 11], which means that there are areas of crystalline order being intermixed with amorphous ones. Typically the amount of amorphous regions varies in plant cellulose between 40 and 60%. Although cellulose is hydrophilic and considerable swelling occurs in water, it is insoluble in water and most organic solvents, but is biodegradable. Since cellulose is chemically a very stable material, the production of aerogels from cellulose needs a technology or processing route to disintegrate the cellulose into the elementary fibrils and eventually down to the polymeric level without degradation. It then has to be rebuild into a suitable low density, open porous gel that can be dried to obtain a 3D meso-porous microstructure typical for aerogels.

There are several solvent for cellulose which are in principle able to break the intermolecular hydrogen bonds. For aerogels three dissolving agents are widely used:

- NaOH/water with additions of e.g. urea, thiourea, polyethylene-glycol (PEG), ZnO or LiOH with similar additives as in the sodium hydroxide case,
- ionic liquids, most frequently based on N-methyl-morpholine-N-oxide (NMMO) with suitable stabilizers
- salt-hydrate melts, like $ZnCl_2 \cdot 3 H_2O$ or $Ca(SCN)_2 \cdot 4 H_2O$ and others.



Figure 5.2.9: Schematic of the process developed by Jin and co-workers [12] to produce cellulose aerogels. Instead of rhodanide one can use also other salts, like zinc chloride tri- or tetrahydrate.

In this brief overview only the salt-hydrate melt route is discussed. Jin and coworkers [12] developed this technique to produce high-quality cellulose aerogels. A solution of calcium thiocyanate (rhodanide) and water with a molar ratio of 1:4 is brought to a temperature of around 110 $^{\circ}$ C and then dissolves cellulose probably by complexing the hydroxyl groups of the cellulose molecule. This particular salthydrate cellulose solution has a reversible sol-gel transition at approximately 80 $^{\circ}$ C, meaning on cooling the solution to room temperature the gel is formed. A schematic of the process developed by Jin and co-workers [12] is shown in Figure 5.2.9.



Figure 5.2.10: Density of cellulose aerogels prepared by Hoepfner et al. [13] using the route of Jin [12].

Hoepfner et al. [13] used the process of Jin to produce monolithic cellulose aerogels. They also used a rhodanide-hydrate solution in water with a concentration near the coordination number of the cation and dissolved microcrystalline cellulose of a degree of polymerization (DP = 150). The hot cellulose solution was poured into polyacrylic multi-wall sheets with a cross section of 15×15 mm yielding monoliths with a length of around 100 mm. The cellulose was then regenerated by immersion in ethanol and after solvent exchange and washing out of the calcium salt the gels were dried supercritically.

Monolithic cellulose aerogels are typically white, soft, and easily deformable by indentation. Figure 5.2.10 shows the average density of aerogels aged in ethanol before supercritical drying. The density varies between 10 and 60 kg/m^3 with the cellulose concentrations varying between 0.5 and 3 wt%. Note that the density is only eight times higher than the density of air and is in the range of styrofoams.

The microstructure of cellulose aerogels is completely different compared with silica or RF-aerogels. Fig. 5.2.11 shows the typical fibrillar structure, meaning polymer strands of cellulose rearrange themselves into fibrils of 10–20 nm in diameter and they are connected in 3D like an amorphous spider web or a fleece. At the point of intersection the fibrils are chemically bonded and thus the nano-fleece can transfer loads.



Figure 5.2.11: The left picture shows a SEM micrograph of a cellulose aerogel with 2 wt.% and the right one with 4 wt.% cellulose prepared after the route of Jin.

Properties

The properties of aerogels are determined by their microstructure, which is characterized by first their porosity (total pore volume or envelope density), by the size of the particle network, the bridge size connecting them and of course the material the nanoparticles consist of.

The most simple property is the specific surface area, since this is mainly determined by the particle size. Specific surface area is defined as the surface of

a body *A* divided by its volume *V*, $S_V = A/V$. One can also define the specific surface area with respect to an arbitrary volume V_T enclosing the sphere under consideration. Then the specific surface area would be $S_V^T = A/V_T = S_V \phi$, with ϕ the volume fraction of solid inside the volume V_T . Typically one does not measure the specific surface area per unit volume, but the specific surface area per mass S_m . Both are related as $S_V^T = S_m \rho_e$, with ρ_e the envelope density of the porous body. The specific surface area per unit volume is always in a very simple way related to a characteristic length *D* of the body, namely we have $S_V = \gamma/D$, with $\gamma = 6$ for sphere and cubes, and $\gamma = 2$ for a long cylinder and *D* denotes the diameter. Thus the specific surface area of an aerogel is simply related to the size of its particles. Since the size is in the nanometer range, the surface area is always in the range of a few thousand square meters per gram. The absolute value decreases if the connecting bridges between that particles are thick and the volume fraction of solid increases.



Figure 5.2.12: Young's modulus of several types of aerogels as a function of envelope density drawn with data from [6, 7, 8, 9].

The mechanical properties like Young's modulus and fracture strength depend to a strong extend of the microstructure. Since aerogels are open porous bodies, on expects that the larger the porosity, the smaller the fracture strength and the elasticity. One also would expect, that especially silica is brittle as glass and even more brittle due to the huge quantity of pores. Porous bodies are typically not tested in tension but in compression. In such a test one observes first a linear increase of stress with compressive strain, then a change to a regime in which the stress remains almost constant (a test sample decreases its height at almost constant stress) and finally a strong increase in stress at almost not further increase in strain due to compaction of the porous body. This behaviour is also found in aerogels. However, the plateau regime will be absent in the case of pure brittle behaviour, which is typically for aerogels of high density. The smaller the density the more developed is the plateau. In that stage a lot of particle bridges or strings break and collapse. Models allowing to relate simple quantities of a porous body to its mechanical behavior were developed by Gibson and Ashby [2]. They derive that the fracture strength σ_F can be expressed as a power law of the envelope density, namely $\sigma_F \propto \rho_e^{3/2}$ and the elastic modulus should scale like $E \propto \rho_e^2$. In aerogels such simple power laws are observed but with different exponents. Young's modulus is much stronger dependent on the envelope density. This is caused by the network, which contains dead ends or dangling string of pearls. Fig. 5.2.12 shows a collection of results from the literature for silica aerogels, RF-aerogels (see below) and carbon aerogels.

For silica aerogels a trend is $E \propto \rho_e^{3.6}$ and for RF-aerogels a relation is observed like $E \propto \rho_e^{2.9}$. For cellulose aerogels a relation of the kind $E \propto \rho_e^{1.8}$ is observed, which is closer to the scaling relation derived by Gibson and Ashby. For the yield strength, which is defined as the stress after which a certain non-reversible strain is achieved, typically 0.2%, many aerogels also follow a power law relation with an exponent bigger than that given by the rules of Gibson and Ashby, namely $\sigma_F \propto \rho_e^n$, with 1.5 < n < 2. A recent study on the mechanical properties of silica aerogels as they depend on envelope density was performed by Wong et al. [21] and a multi-scale continuum model describing the whole stress-strain curve of cellulose aerogels was recently developed by Rege et al. [22].

The thermal conductivity of a porous material consists always of three terms: heat conduction via the solid phase, heat conduction or even convection through the pore space and radiative transport, as depicted in fig. 5.2.13 (for a detailed review on aerogels see [23]). In all aerogels the heat conduction via the solid network depends strongly on the type of network forming the gel. In a particular network like in silica or RF aerogels, the volume fraction solid, the size of the particles and their bridges (necks) determine the contribution of the solid phase to the total thermal conductivity. The gas phase transport in aerogels is very special, since the pores are that small, that the gas molecules hit with the pore walls more often than between themselves. Such a transport is called a Knudsen transport. The heat conduction is then determined by the ratio of the pore size d_p to the mean free path of a gas molecule ℓ (which is determined by temperature and pressure), the so so-called Knudsen number Kn. The gas phase thermal conductivity can be expressed by the following equation

$$\lambda_g = \frac{\lambda_{g0}\phi_p}{1+\alpha Kn} \tag{5.2.1}$$

Here λ_{g0} is the thermal conductivity of the gas in the pores not taking into account any Knudsen effect, α is a constant depending on the gas, $\alpha \approx 2$ for air. The Knudsen number scales with the envelope density, since the pore size varies with it

$$Kn = \frac{\ell}{d_p} \approx \ell \rho_e^{\gamma}$$
(5.2.2)

and the exponent γ may vary between 1/2 and 1. This relation means, the smaller the pore size, the larger the Knudsen number and the smaller the thermal conductivity through the pores. It also means, preparing an aerogel with low thermal conductivity asks to make a material with a pore size lower than the mean free path of air, which is at room temperature 69 nm.

The radiative contribution to thermal conductivity depends on the refractive index of the material, the temperature and of course the envelope density. A calculation of radiation transport through a porous medium is complicated [20], but eventually one can derive, that the contribution to thermal transport is proportional to the third power of temperature and inversely proportional to the envelope density [24]. If one sums up all three terms, one can calculate the total thermal conductivity of for instance RF and silica aerogels. The result of such a calculation is shown in fig. 5.2.14.



Figure 5.2.13: The thermal conductivity of porous materials is determined by three contributions: through the solid phase (left), the gas phase, pores (middle), and radiative transport. In the rightmost picture, the red bar at the top shall indicate a higher temperature compared with the blue bar at the bottom indicating a lower temperature. Radiative transport goes from the hot side to the cold side and photons diffuse through the nano-porous network.



Figure 5.2.14: The variation of the total thermal conductivity of silica and RF aerogels with envelope density measured in kg/m^3 .

Industrial applications

Today man industrial applications of aerogels, especially silica, but also RF and carbon aerogels are on the market. Aerogels are used

- · for thermal insulation in homes, vehicles, pipelines and packaging
- · as components in electronic devices like capacitors and batteries
- in foundry technology as binder for foundry sands, or as a filler for foundry sands
- in architecture for diffuse, shadow free illumination or as light high isolation concrete
- · in cosmetics to adjust the viscosity of fluids and creams
- in apparel and sportswear, like tennis rackets, security shows, sport shoes, inlay for winter shoes
- in space applications for super isolating space suits, anti-sloshing filling of tanks or isolation of cryogenic tanks

The outstanding low thermal conductivity of both silica and RF aerogels had immediately lead to industrial applications. As mentioned above, silica as well as RF aerogels are either brittle or deform irreversibly under even small loads. One way to overcome this problem is a reinforcement with a fiber felt. Glass fiber or polymeric felts are readily available on the market. Such a fiber mat is infiltrated with a silica sol and this is brought to gelation, coiled and after hydrophobization with TMCs and solvent exchange supercritically dried. The resulting material is a silica aerogel filled with glass fibers. Industrially such silica aerogel fiber mats are available with a width of 150 cm and a thickness up to 10 mm and lengths up to 60 m. Such aerogel mats are used as isolation material around pipes, mainly oil pipes and for isolation of houses. The advantage over conventional materials like polyurethane and polystyrol foams, is that the material are first superhydrophobic, do not burn or melt, there is no fire risk, and especially, that their thermal conductivity can be as low as 0.015 to 0.018 W/mK and are therefore by a factor of 2 better than the aforementioned foams or glass or rock wool [25, 14].

Aerogel granulates were the first produced already in the late eighties of the last century. They are still produced since more than two decades and have many applications [26]. For instance filling of double polyacrylic wall sheets with silica granulates reduces not only the thermal conductivity but also leads in daylighting applications of roof windows to a shadowfree and diffuse light. Aerogels granulates were recently used as filler materials in high performance concrete to then allow to build wall which are strong and also highly insulating. Silica aerogel granulates are also available on the market dispersed in plaster to make wall insulations. They outperform conventional plasters by a factor of three in isolation [27, 14].

RF-aerogels are used by American Aerogels to isolate bags and boxes used to transport human tissue or organs. They outperform conventional isolation boxes to keep the organic material at the desired temperature range by more than a factor of two [28].

Perspectives

The future of aerogels has just started, although they are known since 90 years and had a first revival in the eighties of the last century. But interestingly enough the number of papers on aerogels increased in the last decade almost exponentially. As mentioned, the first new topic is polymeric (polyurethanes, polyimides) and especially biopolymeric aerogels (cellulose, chitosan, chitin, alginates, agarose, pectin, egg-white) and the second interesting topic is hybrid aerogels, meaning in an aerogel of for instance pectin or cellulose the pores are filled with another aerogel, like silica [29]. The mixture of two aerogels gives new properties and new applications. A third interesting development in the last years is, to improve the processing, and that means especially the gelation, solvent exchange and drying, such that the currently costly production of aerogels becomes much cheaper and then allows for more applications. This is especially true for applications as superisolations in houses. The competition to well established materials, like polystyrol foams and mineral wool requires to reduce costs by a factor of 5 to 10. Also the newly developed superstrong composites of high performance concrete with silica granulates [30, 31] suffer from being to costly currently. New routes for silica aerogel production are necessary and are currently being developed. In the last decade also silica aerogels were considerably improved. Although silica is mostly brittle, the whole concept of methods and technologies currently used in the silica industry can be applied to silica aerogels as well. This means, that instead of a tetra-functional alkoxide di- and tri-functional silanes can be used or a combination of them. This led in the last decade to the development of superflexible and superhydrophobic aerogels which are much easier and cheaper produced than conventional silica [32, 33, 34].

There are many applications of aerogels, as a bulky nanostructured material possible, like applications in food industry and as a transport medium for medical drugs, as template for tissue engineering or as filters for waste water or oil absorbers and of course carbon aerogels, although developed principally thirty years ago, are still not at their end, since their pore space as a mixture of mesoand micro-pores can be adjusted to the electrolyte used in supercapacitors or rechargeable batteries. Therefore the future of aerogels is just at the beginning. To make the future bright, it needs the concerted action of chemists, physicists, material scientists and engineers and applications might drive further developments.

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5.3 Reliability, fraud and misunderstandings in Science. The four "Fs"

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KEYWORDS: bad science, reproducibility, cost of misconduct, predatory journals.

Introduction

It's common understanding, that scientific investigations and related publications are based on facts. Further, that reported experiments are reproducible and results are always reliable. However, recent observations both, in the scientific literature and during industrial product marketing, have raised the question of "What is true?". The reason for this question refers to the public press, where recently reports on scientific fraud, falsifications and misuse of polymers (PIP scandal) have appeared, in other words reports on *fake news in science*.

Scientists and respected institutions profit from public trust. It is the fundament for the provision of research grants or support budgets. Public trust does not hinder or exclude well-founded doubts and scepticisms. However, uncertainties among scientists and the public may arise, when even justified doubts and scepticisms lead to a polarization between pressure groups, or if arguments in favour or against scientific observations are used to support the position of either stakeholder group. The slogan "Junk science in the courtroom" has become a familiar quotation [1], when scientifically based opposite opinions are used as testimonies for polarized groups in court trials.

It's also common knowledge, that historical flaws have eroded the *Golden Picture of Science* in the past. Well known and famous scientists, such as Galileo Galilei (1564–1641) reported on scientific experiments, which he had never performed. Gregor Mendel (1822–1884), the father of genetics, manipulated his experiments on peas in such a way, that results supported his (finally correct) concepts. Robert Millikan (1868–1953) neglected a series of those experimental results, which did not fit into his basic concepts on electrical charge. These examples are taken only as a few apart from many others.

Research on modern life sciences requires highly complex investigational techniques and needs a close collaboration between biochemists, physicists, biologists, engineers and business men in particular. To keep experimental precision and reliability high under these circumstances is not easy. But the development

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of a product for human therapies must always be performed under reliable and reproducible bystander conditions and under the premise "Better safe, than sorry"! Only these factors will guarantee that subsequent clinical consequences in patients can be avoided. The central message of the new European Medical Device Regulation (EU-MDR) from 2017 refers to this [2].

As already said, reported results in life sciences must base on reliable and reproducible investigations. In contrast, Bad Science leads to dubious conclusions not only by scientists, but also by both, political authorities, who take decisions for regulatory frameworks, or companies who spend failing investments for new products.

As an example, many scientific publications lack information on descriptive details, which might lead to misunderstandings, bias or errors. For example, why do scientists use abbreviations in their life-sciences publications, which are not generally understood? Why do authors use complicated chemical formulae in the public press, such as e.g. (S)-N-Methyl-1-phenyl-propan-2-amine, which cannot be validated by an amateur? Finally, why do specialists use the formula "Methamphetamine" in the public press? Is it, because they want to disguise their research topic and not publicly speak of "crystal meth"? Of course, scientific publications are dedicated to an educated readership, but the public voice is eager to use information for a possibly biased view on urgent events.

What is Bad Science and what might be its impact?

Bad Science can be defined in a multidisciplinary approach. Different stakeholders do collaborate here in a bad way. Following J. Best in his editorial in Science magazine [3], *bad science* deals with:

- reporters, who fail to understand the research they purport to summarize;
- editors, who favour compelling headlines that distort the story content;
- professional Journals, that issue press releases to promote their content;
- onferences, that call attention to preliminary findings;
- researchers, who talk about their work in the media limelight before it has gone to peer review;
- ghostwriters, hired by pharmaceutical corporations, to produce articles reporting selective and favourable results.

With *bad science*, a simple lie is better, than a complex truth, and obviously more appreciated by the general public. Interestingly, and as reported in a recent publication by Vosoughi et al., the spread of false news is then faster than that of true information [4].

In this paper, I would like to provide examples for the four "Fs" of scientific misconduct, draw conclusions and provide recommendations for quality control and quality management in research on life sciences.



Figure 5.3.1: The "Sloppy Science Pyramid" represents different levels of scientific misconduct.

The four "Fs" of scientific misconduct

Scientific misconduct is a multifaceted phenomenon and not easy to categorize. I'd like to introduce here the four "Fs", namely f raud, f ake, f iction and f alsification. Examples from the most recent literature, as well as from news from the life science market will illustrate this notion and hopefully sensitize the reader for recognizing a scientific misbehaviour.

Fraud In 2018, Harvard University and Harvard Medical School called on journal editors to retract 31 of scientific papers, published by the renowned cardiac researcher Piero Anversa. In the time course of their investigations, they found that these papers contained data that had been manipulated or fabricated. Expression of concerns in this respect were also published by the New England Medical Journal [5], by Science [6] and in Nature [7]. Early doubts about the reliability of Anversa's data have already been published in Nature 2014 [8]. As a consequence, the US government and the NIH halted all clinical stem-cell studies in late 2018. The decision was communicated in a statement released on October 29, 2018 and read "the clinical trials are halted out of an abundance of caution to ensure that the study continues to meet the highest standards for participant safety and scientific integrity." Better safe, than sorry, as already said above. What was the reason?

Piero Anversa and his colleagues suggested in 2002, that a type of stem cells in the heart, called c-kit cells, could regenerate damaged heart muscle. Papers reporting on these findings were retracted because they included falsified and fabricated data [6]. One of the hosting clinics of Piero Anversa, Brigham and Woman's Hospital in Boston even agreed to pay 10 million USD to settle charges, that Anversa and two colleagues fraudulently obtained federal funding. The clinical CONCERT-HF trial of the US National Heart, Lung and Blood Institute (NHLBI) which is currently halted, started in 2015. In this clinical trial, c-kit cells or combinations of c-kit cells with bone marrow cells, were administered to up-to-now 125 patients with chronic heart failure.

Fake "Predatory journals" have become a common platform for fast publications and their number has considerably increased in recent years. This kind of journals offers open access to their content without any subscription fee and pretends to offer adequate scientific information. Publications, however, are accepted without performing a standard peer-review process or deliver other editorial services. Authors get their paper accepted after having paid for article processing charges. They hope that their papers have a widespread and fast distribution due to the open access modality, which helps to increase their publication list and allows for grant application. Even cheating based on commercial interests is common in predatory journals, pretending in a pseudo-scientific way, that a specific technology, a pharmaceutical drug or a life science product is advantageous as compared to a competitor. Scientists, who publish in "predatory" journals are, for the most part, young and inexperienced researchers from developing countries.

The quality of such journals was recently challenged by a group of Polish scientists from Wroclaw University [9]. In 2015, these scientists created a profile of a fictitious scientist named Dr hab. Anna *O. Szust* and applied on her behalf to the editorial boards of 360 journals. Oszust is the Polish word for "a fraud". They gave her fake scientific degrees and credited her with spoof book chapters. Her academic interests included, among others, the theory of science and sport, cognitive sciences and methodological bases of social sciences. The group in Wroclaw also created accounts for Dr Szust on Academia.edu, Google+ and Twitter, and made a faculty webpage at the Institute of Philosophy at the Adam Mickiewicz University in Poznań, Poland. The page could be accessed only through a link they provided on her cv. Forty predatory journals accepted her in their editorial board and at least a dozen requested some form of payment or profit in return. Despite being informed about this fake, Szust is still seen as editor on 11 journals websites and as a member of conference organizing committees in 2018 [9].

Fiction Facts have become fiction, which can be illustrated in the following example. Elizabeth Holmes, a young us American business lady and active in the realm of biotechnology, founded and later headed a company in California, called *Theranos* in 2003 [10]. This company made profit with a device for blood sampling and blood analyses. Holmes intended to revolutionize phlebotomy, a

process of making an incision in a human vein with a needle. Her idea was to optimize blood sampling by pricking the fingertip and run thirty lab-tests based on gene-tests on only one drop of blood, thus to be fast, efficient and reliable. Many investors found that concept convincing and put large scale money in this company for a fast profit. Holmes was able to raise the public awareness of her company and provoked huge profit expectations in the health care business. Her trick to appoint well known politicians as members of her supervisory board, was successful. With Henry Kissinger and George Schultz, both former ministers of foreign affairs in the USA, the company's stock exchange value raised to more than 10 billion USD in a short period of time. In 2015, Time Magazine listed her among the one hundred most influential persons in the world.



However, scientists and hematologists have questioned soon, whether the $20\,\mu$ L volume of a drawn blood droplet would be sufficient to run 30 lab-tests on gene analyses and whether the subsequent need to increase the sample volume by dilution would hamper the precision of her mini-lab. This doubt led to

investigations which confirmed in 2016, that experimental reproducibility and precision analyses of the mini-lab indeed, were out of range and not reliable [10]. Finally, John Carreyrou, a journalist from the renowned Wall Street Journal [11] was able to shed light on details, showing that technology and concept of Theranos' mini-lab didn't work out and that results from blood analyses were far beyond standards or even reproducibility. In contrast to public announcements and adverts of the Theranos company pretending the precision of its mini-lab, Carreyrou published his findings in the Wallstreet Journal on October 16, 2015 [12]. The story finally ends with Elizabeth Holmes being accused for large-scale fraud by the US Stock Exchange Security Agency. As a consequence, the Agency imposed a fine of 500,000 USD to Mrs. Holmes, combined with a ban on running a company in the next 10 years. Theranos, finally, was dissolved as a company in 2018 after its formerly 800 employees have quit their positions.

Falsification The quality of scientific publications considerably depends on the quality and engagement of peer reviewers. Those scientists usually come from the same field of research, serve under anonymous conditions and without any personal financial profit. This task is time consuming and journal editors are usually faced with problems of finding a sufficient number of reliable and knowledgeable peer-reviewers. It's common practice, that authors are asked to submit names of possible reviewers in order to facilitate and speed up the peer reviewing process. Of course, the editor is always free to decide in favour or against a suggested reviewer. How is it possible to fake this peer-review process?

A Chinese scientist has set up a simple procedure [13]. He gave journals

recommendations for peer reviewers for his manuscripts, providing them with names and e-mail addresses. However, the provided information referred to e-mails he had created himself, so the request for peer-review went directly to him or to his colleagues. No surprise that editors received favourable reviews, sometimes within hours after the reviewing request has been sent out [13].

Consequences of sloppy science

A scientist, whose task is to develop products for life sciences in industry, is confronted daily with a dilemma and questions, such as: "Can you believe what you read?" Not only patents, but also scientific publications count for the state-of-the-art in technology and determine priorities for intellectual property (IP), inventions and a possible subsequent economic exploitation. Products in life sciences must be safe, reproducible and traceable in order to be competitive. Therefore, scientific publications must be reliable in terms of their hypotheses, their experimental set-up and observed results. In order to develop a life science product successfully, scientists and engineers must be able to rely on the validity of published information. If not, companies will waste money, lose market share against competitors whilst their scientists and engineers are made responsible for any type of product failure and for adverse events in patients. Thus, knowledge and a sensitivity for possible scientific fraud, fiction, fake or falsification in the literature is obligatory.

The web page *Retraction Watch* serves as a practical tool in this respect. It is made available by the US *Center for Scientific Integrity* with the intention to promote transparency and integrity in science and scientific publishing, and to disseminate best practices and increase efficiency in science. Surprisingly, information on scientific fraud and abuse of scientific information appears here almost daily. Papers from predatory journals are often retracted, however, even renowned journals, such as Science, Nature, The New England Journal, The Lancet or Cell suffer from manipulations [14].

What happens, if experiments and reports in the scientific literature are not reproducible and thus, invalid? Invested money, used resources and labor time would be wasted at the expense of high cost for both academia and industry. Such a scenario has been assessed by L. Freedman in 2015 [15]. Here is a citation from this paper:

"Multiple systemic causes contribute to irreproducibility and many can ultimately be traced to an underlying lack of a standards and best practices framework. However, it is reasonable to state that cumulative errors in the following broad categories – as well as underlying biases that could contribute to each problem area or even result in entire studies never being published or reported, are the primary causes of irreproducibility: (1) study design, (2) biological reagents and reference materials, (3) laboratory protocols, and (4) data analysis and reporting. Datasets show a cumulative irreproducibility rate that exceeds 50%. Using a highly conservative probability bounds approach, we estimate that the cumulative rate of preclinical irreproducibility lies between 18% (the maximum of the low estimates, assuming maximum overlap between categories), and 88.5% (the sum of the high estimates, assuming minimal overlap)." [15]



Figure 5.3.2: Reproducibility of preclinical experiments published in the scientific literature is not always guaranteed. A high level of irreproducibility was found in a series of publication as assessed by companies such as Amgen and Bayer Healthcare as well as by and other authors [15]. The respective citations where the analyses can be found are given in the subline.

As a consequence, an analysis of past studies indicated that the cumulative prevalence of irreproducible preclinical research exceeds 50 %, resulting in approximately 28.2 billion USD/year spent on preclinical research that was not reproducible in the United States alone. 36.1 % of this amount referred to undefined biological reagents and reference materials, 27.6 % to an inadequate study design, 25.5 % to data analyses and reporting and finally 10.8 % to unprecise laboratory protocols [15]. The question arises about what could have been done with all that money lost due to irreproducible results?

Search for action and conclusion

Replication must become the norm [16] in scientific investigations. Commonly approved checklists must be set and duplicated images should be detected and avoided [17]. Scientists and not only quality assurance managers, who are responsible for scientific experiments in life sciences, should be obliged to control experimental details and check for reproducibility [18] in case of:

- *Disorganized sample storage*: Clear labelling and proper organisation for incubators and freezers. Everybody in the lab should be able to identify a sample, where it came from, who did what to it, how old it is and how it should be stored.
- *Inadequate data logging*: Data should be logged in a lab note book, not scribbled onto memo paper. Notebooks should be bound or digital; loose paper can too easily be lost or deliberately removed.
- *Variable experiments*: Protocols should be followed to the letter or deviations documented. If reagents need to be kept on ice while in use, each lab member must comply.
- *Unsecured data analysis*: Each lab member should have their own password for accessing and working with data to make it clear who works on what and when. Some popular spreadsheet programs can be locked down to that manipulating data even accidentally is difficult.
- *Missed maintenance*: Instruments should be calibrated and maintained according to regular, documented schedules. Cell cultures to be regularly supervised for dilution, pH and temperature and this information to be documented.
- *Old and undated reagents*: these can affect experimental results. Scientists should specify criteria for age and storage of all important reagents.

Finally, and as a recommendation, scientists should provide answers to the following seven questions in order to obtain reliable results before submitting a manuscript for publication:

- 1. Was there a clearly defined hypothesis to be proven? No HARKing!¹ No WPW-research!²
- 2. Were experiments performed blinded?
- 3. Were basic experiments repeated?
- 4. Were all results presented? No cherry-picking of best-looking results.
- 5. Were there positive and negative controls? Need for running parallel experiments as comparisons which should succeed and the other should fail, if the underlying hypothesis is correct.
- 6. Have valid ingredients been used? E.g. source of antibodies, enzymes clearly marked?
- 7. Were statistical tests appropriate?

When following these recommendations, they would allow for the necessary higher reliability, better experimental reproducibility and higher safety of products applied in life sciences.

¹ HARKing – hypothesizing after the results are known

² WPW – what happens when?

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6 Monographic articles

6.1 Manufacturing of substitutes for spongy bone with increased absorbability

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KEYWORDS: porous implant, polylactide, Eudragit®, freeze-extraction method.

Abstract

Composite scaffolds with increased hydrophilicity were prepared for the cancellous bone regeneration by the freeze-extraction method. As a construction material, a poly-L-lactide (PLLA) was applied. As a hydrophilic, modifying agent a methacrylic acid copolymer under trade name Eudragit® was used. A preliminary investigation and the optimization of the process were performed. For the obtained scaffolds, regression equations determining the effect: Eudragit® E100/PLLA weight ratio; volume ratio of methanol (porophore)/PLLA solution in dioxane on the interconnected porosity and the mass absorbability of obtained implants, were calculated.

Introduction

A commonly used treatment for large bone defects is a transplant, which involves taking a part of the tissue and prefixing it in the place of the defect. Autogenic grafts, i.e. from the treated patient, most often from the iliac crest, are considered to be the "gold standard" of bone implantology [1]. Despite common practice, this treatment carries a risk of infection of the site of transplantation, hemorrhage or nerve damage. Therefore, instead of transplanting live organs, other substitutes are used, such as biocompatible metals, ceramics and polymers [2]. The polymers have elastic and frictional properties that bring them closer to the properties of the synovial joint tissue, which is why they quickly gained wide acceptance of surgeons. In addition, polymer implants have a low mass. Because polymeric materials are more resilient than metallic and ceramic materials, they absorb a larger percentage of the load. The result is the prevention of bone atrophy (disappearance). Resorbable polymers gain the advantage because they are gradually replaced by the host bone and there is no need for a second operation. Due to the biocompatibility and the ability to control the degradation time,

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the polyesters (for example polylactide, polycaprolactone, copolymers of lactic acid and glycolic acid) occupy an important position among polymers used in bone regeneration [3–8]. These polymers were used with positive results not only in preclinical studies in animals but also in clinical trials in humans [9].

One of the polyesters is polylactide (PLA), which is widely used in medicine. PLA was initially used in controlled release systems of the active substance. Then in hydrogels, for the production of orthopedic screws, as well as in tissue engineering. The mechanical properties of polylactide are within the range of mechanical properties of spongy bone, which is why it may be important in the treatment of this bone. Moreover, polylactide has already demonstrated its osteogenic properties and capabilities of healing bone defects [10, 11]. However, polylactide is a hydrophobic polymer and has insufficient osteoconductive and osteoinductive properties in terms of large bone defects [9]. Consequently, synthetic PLA scaffold should be applied together with osteoinductive/osteogenic materials, such as platelet-rich plasma (PRP) [12, 13]. To overcome the problem of the poor impregnability of PLA with hydrophilic substances, modification of polylactide surface may be applied to make PLA more wettable and therefore to obtain better biological activity of PLA.

Methacrylic acid copolymers are used in the drug form technology [14, 15] and are known under trade name Eudragit[®]. They are an auxiliary substance in tablets, i.e. they facilitate swallowing, mask an unpleasant taste, release the active substance with a delay in a specific section of the gastrointestinal tract. The presence of many lateral ester groups imparts methacrylic acid copolymers greater hydrophilic properties than in the case of polylactide. In addition, depending on the substituent, hydrophilic polymethacrylates with anionic (carboxylate group) or cationic (trimethylammonium group) properties may also be available. The presence of suitable moieties as hydroxyl, carboxyl, amino groups have proven an effect on adhesion, differentiation of osteoblasts. Therefore, these polymers were considered by our group as an additive to PLA implants.

A proper bone substitute must meet a number of requirements. Biocompatibility is essential, which means the maintenance of cellular activity without inducing a local or systemic immune response of the body. Biodegradability enables distribution of the implant material into non-toxic products excreted from the body. Mechanical properties and internal structure should be proper for the tissue to be regenerated. Literature data show that a bone substitute must have interlinked pores of > 100 μ m (optimum pore size: 200–350 μ m) and interconnected porosity of > 80% [16, 17].

The requirements set for a given tissue can be achieved not only by choosing the implant material but by choosing the right method of production. Among the methods of manufacturing polymer bone implants are phase inversion (including thermally induced phase separation (TIPS) [18], freeze extraction variant [19]), salt leaching [20], emulsion method with lyophilization [21], gas foaming [22], electrospinning [23] and rapid prototyping techniques (as 3D printing, stereolithography (SLA), selective laser sintering (SLS), fused deposition modelling (FDM)) [24]. Methods were compared in Tab. 6.1.1.

Method		Advantages		Disadvantages	
Phase inversion	TIPS	• the ability to change many factors affecting the structure	-	sensitivity to changing environmental	thermally sensitive polymers excluded
	Freeze extraction	 interconnected porosity, > 80% macro-, microporosity 	sample flexibility	conditions	solvent limited choice
Salt leaching		• pore size and porosity control		porophore residuesflat scaffold limitationclosed pore structure riskfragility	
Lyophilization		• high porosity, > 90%		limited pore size, < 200 μmclosed pore structure	
Gas foaming		 preparation facility solvent free high porosity, > 90% 		 closed pore structure nonporous surface limited pore size, < 100 µm pore structure collapse risk 	
Electrospinning		 preparation facility high porosity		limited pore size, < 20 μmflat structure	
Rapid prototyping techniques	3D printing	 material assortment short duration possible cell employment unlimited shape 		substrate residues risklow resolutionexpensive apparatus	
	SLA	 high resolution short duration		 limited materials choice expensive apparatus cytotoxicity risk 	
	SLS	material assortmenthigh resolutionshort duration		thermal degradation riskexpensive apparatus	
	FDM	mechanical strengthsolvent free		thermal degradation risklimited materials choiceexpensive apparatus	

 Table 6.1.1: Comparison of scaffolds obtainment.

Freeze extraction method allows obtaining scaffolds of good flexibility compared to rapid prototyping techniques and salt leaching [25–27]. This feature allows the surgeon to adapt the implant size to the defect site in the operating room. Moreover, the adaptation of the process conditions leads to the proper internal structure of a scaffold.

In this work, a novel implant was obtained, which was consisted of two materials: polylactide and methacrylic acid copolymer. The influence of the addition of three methacrylic acid copolymers on implants mass absorbability and interconnected porosity was examined. Subsequently, using the design of experiments (DOE) [28–30], preparation of polylactide cancellous bone implants modified with methacrylic acid copolymer was optimized to obtain a scaffold with the maximal mass absorbability at the interconnected porosity of more than 90%. We suggest using the implant as a platelet reach-plasma carrier. The maximization of mass absorbability is important due to the possibility of inserting a greater volume of the platelet-rich plasma into the scaffold.

Materials and methods

Materials Poly-L-lactide (PLLA) of M_n 86 000 g/mol NW 2003D was distributed by Nature Works. Eudragit®E100 (methyl methacrylate, dimethylaminoethyl methacrylate, n-butyl methacrylate copolymer 1:2:1) of M_w 47 000 g/mol was kindly donated by EVONIK Industries. Eudragit®s100 (methacrylic acid, methyl methacrylate copolymer 1:2) of M_w 125 000 g/mol, Eudragit®L100 (methacrylic acid, methyl methacrylate copolymer 1:1) of 125 000 g/mol were distributed by EVONIK Industries. 1,4-Dioxane, methanol were distributed by POCh sA 2-propanol was distributed by Chempur. Ultrapure water with 18.2 M Ω cm resistivity was obtained using Milli-Q device.

Preparation of implant-forming solutions The PLLA solution was prepared in 1,4-dioxane at a concentration of 3 wt% PLLA was dissolved in dioxane during 24 h with constant stirring using a magnetic stirrer without heating. Then a suitable methacrylic acid copolymer (Eudragit®E100 or Eudragit®S100 or Eudragit®L100) was added in a 4:60 or a 4:6 weight ratio relative to PLLA. After complete dissolution of Eudragit®, the porophore (methanol or 2-propanol) was added in a 1:10 volume ratio relative to PLLA/dioxane solution. The mixture was stirred the next 24 h at 25 °C, with a speed of 200 rpm.

Preparation of implants The PLLA solutions in dioxane with additives were poured into the polyethylene forms at 25 °C. Then the forms were cooled at a temperature of -18 °C for 24 h. The frozen solutions were removed from the forms and extracted in a 300 mL of a gelling bath at -18 °C (methanol/water in a 4:6 volume ratio) or 4 °C (water) for 5 days, without stirring. Then samples were vacuum dried at 45 °C, 10 mbar for 24 h [31, 32].

Analytical methods

Implant interconnected porosity and mass absorbability

The implants were weighed using Mettler Toledo xs 104 scales. Dry scaffolds were weighted in air (m_s) . Then scaffolds were impregnated in the isopropanol/water solution in a 4:6 volume ratio (*vac*, 30 min). Impregnated scaffolds were weighted in isopropanol/water solution (m_{ww}) and finally the scaffolds impregnated in isopropanol/water solution were weighted in air (m_w) .

Interconnected porosity (P_o) was defined according to the Formula 6.1.1.

$$P_o = \frac{V_3}{V_1 + V_2 + V_3} \cdot 100\%$$
(6.1.1)

 V_1 is the volume of material without pores, V_2 is the volume of all closed pores in the material, V_3 is the volume of all interconnected pores in the material. On the basis of Archimedes' law, the Equation 6.1.2 is true.

$$(m_{s} - m_{ww}) \cdot g = (V_{1} + V_{2}) \cdot d_{0} \cdot g \tag{6.1.2}$$

Where g is the standard gravity, d_0 is the density of the liquid at the measurement temperature. The volume of open pores was defined as in Equation 6.1.3.

$$V_3 = \frac{(m_w - m_s)}{d_0} \tag{6.1.3}$$

After substitution of Equations 6.1.2 and 6.1.3 to Equation 6.1.1, the implant interconnected porosity was calculated according to the Formula 6.1.4.

$$P_o = \frac{m_w - m_s}{m_w - m_{ww}} \cdot 100\%$$
(6.1.4)

Mass absorbability (N_m) was determined according to the Formula 6.1.5.

$$N_m = \frac{m_w - m_s}{m_s} \cdot 100 \%$$
 (6.1.5)

Results and discussion

Poly-L-lactide bone implants with the addition of a suitable methacrylic acid copolymer were obtained. Implants were in the form of a cylinder with a volume of about 10 cm^3 (Fig. 6.1.1).

Three types of methacrylic acid copolymer were used: methyl methacrylate, dimethylaminoethyl methacrylate, n-butyl methacrylate copolymer (group ratio of 1:2:1 – Eudragit®E100), methacrylic acid, methyl methacrylate copolymer (group ratio of 1:2 – Eudragit®S100, group ratio of 1:1 – Eudragit®L100). As a preparation method phase inversion with freeze extraction variant was applied. Two types of porophore were used: methanol and 2-propanol.



Figure 6.1.1: Poly-L-lactide spongy bone implant modified with Eudragit®E100.

Selection of a porophore PLLA implants with the addition of three types of Eudragit® in a weight ratio of 4:60 to PLLA were prepared. As a porophore methanol (MeOH) or 2-propanol (iPrOH) were added. Methanol/water gelling bath was used. Prepared samples were hydrostatically weighted to estimate its mass absorbability and interconnected porosity. Results are presented in Fig. 6.1.2.



Figure 6.1.2: Dependence of implants mass absorbability (left side) and implants interconnected porosity (right side) on the type of Eudragit® and porophore – methanol (MeOH), 2-propanol (iPrOH). Error bars represent a standard deviation of the mean of three samples.

In all cases, mass absorbability was greater when MeOH was used. Obtained mass absorbability values were in the range of 1500–1800 % and corresponded with porosity values in the range of 93–96 %. The greater absorbability the greater porosity was observed. Differences between used Eudragits® were not significant. In the next experiments, MeOH was employed as a porophore, because of obtainment of greater absorbability values.

Eudragit selection PLLA implants with the addition of three types of Eudragit® in a weight ratio of 4:60 and 4:6 to PLLA were obtained. As a porophore MeOH was used. Water/methanol gelling bath was applied. Prepared samples were hydrostatically weighted to determine the effect of a type and amount of Eudragit® on the mass absorbability and the interconnected porosity of implants (Fig. 6.1.3).



Figure 6.1.3: Dependence of implants mass absorbability (left side) and implants interconnected porosity (right side) on the type and amount of used Eudragit®. Eudragit®/PLLA ratio was 4:60 and 4:6. The green line is an outcome for an implant obtained without porophore and Eudragit®. Error bars represent a standard deviation of the mean of three samples.

Obtained mass absorbability values were in the range of 1000–1800 %, interconnected porosity values were in the range of 92–96 %. Absorbability and porosity values were compared to a sample which was prepared without a porophore and Eudragit® (1300 %, 94 %). In most cases, Eudragit® addition influences mass absorbability reduction. Influence on porosity is not clear. The greatest absorbability increase was observed in the case of Eudragit®E100 addition in the weight ratio of 4:6. For this reason, Eudragit®E100 was selected for further research. Furthermore, the presence of amino groups in this polymer can increase the differentiation of osteoblasts [33].

Influence of mass ratio of Eudragit®E 100 to PLLA on the implant mass absorbability and interconnected porosity PLLA implants with a various mass ratio of Eudragit®E100 to PLLA were obtained. Samples were prepared with the addition of porophore (MeOH) in a volume ratio of 1:10 to PLLA solution on dioxane. Water gelling bath was applied to reduce Eudragit® loss during gelation. Prepared samples were hydrostatically weighted to determine the effect of Eudragit®E100 mass ratio to PLLA and the addition of porophore (methanol) on the mass absorbability and interconnected porosity of implants (Fig. 6.1.4).



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Figure 6.1.4: Dependence of implants mass absorbability (left side) and implants interconnected porosity (right side) on the amount of used
 Eudragit®E100. Eudragit®/PLLA mass ratio was 4:60. Porophore/PLLA solution in dioxane volume ratio was 1:10. The green line is an outcome for an implant obtained without porophore and Eudragit®. Error bars represent a standard deviation of the mean of three samples.

The greatest value of absorbability exceeding 2000 % was obtained in the case of implant prepared only with a porophore (MeOH). A sample prepared with Eudragit®E100 and porophore addition was characterized by lower absorbability. All implants (with porophore or Eudragit®) were marked by greater absorbability compared to implant prepared without any additive. Because of ambiguous interpretation (no linear dependence), it was decided to optimize the process with the aid of design of experiments. Eudragit®E100 addition was not abandoned because of the potential improvement of biological properties of the implant described in details above.

Optimization The effect of the Eudragit®E100 to PLLA weight ratio (x_1) , the volume ratio of the methanol (porophore) to PLLA solution in dioxane (x_2) on the mass absorbability (y_1) and the interconnected porosity (y_2) of obtained implants was investigated. The volume of the PLLA solution in 1,4-dioxane was constant. The optimization criterion was the mass absorbability maximization with the interconnected porosity of not less than 90 %. The optimization was performed based on the 2^2 rotatable design. Input and output variables are shown in Tab. 6.1.2.

A 13-run design was used, which consisted of a 2^2 factorial design (4 runs with two input variables in all combinations of +1 and -1 levels), four star points (4 runs with input variables at combinations of -1.414 or +1.414 levels with 0)
	Variable	Natural variable	Unit	Coded variables					
	Variable		om	-1.414	-1	0	+1	+1.414	
Input	x_1	weight ratio of Eudragit®E100 to PLLA	_	0.10	0.16	0.32	0.48	0.54	
	x_2	volume ratio of porophore to PLLA solution in 1,4-dioxane	-	0.03	0.05	0.10	0.15	0.17	
Output	$egin{array}{c} {\mathcal Y}_1 \ {\mathcal Y}_2 \end{array}$	mass absorbability interconnected porosity	% %			max > 90 %			

Table 6.1.2: Identification of input and output variables with a codification of input variables.

and five replicates for the center of the design (5 runs with all two variables at 0). All other variables were constant (standard conditions). The experiments were performed in a random order, and both of the response variables, y_i , were measured for each experiment. Tab. 6.1.3 shows the design matrix along with the results.

In order to shorten the discussion, the statistical analysis details are not presented in this paper. Here, we present the linear models (without insignificant coefficients) and the most important diagrams only.

Absorbability, \hat{y}_1 (%)

$$\hat{y}_1 = 1732 \cdot x_0 + 281 \cdot x_1 x_2 - 138 \cdot x_1^2 - 158 \cdot x_2^2$$
 (6.1.6)

The diagram of the relation between the mass absorbability, \hat{y}_1 , and weight ratio of Eudragit®E100 to PLLA, x_1 , and the volume ratio of porophore to PLLA solution in 1,4-dioxane, x_2 , is shown in Fig. 6.1.5.

Interconnected porosity, \hat{y}_2 (%)

$$\hat{y}_2 = 95.4 \cdot x_0 - 1.02 \cdot x_1^2 \tag{6.1.7}$$

The diagram of the relation between the implant interconnected porosity, \hat{y}_2 , and Eudragit®E100 to PLLA weight ratio, x_1 , is shown in Fig. 6.1.6.

Summary of the optimization The effect of Eudragit®E100 to PLLA weight ratio (x_1) , volume ratio of methanol (porophore) to PLLA solution in dioxane (x_2) on the mass absorbability (y_1) and the interconnected (y_2) porosity of the obtained implants was investigated. Using the estimated function (6.1.6), it was found that, within the design limits, it is the interaction between Eudragit®E100/PLLA

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Trial					2	2	Mass absor- bability (%)		Interconnected porosity (%)	
no.	<i>x</i> ₀	<i>x</i> ₁	x_2	$x_1 \cdot x_2$	$(x_1)^2$	$(x_2)^2$	<i>y</i> ₁	\hat{y}_1	y_2	\hat{y}_2
1	1	-1	-1	1	1	1	1790	1740	95.2	94.8
2	1	1	-1	-1	1	1	1050	1020	93.6	93.5
3	1	-1	1	-1	1	1	1320	1290	93.3	93.7
4	1	1	1	1	1	1	1710	1690	94.4	94.9
5	1	-1.414	0	0	2	0	1530	1570	93.4	93.4
6	1	1.414	0	0	2	0	1310	1340	93.5	93.3
7	1	0	-1.414	0	0	2	1300	1340	94.6	95.0
8	1	0	1.414	0	0	2	1460	1490	95.9	95.3
9	1	0	0	0	0	0	1750	1730	95.6	95.4
10	1	0	0	0	0	0	1840	1730	95.7	95.4
11	1	0	0	0	0	0	1560	1730	94.6	95.4
12	1	0	0	0	0	0	1800	1730	95.7	95.4
13	1	0	0	0	0	0	1700	1730	95.2	95.4

Table 6.1.3: The 2² rotatable design: experimental matrix^a and results^b.

a – Standard conditions: all experiments were performed using the same raw materials and volume of PLLA solution in 1,4-dioxane; b – All \hat{y}_i were calculated using a linear model.



Figure 6.1.5: The relation between the mass absorbability (\hat{y}_1) and the weight ratio of Eudragit®E100 to PLLA (x_1) and the volume ratio of porophore to PLLA solution in 1,4-dioxane (x_2) .



Figure 6.1.6: Interconnected porosity (\hat{y}_2) dependence in function of Eudragit®E100 to PLLA weight ratio (x_1) .

weight ratio and the volume ratio of porophore/PLLA solution in dioxane (x_1x_2) that has the strongest influence on the implant mass absorbability. The x_1 and x_2 variables do affect the implant mass absorbability only squared. Because of the positive value of the x_1x_2 variable coefficient, extreme variable values results in decreasing mass absorbability. Negative values of x_1 and x_2 squared variables coefficients result in correcting mass absorbability by reducing it. Therefore, the greatest values of mass absorbability correspond to the values of variables approaching the center of the design. A graph in the form of a saddle was obtained on the basis of the regression equation (Fig. 6.1.5).

In the interconnected porosity equation (6.1.7) x_1 variable in the square is the only factor. It indicates that only Eudragit®E100 to PLLA weight ratio affects the implant interconnected porosity. The negative coefficient value of x_1^2 variable results in decreasing the implant interconnected porosity along with the increasing value of the x_1^2 variable module. Therefore, the greatest values of interconnected porosity correspond to the x_1^2 variable values equal to 0. A graph in the form of a parabola was obtained on the basis of the regression equation (Fig. 6.1.6).

It should be noted that this optimization is appropriate only within the previously established range of the variables and it should not be extrapolated beyond that range.

The maximization of the mass absorbability of implants with an interconnected porosity of not less than 90 %, leads to the following optimal conditions:

- Eudragit®E100 to PLLA weight ratio of 1:3 ($x_1 = 0$);
- volume ratio of porophore to PLLA solution in 1,4-dioxane of 1:10 ($x_2 = 0$).

The results are as follows: $\hat{y}_1 = 1732 \%$, $\hat{y}_2 = 95.4 \%$. Experiments no. 9–13, which were performed under the same conditions, were accepted as confirmatory experiments. It had the following average results: $y_1 = 1732 \%$, $y_2 = 95.4 \%$.

Conclusions

A novel method for the preparation of composite poly-L-lactide/Eudragit®E100 bone implants with increased absorbability was developed. In our group, a spatial implant with a volume of 10 cm^3 , interconnected porosity above 90%, microporosity (pore size of ten micrometers) and macroporosity (pore size of 200–250 µm) was obtained [31, 32]. These features make the implant suitable for spongy bone regeneration. What is more this method does not require special equipment and costs of used solvents are low.

Among used methacrylic acid copolymers Eudragit®E100 gave the best results of implants mass absorbability. However, the greatest mass absorbability value of implant was obtained using only methanol (porophore) as an additive during the manufacturing process. Still, it was believed the addition of Eudragit®E100 is essential to improve osteogenic properties of the implant, because of favourable groups in the structure. Therefore, it was decided to use Eudragit®E100 as an additive despite the slightly lower mass absorbability values observation. Further research is planned to investigate the influence of Eudragit®E100 addition on cytotoxicity and proliferation of osteoblasts. Also, methanol was used due to a beneficial influence on absorbability of the implant. Because of the unclear influence of the addition of methanol and Eudragit®E100 on implant mass absorbability, it was decided to optimise the process using a mathematical model.

The process was successfully optimized with the aid of the DOE. After carrying out a 2^2 rotatable design, the mathematical models describing the influence of input variables: weight ratio of Eudragit®E100 to PLLA; volume ratio of porophore to PLLA solution in 1,4-dioxane, on the mass absorbability and the interconnected porosity of obtained implants, were calculated. Both regression equations are adequate, which is confirmed by the fact that the differences between the results and the calculated values are small. The first model enables the control over implant mass absorbability, the maximization of which ensures the insertion of the largest possible volume of the platelet-rich plasma into the scaffold. the second model enables control over composite implant interconnected porosity. The suitable interconnected porosity (over 90%) enables the nutrients to migrate into the scaffold and the cell metabolites to migrate out of it. The scaffold design with optimal properties including interconnected porosity and mass absorbability provides an implant which meets the requirements for the cancellous bone regeneration.

Under optimal conditions: Eudragit®E100 to PLLA weight ratio of 1:3, volume ratio of porophore to PLLA solution in 1,4-dioxane of 1:10, the poly-L-lactide bone implant modified with Eudragit®E100 having the interconnected porosity of 95.4 % and mass absorbability of 1732 % was obtained confirming that the calculated equations describe the entire process very well.

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6.2 Development of a force field for the simulation of liquid diiodomethane

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KEYWORDS: computer simulations, molecular dynamics, diiodomethane, force field.

Abstract

Computer simulations play an increasingly important role in understanding the structure of matter and the course of physicochemical processes. It is a powerful research tool in the hands of physicists, chemists, biologists, engineers, as well as specialists from many other fields. In order to conduct a computer simulation, it is necessary to know – at least to a minimum extent – the basics of its functioning.

Unfortunately, most of the currently available literature items are written in an advance scientific language which can make it very difficult for a novice researcher to run a computer experiment, or even in extreme cases – to reject this technique as a research tool.

This work presents a proposal for a three-site model of diiodomethane with appropriate parameters of the force field. The developed model can be used in computer simulations of systems containing liquid diiodomethane – for example during wettability and surface free energy (SFE) measurements.

Introduction

The basic research tool of chemistry – as a science – is an experiment during which the properties of matter and its transformation are studied. However, in some cases, for example due to the technical impossibility of reproducing the process conditions, the experiment cannot be carried out, or the results obtained with it will not be consistent with reality. That is why – especially in the last few decades – computer simulations have become a powerful tool in the hands of chemists. The rapid development of computational techniques and – especially during the last two decades – a significant increase in the computing power of computers enabled computer simulations of large-sized systems in an acceptable time. Even when an experiment is possible to be carried out in laboratory conditions, a computer simulation is an ideal complement and may soon become its substitute.

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Matter as a structure and processes occurring in it are very complicated real systems. When planning a computer simulation, we must take into account the fact that it is technically impossible to consider all the properties of the tested systems. For example, in the case of general equations of statistical mechanics, even for small macroscopic systems, it is necessary to solve integrals with a multiplication of 10^{20} . This issue is not analytically or numerically solvable at the present stage of knowledge and technology. It is therefore necessary to focus only on those properties of the system, which from our point of view are important in the specific research work. This will allow the development of a model system, i.e. a simplified model of the real system. Having such a model, the possessed powers and computing techniques at the current stage of civilization development are sufficient to conduct a computer experiment.

Computer simulations and theoretical approximations made on the model give the results of calculations, the comparison of which is called the theory test. However, in order to fully illustrate the research problem, an experiment on the real system should be performed in parallel. The obtained results are compared with the results of modeling – it is a test of the model that allows to assess the accuracy of the developed model systems (the more consistent results, the more accurately developed model). Often this step is repeated several times (each time after introducing corrections to the model), until satisfactory agreement between the results of the experiment and the simulation is obtained. It is only after this stage that we obtain a verified model system that can be used for further computer experiments.

Model systems can be discrete or continuous, and stochastic or deterministic. Stochastic simulation models the behavior of the system based on random factors selected for the purpose of obtaining a model similar to the parameters of the real system. A method suitable for conducting stochastic simulations is the Monte Carlo method [1], which due to the more complicated principle of operation will not be discussed in detail here. On the other hand, deterministic simulation consists in iterative solving of systems of differential equations at given time intervals describing the mathematically tested system.

Molecular dynamics simulations Molecular dynamics (MD) is the method usually used to carry out deterministic simulations. It is devoid of element of randomness – the studied systems are unambiguously described using mathematical formulas. Molecular dynamics, as the name suggests, is a dynamic method, i.e. it is very well suited to modeling traffic-related situations that evolve over time. In a simplified form, MD consists in predicting the trajectory of all objects included in the studied system by means of solving in the time intervals systems of motion equations based on the Newton's second law of motion; it is a study of the evolution of the state of the system in time using the laws of classical dynamics.

Before starting the simulation, initial velocities are assigned to the particles (e.g. according to the selected probability distribution for a given temperature), and then in defined time steps the forces acting on each particle are calculated according to the applied force fields [2].

During computer simulation using the molecular dynamics method, the solving of motion equations for a system takes place using various numerical methods. Each particle is subject to classical equation of motion:

$$F_i = m_i \frac{d^2 r}{dt^2} \tag{6.2.1}$$

where: F_i – strength acting on the *i*-th body; m_i – mass of the *i*-th body; $\frac{d^2r}{dt^2}$ – acceleration of the body.

The impact force for particle pairs can be calculated using the appropriately selected potential:

$$F_i = -\nabla_i V_{ij} \tag{6.2.2}$$

where: ∇_i is a del operator (nabla symbol) which is a gradient operator and V_{ij} is the potential energy between *i*-th and *j*-th body.

Thus, knowing the position of the particles in the simulation box at the moment, one can calculate the resultant forces acting on each of them.

In order to enable the start of simulation, i.e. integration of systems of motion equations, appropriate initial conditions should be imposed on the system: give the positions of particles (*r*) and velocity (*v*) at the moment of simulation start (t_0). By integrating the equations of motion with the timestep Δt we will get expressions on the velocity and position of the particles at time *t*:

$$v(t) = v(t - \Delta t) + \frac{F\Delta t}{m}$$
(6.2.3)

$$r(t) = r(t - \Delta t) + v(t - \Delta t)\Delta t + \frac{F\Delta t^2}{2m}$$
(6.2.4)

The equations of motion are ordinary differential equations of the second order. There are many numerical methods that allow for effective solution of such a problem. The most frequently used are various modifications of the Verlet integration, which in the basic form looks as follows:

$$v(t) = \frac{r(t + \Delta t) - r(t - \Delta t)}{2\Delta t}$$
(6.2.5)

$$r(t + \Delta t) = 2r(t) - r(t - \Delta t) + \frac{F(t)}{m} \Delta t^{2}$$
(6.2.6)

Verlet integration is reversible in time; this is an example of a multi-step algorithm – the next step is calculated using the data from the previous one.



Figure 6.2.1: The simplified description of the standard molecular dynamics simulation algorithm.

The Verlet integrator provides good numerical stability, as well as other properties that are important in physical systems such as time reversibility and preservation of the symplectic form on phase space, at no significant additional computational cost over the simple Euler method. However, systems of multiple particles with constraints (for example, potentials constraining them to a specific distance or attractive forces) are simpler to solve with Verlet integration than with Euler methods.

Force fields For simulation systems composed of many particles, it is necessary to use a model description of interactions between pairs or even three of particles. The force field is a mathematical function along with a selected set of parameters that describes the potential energy of the particles forming a system.

Having a given system of particles identically interacting with one another, its potential energy can be expressed in the form of functions of position's vectors of individual particles:

$$V(r_1, \dots, r_N) = \sum_{i=1}^{N} U_1(r_i) + \sum_{\substack{i,j=1\\i < j}}^{N} U_2(r_i, r_j) + \sum_{\substack{i,j,k=1\\i < j < k}}^{N} U_3(r_i, r_j, r_k) + \dots$$
(6.2.7)

where: $U_1(r_i)$ – potential of a particle in the external force field; $U_2(r_i, r_j)$ – twobody (bimolecular) potential; $U_3(r_i, r_j, r_k)$ – three-body potential. In practice, the calculation is limited to two or three first sums in equation (6.2.7).

There are many force fields used in the molecular dynamics method; some of them are so specific that they are only suitable for specific applications. Below, only two examples of potentials will be described in detail: the most frequently used two-body potential – the Lennard-Jones potential, and an exemplary threebody potential – the Stillinger-Weber potential. **Lennard-Jones potential** The Lennard-Jones potential (called also the L-J potential or 12-6 potential) is a mathematically simple model that approximates the interaction between a pair of neutral atoms or molecules. It is widely used as a model to describe the energy of intermolecular interactions during various types of simulations:

$$V(r_{ij}) = 4\varepsilon \left[\left(\frac{\sigma}{r_{ij}} \right)^{12} - \left(\frac{\sigma}{r_{ij}} \right)^6 \right]$$
(6.2.8)

where: $V(r_{ij})$ is the potential energy *i*-th and *j*-th molecule; ε is the depth of the potential well; σ is the finite distance at which the inter-particle potential is zero; *r* is the distance between the *i*-th and *j*-th particle (distance parameter, which is characteristic for individual atoms).



Figure 6.2.2: The graph of strength versus distance for the Lennard-Jones potential

The potential consists of two components: repulsive $\left(\frac{\sigma}{r}\right)^{12}$, and attractive $\left(\frac{\sigma}{r}\right)^{6}$, which can be used independently to describe the atomic-attractive attraction. The combination of both components allows the use of the above formula as a model of atoms bonded in a molecule.

The characteristic properties of the potential are:

- while $r_{ij} \approx 0 \rightarrow V \approx \infty$ it results in the lack of the possibility of "overlapping" of the interacting particles;
- while $r_{ij} \approx \infty \rightarrow V \approx 0$ particles located infinitely far from each other do not interact;
- while $r_{ij} \approx \sigma \rightarrow V \approx 0$;
- while $r_{ij} \approx r_{min}$ the potential reaches the minimum value (equilibrium position).

Stillinger-Weber potential Stillinger-Weber potential is an empirical, threebody model of interactions developed for silicon structure modeling [3]:

$$V = \sum_{\substack{i,j=1\\i < j}} U_2(r_{ij}) + \sum_{\substack{i,j,k=1\\i < j < k}}^N U_3(r_{ij}, r_i k, \alpha_{ijk})$$
(6.2.9)

where α_{ijk} – angle between three interacting molecules/particles. The two-body part takes the form:

$$U_{2}\left(r_{ij}\right) = A_{ij}\varepsilon_{ij}\left[B_{ij}\left(\frac{\sigma_{ij}}{r_{ij}}\right)^{p_{ij}} - \left(\frac{\sigma_{ij}}{r_{ij}}\right)^{q_{ij}}\right]\exp\left(\frac{\sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right)$$
(6.2.10)

where *A*, ε , *B*, σ , *p*, *q*, *a* – appropriate numerical parameters. The three-body part describes the equation:

$$U_{3}(r_{ij}, r_{ik}, \alpha_{ijk}) = \\ = \lambda_{ij} \varepsilon_{ijk} \left[\cos \alpha_{ijk} - \cos \alpha_{0_{ijk}} \right]^{2} \exp\left(\frac{\gamma_{ij} \sigma_{ij}}{r_{ij} - a_{ij}\sigma_{ij}}\right) \exp\left(\frac{\gamma_{ik} \sigma_{ik}}{r_{ik} - a_{ik}\sigma_{ik}}\right)$$
(6.2.11)

where A, ε , B, σ , p, q, a – appropriate numerical parameters; α_{ijk} – angle between three interacting molecules/particles. Potentials of this type can be used in the case of modeling interactions in solid bodies (crystals) with symmetry other than the regular system (sc, BCC, FCC).

Periodic boundary conditions (PBCs) For many simulated systems (e.g. bulk systems) the presence of the edges of the simulation box is undesirable due to the surface effects appearing there. Particles located near the edge of the box can accidentally lower them, have fewer neighbors than those closer to the center, and are affected by non-symmetrical force fields. To prevent these phenomena, a procedure based on the surroundings of the simulation box is used, its replicas giving the so-called periodic boundary conditions.



Figure 6.2.3: Illustrating periodic boundary conditions in two-dimensional system.

Methods of thermostating systems To ensure a constant temperature in the system during simulation, use one of the following methods:

- · Berendsen thermostat,
- Nosé-Hoover thermostat,
- Andersen thermostat.

The temperature during the simulation is defined as the average after the kinetic energies of all atoms, therefore it is impossible to determine it exactly. The average temperature is the parameter that can be controlled.

The simplest procedure that ensures temperature stability is its scaling. This is done by multiplying the speed of each molecule by a certain factor λ :

$$\vec{v}_i(t) \to \lambda \vec{v}_i(t)$$
 (6.2.12)

which is determined on an ongoing basis based on the calculated actual system temperature:

$$\lambda = \sqrt{\frac{T_0}{T(t)}} \tag{6.2.13}$$

Berendsen's thermostat is also the same, which is more realistic than regular speed scaling, that it reflects natural temperature fluctuations:

$$\lambda = \sqrt{1 + \frac{dt}{\tau} \left(\frac{T_0}{T(t)} - 1\right)}$$
(6.2.14)

where the $\tau > 100 dt$ parameter is selected individually.

The Andersen thermostat is implemented by replacing the speed of a randomly selected particle with the speed derived from the Maxwell-Boltzmann distribution at the set temperature. The thermostat does not change the equations of motion, but generates a distribution corresponding to the correct velocity distribution for the canonical ensemble only for positions; its application causes erroneous determination of dynamic quantities during simulation [2].

The Nosé-Hoover thermostat introduces an additional degree of freedom to the system. If we express the Hamiltonian system as follows:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r)$$
(6.2.15)

after using the Nosé-Hoover thermostat it will take the form:

$$H = \sum_{i=1}^{N} \frac{p_i^2}{2m_i} + U(r) + \frac{1}{2}Q\xi^2 + 3Nk_BT\ln(s)$$
(6.2.16)

where: p_s – the momentum coupled with the thermostat; Q – the element interpreted as the mass of the thermostat; $\xi = \frac{p_s s}{Q}$ – the coefficient described by Hoover, referred to as the coefficient of friction. Changing the Hamiltonian by introducing an additional degree of freedom also forces a change in the equations of motion when using this thermostat.

Due to the good reproduction of particle velocity distributions, reversibility over time, good canonical performance and many implementations, the Nosé-Hoover thermostat is a willingly used thermostat when conducting various types of simulations [2].

Diiodomethane and its applications Diiodomethane (chemical formula: CH_2I_2) is a liquid which is an iodine derivative of the methane. Diiodomethane is a colorless liquid; however, it decomposes upon exposure to light liberating iodine, which colours samples brownish. Because of its high density, diiodomethane is used in the determination of the density of mineral and other solid samples. It can also be used as an optical contact liquid for determining the refractive index of certain gemstones. In organic chemistry diiodomethane is a reagent in the Simmons-Smith reaction, serving as a source of the free radical methylene (carbene) during synthesis.

First and foremost, it is used as a one of testing liquid during wettability and surface free energy (SFE) measurements. It is the most commonly made by measuring the contact angle of the tested surface by a drop of liquid. That method is popularity because of the simplicity of the testing (it does not require complicated apparatus) and many modifications (SFE determination by means of the Young equation, state equations, SFE division into independent components). The measurements of this value are very important issue, because research on the properties of the surface layer of different materials is the basis for assessing their characteristics.

Most typically contact angle is measured with two different liquids. The selection of the measurement liquid is important for reliable results. Water is an obvious choice due to its non-toxicity and availability. Water also has high surface tension (72.8 mN/m) which makes it an ideal liquid for contact angle measurement as it forms an angle with most of the substrates (it does not wet the surface completely). Water is highly polar in nature thus it has a large polar component (51 mN/m) compared to many other liquids. The selection of the second liquid is much more cumbersome. It should be dispersive as using two polar liquids would exaggerate the polar component of the surface. The main problem with most of the dispersive liquids (like hydrocarbons) is that their surface tension is much lower than surface free energy of the solid surface making them wet the surface completely (i.e. contact angle is zero). Thus, more exotic liquids need to be used. Diiodomethane with the surface tension of 50.8 mN/m is the most used one.



Figure 6.2.4: Molecular model of diiodomethane – van der Waal's based representation; carbon (C) in black, iodine (I) in dark gray and hydrogen (H) in white.

Methods and results

In this work a new forcefield for describing behavior of bulk liquid diiodomethane was proposed. Three-site model of diiodomethane molecule based on OPLS-AA (Optimized Potentials for Liquid Simulations – All Atom) forcefield and one of modification of OPLS-UA (Optimized Potentials for Liquid Simulations – United Atom) forcefield was developed.

We simulated diiodomethane with 1000 molecules in a box of $52.0 \times 52.0 \times 52.0$ Angstroms dimensions. The periodic boundary conditions were applied in all



Figure 6.2.5: Three-center model of diiodomethane molecule proposed in this work

directions. Simulation was started from the Maxwell-Boltzmann velocity distribution for all molecules at 298 K. Canonical ensemble (NVT) was used with the Nose-Hoover thermostat maintaining the constant system temperature at 298.15 K. This ensemble (NVT) is a collection of systems whose thermodynamic state is characterized by a fixed number of atoms (N), a fixed volume (V), and a fixed temperature (T).

The simulation ran for 2.5 ns in order to equilibrate system, and after that time averaging of desired properties was performed for 500 ns. The simulation was performed using the LAMMPS package with 0.5 ps timestep.

All interactions between atoms were described by standard 12-6 Lennard-Jones and Coulombic potentials with 10 Angstroms cutoff. The Lennard-Jones parameters for CH_2 -I interactions were calculated by L-B mixing rule [4] given as:

$$\sigma_{ij} = \frac{\sigma_{ii} + \sigma_{jj}}{2} \tag{6.2.17}$$

$$\varepsilon_{ij} = \sqrt{\varepsilon_{ii}\varepsilon_{jj}} \tag{6.2.18}$$

where ε is the depth of the potential well, σ is the finite distance at which the inter-particle potential is zero, *i* and *j* according to molecules of known parameters.

q(e)	$ \begin{array}{c} \sigma \left(\mathrm{CH}_{2} \right) \\ \mathrm{(A)} \end{array} $	ε (CH ₂) (kcal/mol)	σ(I) (A)	ϵ (I) (kcal/mol)	C – I bond (A)	I – C – I angle (deg)
0.4	3.905	0.118	3.75	0.6	2.182	116.2

Table 6.2.1: Forcefield and model parameters [5].

The radial distribution function (RDF) describes how the atomic density varies as a function of the distance from one particular atom.



Figure 6.2.6: The radial distribution function $(gCH_2 - CH_2)$ computed during simulation.

Property	Experimental value	Calculated value
density (g/cm ³)	3.325 [6]	3.163
dipole moment (D)	1.08 [7] 1.16 (quantum calculations)	1.845

Table 6.2.2: The density of liquid phase and dipole moment at 298 K.

Discussion and conclusions

The radial distribution function of a liquid is intermediate between the solid and the gas, with a small number of peaks as short distances, superimposed on a steady decay to a constant value at longer distances. Calculated radial distribution functions are in good agreement with the data shows liquid state. At short distances (less than atomic diameter $-\sigma$) g(r) is equal to zero. This is due to the strong repulsive forces. The first (and the largest) peak occurs at approximately 5.43 Angstroms, with g(r) having a value of about 3.5. This means that it is three to four times more likely that two molecules would be found at this separation. The radial distribution function then falls and passes through a minimum value around approximately 6.0 Angstroms. At long distances the radial distribution function approaches one which indicates there is no long-range order.

However, it is necessary to determine more physicochemical parameters (such an enthalpy of vaporization, self-diffusion coefficient, dielectric constant, surface tension) and compare them with the experimental data in order to carry out a full test of the model. It may show that more complex model will be required – taking into account the large dipole moment of the molecule (for example model with Drude particle).

The developed force field can be used in the future to description more complex systems containing diiodomethane, for example to simulations of adsorption or wetting.

Computer simulations of matter are a complementary research method in relation to the classical experiment. By conducting computer simulation using the molecular dynamics method, solving the equations of motion with numerical methods for individual molecules with the help of a suitably prepared program makes it possible to study the evolution of the system over time and determine its physicochemical properties. Considering the constantly and rapidly increasing computing power of computers, this method can be very helpful in situations where it is not possible to carry out a classical experiment. However, one should take into account the necessity of a good preparation of the model (including description of interactions in the system), because the quality of the results will depend on this.

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6.3 Reconstruction of particle size distribution based on a finite number of distribution's moments in the Matlab environment

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KEYWORDS: distribution reconstruction, distribution's moments, Matlab.

Abstract

The moment method is very effective and convenient for solving the population balance, however its disadvantage is the lack of knowledge about the statistical distribution of particle size. This inconvenience poses a challenge to reconstruct these distributions, which is the goal of the work.

Over the years, various attempts have been made to deal with this issue. This work focuses on the analysis of reconstruction based on predetermined formulas of statistical functions, and at a later stage on the reconstruction based on the "statistically most likely" [1] function and a new function. For this purpose, the Matlab environment and the numerical procedures in it were used.

Based on the calculations made, interesting conclusions about the use, advantages and limitations of the above methods were obtained. It was found that simple statistical relationships are useful only in a narrow group of distributions of a simple character, while distributions of more complex shape should be solved on the basis of more complex relationships. The method "statistically most likely" and new function were compared. The first method better maps the distribution of variability in the linear scale, while the second method in the logarithmic scale. The methods also differ in that the "statistically most likely" method is less sensitive to the initial parameters in the numerical procedure, but more sensitive to the integration range, while the new function is almost insensitive to the integration range, but sensitive to the initial values. During the calculations, it was decided to focus on adjusting the logarithms of the differences in moments. Based on the experience, it was found that the most universal numerical procedure was the "Levenberg-Marquardt" algorithm.

In summary, the numerical procedures used have the potential to be used in CFD programs as an extension to population balance settlement procedures. The procedures created would help to assess the process in terms of particle size, which can be particularly useful in the powder industry.

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Introduction

The issue of reconstruction of statistical distribution based on a finite number of moments in mathematics is known as the problem of moments where the moment m_i is:

$$m_j = \int_0^\infty L^j f(L) \, dL, \quad \text{for} \, j = 0, 1, \dots, N - 1 \tag{6.3.1}$$

where *L* is particle size and f(L) is number distribution of particle size.

The problem of moments was first mentioned in Chebyshev [2]. The difficulty of solving it arises from the fact that the problem is ill-conditioned, just like the problem of Hausdorff moments [3,4,5]. Despite these limitations, reconstruction attempts were made on the basis of the knowledge of a finite number of moments. The simplest approach is to assume a distribution form among known statistical functions and to match constants based on up to three first moments. This method of solving will be moved first. A more difficult approach, but more accurate is the adjustment of parameters to new functions, where one of the first is the Pope function [6]. More advanced proposal for particle size distribution was presented by Bałdyga and Orciuch [1].

Methods

Basic statistical functions In order to solve the problem of reconstruction of the distribution, the simplest approach is to assume the form of a known statistical function or their superposition. For this purpose, it is best to use functions such as Gaussian normal distribution, half-normal distribution, log-normal distribution, etc. Such distributions can be calculated on the basis of the maximum of three first moments. And so for the basic functions we get the following patterns [7]:

$$\overline{L} = \frac{m_1}{m_0} \tag{6.3.2}$$

$$c_{\nu} = \sqrt{\frac{m_0 m_2}{m_1^2} - 1} \tag{6.3.3}$$

$$\sigma = \overline{L}c_{\nu} \tag{6.3.4}$$

where \overline{L} is arithmetical mean, c_v is coefficient of variation and σ is standard deviation.

1. Gaussian normal distribution (calculated from moments: m_0, m_1, m_2):

$$f(L) = \frac{1}{\sigma\sqrt{2\pi}} \exp\left(-\frac{\left(L - \overline{L}\right)^2}{2\sigma^2}\right)$$
(6.3.5)

2. Half-normal distribution (calculated from moments: m_0, m_1, m_2):

$$\phi = \sqrt{\frac{\pi - 2}{2\sigma^2}} \tag{6.3.6}$$

$$f(L) = \frac{2\phi \exp\left(\frac{-L^2\phi^2}{\pi}\right)}{\pi}$$
(6.3.7)

where ϕ is a auxiliary parameter for half-normal distribution.

3. Log-normal distribution (calculated from moments: m_0, m_1, m_2):

$$\sigma_g = \exp\left(\sqrt{\ln(c_v^2 + 1)}\right) \tag{6.3.8}$$

$$\overline{L}_g = \frac{L}{\exp\left(0.5\ln^2\sigma_g\right)} \tag{6.3.9}$$

$$f(L) = \frac{1}{L \ln \sigma_g \sqrt{2\pi}} \exp\left(-\frac{\ln^2\left(\frac{L}{\overline{L}_g}\right)}{2ln^2 \sigma_g}\right)$$
(6.3.10)

where $\sigma_{\rm g}$ is natural logarithm of standard deviation and $\bar{L}_{\rm g}$ is natural logarithm of mean.

4. Gamma function (calculated from moments: m_0, m_1, m_2):

$$\mu = \frac{\bar{L}^2}{\sigma^2} \tag{6.3.11}$$

$$\Gamma(\mu) = \int_0^\infty z^{\mu-1} e^{-z} dz$$
 (6.3.12)

$$f(L) = \frac{\mu^{\mu} L^{\mu-1} \exp\left(-\frac{\mu L}{\bar{L}}\right)}{\Gamma(\mu) \bar{L}^{\mu}}$$
(6.3.13)

where μ is a shape parameter.

5. Exponential function (calculated from moments: m_0, m_1):

$$f(L) = \frac{\exp\left(-\frac{L}{\tilde{L}}\right)}{\tilde{L}}$$
(6.3.14)

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6. Rayleigh's function (calculated from moments: m_0, m_1):

$$s = \overline{L} \sqrt{\frac{2}{\pi}} \tag{6.3.15}$$

$$f(L) = \frac{L \exp\left(-\frac{0.5L^2}{s^2}\right)}{s^2}$$
(6.3.16)

where *s* is standard deviation for Rayleigh's function.

"Statistically most-likely" function The method "statically most-likely" proposed by Bałdyga and Orciuch [1] based on the work of Pope [6] allows for effective reconstruction of the distribution for cases where we can obtain a function whose peaks are wide. The form of the function is presented as below:

$$f(L) = B_0 \exp\left(\sum_{i=0}^N A_i L^i\right)$$
(6.3.17)

The constant B_0 can be combined with the constant A_0 , which gives us:

$$f(L) = \exp\left(\sum_{i=0}^{N} A_i L^i\right)$$
(6.3.18)

The constant A_0 in the equations above have different values then in equation (6.3.17), it is advisable to use the second relationship without the constant B_0 .

Based on the knowledge of N moments from m_0 to m_{N-1} , we can calculate the values of N coefficients A_i $(A_0, A_1, ..., A_{N-1})$ from the following systems of equations:

$$\int_{0}^{\infty} L^{j} \exp\left(\sum_{i=0}^{N} A_{i} L^{i}\right) dL - m_{j} = 0, \quad j = 0, 1, \dots, N - 1$$
(6.3.19)

Alternatively, in case of wide distribution, it is recommended to change the system of equations as below:

$$\ln\left[\int_{0}^{\infty} L^{j} \exp\left(\sum_{i=0}^{N} A_{i} L^{i}\right) dL\right] - \ln m_{j} = 0, \quad j = 0, 1, \dots, N - 1$$
(6.3.20)

In order to optimize calculations, normalization is recommended because better numerical convergence is obtained for numbers close to one [8]. To this end, we will use the following normalization scheme:

We introduce the moments m_i according to the dependencies below.

• 1st stage:

$$m_j' = \frac{m_j}{m_0}, \quad j = 0, 1, \dots, N-1$$
 (6.3.21)

Then, change the moments m_i to m_i as below.

• 2nd stage:

$$m_j'' = \frac{m_j'}{(m_1')^j}, \quad j = 0, 1, \dots, N-1$$
 (6.3.22)

Renormalized formula reads:

$$f(L) = \frac{m_0^2}{m_1} \exp\left(\sum_{i=0}^N A_i \left(L\frac{m_0}{m_1}\right)^i\right)$$
(6.3.23)

New function The third approach is the distribution developed on the basis of a log-normal distribution and "statistically most likely distribution" presenting as follows:

$$f(L) = \frac{1}{L} \exp\left[\sum_{i=0}^{N} A_i (\ln L)^i\right]$$
(6.3.24)

This distribution is particularly well suited to the bi- or multi- modal distributions where the peaks are very narrow. However, for the equation (6.3.24) presented above, numerical convergence is difficult to achieve, which is why we decided to use the property of a logarithm to transform it into a form (6.3.25):

$$f(L) = \frac{1}{L} \exp\left[A_0 - \sum_{i=1}^{\frac{N}{2}-1} A_i \left(\ln L + B_i\right)^{2i}\right]$$
(6.3.25)

Where A_0 , A_i , B_i are constants of the function.

First stage of normalization, eq. (6.3.21), was applied on the function eq. (6.3.25). Renormalized formula reads:

$$f(L) = m_0 \frac{1}{L} \exp\left[A_0 - \sum_{i=1}^{\frac{N}{2}-1} A_i \left(\ln L + B_i\right)^{2i}\right], \text{ for } j = 0, 1, \dots, N-1 \quad (6.3.26)$$

Description of numerical methods

Basic statistical functions The program reconstructing distributions based on basic statistical functions uses the dependence (6.3.2–6.3.16) and basic arithmetic operations and do not need to be explained.

"Statistically most-likely" function The program solving the "statistically most likely" distribution was written in the Matlab environment and uses mainly the Optimization Toolbox and the numerical procedures implemented there. The main challenge during the creation of this program was the selection of appropriate numerical procedures in order to make calculations and the selection of key parameters from the point of view of the calculation process. The decisive factors are:

Three different forms of the system of equations were considered:

$$\int_{L_{min}}^{L_{max}} L^{j} \exp\left(\sum_{i=0}^{N} A_{i}L^{i}\right) dL - m_{j}^{\prime\prime} = 0, \text{ for } j = 0, 1, \dots, N-1$$
(6.3.27)

$$\ln\left[\int_{L_{min}}^{L_{max}} L^{j} \exp\left(\sum_{i=0}^{N} A_{i} L^{i}\right) dL\right] - \ln m_{j}^{\prime\prime} = 0, \text{ for } j = 0, 1, \dots, N-1 \qquad (6.3.28)$$

$$\frac{\int_{L_{min}}^{L_{max}} L^{j} \exp\left(\sum_{i=0}^{N} A_{i} L^{i}\right) dL}{m_{j}^{\prime\prime}} - 1 = 0, \text{ for } j = 0, 1, \dots, N - 1$$
(6.3.29)

In the case of functions with a simple form and values of normalized moments close to one, the equation (6.3.27) is faster for calculations and more accurate. However, for the cases where the normalized moments were still far from unity, the equation (6.3.28) turned out to be better, which allows for greater numerical convergence. Equation (6.3.29) was of marginal significance, sometimes serving as a transition element between equation (6.3.27) and (6.3.28), being optimal for the class of functions between the restriction for (6.3.27) and (6.3.28).

At the stage of calculations three different algorithms implemented in the Matlab environment were tested: Levenberg-Marquardt, trust-region-dogleg and trust-region. All of them are large-scale algorithms. Based on the calculations, it was found that the most universal and the fastest numerical procedure was the Levenberg-Marquardt algorithm, which focuses on searching a direction leading to minimum sum of squares of differences, which was especially effective for the eq. (6.3.28). The second algorithm was trust-region-dogleg, which found a narrow application for some functions that reach a minimum close to zero between peaks, and are calculated only according to equation (6.3.27). The trust-region has proved ineffective, it is not recommended to use this method.

We were using a implemented function integral which is based on global adaptive quadrature mechanism. This method gave us fast results with sufficient precision.

The most difficult element in the "statistically most likely" method turned out to be the selection of integration limits L_{min} and L_{max} , which determined

convergence or lack thereof. For this purpose, a distribution based on basic statistical functions was used to initially estimate the integration limits and improve them until a satisfactory convergence was achieved. The initial values of A_i were tested in different variants, depending on the set of moments. However, after many attempts, it was found that the values equals to zero are the most universal, because in almost every case it allowed for numerical convergence. In the narrow distributions, the start parameters were selected by trial and error.

New function The program reconstructing the proposed function has been written in the same environment and uses the same procedures as the "statistically most likely" distribution program. The creation of the program consisted in the selection of appropriate numerical procedures in order to make calculations with the appropriate choice of parameters as in the previous method. The decisive factors are:

$$\ln\left[\int_{L_{min}}^{L_{max}} L^{j-1} \exp\left(A_0 - \sum_{i=1}^{\frac{N}{2}-1} A_i \left(\ln L + B_i\right)^{2i}\right) dL\right] - \ln m_j' = 0, \text{ for } j = 0, 1, \dots, N-1$$
(6.3.30)

$$\frac{\int_{L_{min}}^{L_{max}} L^{j-1} \exp\left[A_0 - \sum_{i=1}^{\frac{N}{2}-1} A_i \left(\ln L + B_i\right)^{2i}\right] dL}{m_j'} - 1 = 0, \text{ for } j = 0, 1, \dots, N-1$$

(6.3.31)

In almost every case the equation (6.3.30) was proved to be effective, the meaning of eq. (6.3.31) was marginal. Only the first stage of normalization eq. (6.3.21), was used, however it is optional and does not significantly affect the speed and accuracy of calculations. It was used almost entirely from the Levenberg-Marquardt algorithm, due to its versatility and the ability to solve redefined systems in order to validate reconstruction results.

The numerical integration limits, in contrast to the "statistically most likely" method, could be roughly chosen based on the orders of predicted quantities, which can be easily estimated on the basis of basic statistical functions. The most difficult was the selection of initial values that had to be selected by trial and error, but in most cases, the constant A_i was worth choosing at a level close to unity beyond the constant A_0 , which could be larger. And the constant B_i was close to the logarithm of the natural inverse of the mean value. The accuracy of solving the system of equations was similar to the method "statistically most likely" in the same form of the system under consideration.

Results

Basic statistical functions The table 6.3.1 presents the values of the test distribution moments, which are indicated in the charts as originals. They served as a material to verify the effectiveness of the previously mentioned methods of reconstruction of distribution. Distribution's moment data sets (Tab. 6.3.1) were an

Set	$m_0\left(rac{1}{\mathrm{m}^3} ight)$	$m_1\left(rac{\mathrm{m}}{\mathrm{m}^3} ight)$	$m_2\left(rac{\mathrm{m}^2}{\mathrm{m}^3} ight)$	$m_3\left(rac{\mathrm{m}^3}{\mathrm{m}^3} ight)$	$m_4\left(rac{\mathrm{m}^4}{\mathrm{m}^3} ight)$	$m_5\left(rac{\mathrm{m}^5}{\mathrm{m}^3} ight)$	$m_6\left(rac{\mathrm{m}^6}{\mathrm{m}^3} ight)$	$m_7\left(rac{\mathrm{m}^7}{\mathrm{m}^3} ight)$
1	7.78E+08	5.07E+05	3.83E+02	3.14E-01	2.78E-04	2.66E-07	2.76E-10	3.10E-13
2	1.22E+10	1.30E+06	5.14E+02	5.61E-01	8.21E-04	1.32E-06	2.25E-09	3.97E-12
3	4.19E+21	3.50E+12	2.92E+03	2.45E-06	2.05E-15	1.72E-24	1.45E-33	1.22E-42
4	2.00E+14	4.12E+07	9.62E+00	2.47E-06	6.91E-13	2.24E-19	1.09E-25	1.09E-31

Table 6.3.1: Sets of distribution's moments.

alyzed. Statistical distributions were reconstructed according to formulas (6.3.2-6.3.16) based on these data. The calculated values are compiled in the form of table 6.3.2 and figures 6.3.1-6.3.8:

 Table 6.3.2: Reconstruction results with basic statistical functions for moment sets 1–4.

Data/set	1	2	3	4
$\overline{m_0\left(\frac{1}{m^3}\right)}$	7.78E+08	1.22E+10	4.19E+21	2.00E+14
$m_1\left(\frac{m}{m^3}\right)$	5.07E+05	1.30E+06	3.50E+12	4.12E+07
$m_2\left(\frac{m^2}{m^3}\right)$	3.83E+02	5.14E+02	2.92E+03	9.62E+00
$c_v(-)$	3.99E-01	1.65E+00	3.36E-02	3.65E-01
$\phi\left(\frac{1}{m}\right)$	2.91E+03	4.31E+03	2.69E+10	1.00E+07
$\mu(m^2)$	6.29E+00	3.66E-01	8.86E+02	7.50E+00
s(m)	5.20E-04	8.47E-05	6.66E-10	1.64E-07
$\sigma(m)$	2.60E-04	1.75E-04	2.81E-11	7.52E-08
σ_g (m)	1.47E+00	3.15E+00	1.03E+00	1.42E+00
$\overline{\tilde{L}}(m)$	6.52E-04	1.06E-04	8.35E-10	2.06E-07
$\bar{L}_{g}(m)$	6.05E-04	5.50E-05	8.35E-10	1.93E-07

Figures 6.3.1–6.3.8 show the result of reconstruction with basic statistical functions compared to the original distributions with moments listed in Tab. 6.3.1. The results are presented in the form of density of distributions, which is defined as distribution function f(L) divided by m_0 . As we can see all of basics functions are able to reconstruct only one peak. The maximum value of reconstructed dis-

tribution is different in all cases. For example the highest values provides the lognormal function. The most useful functions are gaussian, log-normal and gamma. The reconstruction based on exponential function are the worst. The main drawback of half-normal and exponential distributions is that the maximum value of this function is for L = 0.



Figure 6.3.1: Reconstruction results with basic statistical functions for moment set 1.

Figure 6.3.1 shows that distributions: gaussian, log-normal, gamma function and to some extent the Rayleigh's function are able to reconstruct the peak in the wider pick of the two-modal distribution. Exponential and half-normal distribution are not completely similar to the original function.

When the distribution's picks are close to each other (Fig. 6.3.2) the Rayleigh's function best reconstructs the peak in the larger size range, and the log-normal peak for smaller sizes. The other functions are not in any way similar to the original function.



Figure 6.3.2: Reconstruction results with basic statistical functions for moment set 2.



Figure 6.3.3: Reconstruction results with basic statistical functions for moment set 3.

Third set of moments describes the one-pick narrow distribution shown on fig. 6.3.3. The gaussian and log-normal distributions ideally reconstruct the original one. The Rayleigh's function artificially blurs the peak into a wide range, while the half-normal one represents an image not entirely similar to the original. The gamma distribution was omitted, because the data caused numerical errors in the reconstruction.



Figure 6.3.4: Reconstruction results with basic statistical functions for moment set 4.

One-pick wide distribution is shown on figure 6.3.4. The gaussian and gamma distributions present the results closest to the original, not much worse result slightly overestimating the peak and moving it towards smaller sizes presents the log-normal distribution. The Rayleigh's function understates the peak and blurs it significantly to smaller sizes. Half-normal and exponential distributions are completely different than the original.

"Statistically most likely" function and new function comparison

Figure 6.3.5 shows that both methods reconstruct the wider peak in a larger size in a good way. On the other hand, in the smaller size range, the new function is evidently better for this data set, reconstructing the second peak. Maximum value of this peak, however, is overestimated.



Figure 6.3.5: Reconstruction results with "statistically most likely" and new function for moment set 1.

In the case of second set of distribution's moments, the methods return quite different results (Fig. 6.3.6). The "statistically most likely" function is closer to the peak for larger sizes, and the new function better captures the second peak for smaller sizes. But both methods cannot recognize two picks which are close to each other.



Figure 6.3.6: Reconstruction results with "statistically most likely" and new function for moment set 2.



Figure 6.3.7: Reconstruction results with "statistically most likely" and new function for moment set 3.

As can be seen from figure 6.3.7, both methods present an almost identical and good result, when distribution has one, narrow pick.

Figure 6.3.8 presents reconstruction of wide, one-pick distribution. "Statistically most likely" method fails only for smallest sizes. New function matches only the diminishing part of the original distribution.



Figure 6.3.8: Reconstruction results with "statistically most likely" and new function for moment set 4.

Tables 6.3.3–6.3.6 present the reconstruction results using the "statistically most likely" function (SML) reconstructed from the first 8 distribution's moments and a new function reconstructed from the first 7 distribution's moments with relative errors. Tables 6.3.7–6.3.8 show the calculated values of constants in reconstructed distributions, eq. (23) and eq. (26), while tables 6.3.9–6.3.10 show the integration limits used in the calculations.

 Table 6.3.3: Reconstruction results with "statistically most likely" and new function for moment set 1.

Moment	0	1	2	3	4	5	6	7
Original	7.78E+08	5.07E+05	3.83E+02	3.14E-01	2.78E-04	2.66E-07	2.76E-10	3.10E-13
SML	7.78E+08	5.07E+05	3.83E+02	3.14E-01	2.78E-04	2.66E-07	2.76E-10	3.10E-13
Error (%)	1.63E-11	3.29E-11	7.06E-11	1.63E-10	3.86E-10	9.08E-10	1.55E-09	3.22E-09
New	7.78E+08	5.07E+05	3.83E+02	3.14E-01	2.78E-04	2.66E-07	2.76E-10	-
Error (%)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	-3.56E-13	-

 Table 6.3.4: Reconstruction results with "statistically most likely" and new function for moment set 2.

Moment	0	1	2	3	4	5	6	7
Original	1.22E+10	1.30E+06	5.14E+02	5.61E-01	8.21E-04	1.32E-06	2.25E-09	3.97E-12
SML	1.22E+10	1.30E+06	5.14E+02	5.61E-01	8.21E-04	1.32E-06	2.25E-09	3.96E-12
Error (%)	-1.59E-02	1.43E-02	-2.91E-02	6.25E-03	4.08E-02	-5.28E-03	-5.56E-02	2.93E-02
New	1.22E+10	1.30E+06	5.14E+02	5.61E-01	8.21E-04	1.32E-06	2.25E-09	-
Error (%)	0.00E+00	0.00E+00	0.00E+00	1.78E-13	-1.19E-13	0.00E+00	4.42E-13	-

 Table 6.3.5: Reconstruction results with "statistically most likely" and new function for moment set 3.

Moment	0	1	2	3	4	5	6	7
Original	4.19E+21	3.50E+12	2.92E+03	2.45E-06	2.05E-15	1.72E-24	1.45E-33	1.22E-42
SML	4.19E+21	3.50E+12	2.92E+03	2.45E-06	2.05E-15	1.72E-24	1.45E-33	1.22E-42
Error (%)	-1.12E-04	1.57E-04	3.99E-04	-1.01E-03	8.88E-04	-6.24E-04	4.56E-04	-1.58E-04
New	4.19E+21	3.50E+12	2.92E+03	2.45E-06	2.05E-15	1.72E-24	1.45E-33	-
Error (%)	-3.11E-05	2.18E-05	3.29E-04	-9.25E-04	1.05E-03	-5.67E-04	1.20E-04	-

 Table 6.3.6: Reconstruction results with "statistically most likely" and new function for moment set 4.

Moment	0	1	2	3	4	5	6	7
Original	2.00E+14	4.12E+07	9.62E+00	2.47E-06	6.91E-13	2.24E-19	1.09E-25	1.09E-31
SML	2.00E+14	4.11E+07	9.63E+00	2.47E-06	6.91E-13	2.23E-19	1.09E-25	1.09E-31
Error (%)	-1.39E-01	3.94E-01	-1.11E-01	-2.84E-01	-3.81E-02	2.78E-01	-1.28E-01	3.26E-02
New	2.00E+14	4.12E+07	9.62E+00	2.47E-06	6.91E-13	2.24E-19	1.09E-25	-
Error (%)	0.00E+00	0.00E+00	0.00E+00	0.00E+00	2.92E-13	0.00E+00	0.00E+00	-

Table 6.3.7: Reconstructed parameters for "statistically most likely function".

Set	A ₀ (-)	A ₁ (-)	A ₂ (-)	A ₃ (-)	A ₄ (-)	A ₅ (-)	A ₆ (-)	A ₇ (-)
1	8.912E-1	-4.377E+1	1.430E+2	-1.855E+2	1.212E+2	-4.250E+1	7.604E+0	-5.429E-1
2	-7.654E-1	2.563E+0	-3.283E+0	9.891E-1	-1.360E-1	9.575E-3	-3.354E-4	4.631E-6
3	-6.389E+1	2.094E+1	3.899E+1	2.763E+1	2.157E+1	-5.273E+0	-2.377E+1	-1.373E+1
4	-2.785E+0	4.595E+0	-7.824E-1	-1.079E+0	7.892E-2	1.266E-2	3.535E-4	-1.366E-4

Set	A ₀ (-)	$B_1(-)$	A ₁ (-)	$B_2(-)$	A ₂ (-)	B ₃ (-)	A ₃ (-)
1	2.816E-1	7.298E+0	6.503E+0	7.240E+0	-7.742E-1	7.742E+0	5.700E-2
2	-1.355E+0	9.092E+0	1.351E+0	8.449E+0	-8.929E-1	8.368E+0	1.495E-1
3	1.880E+0	2.090E+1	3.359E+2	2.094E+1	1.081E+4	2.143E+1	-2.685E+1
4	1.764E-1	1.524E+1	1.044E+1	1.498E+1	-5.744E+0	1.490E+1	1.010E+0

 Table 6.3.8: Reconstructed parameters for new function.

Table 6.3.9: Limits of integration for "statistically most likely function".

Set	Lower limit of integration <i>L_{min}</i> (m)	Upper limit of integration L_{max} (m)
1	0	3.26E-03
2	0	2.21E-03
3	0	2.09E-09
4	0	2.06E-06

Table 6.3.10: Limits of integration for new function.

Set	Lower limit of integration L_{min} (m)	Upper limit of integration L_{max} (m)
1	1.00E-07	1.00E-02
2	1.00E-09	1.00E-02
3	1.00E-10	1.00E-08
4	1.00E-11	1.00E-04

Conclusions

Two advanced methods were considered: "statistically most likely" and new function. The applied methods of the reconstruction, allow for a relatively effective reconstruction, with the "statistically most likely" method being faster compared to the wide peaks, when we do not have a large discrepancy with respect to unity for the moments after the 2nd stage of normalization, and the original function fulfills its function in the remaining cases. Thanks to this, both methods complement each other and have their own advantages and limitations. In the case of the "statistically most likely" method, the main limitation is the difficulty in choosing the right integration limits, and in the second place the initial values. On the other hand, new function is very flexible in relation to the integration limiits and only the appropriate selection of initial values is required. Both methods can be very accurate. The basic statistical functions do not allow reconstruction with proper accuracy, however, it is useful to estimate the start parameters and integration limits for more advanced reconstruction methods.

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6.4 Properties of 3Y-TZP/Al₂O₃ composite as a solid electrolyte material for a new generation of electrochemical devices

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Abstract

In the presented study, 3Y-TZP sinters with 1, 5, 10 and 15 mol% of Al_2O_3 were prepared in two different ways from a 3-YSZ powder synthesized using the citrate process. The first method involved the introduction of aluminum via chemical synthesis, while the second one was based on the impregnation of the 3-YSZ power with aluminum nitrate. All samples were sintered at the temperature of 1773 K. The microstructure, chemical and phase composition, and electrical properties of the prepared composites were investigated. The findings indicate that the conductivity of the grain interiors in 3Y-TZP/ Al_2O_3 sinters measured at 573 K is ca. 30-74% higher than that of grain boundaries for all investigated composites. At 723 K, this tendency is reversed – the conductivity of grain boundaries is ca. 18-63% higher than that of the grain interiors. A higher alumina content results in reduced total conductivity for the 3Y-TZP samples modified with alumina in either of the two investigated ways.

Introduction

Solid oxide fuel cells (SOFCS) are currently the most efficient devices used for the conversion of chemical fuels directly into electrical power [1–4]. The type of SOFCS that would prove the most beneficial if they were to achieve widespread popularization are planar cells. In this type, a single cell consists of an oxide electrolyte sandwiched between an anode and a cathode. To achieve a high-power output of a single cell, the ohmic losses in the layer placed between the cathode and the anode should be minimized. Hence, electrolyte materials that ensure fast oxide ion transport must be used [3–5].

Due to the specific operating conditions of ceramic fuel cells, the criteria for the preselection of electrolyte materials are far more strict than in the case of other soFC components. Hence, the electrolyte should be characterized by the

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following properties: long-term stability in reducing and oxidizing atmospheres, oxide ion conductivity higher than $10^{-2} \,\mathrm{S \, cm^{-1}}$ at the cell's operating temperature, good mechanical strength, high interfacial gas-solid reaction kinetics, high density. In addition, it cannot exhibit any porosity, which would cause the leakage of oxidant and fuel gases, and it should be easy to manufacture and inexpensive to maintain [2–5].

The most commonly used oxygen-conducting solid electrolytes are zirconiabased materials. They can take on of three crystal forms depending on temperature: monoclinic (at room temperature), tetragonal (above 1443 K) and cubic (at 2643 K and above). It was discovered that doping pure zirconium oxide with lower valance oxides such as MgO, La₂O₃, CaO, Sc₂O₃ and Y₂O₃ reduces the amount of the monoclinic phase at room temperature and favors the formation of the cubic and tetragonal ones [5–6]. Furthermore, the addition of one of these dopants increases conductivity due to the creation of additional load carriers according to the following equation (6.4.1) [5]:

$$\operatorname{Me}_2\operatorname{O}_3 \xrightarrow{\operatorname{ZrO}_2} 2\operatorname{Me}_{\operatorname{Zr}}' + \operatorname{V}_{\operatorname{O}}^{\bullet\bullet} + 3\operatorname{O}_{\operatorname{O}}^{X}$$
 (6.4.1)

where V_0 represents the oxygen vacancy for every two atoms of metal (Me) incorporated into the lattice.

Currently the most common material used as a soFC electrolyte is yttriastabilized zirconia (YSZ). Three types of such materials may be distinguished depending on the structure: fully stabilized zirconia (FSZ), partially stabilized zirconia (PSZ) and tetragonal zirconia polycrystals (Y-TZP). The first type (FSZ) has a cubic structure and exhibits high ionic conductivity at elevated temperatures. Regardless of this advantage, its widespread commercial application is limited due to its high operating temperature (1073–1273 K), low mechanical strength and poor resistance to thermal shocks. The third type (Y-TZP) with 1 to 3 mol% Y_2O_3 content has submicron-sized tetragonal grains and is known as ceramic steel on account of its very high mechanical strength and fracture toughness [2–3,7–9].

The reasons why the 3Y-TZP composite is applied as an electrolyte in intermediate-temperature solid oxide fuel cells (IT-SOFCS) instead of cubic FSZ include its significantly higher mechanical strength and its lower activation energy of electrical conductivity, which is associated with higher electrical conductivity at temperatures below 973 K. At moderate temperatures below 973 K, the grain interior of 3Y-TZP has higher conductivity than that of FSZ or PSZ. However, the total conductivity of 3Y-TZP is lower due to the high contribution of grain boundary resistivity, known as the blocking effect [9–14].

In general, the literature on the subject proposes two reasons for the blocking effect. One of them is related to the presence of impurities (mainly silicon) that are segregated at grain boundaries. Silicon can form a glassy layer that surrounds the zirconia grains. The formation of this continuous glassy layer makes
it difficult for oxygen ions to move across grain boundaries in this insulating layer [12,15,18]. The second reason for this phenomenon is the segregation of yttrium cations at the ZrO_2 grain boundaries, which results in the formation of a Schottky barrier [11,16-18].

Many efforts have been made to reduce the blocking effect in 3Y-TZP. It was found that when alumina is added above its solubility limit to the zirconia material, it acts as a silicon scavenger. Furthermore, this allows the mechanical strength of such an electrolyte to be improved and to make it suitable as a support material in IT-SOFC [19–21].

The aim of the presented work was to determine how the addition of 1, 5, 10 and 15 mol% of Al_2O_3 , which is an insulator itself, affects the ionic conductivity of a 3Y-TZP material synthesized using the citrate process.

Materials and methods

Synthesis of 3-vsz powder and preparation of 3v-tzp/**Al**₂**O**₃ **sinters** Composite 3v-tzp sinters containing 1, 5, 10 and 15 mol% of Al₂O₃ were obtained from a 3-vsz powder synthesized using the citrate method. Two types of samples were prepared.

In the case of the first type (series C), aluminum was introduced during the chemical synthesis of the 3-vsz powder. The saturated solutions of aluminum, yttrium and zirconyl nitrates were mixed at the appropriate ratio. The required amount of citrate acid was added and the whole mixture was stirred at 343 K for 8 hours. The solution was then dried in the oven at 523 K for 24 hours to obtain a brown gel. The final product underwent 1hour of thermal treatment in air at 873 K. Four samples were obtained using the described procedure (alumina content indicated in parentheses): C-1 (1%), C-5 (5%), C-10 (10%), and C-15 (15%). A sample without any alumina content (C-0) was used for reference.

For the second type (series I), the 3-vsz powder was obtained as in the case of series C, with one exception – aluminum nitrate was not used during synthesis. The obtained 3-vsz powder was ground in the mortar and then impregnated with the ethanol solution of aluminum nitrate. The prepared suspension was vigorously stirred at 323 K for 2 hours using an ultrasound stirrer and then dried in the oven at 373 K for 24 hours. The powders were calcined at 873 K for 1 hour in air. As before, four samples with different alumina content were obtained: I-1 (1%), I-5 (5%), I-10 (10%), and I-15 (15%).

In order to obtain sinters, all of the prepared powders were crushed in an agate mortar, milled in an attritor, and formed into disc pellets. Isostatic pressing was then applied to produce green bodies, which were subsequently sintered for 2 h in air at 1773 K.

Research methods Phase composition studies were performed via X-ray diffraction (xRD) using a Philips X'Pert Pro diffractometer. The HighScore Plus application coupled with the X'Pert diffractometer software, the PCPDFWIN database (v. 2.3), and ICSD identification cards were used to identify phases, while the content of each phase was determined using the Rietveld method.

Microstructural and chemical analyses were carried out using the Nova NanoSEM 200 (FEI Europe) scanning electron microscope combined with an energy-dispersive X-ray spectroscopic (EDAX) analyzer. Prior to morphological observations, the samples were polished.

The electrical conductivity of the samples was measured by means of electrochemical impedance spectroscopy (EIS) using a computer-controlled Solartron (FRA 1260 and dielectric interface 1294). For the EIS test, Pt paste was deposited on both sides of each disc and then fired at 973 K for 2 hours. Data were collected in the frequency range of 0.1 Hz–1 MHz over the temperature from 673 to 973 K and in increments of 323 K. The impedance spectra were analyzed using the ZPLOT software package provided by Solartron.

Results and discussion

Phase composition A study of the unmodified sinters and the ones modified with aluminum revealed that their phase composition varied depending on the aluminum content and the way in which it had been added to the 3Y-TZP material (Table 6.4.1). As an example, Fig. 6.4.1 shows the X-ray diffraction pattern of 3Y-TZP doped with 15 mol% of Al₂O₃ (C-15) obtained after 2 h of sintering in air at 1772 K.

	Detected					
Sample	t-ZrO ₂	$c-ZrO_2$	m -ZrO $_2$	corundum		
C-0	87.2	87.2	6.2	-		
C-1	85.4	85.4	7.9	-		
C-5	80.3	80.3	9.5	4.3		
C-10	77.1	77.1	7.4	8.3		
C-15	75.8	75.8	6.6	12.4		
I-1	74.6	74.6	21.1	-		
I-5	79.1	79.1	11.7	4		
I-10	72.9	72.9	15.1	7.3		
I-15	67.3	67.3	16.9	12.2		

Table 6.4.1: Relative mass fractions of phases formed after sintering
3Y-TZP and 3Y-TZP/Al2O3 materials.



Figure 6.4.1: The X-ray diffraction pattern of 3Y-TZP doped with 15 mol% of Al_2O_3 (C-15).

The tetragonal phase was predominant in all samples, and its mass fraction ranged from around 67 to 87%. In addition, certain amounts of the cubic and monoclinic phases were found. The amount of the monoclinic phase was considerably larger in the case of series I samples. The mass fraction of corundum in both series was slightly lower than what the nominal composition would suggest.

Microstructure

Figs 6.4.2 and 6.4.3 present the surface morphology of two types of samples with a 10 mol% Al content, namely C-10 and I-10.

As can be noticed, aluminum was distributed evenly in the sinter obtained via impregnation. In the sinter received by adding aluminum during the citrate process, black, isolated clusters had formed. These clusters were not distributed evenly. Grain size was similar in both cases, and it ranged from 0.2 to $0.5 \,\mu$ m. In some areas of the studied sinters, pores can be found. These pores had formed during sintering due to the presence of hard agglomerates.

6.4. Properties of 3Y-TZP/Al₂O₃ composite as a solid electrolyte material...



Figure 6.4.2: SEM micrographs of 3Y-TZP doped with $10 \mod \%$ of AI_2O_3 (C-10). Magnification of $\times 5000$ (a) and $\times 30000$ (b).



Figure 6.4.3: SEM micrographs of 3Y-TZP doped with 10 mol% of Al_2O_3 (I-10). Magnification of \times 5000 (a) and \times 30000 (b).

Electrochemical properties Electrical conductivity is a crucial property with regard to the application of a material as an electrolyte in sorcs. Fig. 6.4.4 shows an example of a Nyquist plot representing the impedance of the C-0 sinter and a scheme of the corresponding equivalent circuit.

The spectra were obtained at 573 K. Two partially overlapping circles that are displaced from the origin of the coordinate system can be distinguished. In accordance with the well-established interpretation, the semicircle located at the lowest frequencies was attributed to the transport properties of grain boundaries, while the second semicircle was attributed to the properties of the grain interior [22]. Electrical conductivity was calculated using the following equation (6.4.2):

$$\sigma = \frac{L}{R \cdot S} \tag{6.4.2}$$

where L represents sample thickness, R stands for total resistance, and S is the electrode area of the sample.



The Arrhenius plots shown in Fig. 6.4.5 represent the temperature dependences of the total conductivity of all studied sinters.

Figure 6.4.4: Nyquist plot recorded at 573 K for the C-0 sinter and the associated equivalent circuit.



Figure 6.4.5: Arrhenius dependence of total electrical conductivity (σ_i) of all studied samples.

Electrical conductivity increases with temperature, which confirms that these materials are characterized by a thermally activated process. The highest total conductivity in the entire temperature range was observed for the 3Y-TZP sinter which had not been modified with aluminum oxide (C-0) and for the sinter containing 1 mol% of aluminum introduced via chemical synthesis (C-1); the lowest values were observed for sinters C-10 and C-15. This can be explained by the fact that sinters C-0 and C-1 contain the highest mass fraction of tetragonal ZrO_2 (> 85%), while the mass fraction of this phase in sinters C-10 and C-15 is around 76–77% (Table 6.4.1). Slight differences in total conductivity were observed for the series of sinters for which aluminum was introduced via impregnation (I-1, I-5, I-10, I-15). One of the reasons for this is the uniform distribution of alumina in the matrix of the 3Y-TZP phase (Fig. 6.4.3), observed despite the different mass fractions of tetragonal zirconia in these composites (Table 6.4.1).

In conclusion, a higher alumina content resulted in reduced total conductivity in the investigated temperature range regardless of the method used to introduce aluminum into the 3Y-TZP material. This is illustrated in Fig. 6.4.6, which shows the electrical conductivity measured at 573 K for two series of samples. Sinters with aluminum added via the citrate process exhibited lower conductivity than the sinters synthesized through impregnation.



Figure 6.4.6: Dependence of electrical conductivity on AI_2O_3 content in the investigated sinters, as measured at 573 K.

Table 6.4.2 presents some of the values of electrical conductivity measured at 573 and 723 K for the grain interiors and grain boundaries in two series of the studied materials.

	Electrical conductivity (S/cm)					
	measurement at 573 K		measurement at 723 K			
Sample	grain interior	grain boundary	grain interior	grain boundary		
C-0	6.82×10^{-6}	6.94×10^{-6}	2.79×10^{-4}	5.24×10^{-4}		
C-1	4.34×10^{-6}	2.32×10^{-6}	1.65×10^{-4}	1.84×10^{-4}		
C-5	2.57×10^{-6}	1.79×10^{-6}	1.04×10^{-4}	1.26×10^{-4}		
C-10	1.18×10^{-6}	5.18×10^{-7}	2.87×10^{-5}	7.69×10^{-5}		
C-15	1.07×10^{-6}	2.84×10^{-7}	1.47×10^{-5}	3.22×10^{-5}		
I-1	4.94×10^{-6}	3.16×10^{-6}	1.61×10^{-4}	2.19×10^{-4}		
I-5	4.58×10^{-6}	2.17×10^{-6}	1.34×10^{-4}	2.30×10^{-4}		
I-10	3.16×10^{-6}	2.22×10^{-6}	1.18×10^{-4}	1.56×10^{-4}		
I-15	2.08×10^{-6}	1.08×10^{-6}	6.48×10^{-5}	1.47×10^{-4}		

Table 6.4.2: Constituents of electrical conductivity measured at 573 K and 723 Kfor two series of the investigated materials.

An analysis of the impedance spectra carried out at 573 K revealed that the conductivity of grain interiors was higher than that of grain boundaries in the case of all studied $3Y-TZP/Al_2O_3$ composites, which was not the case for the unmodified 3Y-TZP sinter. On the other hand, for the measurement temperature of 723 K the relation between conductivity values observed for the grain interior and grain boundaries was reversed.

Conclusions

In this study, composite 3Y-TZP sinters containing 1, 5, 10 and 15 mol% of Al_2O_3 were obtained from a 3-YSZ powder synthesized using the citrate method. Two series of samples were prepared. In the case of the first type, Al was added during the citrate process, while for the second type of samples Al was introduced via impregnation after the citrate process.

The tetragonal phase was predominant in all samples and certain amounts of the cubic and monoclinic phases were also found.

The conductivity of the grain interiors in 3Y-TZP/Al₂O₃ sinters measured at 573 K was ca. 30-74% higher than that of grain boundaries for all investigated composites. At 723 K, an opposite tendency was observed – the conductivity of grain boundaries was ca. 18-63% higher than that of the grain interiors. It was also evident that a higher alumina content was associated with reduced conductivity. Sinters with more than $1 \mod \%$ aluminum added via the citrate process were characterized by lower conductivity than the sinters synthesized through impregnation.

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6.5 Preparation and analysis of the surface of modified steel materials and their applications as a surface for endothelial cell culture

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Abstract

Endothelial cells are commonly used in modern laboratory research. They are widely applied in many fields of science, but they play their most important role in the biomedical engineering research. We are constantly working on the best ways to use endothelial cells to improve the properties of synthetic implants, such as biocompatibility with the patient's body.

Presented work concerns the use of 316L stainless steel materials for the cultivation of endothelial cells of HMEC-1 cell line in order to select the most appropriate parameters encouraging cells to adhere and grow. The first step in the modification of pure metal discs was to obtain the PEGDMA (polyethylene glycol dimethacrylate) layer by electropolymerization. Then carboxyl groups were attached to the polymer layer and process parameters were tested. The aim of second step was to make a reaction between the carboxyl groups from the surface of the steel discs and the amino groups from the aminoacids of the peptide with the REDV sequence that is recognized by endothelial cells as a suitable surface for adhesion and proliferation.

Modified materials were analyzed using goniometer, Fourier-transform infrared spectroscopy and bicinchoninic acid assay. Later, endothelial cells were cultured on the materials for 3 and 5 days. Then they were fixed and dyed with antibodies with fluorophore to visualize nuclei, vinculin and von Willebrand factor. The observation of visualized structures was carried out using a scanning confocal microscope. Finally, it was possible to assess the best conditions in which HMEC-1 line could anchor, develop and functionalize.

As a result of these tests, it was possible to see that endothelial cells grow better on the steel with peptide coating rather than on uncoated material. Adhesive sequences encourage cells to adhere and metabolize and higher concentration of REDV and higher parameters of carboxylation give better results of the analysis.

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Introduction

Nowadays, biomaterials are widely applied in medicine as a replacement for bone tissues, cartilage, hydrogels. It is possible because of the development of the interdisciplinary field of science which is tissue engineering [1]. The main subject of intensive research in this field is the selection of the appropriate material and its modification depending on the subsequent application. Its main purpose is to discover modern solutions that allow to regenerate or in some cases completely replace damaged tissues or organs.

The process of creation of biomaterials is mainly based on the coverage of suitable matrix constructed, i.e. from a polymer, ceramic or metal coating that encourage cells to adhere and develop on its surface and then to grow a confluent monolayer of cells previously taken from the patient's body. This way a hybrid material is created that can actively and for a long time exist and function in the patient's body [2]. However, this process is very complicated, because implants must be characterized by biocompatibility, lack of toxicity, and these are just a few of the many requirements that are demanded. Therefore, there is a growing necessity for finding biomaterials with the appropriate features [3].

Stainless steel is a family of steel alloys with a minimum mass of 10.5 % of chromium. It is characterized by high resistance to corrosion and high temperature and that is because of the presence of a thin layer of chromium (III) oxide on a surface that is impermeable to water and air. This layer is renewable because chromium in the steel reacts quickly with oxygen and humidity in the environment to recreate the oxide layer [4].

Stents are one of many examples of biomaterials applications in medicine. Stents are small tubes that help to treat damaged arteries in human body. They are used in angioplasty – this term refers to the procedure to introduce a small balloon with a stent into the body. The balloon is supposed to expand the lumen of the blocked vessel (artery) while the stent is to prevent the collapse of these walls after removing the balloon [5]. There are 3 types of stents: BMS (Bare metal stent), DES (Drug eluting stent) – stent that elutes the drug in the patient's body like everolimus, paklitaksel to block cell proliferation and prevent restenosis, BVS (Bioresorbable vascular stent) – i.e. polilactide [6].

Stent implantation is followed by some problems. Restenosis is a very important issue – this term refers to narrowing of the blood vessel previously subjected to stenting because of endothelial cell proliferation [7]. Corrosion of steel leads to nickel ions release which might have an influence on tissues. Moreover, the risk of thrombosis is rising after the implantation of foreign body into the blood vessel [8]. That is why it is very important to find a material with appropriate surface properties that will allow free growth of eukaryotic cells without showing toxic properties. Therefore the aim of the research was to determine the process parameters to modify the surface of stainless steel discs in order to obtain the good medium for endothelial cells growth. The aim of the research was to cover disks made of 316L stainless steel with a diameter of 14 mm and a thickness of 0.6 mm with a polymer coating containing covalently attached peptide molecules. REDV is one of the adhesive sequences – complex, dynamic protein containing integrin placed in the basic membrane. They form a connection between the cytoskeleton and the extracellular matrix. These sequences may include over 100 different proteins, which demonstrates the functional diversity. Von Willebrand Factor (vWF) is a glycoprotein involved in haemostasis and vinculin is a cytoskeletal protein associated with cell-matrix and cell-cell connections where it is one of several interacting proteins involved in anchoring F-actin to the membrane [9]. The analysis of these two proteins informs whether the cells adhere to the surface of material and may also allow to evaluate endothelial cell metabolism.

The first step of the research was to modify the surface of stainless steel discs in order to prepare them for later cell culture. Then, the HMEC-1 cell line was cultured on the materials. The next step was to label proteins and nuclei in order to analyze the growth and proliferation of cells on the materials with the use of scanning confocal microscope.

Materials and methods

The coating of steel with polymeric layer with the use of electropolymerization method was performed according to the protocol described in previous paper [7]. During electropolimerization, an electric field starts the decomposition of the initiator and radical polymerization of a substrate. A crosslinked PEGDMA film, that is the final product, should adhere to the surface of steel due to the fact that primary and secondary bonds are forming between the steel and polymer coating and interfacial contact is increased. The initial modification was based on polishing the disks (washing the discs with water and detergent, cleaning them using a sonicator and drying in an incubator at 40 °C). The first step in the modification of pure discs was to obtain the PEGDMA (polyethylene glycol dimethacrylate) (Sigma) layer by electropolymerization. For this purpose, 2 discs were hanged on wire and placed in vessels containing of sodium sulfate (Chempur) and ammonium persulfate (Sigma, 98%, reagent grade) dissolved in sulfuric acid (Chempur, 98 %) solution. The carbon electrode was connected to the "+" pole and the discs to the "-" pole. The vessel was placed on a magnetic stirrer, Tween®20 (Sigma, 0.05 % (v/v)), EGDMA (ethylene glycol dimethacrylate) (Sigma, 98%) and PEGDMA were added to the solution. The power supply was turned on so that the current was 0.03 A and the reaction was carried out for 30 min, then the materials were removed from the solution and rinsed with distilled water.

The aim of the next stage was to attach carboxyl groups to the polymer layer and to test the process parameters, such as the reaction time with acrylic acid and the concentration of acrylic acid. In a new vessel, a reaction solution was prepared followed by Tween®20, EGDMA and the appropriate amount of acrylic acid (Sigma, 99%) according to the table 6.5.1.

Electropolimerization time (min)	Final concentration of acrylic acid in reaction solution (% (v/v))	Volume of acrylic acid in reaction solution (mL)
5	1	0.735
30	3	2.205

 Table 6.5.1: Variants of modification of stainless steel discs.

The electropolymerization reaction was carried out for 5 or 30 minutes in a solution containing above concentration of acrylic acid. Subsequently, the materials were rinsed with distilled water, air dried for about 24 hours and annealed by placing them in a heater at 150 $^{\circ}$ C for 10 minutes.



Figure 6.5.1: Steel discs after the first step of modification.

The aim of step 2 was to make a reaction between the carboxyl (COOH) groups from the surface of the steel discs and the amino (NH_2) groups from the aminoacids of the peptide. The reaction between these groups is not easy, so a special method that is known and widely applied – the EDC (N-(3-dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride) (Sigma)/sulfo-NHs (N-hydroxysuccinimide) (Thermo Scientific) protocol – was used. The process includes two stages. In the first stage, a sulfo-NHs ester that easily reacts with the NH₂ group of the peptide was obtained. Two different concentrations of REDV peptide were used in order to choose the best one for cell proliferation.

In the next step the culture of HMEC-1 cell line was carried on the modified materials. HMEC (Human Microvascular Endothelial Cells) (LGC Standards) is isolated from human tissue transfected with the plasmid vector. HMEC cells are adherent and produce proteins such as von Willebrand factor (vWF) or vinculin,



Figure 6.5.2: The second step of modification of stainless steel.



Figure 6.5.3: Scheme of 24-well plate with variants of modification of stainless steel. where: ss - stainless steel without modification; 5', 30' – time of electropolimerization reaction with acrylic acid; COOH – disks functionalized with carboxyl groups; REDV 5 mM, 0.5 mM – disks functionalized with peptide with REDV sequence of appropriate concentration.

which enable the use of this line as a model for the determination of endothelial cell growth and activity. As well as the popular HUVEC cells (*Human Umbilical Vein endothelial cells*), they are used to grow on polymeric and metal materials to strengthen the biocompatibility of prostheses and implants used in medical procedures [10].

Firstly, HMEC-1 cells were thawed, suspended in MCDB-131 medium (Gibco[®] by Life Technologies) supplemented according to the provider's protocol and incubated in 5 % CO₂, 37 °C. After two days, the cells reached confluence and were subcultured in the ratio 1:4. Four days after the passage, the cells were tripsinized, centrifuged and suspended in the fresh MCDB medium. Each tested material: ss, ss-COOH variants and ss-REDV variants were placed in a well plate and seeded with HMEC-1 cells in a concentration of 8 × 10⁴ cells/mL.

The culture was carried out for 3 and 5 days to discover whether longer time of culture results in better growth and proliferation of endothelial cells. After the culture, the materials were labelled with antibodies. The primary antibody binds to a specific antigen, which in case of tests performed were the proteins produced in HMEC-1 cells – vinculin and vWF, and the secondary antibodies bind to primary antibodies. Both anti-vinculin and anti-vWF primary mouse monoclonal antibodies were compatible with goat anti-mouse secondary antibodies that were coupled with fluorophores, respectively, Alexa Fluor 488[®] (ThermoFisher Scientific) fluorophore for vinculin and Alexa Fluor 647[®] (ThermoFisher Scientific) for vWF. The nuclei were visualized with the use of DAPI (4′,6-diamidino-2-phenylindole) (Invitrogen).

The procedure of labelling with antibodies lasted 3 days. Firstly, the materials were prepared for incubation with the first vinculin antibody solution (10 μ g/mL) (Abcam, ab18058) for 24 h at 4 °C. The next day the materials were rinsed with PBs and incubated with second antibody (2 μ g/mL) (Abcam, ab150113) for 1 hour. After that, the materials were washed with PBs, transferred to a new multi-well plate and then incubated with the 1st antibody to vWF (10 μ g/mL) (Abcam, ab20435) for 24 h at 4 °C. Subsequently, the materials were washed with PBs and later they were incubated with the second-order vWF antibody (2 μ g/mL) (Abcam, ab150119) for 1 hour. The next step combined the staining of the cell nucleus with diluted 4',6-diamidino-2-phenylindole (DAP1) with anti-aging agent and fixing of preparations for observation on a confocal microscope.

The use of fluorescent microscope or scanning confocal microscope is the most common method of the analysis of cell culture. Fluorescent microscopy is a variety of light microscopy, which is based on the phenomenon of fluorescence, i.e. the emission of visible light through the object irradiated with ultraviolet, green and blue rays, which allows detection and visualization of a signal from a fluorochrome [11]. Fluorochrome is a substance capable of emitting fluorescent light when excited by wavelengths of a certain length. The analyzed samples may show natural fluorescence or "artificial" after labeling with fluorescent dyes. This way it is possible to see the growth and development of cells in the culture.

Fourier-transform infrared spectroscopy (FTIR) analysis and goniometer were used to test the surface of modified materials. FTIR is a technique used to measure the absorption or emission of infrared radiation through a solid, liquid or gas. The FTIR spectrometer simultaneously collects high resolution spectral data over a wide spectral range, which gives a significant advantage over a dispersive spectrometer that measures intensity over a narrow wavelength range at once. The term Fourier's spectroscopy comes from the mathematical term Fourier transform, thanks to which it is possible to transform data into real spectrum. ATR (Attenuated Total Reflectance) refers to a technique in IR (infrared) spectroscopy that studies absorption by infrared radiation chemical molecules [12].

Goniometer was used to analyze the wettability of the surface of modified materials. Wettability is a very important physical property that characterizes the surface of materials in terms of their interaction with liquids. The value of wettability determines the basic functions of a given material. In the case of biomaterials, from the point of view of the body's response, the key are the phenomena occurring at the interface between the implant and the cells. Determination of the wettability of a given surface allows the evaluation of cell responses in vivo and the appropriate shaping of a given surface to obtain a biocompatible implant with appropriate properties [13].

Results

FTIR-ATR FTIR-ATR (Fourier-transform infrared spectroscopywith attenuated total reflection) analysis was performed for uncoated steel discs with a polymer coating and polymer-peptide coating using a Nicolet 6700 FT-IR spectrometer (Thermo). Each image presents one representative spectrum chosen from the spectra taken from 6 different places on the studied material. Thanks to FTIR-ATR spectroscopy, functional groups comprised in the compounds present in the surface can be determined.

For the 5-minute electropolymerization, as the concentration of acrylic acid on the 316L steel increases, the values of absorbance remain roughly similar. From these spectra it can be assumed that carboxylic groups are present (1100 cm^{-1} and $3000-2800 \text{ cm}^{-1}$).

For the 15-minute electropolymerization, as the concentration of acrylic acid on the 316L steel increases, higher absorbance values can be observed.

The analysis of discs subjected to 30 minute electropolymerization reaction at the highest concentration of acrylic acid is significantly different from the other variants, because the peaks are much more intensive and the absorbance reaches much higher values than in case of the other spectra. The presence of carboxylic groups ($3600-3000 \text{ cm}^{-1}$ and 1750 cm^{-1}) is noticeable, they occur in a much larger quantity than in the case of other variants.

In the spectra of the surface of the samples with the covalently attached peptide, there is no characteristic signal of peptide bond. On the basis of the FTIR analysis it cannot be unequivocally determined whether the peptide has joined the polymer coating on the steel surface. The ss-REDV spectra has lower quality than ss-COOH spectra, which can be seen by comparing the intensity of sig-



Figure 6.5.4: FTIR-ATR spectrum for pure stainless steel 316L.



Figure 6.5.5: FTIR-ATR spectrum for steel after 5 minutes reaction with different concentration of acrylic acid – 1, 2 and 3%.



Figure 6.5.6: FTIR-ATR spectrum for steel after 15 minutes reaction with 1, 2 and 3% of acrylic acid.



Figure 6.5.7: FTIR-ATR spectrum for steel after 30 minutes reaction with 1, 2 and 3% of acrylic acid.



Figure 6.5.8: FTIR-ATR spectrum for steel after 5-minute electropolimerization with 1 % of acrylic acid and different concentration of peptide REDV – 0.5 mM and 5 mM.



Figure 6.5.9: FTIR-ATR spectrum for steel after 30-minute electropolimerization with 3 % of acrylic acid and different concentration of peptide REDV – 0.5 mM and 5 mM.

nals from the same functional groups (lower values of absorbance in the case of ss-REDV). This may be a result of the swelling phenomenon of the polymer coating due to the peptide attachment reaction, which increases the porosity of the material surface and thus the quality of the analysis.

The analysis of contact angle The analysis of contact angle was prepared in 6 replicates in 6 different places on the surface of each disc. The table below presents the average values of the contact angle for individual variants of steel surface modification.

		time (s)		
Variant		1	60	
SS		84.58 ± 10.13	82.47 ± 11.75	
5'1%		37.34 ± 5.15	34.47 ± 3.21	
5' 2%		45.81 ± 4.91	40.03 ± 3.39	
5' 3%		45.79 ± 5.12	40.11 ± 4.61	
15' 1%		46.82 ± 6.34	43.04 ± 4.19	
15' 2%	COOH	44.70 ± 8.31	40.85 ± 6.43	
15' 3%		40.56 ± 6.09	38.17 ± 6.03	
30' 1%		40.37 ± 12.35	37.63 ± 12.35	
30' 2%		42.31 ± 3.79	40.28 ± 3.22	
30' 3%		49.21 ± 4.26	47.83 ± 4.59	
5' 1%	redv 0.5 mM	36.27 ± 0.88	31.23 ± 4.20	
	Redv $5 \mathrm{mM}$	33.99 ± 0.66	32.32 ± 8.05	
30' 3%	redv 0.5 mM	44.51 ± 6.23	34.99 ± 6.29	
	redv 5mM	54.26 ± 10.56	46.51 ± 12.77	

 Table 6.5.2: The average values of the contact angle for individual variants of steel

 surface modification after 1 second and 60 seconds of contact between water droplet

 and the material surface.

Large values of standard deviation may indicate irregularities of the surface of discs without cover as well as with the polymer and polymer-peptide coating. The average value of the contact angle was averaged from 6 results in different parts of the discs which in places significantly differ from each other.

The high value of the contact angle in the case of pure 316L stainless steel indicates the high roughness of its surface. This analysis confirms that the surface of stainless steel is poorly hydrophilic [14]. The wettability of the surface of steel discs covered with a layer of polymer with the addition of acrylic acid in low concentration (1 % ss-COOH) is higher than in the case of uncoated steel.

The materials coated with the polymer in higher concentrations (2 and 3 %) have respectively higher values.

Regardless of the concentration of the peptide at the 5' 1 % modification, the contact angles are similar to each other after 1 second and after one minute. At lower peptide concentration (0.5 mM) the contact angle is lower and this indicates that the wettability of the steel surface is better than at higher concentration (5 mM). The contact angle reaches lower values for 5' 1%, i.e. a shorter electropolymerization time and lower acrylic acid concentration, at both peptide concentrations than with the 30' 3 % variant. In this case, the contact angles are close to the analogous variant of the modification without the present peptide. The value of the contact angle for ss-REDV materials is lower than for most ss-COOH materials. This means that ss-REDV materials are more hydrophilic than ss-COOH due to the presence of peptide molecules on their surface. The only exception is one variant of the ss-COOH modification (5' 1%), which is characterized by an equally high hydrophilicity as the ss-REDV variants.

Scanning confocal microscope The analysis of the tested materials with the use of scanning confocal microscope was carried out in order to determine the course of growth, metabolism and cell proliferation of the HMEC-1 cell line. All photos were taken at 200× magnification. On the left side there are pictures of discs taken after 3-day culture, on the right side – after 5-day culture.

Firstly, steel discs with no coating (ss) were analysed (Fig. 6.5.10). The monolayer of cells cannot be seen in the pictures but there is a lot of nuclei (bright spots) and proteins after 3-day culture. Moreover, the cell nuclei are round and clearly visible, but their shape indicates that the cells did not adhere to the surface. Vinculin and vWF are barely visible in the right picture. In the 5-day culture individual cell nuclei and proteins are visible only in the central part of the material. Bright areas seen on the picture is the surface of steel, visible in fluorescence analysis because of non-specific bonding of antibodies in the absence of cells.

Next, the steel discs with polymer coating were analysed (Fig. 6.5.11). In the left picture nuclei are visible, there is a lot of vinculin and vWF. However in the right picture it can be assumed that the labelling did not go well. It is supposed that the coating on discs absorbed the dye.

Some of nuclei, vinculin and vWF are visible in the left picture (Fig. 6.5.12), however in the right one there are only some proteins and DAPI was absorbed by polymer on the disc.

When it comes to the materials with the polymer-peptide coating (Fig. 6.5.13, 6.5.14, 6.5.15) it is visible that peptide encouraged endothelium to grow and proliferate. Steel discs with lower concentration of peptide (0.5 mM) give better results after 3 day culture than after 5 day culture. The amount of stained cell nuclei is satisfactory in the case of a shorter culture, while with a longer culture only a few individual nuclei can be seen.

6.5. Preparation and analysis of the surface of modified steel materials...



Figure 6.5.10: Stainless steel with no coating. 3-day culture in the left picture (A), 5-day in the right (B).



Figure 6.5.11: Materials after 5 minutes of electropolymerization with 1% of acrylic acid. 3-day culture in the left picture (C), 5-day in the right (D).



Figure 6.5.12: Materials after 30 minutes of electropolymerization with 3% of acrylic acid. 3-day culture in the left picture (E), 5-day in the right (F).



Figure 6.5.13: Materials after 5 minutes of electropolymerization with 1% of acrylic acid and 0.5 mM peptide with REDV sequence. 3-day culture in the left picture (G), 5-day in the right (H).

A higher concentration of peptide with a lower electropolymerization variant in the case of shorter cultures give worse results, while in the case of longterm cultures definitely better, especially when it comes to vWF and vinulin. The amount of proteins indicate a large amount of actively metabolizing endothelial cells. Longer time of electropolymerization and higher concentration of carboxyl groups did not affect the amount of proteins produced. The variant with the highest parameters of electropolymerization and peptide concentration (Fig. 6.5.16) give the best results, but only after 3 day culture. Longer time of culturing do not result in better cell growth and proliferation.



Figure 6.5.14: Materials after 5 minutes of electropolymerization with 1% of acrylic acid and 5 mM peptide with REDV sequence. 3-day culture in the left picture (I), 5-day in the right (J).



Figure 6.5.15: Materials after 30 minutes of electropolymerization with 3% of acrylic acid and 0.5 mM peptide with REDV sequence. 3-day culture in the left picture (K), 5-day in the right (L).



Figure 6.5.16: Materials after 30 minutes of electropolymerization with 3% of acrylic acid and 5 mM peptide with REDV sequence. 3-day culture in the left picture (M), 5-day in the right (N).

Discussion

A short incubation time of endothelial cells on materials has a beneficial effect on cell adhesion to the surface, its proliferation and development. During 3-day culture, satisfactory results were obtained, this time showed noticeable growth and development of endothelial cells on the steel material subjected to modification in comparison to pure steel. The properties of 316L stainless steel such as roughness and hydrophilicity of the surface can explain why endothelial cells anchored to the pure steel with no coating. However, the cells did not adhere to the surface as in the case of steel surfaces coated with polymer and peptide with REDV sequence.

After the analysis of all the figures, it can be concluded that the presence of REDV peptide on the surface of the materials encourages endothelial cells to adhesion and development, confirming the earlier opinion about adhesive sequences as effective in mediating the adhesion, proliferation and organization of endothelial cells. According to the literature, peptides containing adhesive sequences promote the growth and binding of endothelial cells, as well as the rate of their spreading on the surface of the materials [15]. The circular shape of the cell nuclei observed in the images depicting the surface of ss and ss-COOH materials compared to materials with peptide and the negligible amount of vinculin and vW factor indicates that these surfaces are a worse substrate for adhesion and proliferation of endothelial cells.

The purpose of the presented work was to obtain a polymer-peptide coating on the surface of 316L stainless steel discs by electropolymerization. The presented analysis of the results shows that the conducted procedure allows to obtain this type of coverage of materials. Examination of various process parameters such as reagent concentrations and reaction time made it possible to select and obtain the most suitable surfaces for culturing HMEC-1 endothelial cells. The use of infrared spectroscopy and the examination of the contact angle allowed to analyse the surface of the obtained materials, whereas the use of confocal scanning microscopy enabled the assessment of development of endothelial cells on the tested substrates. Accurate analysis of images from the confocal cell culture microscope of the HMEC-1 cell line has confirmed the earlier conclusion that various parameters of metal surface modification affect the growth, development and metabolism of endothelial cells.

It was assumed that a longer cell culture, in the case of the 5-day study presented, would yield better results of analysis. However, photos from the confocal microscope show that this is an unconfirmed thesis. The polymer-peptide coating absorbed the dye in some variants, so a second analysis should be carried out. The figures that actually presented some of the cell nuclei and vinculin may indicate that the rate of growth and rapid proliferation of endothelial cells were the reason why their amount was so small. With such a long breeding time, too many cells grew and adapted to the material. Presumably, at the time of observation, some of the cells have been already dead, so they did not produce proteins, which resulted in poor visibility of the stained factors in the photos from the confocal microscope. Demonstration of differences in the growth of endothelial cells in the presence and absence of REDV peptide was successfully performed. Both in the case of 3 and 5-day cultures, the presence of the peptide improved the analvsis results, allowed the cells to achieve some degree of confluence and properly metabolize. With longer cultures at higher modifications, i.e. a 30-minute electropolymerization reaction at high concentrations of carboxyl groups, von Willebrand factor and vinculin were very clearly visible, which may indicate a very large number of metabolizing cells, but the cell nuclei themselves could not be captured. Presumably, the 5-day culture time is too long for endothelial cells with such high variants of modification. It is possible that the cells grew very quickly and occupied a larger part of the breeding area, they grew very densely and already while taking pictures some of the cells were dead. It is advisable to conduct further analysis to improve the process parameters in order to obtain a complete coverage of the surface of the steel discs with endothelial cells. Obtaining a confluent cell monolayer on the surface of the material would be a great step towards the development of metal biomaterials with a high level of biocompatibility.

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Abbreviations

- вмs bare metal stent
- вsa bovine serum albumin
- вvs bioresorbable vascular stents
- COOH carboxyl group
- DAPI 4',6-diamidino-2-phenylindole
- DES drug eluting stent
- EDC N-(3-Dimethylaminopropyl)-N'-ethylcarbodiimide hydrochloride
- EGDMA ethylene glycol dimethacrylate
- FTIR-ATR Fourier-transform infrared spectroscopy attenuated total reflectance
- HMEC-1 human microvascular endothelial cells
- HUVEC human umbilical vein endothelial cells
- мсрв medium
- MES 2-(N-morpholino)-ethanesulfonic acid
- + NH_2 amino group
- PBS phosphate-buffered saline
- РЕGDMA poly(ethylene glycol) dimethacrylate
- PFA paraformaldehyde
- REDV aminoacid sequence; arginin-glutamic acid-aspartic acid-valine
- sulfo-NHS N-hydroxysulfosuccinimide
- vWF von Willebrand factor

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6.6 Magnesium Hydrides used in Hydrogen Storage Technology

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Keywords: magnesium hydrides, hydrogen storage, alternative energy sources, magnesiumiron hydride (Mg₂FeH₆).

Abstract

Currently, three ways of storing hydrogen are known: in the gas phase (compressed hydrogen), in the liquid phase (condensed hydrogen, additionally stored at very low temperatures around 20 K) and in the solid phase (adsorption or absorption of hydrogen in solids, chemical reactions) [1-4]. The last of these methods is the youngest technique and constantly researched and developed, but with this technique the greatest hopes are connected because it is the most secure. The value of the pressure used in this technique is from a few to a dozen bars, and the hydrogen is strongly connected with the solid phase, that even at any leakage, it will release very slowly, which will immediately detect the threat [2–6].

Most of the materials used in this method are powders – because in this form the material is characterized by a highly developed specific surface area, thanks to which hydrogen reacts with it more easily. Various materials are used in this technique, including nickel (LaNi₅) or chromium (ZrCr₂) alloys, borohydrides (NaBH₄), carbon materials (nanotubes, fullerenes, graphene, activated carbon) but also magnesium compounds [5–11].

Due to the high hydrogen absorption capacity (up to about 7.6 wt% in the case of MgH₂) and the reversibility of the reaction, magnesium hydrides are the most promising materials for solid phase hydrogen storage [12,13]. The highest ability to absorb hydrogen among all hydrogen compounds is MgH₂, unfortunately it is characterized by slow kinetics of absorption and hydrogen release, as well as a high temperature of H₂ release (673 K) [14–16]. Therefore, ternary magnesium hydrides are more popular, so this group of material were described in more detail. A very interesting material is Mg₂FeH₆. This compound is characterized by the highest hydrogen content among all known hydrogen compounds – 150 kg/m³ by volume and hydrogen content by 5.46 %. These parameters have a direct impact on the fact that it is one of the most studied compounds in the aspect of hydrogen storage [13–18].

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Hydrogen storage technologies

The energy from hydrogen can be obtained in two ways: as a result of combustion reactions as well as using appropriate fuel cells. However, to obtain energy from hydrogen, it should be stored in a correct and effective way. As previously mentioned, 3 methods of hydrogen storage are currently used [3-9].

Hydrogen is a very small molecule that is able to diffuse through porous materials, rubber, and at elevated temperatures even through steel. It easily leaks through even minimal gaps or leaks and cracks. Hydrogen is also very light, so its diffusion in the air is very fast, much faster than natural gas or gasoline. Therefore, very important are the aspects of hydrogen storage in various phases [2–7].

Hydrogen storage in the gas phase (compressed H₂) Hydrogen is characterized by high calorific value with low energy density – therefore, when using it as a source of energy in gas form, it is necessary to compress it. This treatment is necessary to obtain a tank with a sufficiently large mass of stored hydrogen. This process involves a large amount of energy that needs to be supplied from outside [1,6,9]. Unfortunately, the low density of hydrogen contributes to the fact that even under high pressure, a small amount of useful energy is accumulated. Which directly affects the use of large volume hydrogen tanks and increase storage costs. Hydrogen gas is stored at a temperature of about 298 K - in the pressure range of 150 to 800 bar [8,10]. The pressure value depends mainly on the target application of the tank. For example, for mobile systems that do not require high power, the lowest pressure values are used, but with the use of a tank in buses or cars, the pressure increases to around 350 bar. In stationary applications, pressures reach up to 800 bar [3–5]. Stationary tanks are mainly made of steel, however, when used in mobile applications, weight is very important, which is why tanks are much lighter than steel. They are made primarily of composites based on lightweight plastics. Thanks to that, it is possible to reduce the weight of such a tank by up to 50–75 %. The use of such high pressures is still a psychological barrier in the aspects of safe use of tanks, which is obviously due to the high flammability and explosiveness of hydrogen, which may occur in the event of incorrect storage [1,5,8].

Hydrogen storage the liquid phase (condensed H₂) The conversion of hydrogen from the gas to liquid phase (condensation) increases the hydrogen energy density. The condensation process is unfortunately much more expensive than compression, because it involves a significant increase in energy expenditure – it is estimated that the energy consumption needed to condense hydrogen is by 30-40% more than for compression [4–6]. As a result, the efficiency of the process is low. An additional problem is that liquid hydrogen must be stored at a very low temperature (about 20 K), which obviously increases material costs.

Such tanks should be constantly cooled and thermally insulated from the environment [1-,7,9]. The most commonly used coolant for this purpose is liquid nitrogen. Liquid hydrogen storage tanks can also not be used in applications where hydrogen is not collected continuously - because it involves hydrogen losses due to evaporation. Storage of hydrogen in the liquid phase, however, allows to obtain a much higher density, both mass and volume of hydrogen, than in the case of storage in the gas phase. The advantage of such tanks is the fact that less fuel is lost - about 5-25 % less hydrogen is able to "escape" from the tank when it is in the liquid phase. Currently, both stationary and mobile hydrogen are used in the industry. Stationary magazines usually have a cylindrical shape, are equipped with appropriately selected containers composed of two vessels isolated from each other (internal and external tank) - these tanks are characterized by a high ratio of diameter to length. Mobile tanks are very similar to stationary ones, but due to their use in motor vehicles they must be characterized by greater compactness and adequate equipment. In order to minimize fuel losses to below 1 %, mobile tanks are often covered with a special insulating film (in the amount of 200 to 300 layers). Despite the many advantages of liquid hydrogen tanks, they are still not very economical. The cost-effectiveness of this hydrogen storage method depends mainly on the capacity and weight of the tank, but also on the material that builds and insulates the storage. From the economic point of view, only tanks high capacity is profitable [2,6,10].

Hydrogen storage in the solid phase The most promising, economical and safe method is the storage of hydrogen in the solid phase. When hydrogen is stored in this technique, much lower pressures are used than for the method of hydrogen storage in the gas or liquid phase – there are several bars here, not several hundred, which is the case with the other two methods. The tank with stored hydrogen does not need to be cooled down at very low temperatures (in the order of 20 K – as in the case of hydrogen storage in the liquid phase). Hydrogen joins the solid so strongly that no leakage of this substance from the tank is noticeable, which translates into an increase in the safety and economy of this storage method. The economics of this method are also supported by the fact that solids are highly durable for hydrogen absorption, and the sorption process and desorption is in many cases a reversible process [1,6–10].

Hydrogen can be stored in physical metal hydrides (adsorption and absorption) and in chemical hydrides (formed as a result of chemical reaction), as well as in carbon materials [2,10,11]. In the case of physical metal hydrides, hydrogen may adsorb on the surface of such alloys as, for example, nickel (LaNi₅) or chromium (ZrCr₂) alloys [11] or absorb in powder materials – these are mainly magnesium compounds Mg_2MH_x (where M is: Fe, Co, Ni) or Mg_7TMH_y (where TM is: Ti, V, Nb). Hydrogen can also be stored in the form of chemical com-

pounds (chemical hydrides) that arise as a result of chemical reactions. Thanks to this, it is possible to accumulate much more hydrogen than in the case of metal hydrides. The process of hydrogen release from such compounds is mainly due to the action of water or alcohols. An example of chemical hydrides that has already found industrial application is borohydride (NaBH₄). The release of hydrogen takes place as a result of an exothermic hydrolysis reaction (at room temperature). The greatest advantages of the use of chemical hydrides include the high capacity of stored hydrogen, the disadvantage is the irreversibility of the reaction. The last of the ways of storing hydrogen in solid materials has been storing it in carbon materials. They are mainly highly porous materials, characterized by a large specific surface area, such as graphite, active carbon fullerenes and nanotubes. This method does not have a wider industrial application, however, many studies and experiments are still carried out in this area [1-3,10,11].

Magnesium hydrides

Formation of a magnesium hydride compounds was first recognized by German chemists yet at the end of 19th century but it took more than a half a century before a substantial yields of Mg hydride was obtained from direct synthesis of the elements and the first determination of values for the decomposition pressure on temperature, the enthalpy of formation and the activation energy were obtained [19,20].

Magnesium hydrides and its compounds are an interesting material for hydrogen storage due to such properties as: low process pressure (usually 0.25–10 MPa), reversibility of the hydrogen storage process (possibility of hydrogen absorption and desorption), low process temperature (hydrogen absorption can occur even at room temperature), high hydrogen absorption capacity (up to 7.6 % by weight in the case of MgH₂, relatively low cost and safety of use (no risk related to explosiveness and flammability of the system [20–23].

Magnesium Dihydride (MgH₂) Magnesium dihydrate (MgH₂) can store several times more hydrogen per unit of weight than AB type of hydride (e.g. TiFe). One disadvantage with hydriding metallic Mg is that it does not react with hydrogen at low temperatures and reacts only very slowly at high temperatures (300 °C). Because of the relative inertness with respect to H₂, magnesium was even recommended as a structural metal suitable for contact with hydrogen up to the melting temperature. The natural inertness of Mg to molecular hydrogen it is determined by known facts [20,24-28]:

• Thick surface oxides that cover magnesium metal do not provide sites catalytically active for dissociation of hydrogen molecule, which is known to occur on contact with a metallic surface (clean metallic surface often provides active sites for catalytic breaking of very strong H – H bond) [20,24,25].

• Surface adsorbed impurity gases further slow the kinetics of hydrogen absorption into the bulk grains [20,24,25].

Dehydrogenation of MgH₂ can only be achieved by heating at about 300 °C which is the results of its high enthalpy of dehydrogenation. Stable magnesium dihydride was prepared in 1951 by direct heating of Mg in gaseous hydrogen under high pressures – reaction was slow and difficult to complete [20,23,26]. Therefore, ternary magnesium hydride is more popular and used. There are two types of ternary magnesium hydrides: Mg_2MH_x (where M is: Fe, Co, Ni) or Mg_7TMH_y (where TM is: Ti, V, Nb). However, Mg_2MH_x type hydrides are characterized by good properties in hydrogen storage technology and are used in this field of industry. Therefore, the following part of this article focuses on this group of materials [23–28].

Ternary magnesium-nickel hydride (Mg_2NiH_4) Magnesium-nickel hydride (Mg_2NiH_4) are well known for years. For the first time they were developed in the us Brookhaven National Research Laboratory [20]. The interest in Mg has been stimulated by availability of hydropower required to produce Mg metal in the first place. The new Mg_2Ni alloy has alleviated the problem inherent to Mg metal – poor kinetics of hydrogenation reaction. The presence of intermetallic magnesium compounds on the surface of Mg causes that this reaction can be significantly accelerated. Hydrogen release may occur without major crystallographic transformation when hydride is converted back into Mg_2Ni [20–24]. The crystalline structure of Mg_2NiH_4 is shown in Fig. 6.6.1 - the hydrogen sites of the idealized Mg_2NiH_4 are only partially occupied [25].



Figure 6.6.1: The crystalline structure of Mg₂NiH₄ [25].

Ternary magnesium-iron hydride (Mg₂FeH₆) The beginning of the 90's caused that interest in well-known magnesium hydrides changed. Mg compounds with transition metals (e.g. Fe) started to be more popular. Mg and Fe does not alloy to form Mg₂Fe binary intermetallic by either ingot casting or metal powder sintering procedures, however, when sintering is done in hydrogen, a very stable Mg₂FeH₆, non-interstitial, ternary magnesium-iron hydride forms [20–22]. The new anionic complexes of Fe are stable rendering the desorption temperature too high. When desorbed, the hydrides could not change to the hydrogen-free A₂B alloys because Mg₂Fe do not exist in the binary Mg – Fe systems and in contrast to Mg₂Ni, dehydrogenation reaction occurs through the formation of intermediate MgH₂ [20–22].

 Mg_2FeH_6 is characterized by a cubic crystal structure of the K_2PtCl_6 type, in which octahedral FeH₆ anions are surrounded by a cubic crystal lattice Mg (Fig. 6.6.2) [12–21]. As previously mentioned, this compound is characterized by the highest hydrogen content of 150 kg/m³ in all known hydrogen compounds, and hydrogen mass content of 5.46 %, which makes it one of the most studied compounds in terms of hydrogen storage [16–18].



Figure 6.6.2: The crystalline structure of Mg₂FeH₆ [16].

Magnesium hybrides in automative

Currently, motorization is one of the most dynamically operating and developing industries. The greatest hopes and money are associated with this type of industry. This is because continuous pressure is exerted on the development of the most favorable method of obtaining energy from hydrogen and powering it with cars. What they would like to eliminate in the future the use of oil and gas, which affect environmental pollution [2–7,10]. Therefore, mention should be made of

the use of Mg₂FeH₆ hydride in mobile tanks. Thanks to the use of this type of material, it is possible to reduce the volume and weight of the used tank without changing the capacity of the hydrogen. This is illustrated well in Fig. 6.6.3. The figure shows volume of 4 kg of hydrogen, storage in different phases. The largest volume is occupied by the hydrogen tank in the gas phase, then in the liquid phase. The smallest volume is characterized by solid phase hydrogen containers (physical metal hydrides). In the case of using triple magnesium hydride Mg₂FeH₆ 4 kg of hydrogen takes a volume of only 26 liters [7,10,18–23].



Figure 6.6.3: The volume of 4 kg of hydrogen in various phases [20].

Summary

In conclusion, it should be noted that currently used hydrogen storage technology allows the use of a wide range of materials. Each of the material groups is characterized by different properties and applications. However, one of the most promising material groups for use in solid phase hydrogen storage are ternary magnesium hydrides. This is so because these materials are relatively cheap, available on a large scale. They can store large amounts of hydrogen in small volumes, which is especially important for the automotive industry. In addition, hydrogen storage in this type of materials is safe and economical. The most important and widespread material that has many applications is magnesium iron hydride (Mg_2FeH_6). In the future, more research should be carried out to improve hydrogen storage in this type of material. Researchers should focus on reducing the hydrogen desorption temperature (below 100 °C) so that it can be easily used such tanks in fuel cell vehicles. Magnesium hydrides are a promising material group, however, its advantages should be used in a correct and effective way, because these are materials with high hydrogen sorption capacity, fast kinetics of this reaction and completely safe to use.

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6.7 Comparison of hydrotalcite-like materials prepared by different synthesis methods

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Abstract

Hydrotalcite is a material widely examined as a catalyst in processes such as SCR or methanation. The goal of this research was to compare the crystallinity and structure of the hydrotalcite-like materials prepared by the different synthesis methods.

The chosen preparation techniques were: coprecipitation, urea hydrolysis method and solution combustion synthesis. Two different types of material were prepared by each of the methods. One type of samples was containing Mg – Al species in molar ratio 3:1, the second Ni – Mg – Al with molar ratio 1:2:1. The choice of preparation techniques was dictated by the simplicity of experimental procedure and further possibility of deposition of the material on the catalytic structures, such as monolith. Two elemental compositions were chosen to examine if the same experimental conditions lead to the same type of crystallinity.

The structure of the samples was determined by XRD and FTIR methods hydrotalcites were obtained via coprecipitation and urea method while solution combustion synthesis led to oxides structures such as periclase or spinel.

In order to prepare hydrotalcites via solution combustion method lowering the combustion temperature or stronger alkalization of the resulted powder may be of advantage.

Introduction

Development of industrial processes and energy production is strictly connected with environmental protection. Plenty of catalysis-based technologies were set in order to reduce emission of poisonous substances to atmosphere or produce ecologically-feasible fuels. Materials based on hydrotalcites were tested in processes such as methanation [1, 2, 3] or dry reforming of methane [4, 5] in order to produce methane and syngas, respectively. Also, hydrotalcites were considered as suitable for scR process, to reduce NO_x emission from flue gases [6, 7]. In all the mentioned process, hydrotalcites are very strong competition for carbonaceous materials [8, 9, 10].

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Hydrotalcites, which are layered double hydroxides of divalent and trivalent metals with a general formula $[M^{II}_{1-x} M^{III}_x (OH)_2]_x^+ A^{z-}_{x/z} \cdot nH_2O$ (where: M^{II} and M^{III} are cations of di- and trivalent metals subsequently, A is type of interlayer anions, and *x* is molar ratio [11]) tend to be a good choice for catalytic applications. Composition of such material is flexible, allowing for the preparation of a similar type of crystalline structure with different elements introduced. Active phase can be introduced in two ways, as a metallic cation inside the brucite structure or as an anionic complex inside the space between the brucite layers. The composition of hydrotalcite can be controlled both in the preparation stage and during the further modifications such as ion exchange or impregnation [12, 13].

Depending on the method used, there are a few paths to synthesize hydrotalcite. Most conventional and best-known of synthesis techniques is precipitation under supersaturation conditions, frequently with constant pH. The process can be held with low supersaturation (pH during precipitation of 7–10) and high supersaturation (pH during precipitation of over 10). Two solutions are added dropwise to the flask containing a solution with desired initial pH conditions. This technique is time-consuming because of long time of a coprecipitation itself and, moreover, the sample should be aged for a few hours. The process at low supersaturation results in a product with better crystallinity [12].

Urea method is a solution alternative to coprecipitation. The method does not require a constant control of pH of the solution, but temperature must be controlled. The method is based on the preparation of appropriate solutions containing precursors for hydrotalcite - proper metal nitrates and urea. Depending on the urea-to-nitrate ions ratio, crystallinity of the product may vary [14, 15, 16].

The solution combustion synthesis is considered a very fast methods to obtain nano-size materials, including hydrotalcites. The preparation is based on an explosive reaction between nitrates of proper metals and urea or other substance playing the role of fuel in the combustion reaction (glycine, saccharose, hydrazine etc.). A solution containing the mentioned precursors is combusted in a furnace at high temperature. The combustion of nitrates with urea is highly exothermic and the product is readily crystallized hydrotalcite [13] or mixed oxides [17].

Experimental

The samples were prepared using three different methods: urea hydrolysis, precipitation at low saturation and solution combustion synthesis. Two types of hydrotalcites were prepared, one with magnesium and aluminum in molar ratio 3:1 and the second with magnesium, nickel and aluminum with the ratio of 2:1:1. The following reagents were used: aluminum nitrate nonahydrate (Chempur, purity >98%), magnesium nitrate hexahydrate (Chempur, purity >99%), nickel nitrate hexahydrate (Chempur, purity >98%), urea (Chempur, purity >99.5%), sodium carbonate (Chempur, purity >99.8%).

Synthesis of HTIcs via urea hydrolysis method 20 mL of 1 M solution containing metal nitrates precursors in decided molar ratio was added to a flask with 100 mL of distilled water and urea with molar ratio to nitrate ions of 4:1, basing on the methodology by Zeng et al. [14].

Synthesis of HTIcs via precipitation at low saturation method Preparation was carried according to methodology proposed by Cavani [12], however the cationic composition of desired product was changed to Mg : Al hydrotalcite with metal ions ratio 3:1 subsequently, and Ni : MgAl anion ratio of 1:2:1.

Synthesis of hydrotalcite-like material via solution combustion synthesis Solution with precursors was prepared with $Al(NO_3)_3 \cdot 9 H_2O$ and $Mg(NO_3)_2 \cdot 6 H_2O$ in ratio 3:1, with stoichiometric amount of urea, in accordance to form oxides (Eq. (6.7.2)–(6.7.4)), and 0.2 g Na₂CO₃ per 1g of solid mixture. Such solution was heated to 50 °C for 1 hour under constant stirring. Then, solution was combusted in three different temperatures: 450, 550 and 650 °C for 10 minutes. Powder obtained from each combustion was cooled down and put to the 0.1 M solution of Na₂CO₃ for 5 minutes, under dynamic stirring. After that time, samples were washed with distilled water and dried in 70 °C. Solution for preparation of nickel-containing species was prepared with of $Al(NO_3)_3 \cdot 9 H_2O$, $Ni(NO_3)_2 \cdot 6 H_2O$ and $Mg(NO_3)_2 \cdot 6 H_2O$ in ratio of 1:1:2, with stoichiometric amount of urea.

Molar ratio of ions and temperature chosen methods for all prepared samples are listed in Table 6.7.1.

Characterisation

The samples were characterized by XRD and FTIR methods. XRD was carried on the Panalytical Empyrean diffractometer, equipped with Cu anode as a source of X-ray radiation. The patterns were recorded over the 2θ range 3° to 90° in steps of 0.013°. FTIR spectra of sample in KBr matrix were recorded on a Perkin-Elmer 16PC FTIR spectrometer in the range 4000 to 400 cm⁻¹.

Sample designation	Mg : Al or Ni : Mg : Al ratio	Method	Process temperature (℃)
UMgAl UNiMgAl	3:1 1:2:1	Urea hydrolysis	90-100
CPMgAl CPNiMgAl	3:1 1:2:1	Coprecipitation at low supersaturation	80
MgAl_450 MgAl_550 MgAl_650	3:1	Solution combustion	450 550 650
NiMgAl_450 NiMgAl_550 NiMgAl_650	1:2:1	synthesis	450 550 650

Table 6.7.1: The preparation conditions of the samples

Results and discussion

Synthesis of HTIcs via urea hydrolysis method Urea hydrolysis method is based on reaction 6.7.1, which is a source of carbonate ions, necessary to form hydrotalcite.

$$CO(NH_2)_2 + H_2O \rightarrow NH_4^+ + CO_3^{2-}$$
 (6.7.1)

Urea decomposes at 90 °C, changing the pH of the solution to basic (pH ca. 9–10). The reaction yield and increase in pH depends most of all on $[NO_3^{-}]/[urea]$ ratio. For this experiment ratio of 4 was chosen since according to Zeng et al. [14] it provides a better yield than ratio of 1 or smaller.

In Figure 6.7.1 xRD diffractograms for the samples prepared via urea hydrolysis method are shown. The presence of reflections at 2θ angles of 11.65° and 23.42° confirms the presence of hydrotalcite layers. Reflections at 2θ 34.88°, 39.44° and 46.92° are also typical for hydrotalcite material, containing Mg and Al in lattice. The only crystalline phase found in the samples was hydrotalcite, however intensity of diffraction of UMgAl is stronger than of UNiMgAl.

Figure 6.7.2 shows FTIR spectra for both samples prepared via urea hydrolysis. The spectra for UNiMgAl at wavelength 3300–3600 cm⁻¹ are attributed to H-bonding stretching vibrations of OH group from brucite layer. The range of 1000–400 cm⁻¹ shows vibrations from cation-oxygen bonds and anions from the interlayer: 448cm⁻¹ for Mg – O – Al and 423 cm⁻¹ for Ni – O – Al, 624 cm⁻¹ and 685 cm⁻¹ for CO₃^{2–} vibrations. For a typical hydrotalcite, the band at 1350 cm⁻¹



Figure 6.7.1: XRD diffractograms of UMgAl and UNiMgAl samples

is attributed to carbonate ions, but for UMgAl at 1361 cm^{-1} for UNiMgAl the band is slightly shifted to lower wavelength of 1359 cm^{-1} , which may have arisen from a slight lowering of symmetry of carbonate ions existing in the interlayer not only as a monodentate but also as a bidentate complex [12]. The band at 1624 cm^{-1} may be a confirmation of the bicarbonate ions presence, according to Serna et al. [18]. The peak at 2189 cm^{-1} for UMgAl may have occurred from C = O deformation vibrations.



Figure 6.7.2: FTIR spectra of UMgAl (•) and UNiMgAl (×) samples

Synthesis of HTIcs via precipitation at low saturation method XRD analysis for CPMgAl confirmed the existence of three phases, (i) a hydrotalcite phase confirmed by reflections at 11.27° and 22.78° and weaker reflections at 34.47°, 38.61° and 59.98° 2θ , similarly as for UMgAl. (ii) calcium carbonate, confirmed by very strong reflection at 29.28° and weaker reflections at 43.22° and 47.12°, and (iii) aluminum oxide, probably kappa-alumina, identified by reflections at 14.51°, 34.73°, 38.67° and 42.58°. The presence of calcium carbonate may be explained by a relatively high content of 0.01 % of calcium ions in the used Mg(NO₃)₂ · 6 H₂O.

As seen in Figure 6.7.3 the main phase in CPNiMgAl was hydrotalcite similarly as in the CPMgAl sample, but hydrotalcite phase has lower crystallinity. Reflexes occurring from hydrotalcite layers are strongly decreased. Also, in this sample calcium carbonate is present. On the other hand, no aluminum oxide was found as reflections at 14.51° and 38.67° are lacking.



Figure 6.7.3: XRD diffractograms of CPMgAl and CPNiMgAl samples

Figure 6.7.4 shows FTIR spectra for both samples prepared via coprecipitation at low supersaturation. The curves are almost identical showing peaks with very similar intensity at the same wavenumbers. At $3400-3600 \text{ cm}^{-1}$ peaks typical for O – H stretching vibration are visible. The peaks at 1384 cm^{-1} and 667 cm^{-1} originate from vibrations of CO₃²⁻ anions, the peak at 415 cm^{-1} may be assigned to Mg – O – Al vibrations and the one at 797 cm⁻¹ results from Al – OH bonding [19].



Figure 6.7.4: FTIR spectra of CPMgAl (•) and CPNiMgAl (×) samples

Synthesis of hydrotalcite-like material via solution combustion synthesis Direct combustion of metal nitrates with the stoichiometric amount of urea should lead to formation of mixed oxides, according to Eq. (6.7.2), (6.7.3) and (6.7.4).

$$2 \operatorname{Al}(\operatorname{NO}_3)_3 \cdot 9 \operatorname{H}_2\operatorname{O} + 5 \operatorname{NH}_2\operatorname{CONH}_2 \longrightarrow \operatorname{Al}_2\operatorname{O}_3 + 8 \operatorname{N}_2 + 5 \operatorname{CO}_2 + 26 \operatorname{H}_2\operatorname{O} (6.7.2)$$

$$\begin{array}{c} Mg(NO_3)_2 \cdot 6 \,H_2O + 1.667\,NH_2CONH_2 \longrightarrow \\ & \longrightarrow MgO + 2.667\,N_2 + 1.667\,CO_2 + 8.83\,H_2O \quad (6.7.3) \end{array}$$

$$Ni(NO_3)_2 \cdot 6 H_2O + 1.667 NH_2CONH_2 \longrightarrow MiO + 2.667 N_2 + 1.667 CO_2 + 9.33 H_2O \quad (6.7.4)$$

Davila et al. [20] during the preparation of precursor material heated the solution of nitrates with urea and sodium carbonate, in order to form a paste [20]. In this research, the step with forming a paste was omitted, and the solution was heated for an hour to form complexes. No precipitate was present in the solution before combustion. Such method was chosen as it could be applied to introduce hydrotalcites onto catalytic structures such as monoliths etc.

For the samples prepared via solution combustion synthesis, both XRD and FTIR analysis were made for product just after combustion in order to check which phases were formed, as well as after soaking the combusted powder in sodium carbonate.

Figure 6.7.5 shows XRD diffractograms for MgAl samples after combustion (a), and after soaking of the obtained powder in sodium carbonate solution (b). The sample formed at 450 $^{\circ}$ C differed from those formed at higher temperatures. After combustion, in sample MgAl_450 three significant phases are present: (i) calcium

carbonate, confirmed by reflections at 29.4°, 39.41° and 48.51° 2 θ , (ii) spinel – magnesium aluminum oxide, confirmed by 2 θ values of 37.28°, 45.31° and 66.23, and (iii) aluminum oxide with hexagonal structure identified by reflections at 21.60°, 34.84° and 45.81° 2 θ .



Figure 6.7.5: xRD patterns of MgAl samples (a) after combustion, (b) after crystallisation in sodium carbonate

After soaking of the sample in sodium carbonate solution, the XRD pattern changed. Aluminum oxide phase was still present; but the spinel phase was transformed into hydrotalcite with poor crystallinity, as confirmed with reflections at 11.28° and 22.78° 2θ. Calcium carbonate phase was still detectable, but with lower intensity.

The samples after combustion at 550 °C and 650 °C show the same phase composition. Spinel and periclase phases are present, as confirmed by strong reflections at 36.84°, 44.81°, 59.35° and 65.23° 2θ angles for spinel and 42.92°, 62.30° and 78.63° 2θ for periclase. Alumina is also present. The sample prepared at 550 °C contained additionally calcium carbonate phase, which was absent from the sample prepared at 650 °C. After soaking in sodium carbonate the powders prepared at 550 °C and 650 °C, slightly differed from the fresh powder. Both diffractograms for MgAl_550 and MgAl_650 were practically identical, showing only two phases – spinel and periclase.

No hydrotalcite phase may be seen in Figure 6.7.6. Peaks at 1384–1385 cm⁻¹ originate from carbonate ions. Bands at 603 cm^{-1} and 507 cm^{-1} correspond to Mg-O-Mg stretching vibrations. As it may be noticed, the sample obtained at $650 \,^{\circ}$ C has low content of carbonate ions than the other materials. Also, the band corresponding to O-H group is very weak. The 3419 cm⁻¹ peak of highest intensity originating from O-H group may be observed for the samples prepared in 450 $^{\circ}$ C [21]. It may be assigned to water physiosorbed in the structure [22].



Figure 6.7.6: FTIR spectra of MgAl samples combusted at 450 $^{\circ}$ C (•), 550 $^{\circ}$ C (×) and 650 $^{\circ}$ C (\blacksquare), after combustion

Figure 6.7.7 shows FTIR spectra for the samples after combustion and soaking in sodium carbonate solution. The spectrum of MgAl_450 shows bands typical for hydrotalcite. The peaks at $3400-3600 \text{ cm}^{-1}$ corresponds to the O – H groups. This band is much smaller in two other samples. Also, the peak at 1384 cm^{-1} originating from carbonate ions is much stronger for the sample formed at $450 \degree$ C. This confirms the presence of hydrotalcite structure.



Figure 6.7.7: FTIR spectra of samples combusted at 450°C(•), 550 °C (×) and 650 °C (■), after combustion and crystallisation in sodium carbonate solution

In Figure 6.7.8a, diffractograms of NiMgAl samples prepared at different temperatures are compared. For the powders after combustion, the analysis was made only for the samples formed at 550 °C and 650 °C. Phase composition of these two samples is very similar, the only difference is the presence of calcium carbonate in the NiMgAl_550. At both temperatures following compounds may be found: magnesium nickel oxide confirmed by reflections at 2θ of 37.12°, 43.15°, 62.63°, 75.10° and 79.10°, and nickel aluminum oxide confirmed by the lines at 2θ of 36.96°, 45.06° and 65.50°.

Figure 6.7.8b shows the comparison of XRD patterns for the samples soaked in sodium carbonate solution after combustion. All samples contain nickel alu-

minum oxide and magnesium nickel oxide. The sample NiMgAl_450 has small reflections at 11.65° and 23.42° 2θ typical for hydrotalcites.



Figure 6.7.8: xRD patterns of NiMgAl samples (a) after combustion, (b) after crystallisation in sodiumcarbonate

Figures 6.7.9 and 6.7.10 present FTIR spectra for the NiMgAl samples prepared via solution combustion synthesis after combustion and after crystallization in sodium carbonate, subsequently. The bands are similar to those for the MgAl samples. After combustion, NiMgAl_450 presents strong peaks for carbonate ions and curve related to O-H groups what may be a confirmation of presence of hydrotalcite structure. The weakest number of bonding vibrations is found in sample NiMgAl_650, which confirms oxide form of the sample.

After contact with sodium carbonate solution, the sample NiMgAl_450 shows bands typical for hydrotalcite, however the bands intensity is rather low, indicating relatively low content of this phase. The peaks of O – H and CO_3^{2-} groups are present in all the samples, but with the increase of the combustion temperature their intensity decreases.

Conslusions

This research was focused on the comparison of hydrotalcites preparation techniques. Urea hydrolysis, coprecipitation at low supersaturation and solution combustion synthesis were compared. According to XRD and FTIR analysis only urea hydrolysis method led to formation of hydrotalcite as only crystalline phase. The samples prepared by coprecipitation show lower crystallinity as those from the urea method. Also, phases other than hydrotalcite are present.



Figure 6.7.9: FTIR spectra of NiMgAl samples combusted at 450 $^{\circ}$ C (•), 550 $^{\circ}$ C (×) and 650 $^{\circ}$ C (\blacksquare), after combustion



Figure 6.7.10: FTIR spectra of samples combusted at 450 $^{\circ}$ C (•), 550 $^{\circ}$ C (×) and 650 $^{\circ}$ C (\blacksquare), after combustion and crystallisation in sodium carbonate solution

Hydrotalcite was formed during solution combustion synthesis, but only in the samples which were combusted at 450 °C. Additionally, aluminum oxide and sodium carbonate were present in MgAl_450, and nickel aluminum oxide and magnesium nickel oxide in NiMgAl_450. The MgAl samples prepared at 550 °C and 650 °C showed only the presence of spinel and periclase, while nickel aluminum oxide and magnesium nickel oxide were detected for NiMgAl.

In order to develop solution combustion method to prepare hydrotal cites, lower combustion temperatures of 400 $^\circ\!C$ should by examined. Another possibility could be soaking the powder obtained at higher temperature in sodium carbonate solution with concentration higher than 0.1 M.

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6.8 Modified bentonite-derived materials as catalysts for selective catalytic reduction of nitrogen oxides

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Keywords: pillared bentonite, acid activation, alumina, iron, copper, selective catalytic reduction, NO, ammonia.

Abstract

Recently, excessive emission of adverse nitrogen oxides (NO_x) from the industry is observed. Cationic layered clays, including bentonites have been investigated as potential catalysts for scr DeNO_x systems. Therefore, bentonite-derived catalysts were prepared and tested in the NH₃-scr reaction. Bentonite was activated with HCl or HNO₃. Subsequently, the samples were treated with $C_2H_2O_4$ and pillared with alumina by the ion-exchange. Therefore, the materials were impregnated with iron and copper. The obtained catalysts were characterized by xrD and FTIR. The scr catalytic tests carried out over analyzed samples indicated high conversion rate of NO. Acid treatment and impregnation strongly enhanced the catalytic activity.

Introduction

Nitrogen oxides (NO_x) generated by fuel combustion in stationary and mobile sources are one of the most harmful pollutants of the environment. The actual EU directive 2010/75/EU restrictively limits the permitted amount of NO_x emitted with the exhaust gases [1,2]. The most efficient industrial technology of nitrogen oxides abatement is selective catalytic reduction (scR). The process is based on the reduction of NO_x with the reducing agent (usually ammonia) into nitrogen and water vapor. Although the industrial catalyst V₂O₅-TiO₂-WO₃ or V₂O₅-TiO₂-MoO₃ provides high NO conversion, it has some considerable limitations. First of all, the system exhibits satisfactory catalytic properties only in the narrow temperature window (300–400 °C). Therefore it is applied in the high-dust position, where it undergoes deactivation by SO₂ or fly ash very quickly. On the other hand, location of the catalyst at the tail position or downstream of the electrostatic precipitator requires additional heating of the gases and increases the overall costs of the process. The commercial catalyst is also relatively expensive, moreover vanadium compounds are harmful for the environment and their

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utilization is complicated [2,3]. In view of the above, novel, effective and cheap catalysts need to be found in order to improve the activity in the low temperature range (< 250 °C) and the resistance to SO_2 , As_2O_3 , soot and other poisonous compounds of flue gases.

In recent years, many new materials have been intensively studied as the scr catalysts, including supported metal oxides, exchanged zeolites, hydrotalcitederived materials, modified vermiculites, activated carbons or activated coke [3-8]. Another interesting materials are layered cationic clays. Due to their special properties, including the high specific surface area, ion-exchange properties and stability in high temperature, these materials are considered to be potential catalysts for NH_3 -scr [9–12]. The cationic clays are widespread in nature layered aluminosilicates. The building block of these materials are Si(O, OH) tetrahedra and M(O, OH)₆ octahedra (M: Al^{3+} , Mg^{2+} , Fe^{3+} , Fe^{2+}). The layers are negatively charged and the whole structure is balanced by the interlayer cations (e.g. Na^+ , Ca^{2+}). The representative example of cationic clays is bentonite, in which the isomorphous substitution of Al^{3+} for Si^{4+} in the thetraedral layer and Mg^{2+} for Al^{3+} in the octhaedral layer takes place. The material consists mostly of montmorillonite which is the dioctahedral low charged clay of the smectite group. There are also some amounts of quartz, cristobalite, pyrite, mica and kaolinite in the clay. The majority of bentonites are developed from weathering of volcanoclastic rocks [13]. These aluminosilicates present considerable amount of both Brönsted and Lewis acidic centres, which are the external OH⁻ groups and Al³⁺ ions in the tetrahedral sheet respectively [13,14]. What is more, it is possible to induct redox properties of the materials by the introduction of e.g. Cu²⁺, Fe²⁺ or Ag⁺ ions [10,12,15].

Both the surface acidity and the specific surface area of the clay can be greatly enhanced by the acid activation. Motak [2] carried out the research over the surface properties of acid activated montmorillonites and its catalytic performance in NH_3 -scr. It was proven that pre-treatment with HCl solution increased considerably the specific surface area of the material, which was caused by the partial delamination and resulted in washing out of Al-oxides. Moreover, activated materials impregnated subsequently with copper exhibited increased NO conversion in comparison to the samples non-treated with acid.

Another kind of modification is based on intercalation (pillaring) of cationic clays. It provides the possibility of tailoring the interlayer space by the exchange of cations which compensate the negative charge with inorganic cations that have dimension larger than the original ions. Calcination of pillared clays results in formation of three-dimensionally or disordered (delaminated), microporous structure. What is more, intercalated layered aluminosilicates have considerably larger specific surface area [9,16,17]. Chmielarz et al. [19] studied the influence of pillaring with alumina, titania and zirconia on the structure and catalytic activity in NH₃-SCR of montmorillonites. XDR analysis carried out for the pillared

clays indicated a shift of (0 0 1) reflectance to lower values of 2θ which means successful introduction of metal oxide pillars into the interlayer space, moreover, it was calculated that interlayer distance increased after intercalation. Additionally, pillaring resulted in the considerable increase of sber from 38 m² g⁻¹ to even 279 m² g⁻¹. Catalytic tests carried out for intercalated materials containing copper or iron as an active phase indicated satisfactory conversion of NO in the low-temperature range (< 250 °C) and N₂ selectivity over 90% for all analyzed materials.

Many kinds of metals have been investigated as active phase in scr. Noble metals are considered to be very active when hydrocarbons are used as the reducing agent [19,20,21,22,23]. However, due to their high cost and rapid deactivation, transition metals seem to be more efficient and economic [24,25,26,27,28]. Among transition metals active in the scr process, copper and iron are confirmed to have excellent activity in scr DeNO_x systems, e.g. in zeolites [19,20,21,22,27], activated carbons [34] and layered clays [2,18,12,15]. The subject of this work is to study the influence of the type of acid (HCl or HNO₃) and intercalation with Al_2O_3 pillars on the structure properties of bentonite. The materials were subsequently impregnated with iron and copper and tested as the NH₃-scr catalysts.

Materials and methods

Catalyst preparation The supports of the catalysts based on bentonite were prepared according to two routes:

- (1) bentonite \rightarrow acid activation with HCl \rightarrow acid activation with C₂H₂O₄ \rightarrow pillaring with Al-polycations \rightarrow impregnation with Cu or Fe;
- (2) bentonite \rightarrow acid activation with HNO₃ \rightarrow acid activation with C₂H₂O₄ \rightarrow pillaring with Al-polycations \rightarrow impregnation with Cu or Fe.

The samples of bentonite were dispersed in a solution of HCl (0.8 M) or HNO₃ (0.8 M) with the ratio of clay mass to acid solution of $1 \text{ g}/10 \text{ cm}^3$ and stirred at 95 °C for 2 h. The samples were separated by filtration, washed with distilled water and dried at 120 °C for 24 h and then calcined at 300 °C for 2 h. Subsequently, the next acid activation with organic acid (C₂H₂O₄) was performed. Previously activated samples were dispersed in the oxalic acid (0.12 M) and stirred at 80 °C for 2 h, filtered, washed with distilled water and dried for 24 h at 70 °C. The samples were labeled as BentAlHClMe or BentAlHNO₃Me (where Me: Cu or Fe).

Acid activated samples were pillared with Al-polycations. The aluminium hydroxy-oligometric solution was prepared by slow addition of 0.4 M NaOH to 0.4 M solution of $AlCl_3$ under constant stirring with OH/Al ratio of 2.5 for about 24 h. Then, the pillaring solution was left to age in room temperature for

about 96 h. In the next step pillaring solution was added to the suspension containing 1% m/m of activated bentonite in distilled water until the Al/clay ratio reached the value of 12 mmol of Al per 1 g of bentonite. The mixture was left to react for 4 h. Then the modified samples were separated, washed with distilled water to remove the chloride ions and dried at 120 °C for 24 h.

The next step of preparation was incipient wetness impregnation with a queous solution of Cu(NO₃)₂ or Fe(NO₃)₂ to obtain 5% m/m solution of active phase in respect to the support mass. Obtained catalysts were subsequently dried for 24 h at 120 $^{\circ}$ C and calcined at 300 $^{\circ}$ C for 2 h.

Catalyst characterization

The mineralogical compositions of the samples were determined by the XRD analysis. The measurement was carried out using PANalytical-Empyrean diffractometer equipped with Cu KA ($\lambda = 1.5206$ Å) radiation source. The 2θ spectrum of the diffractometer ranges from 5 to 900 with the step size of 0.02 deg min⁻¹.

Fourier-transform-infrared spectra (FT-IR) were obtained with a Thermo Nicolet 380 FT-IR spectrometer in the region $4000 - 400 \text{ cm}^{-1}$, registered with a resolution of 4 cm^{-1} . The modified bentonite samples were mixed with KBr at the ratio of 1:100 and pressed into disks.

Catalytic measurement

Catalytic NH₃-scR tests were performed at atmospheric pressure in a fixed-bed flow reactor containing 0.2 g of the catalysts. The reaction mixture contained 800 ppm NO, 800 ppm NH₃, 3.5 vol% O₂ and balance He. The total flow of the gas mixture was 100 cm³ min⁻¹. The concentration of NO and N₂O were analyzed by FT-IR detector (ABB 2000 AO series). The reactor was heated to appropriate temperature (150-200-250-300-250 °C, 10 °C/min). A catalyst was kept for 60 min at each temperature. The temperature inside the reactor was controlled by a thermocouple with an electronic temperature controller (Lumel RE19). NO conversion was calculated according to the equation:

$$NO_{conversion} = \frac{NO_{in} - NO_{out}}{NO_{in}} \cdot 100\%$$
(6.8.1)

where NO_{in} is the inlet NO concentration and NO_{out} is the outlet NO concentration.

Results and discussion

X-ray diffraction studies of modified bentonite

The results of structural studies on the modified bentonites are shown in Fig. 6.8.1. and Fig. 6.8.2. For the XRD pattern of natural bentonite, one reflection was observed in the region of $20 < 2\theta < 100$. It corresponds to the ca. 7.30° (2 θ) value from which the (0 0 1) basal spacing was calculated to be 12.30 Å. The reflections observed at $2\theta \sim 19.5^{\circ}$ and $61-62^{\circ}$ correspond to diffraction from (1 0 0) layers of montmorillonite phase present in the bentonite structure [14]. The XRD pattern of samples pre-treated with acid show poorer crystallinity confirmed by less intense reflections on the diffractogram in comparison to the parent clay. It is probably the result of the presence of layers activated with hydrogen ions or the irregular placement of non-activated and activated layers, therefore the clay becomes amorphous to XRD [14]. Additionally, it can be observed that regardless to the type of acid used for the activation procedure, the pattern is similar for both preparation routes. The reflections observed at $2\theta \sim 9^\circ$ suggest that some fraction of the clay was not pillared with Al-polycations, probably due to the short time of pillaring. However, small peak at $2\theta \sim 18.70^{\circ}$ confirms the presence of Al in the interlayer space [12]. The reflections observed $2\theta \sim 26.5^{\circ}$ and 28.5° are caused by the presence of quartz and crystobalite impurities in the clay [19]. The presence of Cu or Fe introduced into the modified bentonite via impregnation is confirmed by the reflectance at $2\theta \sim 35^\circ$, 75° and 35°, respectively [35,36]. Introduction of the transition metals as an active phase of the catalyst did not change the basal spacing of montmorillonite phase present in the samples.

FT-IR studies of acid-activated bentonite

FT-IR spectra of natural and acid activated bentonite are presented in Fig. 6.8.3. The absorption band observed at 3635 cm⁻¹ corresponds to the stretching vibrations of structural OH groups of montmorillonite. Bands present at 929 cm⁻¹, 845 cm^{-1} and 526 cm^{-1} are due to the AlAlOH, AlMgOH and Al – O – Si bending vibrations, respectively, while band at 1040 cm⁻¹ observed for natural bentonite is ascribed to the stretching vibrations of Si-O groups in the in-plane thetraedral sheets [13,38–40]. Absorption bands at 642 and 634 cm⁻¹ correspond to the coupled Al-O and Si-O out-of-plane vibrations, respectively [14]. Alternative explanation of the presence of these bands is the plane deformation of M - O - Sivibrations, where M: Mg or Al [41]. Hence, the analysis indicated that montmorillonite is the dominant phase of bentonite which stays with agreement with the xRD measurement. Band at 3429 cm⁻¹ observed for natural bentonite is assigned to the H₂O molecules of natural montmorillonite corresponding to the stretching vibrations of H-O-H, due to the overtone of a vibration of water observed at 1622 cm⁻¹. For acid activated samples, the bans assigned to water molecules are shifted to 3517 cm⁻¹ and 3524 cm⁻¹ which suggest the overlapping of asym-



Figure 6.8.1: The xRD patterns of the natural bentonite (a) and bentonite pre-treated with HCl + modified with Al pillars (b) and modified bentonite impregnated with Cu (c) or Fe (d).



Figure 6.8.2: The XRD patterns of the natural bentonite (a) and bentonite pre-treated with HNO_3 + modified with Al pillars (b) and modified bentonite impregnated with Cu (c) or Fe (d).

metric and symmetric H-O-H stretching vibrations [14]. Treatment with acid influenced the fundamental vibrations of Si – O and OH groups in comparison to the non-modified samples. For instance, the stretching vibration band characteristic for montmorillonite was shifted up to 3746 cm⁻¹. What is more, a slight shift of the band at 1040 cm⁻¹ also indicated differences in the structure in comparison to the parent clay. Lack of the band at 789 cm⁻¹ suggest the exit of octahedral cations to the tetrahedral layers [41].



Figure 6.8.3: IR spectra of the natural bentonite (a) and bentonite activated with HCl (b) or HNO_3 (c).

Catalytic tests

Acid treated and Al-pillared bentonites were tested as catalysts of selective catalytic reduction of NO with ammonia (NH_3 -scr.). The desired products of these reaction are N₂ and H₂O, while N₂O is the side-product.

Catalytic activity of all of the modified bentonites is presented in Fig. 6.8.4. The samples activated with HNO₃ exhibited significantly higher catalytic activity in NO reduction than materials treated with HCl, regardless the introduced active phase. Moreover, considering the whole temperature range of the catalytic tests, bentonites that contain Fe showed much better catalytic performance in comparison to the samples with Cu. However, in case of the T_{50} , which is the temperature of 50% conversion of NO, both BentAlHNO₃Cu and BentAlHNO₃Fe

samples exhibited similar temperature values (about 190 °C). The highest catalytic activity of 90% at about 300 °C was detected for BentAlHNO₃Fe. Moreover, the NO conversion does not decrease with the increasing temperature, which means that the reaction reaches its equilibrium. Therefore, it can be assumed that this catalyst has a strong potential to be the substitute of the commercial system, V_2O_5 – TiO₂ with WoO₃ or MoO₃ as a promoter. According to the scientific literature, the commercial catalyst reaches the maximum of NO conversion at about 300-450 °C [42,43]. In case of bentonites, similar, or even lower temperature ranges are taking into account. Hence, it is possible that after addition of promoters, which provide the bentonite-based catalysts better stability and selectivity to N_2 , V_2O_5 – TiO₂ could be replaced by these materials in commercial applications. What is more, considering T_{50} of BentAlHNO₃Fe and another commercial zeolite-based catalysts, Cu-ssz and Cu-sAPO, similar values of T_{50} (about 190 °C) were detected [44]. The materials containing copper as an active phase exhibited lower catalytic activity in NO conversion in comparison to Fe-based catalysts. It is clearly visible that BentAlHClCu showed rather poor catalytic activity, exhibiting maximum NO conversion of 42% at 250 °C. It can be assumed that the reason of lower catalytic activity of this sample might be the weaker interaction of HCl with the support, in comparison to HNO₃. Consequently, the cations present in the octahedral layers of bentonite were not successfully leached on the tetrahedral layers. Moreover, the specific surface area might have not increased enough to facilitate the access of reacting molecules to the active centres of the catalyst. Nevertheless, to examine the structure and texture of the materials, additional SBET analysis before and after modification of the samples should be carried out. What is more, it was observed that above 250-300 °C the activity of Cu-based catalysts was significantly limited. According to the scientific literature, it might be caused by the strong potential of copper species in the ammonia oxidation, which is the side process of NH₃-scr [44,45,46].

The concentration of N₂O in the flue gas detected for all catalysts in the temperature range of 100–400 °C is presented in Fig. 6.8.5. In case of HCl treated samples, the amount of N₂O was significantly higher than in case of bentonites activated by HNO₃. The type of metal introduced as an active phase did not influence substantially on the nitrous oxide concentration. However, in the temperature range of 200–350 °C, for both Fe-containing samples, the amount of N₂O was subtly lower. It is possible, that for the samples activated with HNO₃ better dispersion of the active phase, resulting in lower N₂O concentration was obtained. Nevertheless, to prove this expectation, additional H₂-TPR studies should be carried out. Generally, the results indicate that not only catalytic activity, but also selectivity to nitrogen of the catalyst was enhanced after activation with HNO₃ and introduction of Fe as an active phase.

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Figure 6.8.4: Catalytic activity comparison of BentAlHClCu, BentAlHClFe,BentAlHNO3Cu, BentAlHNO3Fe samples. Reaction conditions: NO – 800 ppm,NH3 – 800 ppm, O2 – 3.5 vol.%, balance He.



Figure 6.8.5: N₂O concentration in the flue gas detected for BentAlHClCu, BentAlHClFe, BentAlHNO₃Cu, BentAlHNO₃Fe samples. Reaction conditions: NO – 800 ppm, NH₃ – 800 ppm, O₂ – 3.5 vol.%, balance He.

Conclusions

Bentonites treated with HCl or HNO₃, pillared with Al polycations and impregnated with iron and copper species were tested as the potential NH₃-scR catalysts. The results of catalytic tests were compared to the NO conversion exhibited by the commercial system, $V_2O_5 - WO_3 - TiO_2$ or $V_2O_5 - MOO_3 - TiO_2$. It was observed that especially for samples activated with HNO₃ and containing Fe as an active phase, the temperature of 50% NO conversion was similar to the industrial catalyst. What is more, the results were compared to another commercially used material, Cu-ssz and Cu-sAPO and it was assumed, that comparable NO conversion at similar temperature were obtained. Moreover, it was observed that the type of activating acid strongly influenced not only the catalytic activity, but also the concentration of N_2O in the flue gas. It is probably caused by stronger interaction of HNO₃ with the clay structure resulting in increased specific surface area and enhancement of the pore system. It is expected that the addition of promoters to the bentonite-based catalyst could improve their catalytic activity and decrease the concentration of N_2O .

XRD analysis carried out over prepared catalysts proved the presence of phase characteristic for montmorillonite, which is the main component of bentonite. The results are in agreement with the data presented previously in the scientific literature. It should be mentioned, that the samples activated with acids show poorer crystallinity. It is probably the result of the irregular placement of layers containing H⁺ ions from acid and non-activated layers. Therefore, the structure becomes invisible for XRD. Additionally, it is probably because of the short time of the intercalation procedure. It was observed that introduction of Cu and Fe did not affect the basal spacing of montmorillonite present in the clays.

FT-IR measurement had a significant contribution into the understanding of the structure and bonding in the modified clays. The spectra provided information on the vibration modes of these materials. Characteristic absorption bands assigned to the vibration modes of Si – O, Al – O – Si, Mg – O – Si or H₂O molecules were detected. Acid activation visibly affected the position of characteristic bands, shifting up some of them to the higher values of the wavelength. Additionally, it was proven that acid activation results in leaching of octahedral cations on the tetrahedral sheets.

The results of the following research proved that bentonite, which is the representative of cationic clays, is characterized by complicated structure and phase composition. Modifications, such as acid treatment or pillaring results in formation more complex materials with diversified surface and structure properties. In view of very strong impact of these modifications on the catalytic performance, more detailed studies focused on the influence of acid activation and pillaring on the activity of bentonites in NO conversion are indispensable. Acknowledgement Research financed by Grant AGH.

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6.9 Poly(glycerol sebacate) as prepolymer material for biomedical applications – synthesis and purification method

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KEYWORDS: poly(glycerol sebacate), prepolymer, synthesis, purification, optimization.

Abstract

Polyesters are very interesting materials for scientists looking for biodegradable and biocompatible materials. Currently, one of the newest polyesters, which could be biomaterial for tissue regeneration is poly(glycerol sebacate) (PGS). PGS is a biocompatible, biodegradable, non-immunogenic and non-toxic material. It is postulated to use this polymer with suitable properties as follows: cell scaffold in soft tissue engineering, drug carrier, surgical sealants, and as a contact surface for biomedical sensors. Most of the works are focused on the synthesis of the crosslinked polymer (no isolation of the prepolymer) adapted to perform one function. In our work, we focused on developing a synthesis and purification of a non-crosslinked product, which is called prepolymer. The equipment for industrial polymer production has been proposed. The material was characterized by IR spectroscopy, NMR spectroscopy and the acid and ester numbers were determined for delimitation of esterification degree. The analysis of the final product confirms the purity of the prepgs. The material produced by us can be processed in a simple way for functionalization. This is an incredible advantage appreciated by manufacturers of medical devices.

Introduction

Polymeric materials are broadly used in medicine [1,2]. In regenerative medicine [3] and pharmacy [4] was observed particular increase in interest of biodegradable polymers [5]. Biodegradable polymers could be applicable as wound dressing materials [6] (including hydrogel ones [7,8]), resorbable surgical threads [4], and bone implants [9], as well as connectors and screws for bonding broken bones [10]. Also regeneration of damaged tissue (e.g. cartilage [11], bone [12,13], nerve [14], and epithelial tissue [15]) could be help by polymeric scaffolds [16]. To achieve the attractive aim for medicine, the physical and chemical properties of polymer have to suit with their application. It is hard to do,

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despite the broad bases of known biopolymers. For this reason, it is important to synthesize new polymers with properties, which will be better for the specific application.

Poly(glycerol sebacate) (PGS) was first obtained in 2002 in the Wang Yadong's team and it was immediately postulated that this material should be used in medicine [17,18]. Currently, depending on the reaction parameters, it becomes possible to obtain this material in such forms as: wax, viscous liquid, viscous elastomer and previously known elastomer [19]. PGS become an extremely interesting polymer because of relatively easy way to make significant modifications to the properties of the material. Until this day, many works on the synthesis of PGS (Fig. 6.9.1) have been created, all of them rely on the reaction of polycondensation of glycerol with sebacic acid with the production of a water molecule [17–27].



Figure 6.9.1: Synthesis of poly(glycerol sebacate) [28].

Unfortunately, many works dealing with the synthesis of this polymer provide significantly different polycondensation performance, often leading to significantly different properties of polymers. What is the worst, most works describe the synthesis without separating the product in the form of a prepolymer (prePGS), i.e. polymer chains that would not be cross-linked. For this reason, such significant differences in the synthesis of a given material may occur. Usually, after first synthetic step (obtaining prePGS) there was immediately ongoing second step to obtain, finally, PGS that could not be futher modificated, but which has properties for direct application (Tab. 6.9.1).

Prepolymer allows for chain modifications to obtain a material with satisfactory properties (molar mass, dendrimeric or linear structure). It is very important to have good process of prepgs synthesis, because it naturally will be semiproduct for all medical devices based on Pgs. Converting prepgs to Pgs is very easy and usually relies on vacuum drying, what shows Tab. 6.9.1. Such parameters as time, temperature and pressure allow to obtain Pgs which have required properties to specific application. For example, elastomeric Pgs with Young's Modulus about 0.025–1.200 MPa, is very alike to cartilage tissue (0.02–0.50 MPa). Moreover, elongation at break at 330 % for Pgs and 260 % for vascular tissue also are

no.	1st step		2nd step		
	molar ratio _{G/SA} *	other conditions	molar ratio G/SA	other conditions	ref.
1	1:1	120 °C, 24 h, Ar	1:1	120 °C, 72 h, 0.1 MPa, Ar	[20]
2	1:1	130 °C, 1 kPa, N ₂	2:2.5	 (1) 130 °C, 1 kPa, N₂ (2) 130 °C, 1 MPa, N₂ (3) cooling down to rt 	[21]
3	1:1	120 °C, 24 h, Ar	1:1	120 °C, 48h, 40 mTorr, Ar	[17]
4	1:1	(1) 120 °C, 24 h, 1 Torr, N ₂ (2) 5 h, 40 mTorr	1:1	120 °C, 24 h	[19]
5	2:1,2:2, 2:3,2:4, 2:5	(1) 120 °C, 24 h, Ar (2) 120 °C, 48 h, low pressure	same as before	120 °C, 48 h, low pressure	[22]
6	1:1	130 °C, 24 h, N ₂ or 150 °C, 5 h, N ₂	1:1	130°C, 24–168 h	[23]

Table 6.9.1: Known synthetic methods (without prepcs isolation).

* Molar ratio G/SA - molar ratio glycerin/sebacic acid.

very similar [24]. This polymer with appropriate properties could be used in the following way: scaffolding in soft tissue engineering, drug carrier, surgical sealer, and as a contact surface for biomedical sensors [24,29–31].

Till now, there were not any works about synthesis of prepGs, because of that our group developed synthesis and purification process of prepolymer poly(glycerol sebacate) [28]. The material produced by us can be processed in a simple way for functionalization. This is an incredible advantage appreciated by manufacturers of medical devices. In this work synthesis and purification method will be presented, characterization by IR spectroscopy, NMR spectroscopy and the degree of estrification. Moreover, the equipment for industrial prepolymer production has been proposed.

Materials and methods

All reactions were carried out on a MultiMax (Fig. 6.9.2) production apparatus of the Mettler Toledo company. This apparatus is a system of parallel reactors allowing for the process of optimizing the chemical reaction. The reactor has a

built-in ZnSe prism with a diamond that allows for measurement of the IR spectrum in ATR technology during synthesis. Specialized software, as well as a set of regulators, allows for strict control of the process, thus ensuring repeatability of synthesis. The reactors are made of high quality acid resistant steel and placed in a heating jacket, which ensures chemical resistance and good heat reduction. The MultiMax system ensures uniform mixing by controlling the mechanical stirrer and the same temperature profile in the reaction. Optimization process and real time IR spectra have been written with detail in our previous work [28].



Figure 6.9.2: MultiMax reactors system from Mettler Toledo [32].

Prepolymer synthesis were carried out at temperature of 150 °C for 4 hours. The ratio of glycerol and sebacic acid in each reaction was 2:1 (15.00 g, 74 mmol of sebacic acid, and 13.63 g, 148 mmol of anhydrous glycerine). This parameters were previously optimized to obtain prePGs, which estrification degree was about 82 % [28]. Before the reagents were weighed, the reactor have been filled with nitrogen. Moreover, synthesis was carried out in the flow of this gas (6 L/min).

To purify prepolymer poly(glycerol sebacate) 15 g of preps and 15 mL of dioxane was stirred for 24 hours. Then the solution was poured into 250 mL distilled water at 5 °C. Upon cooling, the suspension was seeped on the cooled Buchner funnel with a double filter. The sediment was dried at 45 °C for 24 hours [28,32].

Pure prepolymer PGS: white solid; IR (ATR, cm⁻¹) 2929, 1714, 1172, 1039; ¹H NMR (400 MHz, CDCl₃) δ /ppm 1.30 (m, 9H) 1.60 (m, 4H) 2.33 (m, 4H) 3.54 (m, 8H) 4.14 (m, 1H) 5.15 (m, 5H); ¹³C NMR (100 MHz, CDCl₃) δ /ppm 24.6, 28.8, 34.1, 63.3, 64.9, 68.2, 70.3, 174.0, 179.1 [28].

IR spectra were obtained using a Bruker Alpha II Platinum atr spectrometer (in atr technics). 1 H and 13 C NMR spectra were obtained using a Mercury-400BB spectrometer (400 MHz).

Esterification degree (*ED*) was calculated on the basis of the following formula [28]:

$$ED = \frac{EN}{EN + AN} \cdot 100\% \tag{6.9.1}$$

where: ED - esterification degree; AN - acid number; EN - ester number.

Acid Number (*AN*): weigh 0.2-0.3 g of the sample, add 25 ml of MeOH and 3-4 drops of thymol blue. Titrate the sample with 0.1 M aqueous solution of NaOH until the colour changes from yellow to blue. Simultaneously, a blank test should be assayed. The analysis was carried out in three replications. The standard error did not exceed 5 %. Calculate the acid number (*AN*) using the formula:

$$AN = \frac{(V - V_0) \cdot M_{\rm KOH} \cdot 56.1}{m} \cdot 100$$
 (6.9.2)

where: AN – acid number (mg/g sample); V_0 – volume of 0.1 M KOH used to titrate the blank test; V – volume of 0.1 M KOH used to titrate the sample; M_{KOH} – KOH titre used for titration (0.1 M); m – mass of the sample.

Ester number (EN): 0.2-0.3 g of the sample was weighed. 15 mL of methanol and 20 mL of 0.1 M of aqueous solution of KOH were added. It was heated in boiling water under a reflux condenser for 1 hour. Upon cooling the solution, the excess of added KOH 0.1 M was titrated with hydrochloric acid in the presence of phenolphthalein. Simultaneously, the blank test was conducted. The analysis was carried out in three replications. The standard error did not exceed 5 %. The ester number (*EN*) is calculated according to the following formula:

$$EN = \frac{(V_0 - V) \cdot M_{\text{HCL}} \cdot 56.1}{m} - AN$$
(6.9.3)

where: EN – ester number (mg/g sample); AN – acid number; V_0 – volume 0.1 M HCl used to titrate the blank test; V – volume of 0.1 M HCl used to titrate the sample; M_{HCl} – HCl titre used for titration (0.1 M); m – mass of the sample.

Result and discussion

The polycondensation of glycerine and sebacic acid (molar ratio 2:1) was examined. The reaction was conducted at 150 °C for 4 h. We decided to run the process without any catalyst, due to the planned medical application of the obtained polymer. During the process reaction was monitored by real time IR spectroscopy. Signals at 1720 cm^{-1} were expanded and shifted toward higher wave numbers, which indicates the formation of ester bonds. The disappearance of the acid originated 1410 cm^{-1} band and an increase in the intensity of the 1185 cm^{-1} ester band were observed.

To purify prepgs the post-reaction mixture was dissolved in dioxane for 24 h in order to completely dissolve the polymer. The solution was then poured into cold water and filtered. The sediment was dried under reduced pressure at 45 $^{\circ}$ C for 24 h. Process is shown in Fig. 6.9.3.



Figure 6.9.3: Block diagram of synthesis and purification method [28].

The analysis of product IR spectra allows to confirm purity poly(glycerol sebacate). The disappearance of the 1685 cm⁻¹ wide band and the occurrence of the 1715 cm⁻¹ band in the product confirms that the polyester has been obtained and the acid is fully reacted. The incomplete disappearance of the band in the range of 3200–3400 cm⁻¹ allows to claim that polymer chain has glycerol hydroxy side groups. The characteristic area of the fingerprint, which cannot be interpreted as average of glycerol and sebacic acid, suggests that the product is free of unreacted substrates. Also, the repeatability of synthesis has been noted, as evidenced by the high similarity of spectra for the products of subsequent reactions.

The ¹H NMR spectra obtained for the prepolymer and polymer differ in the intensity of the signals coming from the glycerol portion relative to the sebacic part. For the prepolymer, a significant increase in the intensity of signals from the alcohol-derived portion is observed. This allows to conclude that the obtained compound is largely composed of a disubstituted glycerine portion, so the ratio of the alcohol and acid portion is close to one. Only a non-crosslinked polymer, i.e. a prepolymer form, can have such a construction.

After purification *AN* of product is smaller (14) than before that process (60). It confirms that acid monomers were isolated from the product. It is very important, because any acid amounts could hydrolize product. It is very undesirable phenomenon for all PGs products, not only for medicine devices. *ED* of final product was about 96 %.

Because prepgs is not commercially available, we decide to propose apparatus to industrial production. Our technology is based on basic and available apparatus such as:

- Z1 glycerine bearing tank (18 L);
- Z2 dioxane bearing tank (65 L);
- Z3 hydrated glycerine tank (16 L);
- Z4 regenerated nitrogen tank (10 L);
- R1 stainless steel reactor with a jacket and a mechanical agitator to conduct polycondensation (15 L);
- R2 stainless steel reactor with a jacket and a mechanical agitator to conduct granulation (130 L);
- F1 filter;
- S1 dryer;
- K1 column with filling for gas drying;
- WC1 shell-and-tube heat exchanger;
- SP1 compressor.

More details shows technological scheme (Fig. 6.9.4).

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Figure 6.9.4: Technological scheme for industrial process of synthesis and purification of prepcs.

A like laboratory the industrial process begins with the polycondensation reaction. The reaction is carried out in a nitrogen flow which is regenerated. After polycondensation, the reaction mixture is cooled to 40° C and then distilled under vacuum to purify the excess of glycerol and the water formed in the reaction. The obtained resin is diluted, which significantly affects the quality of the obtained granulate. The granulation is carried out by precipitating the diluted resin in

demi water. The obtained suspension is filtered and the obtained granulate is dried under mild conditions. The table (Tab. 6.9.2) presents the basic information about each process/unit operation.

Process/unit operation	Parameters
polycondensation	150 °C; 4 h
distillation	40 °C; 1.5 h; 18 mbar
dilute	rt; 0.2 h
precipitation	≈ 10 °C; 0.25 h
filtration	rt; 0.5 h
drying	40 °C; 0.5 h

Table 6.9.2: All process/unit operations parameters.

Calculated production capacity will be at 100 kg/year, if there are 48 charge/year. About 2.2 kg prepgs could be obtain in one charge. Detailed mass balance is shown in table (Tab. 6.9.3).

Process	Input	kg/charge	Output	kg/charge
polycondensation	sebacic acid glycerol	2.4 2.2	post-reaction mixture	4.6
distillation	post-reaction mixture	4.6	liquid exhausted vapors	3.1 1.5
dilute	liquid exhausted dioxane	3.1 6.7	prepolymer solution	9.8
precipitation	prepolymer solution water	9.8 97.3	suspension	107.1
filtration	suspension	107.1	filtrate granulate	104.4 2.7
drying	granulate	2.7	pre¤gs water, dioxane (vapor)	2.2 0.5

Table 6.9.3: Mass balance for industrial process of synthesis and purification of prepos.

Economic calculations and estimation of the scale up risk [34] give a positive answer. Currently, no one is able to offer such a product, moreover the cost of production is low and considering its biomedical application, large profit is very real. Gross profit was estimated at \notin 35 thousand/kg of product. The technical cost of manufacturing (include all cost for production of 1 kg prepas) accounts for 77 % of the product sales price. The raw material costs are about 30 % of the product sales price. All this argue in favour of economic viability. Operations
that raise the risk of scale expansion are drying and filtration. Only in this case the permissible scale-up factor has been exceeded (Tab. 6.9.4). All this indicates the maturity of the project's process of obtaining preps. The calculations were carried out using the MS Excel software.

Process/unit operation	Scale-up factor	Permissible scale-up factor	Risk
polycondensation	480	1000	low
distillation	482	100000	low
dilute	324	1000	low
precipitation	324	1000	low
filtration	324	1000	high
drying	497	100	high

 Table 6.9.4:
 The scale-up risk factors for each processes.

Conclusions

In this work were presented synthesis and purification methods of prePGS. Prepolymer is obtained by using cheap substrates and easy and well known technologies. High purity of product was confirm by IR spectra, ¹H and ¹³C NMR spectra and analyzing acid number, ester number and esterification degree. Technology of prePGS industrial production was proposed. Economic analysis was favorable. Moreover, there were not much risk with enlarging the scale from laboratory to production line. The developed technological process has a good chance of implementation, however, it is necessary to carry out preliminary experiments on a semi-technical scale. Because of high purity and possibility to use prePGS as easily process semi-product to medical PGS this work should has great value for potential investors.

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7 Scientific articles

7.1 Impact of the structure of aggregates on their behavior in non-Newtonian fluids

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KEYWORDS: fractal aggregates, CFD, computational fluid dynamics, non-Newtonian fluid, mucus.

Abstract

The study investigates the impact of aggregate structure on its falling time in non-Newtonian fluid. Various types of aggregates were examined in experimental and theoretical approaches. In order to imitate human bronchial mucus, the carboxymethyl cellulose dissolved in water was used. Aggregates used in experiment were made from glass balls stuck together. Their falling times in the carboxymethyl cellulose were measured. Received values were used to verify theoretical models. Two models were compared – equivalent sphere approach (i) and Moskal-Payatakes model (ii). First of them is a coarse approximation which is based on treating the aggregates as one sphere with the same volume as aggregate. The Moskal–Payatakes model is more precise and it includes such parameters as structure of aggregates and allow to predict trajectory of falling and torque. Equivalent sphere approach gives better results for small and spherical shape aggregates. Results from aggregate made from 10 primary particle give the worst values.

Introduction

Aggregates are complex branched structures formed by solid particles which occur in industry, medicine and everyday life. They are created during e.g. crystallization, milling, dispersion and many others. We may encounter them in medicine, exhaust gases and different powders. To describe their structure, one may use a simplification - equivalent sphere model (aggregate is treated as simple sphere created from all primary particles joined together). Aggregates can make very different forms like linear, branched and spherical. To describe spatial structure, one may use the fractal dimension D_f whose values lie between 1 (linear forms) to 3 (spherical forms).

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The behavior of aggregates is strongly related to its morphological structure. It can be important in many processes e.g. inhalation, filtration or the spread of pollution. There is a large number of publications related to aggregates dynamics (e.g. [1–4]). This work is based on the Moskal and Payatakes model [5].

Experimental procedure

Experiment was conducted with the use of carboxymethyl cellulose dissolved in water with parameters similar to bronchial mucus [6]. The obtained concentration of shear thinning solution was 0.08 g ml^{-1} . To determine rheological parameters of fluid the rheometer MCR102 (Anton Paar) was used. The obtained result is:

$$\tau = \kappa \cdot \gamma^n \tag{7.1.1}$$

with n = 0.70905 and $\kappa = 3.9702 \,\text{Pa} \cdot \text{s}^n$. In the above equation τ – shear stress (Pa), κ – flow consistency index (Pa $\cdot \text{s}^n$), γ – shear rate (s⁻¹), n – flow behavior index (–).

The described medium was placed into a large cylindrical vessel. Its size needed to be much bigger than aggregates to suppress bounded system size influence [7]. The models of aggregates (Fig. 7.1.1) were set singly into the fluid and were free falling. They were made from 3 mm glass beads glued together. When after few centimeters of falling the aggregates reached stationary velocity, the time on a 10 cm distance of falling was measured. Every measurement was repeated 10 times to extract the average value. The obtained results were shown in Tab. 7.1.1.



Figure 7.1.1: Experimental models of aggregates.

Aggregate model	Number of primary particle	Falling time (s)
1v01	1	71
3v01	3	41
3v02	3	39
3v03	3	45
5v01	5	40
5v02	5	32
5v03	5	41
7v01	7	32
7v02	7	33
7v03	7	25
10v01	10	48
10v02	10	46
10v03	10	43

 Table 7.1.1: Experimental average values of aggregates falling time.

Theoretical models

Equivalent sphere approach This model is based on substituting an aggregate with a sphere of the same volume as modeled aggregate. With this simplification we are able to designate a diameter needed to obtain theoretical velocity and then falling time. To calculate it we used a force balance acting on the aggregate. We took to account three forces – drag, gravity and buoyance. Equations for drag force in non-Newtonian fluids were used from [8] for laminar flow. Fractal dimension for our cases that is small and unbranched aggregates amount 3. The calculations are presented below:

$$d_{eq} = \sqrt[3]{\frac{6 \cdot V_{sum}}{\pi}} = \frac{d}{2} N^{\frac{1}{D_f}}$$
(7.1.2)

$$F_g = F_w + F_d \tag{7.1.3}$$

$$F_g = \rho_s V g \tag{7.1.4}$$

$$F_w = \rho_f V g \tag{7.1.5}$$

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$$F_d = \pi d^{2-n} \kappa \, 3^{1.5(n+1)} \frac{u^n}{n^n \left(n+2\right) \left(n^2 - n + 1\right) \left(n^2 - n + 3\right)} \tag{7.1.6}$$

$$u = \sqrt[n]{\frac{gV(\rho_s - \rho_f)[n^n(n+2)(n^2 - n + 1)(n^2 - n + 3)]}{\pi d^{2-n}k \, 3^{1.5(n+1)}}}$$
(7.1.7)

where d_{eq} – equivalent diameter (m); V_{sum} – aggregate volume (m³); d – primary particle diameter (m); N – number of primary particles in aggregate (–); D_f – fractal dimension (–); F_g – gravity force (N), F_w – buoyance (N); F_d – drag force (N); ρ_s , ρ_f – density of solid, fluid (kg m⁻³); g – gravity (m s⁻²). The results are presented in Tab. 7.1.2.

Table 7.1.2: Results from equivalent sphere approach.

Number of primary particle in aggregate	$d_{eq} \times 10^3 \text{ (m)}$	Time (s)
3	4.327	36
5	5.130	24
7	5.739	18
10	6.463	14

Moskal-Payatakes model The Moskal-Payatakes model allows to simulate the translational and rotary movements of aggregates composed of N identical particles in a Cartesian system. The model includes many variables such as radius of primary particle, fractal dimension, moments acting on aggregates, angular velocity and many others. Full description of mathematical model is described in [5]. The important variable of the model is hydrodynamic correlation factor f_i . This factor is applied to the *i*-th primary particle in the aggregate. The range of values of this variable is from 0 to 1. Correlation factor describes how drag force change with the coordination number ξ that is the number of direct neighbors of *i*-th primary particle in the aggregate. The values that it can take are integers from 1 to 26. To obtain f_i we need to divide drag force with various coordination number F_i' by drag force for only *i*-th particle F_i .

$$f_i = \frac{F_i'}{F_i} \tag{7.1.8}$$

To obtain the values of f_i the CFD (Computational Fluid Dynamics) were used. At the beginning the aggregates models were prepared by using Design Modeler software. Then all fluid domain were meshed with using tetrahedral cell. The smallest cells were placed on the aggregate surface with growth rate 1.15. Mesh quality were very good in every case. Correctness of it was also checked by mesh independence study. Simulations were conducted in laminar flow over aggregates. Fluid were flowing over aggregate with velocity calculated from Reynolds number

$$Re = \rho_f \, d^n \, u^{2-n} \, \kappa^{-1} \tag{7.1.9}$$

$$u = \sqrt[2-n]{\frac{Re \cdot \kappa}{\rho_f \, d^n}} = 9.216 \times 10^{-3} \,\mathrm{m/s}$$
 (7.1.10)

with Re = 0.01 (–), n = 0.70905 (–), $\kappa = 3.9702$ Pa · sⁿ, and d = 0.003 m. In above equations Re – Reynolds number for non-Newtonian fluid (–).

Aggregates were modeled as a wall with no slip condition. To get correct results drag force and coefficient were monitored. Calculation were conducted up to stabilization of those parameters. Methodology included designing of *i*-th particle with various coordination numbers in different position relative to *i*-th particle. The results are presented on Fig. 7.1.2.



Figure 7.1.2: The dependency of correlation factor on coordination numbers.

Based on CFD calculation we received a dependency of correlation factor on coordination numbers for examined fluid

$$f_i = 1.04194 \, e^{-\xi/2.8087} - 0.001020 \, \xi + 0.06555 \tag{7.1.11}$$

Using the obtained values we determined falling times of aggregates. They are presented in Tab. 7.1.3.

Aggregate model	Time (s)
3v01	44
3v02	22
3v03	43
5v01	41
5v02	18
5v03	44
7v01	30
7v02	30
7v03	11
10v01	28
10v02	29
10v03	10

Table 7.1.3: Results from Moskal-Payatakes model.

Discussion

Obtain results shows that for aggregates formed in sphere-like shapes (3v02, 5v02, 7v03, 10v03) the equivalent sphere approach is more suitable than Moskal-Payatakes model. Those aggregates are the most similar to one big sphere so it is compatible with theoretical model. In such aggregates it is reasoned to use this approach – it is easier and quicker model which return better results. We can notice that the best results were get for aggregates with lower numbers of primary particle in aggregates. In more branched cases result of this technique return worse match to experiment. What is more, equivalent sphere approach give only one result for each aggregate. Little change in aggregate structure (3v02 and 3v03) makes a large difference in experimental falling time whilst equivalent sphere approach result do not change.

Moskal–Payatakes model give better results for most of cases. The best comparison experimental and model data is for small brunched aggregates. The bigger they are the difference in results is larger. The worst match is for aggregates formed in sphere-like shapes. The results from this model are various for different aggregate structure e.g. 3v01 and 3v03 or 5v01 and 5v03. For aggregate made from 10 primary particle results are greatly different.

Conclusion

The research shows how many variables influence on behavior of aggregate in fluid. Using simple model such as equivalent sphere approach is not enough to predict properly the behavior of formulation. In most cases Moskal–Payatakes model replicates experimental results better. Differences between values may be caused by few reasons. First of all, in the experiments the aggregates were connected with the glue which changed their roughness, mass and shape which directly influence the drag force acting on aggregates. What is more Moskal– Payatakes model do not include non-Newtonian correction.

Results shows that values obtain from equivalent sphere approach differ from experimental results. The best reproduction is for spherical aggregates with fractal dimension close to 3. The more linear the aggregate the bigger the difference in received values.

	Fa	alling time (s)	1		
Aggregate model	Experimental	Moskal- Patayakes model	Equivalent sphere approach	$\frac{t_{exp}}{t_{eq}}$	$rac{t_{model MP}}{t_{eq}}$
3v01	40	44		1.12	1.22
3v02	39	22	36	1.08	0.61
3v03	45	43		1.25	1.19
5v01	40	41		1.67	1.71
5v02	32	18	24	1.33	0.75
5v03	41	44		1.71	1.83
7v01	32	30		1.78	1.67
7v02	33	30	18	1.83	1.67
7v03	25	11		1.39	0.61
10v01	48	28		3.43	2.00
10v02	46	29	14	3.29	2.07
10v03	43	10		3.07	0.71

Table 7.1.4: Comparison of results obtained by different model
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The research proves that modelling aggregates behavior is difficult but also very important. There are many factors which should be taken to account whilst modeling aggregate morphology such as coordination number, their position relative to others, description of forces acting on primary particles, their durability and roughness. To predict aggregates behavior mathematical model which includes many parameters is necessary. In the future it is planned to expand Moskal–Payatakes model to non-Newtonian correction and maybe take into account mechanical properties like durability.

Acknowledgements

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7.2 Validation of the RANS turbulence model for CFD simulations of the Francis turbine

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Keywords: Francis turbine, power, k- ε , k- ω , vortex rope.

Abstract

CFD simulations in present time are most important part of designing of turbine components. In this paper validation of experimental results for efficiency and power is made. Flow through high head Francis turbine installed in HPP Dubrovnik (Croatia) is considered. Geometry of the spiral casing, guide and stay vanes, runner and draft tube are reconstructed using 3D CAD software Solidworks Simulation was done for three different operational points PL, BEP, and HL using the experimental results from laboratory. In this paper results are compared for three different k- ε variants (Standard, RNG, Realisable), and k- ω for same computational set up. Simulation is made for full scale model with frozen rotor approach. The CFD results for the turbine power and efficiency confirmed the experimental ones at design flow and off-design conditions as well. Realizable k- ε had best results for this kind of flow and computational set up. For PL is shown flow deflection in one side of draft tube, and vortex rope. For HL vortex direction at the draft tube inlet is different than for PL. The opinion and one solution for possible flow improvements in the draft tube has been given.

Introduction

Hydropower Plant Dubrovnik is located 15 km southern of Dubrovnik. In HPP Dubrovnik there are two high head Francis turbines installed power of 126 MW each. HPP Dubrovnik uses water of Trebišnjica River. Dam and intake system is located in Bosnia and Herzegovina; turbines and generators are located in Croatia. Over the last years there was a constant need to improve energetic and cavitation performances of the Francis turbines. Many articles are made for same reason to prove which turbulence model is better for predicting global parameters such as power, efficiency etc. this article will compare three different k- ε models and one k- ω model. For industry this is mainly enough for quality simulations of flow inside the Francis turbines but in scientific world there are the LES approach or hybrid LES/RANS approach.

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Turbine geometry

In HPP Dubrovnik are installed two Francis turbines with vertical shaft. Each turbine has 126 MW installed power. Francis turbine generally consists of: spiral casing, stay vanes, guide vanes, runner and draft tube. New turbines after revitalization at HPP Dubrovnik consists of 24 stay and 24 guide vanes. The runner has 17 blades. The specific speed of the turbine is $n_s = 100$ calculated for the BEP data $\dot{V} = 45 \text{ m}^3/\text{s}$, P = 106 MW, n = 300 r pm. Geometry or this article is generated with CAD software Solidworks [4]. For reconstruction of geometry 2D drawings are used. In reconstruction some simplifications has been done but that simplifications hasn't big contribution to global parameters like power, efficiency etc.

For this article some corrections with number of blades are made. Runner in Fig. 7.2.1 has 15 blades. After revitalisation there are 17 runner blades and geometry of guide vanes are lightly different. Runner reconstruction was most demanding in whole reconstruction. Side view is visible at Fig. 7.2.2. This improvements gives more hydraulic efficiency and more power but are not tested in this article.



Figure 7.2.1: Francis turbine geometry.



Figure 7.2.2: Francis turbine runner.

Case studies

Case studies can be divided in three big sections. Sections were designed considering operational points of Francis turbine. Simulations are made for partial load (PL), best efficiency point (BEP) and high load (HL). For every operational point are made four same simulations with same computational set-up but with different RANS turbulence model. Standard k- ϵ , Realisable k- ϵ , RNG, and Standard k- ω . Most realistic results for efficiency prediction is for cases where Realisable k- ϵ is used. The geometry set-up is shown in Fig. 7.2.1 and the computational set-up is shown in Fig. 7.2.3.



Figure 7.2.3: Computational set-up.

Geometry is divided in three big domains. First of all there are two stationary domains and one rotating domain. Stationary domain 1 consists of: spiral casing, stay vanes and guide vanes. Rotating domain is runner, and stationary domain 2 is draft tube. All simulations are made for full scale model and with frozen rotor approach because there is no significant difference between frozen rotor and sliding mesh approach for global parameters such as power, efficiency and etc. Mesh is structured and divided for every domain. There is 21.5 million overall finite volumes divided like in Table 7.2.1. After initial simulations it is assumed that is needed to extend outlet section for approx. 10 m because numerical problems of backflow.

Mesh is generated by ICEM CFD. For stationary domains and rotating cells are tetrahedrons and for extension there are quads. Grid independency test was done at [1] and this is extension of that work with another turbulence models. It is necessary to emphasize that in [1] mesh grid was approx. 8 million finite volumes but in comparison with grid of 21.5 million finite volumes there is no significant differences for computation of global parameters what is shown in Fig. 7.2.6.

	Mesh se	ctions	
1	2	3	4
Stat. Domain 1 Rot. Domain		Stat. Domain 2	Extension
Number of finite volumes (10 ⁶)			
9.150	10.70	1.250	0.2

Table 7.2.1: Mesh sections.

 Y^+ value is in the log layer, but for standard k- ω it's a little too coarse grid but in result chapter it will be seen that the results for that turbulence model lie better than for standard k- ε for comparison.

Flow in whole simulations was steady with RANS turbulence models in commercial software package ANSYS Fluent.



Figure 7.2.4: Mesh resolution for passage through guide, stay vanes and runner.

In Fig. 7.2.4 is shown mesh grid for main parts of Francis turbine. For hydraulic losses it is very important to have fine mesh around the vanes, and for good prediction of torque too have fine mesh grid at rotating domain. Disk friction losses and leakage losses are modelled in the paper neither their effect on turbine through flow.

Every simulation with k- ϵ turbulence model is performed with standard wall functions. For standard k- ω , production limiter and corrections for shear flow are

used. For all simulations are used simplec software. Discretization schemes for momentum equation and all others is 2nd order upwind. Convergence criteria for residuals in simulations is 10^{-3} , shown in Fig. 7.2.5.

Torque convergence is monitored also like important part of simulation convergence criteria. Boundary conditions for simulations was mass flow rate prescribed at inlet and zero gauge pressure at the outlet. At the inlet only component normal to boundary was enabled. Fluid properties are used for cold water.



Figure 7.2.5: Converge history for PL and realizable k-ε.



Figure 7.2.6: Mesh grid independency test.

In Fig. 7.2.6 is obvious that there is no significant changes at results for finer mesh grids. There is slightly raise of efficiency values for PL, BEP and over predicting value for HL. In Fig. 7.2.6 gray line with squares is experimental [3]. All other lines are constructed for realizable k- ε turbulence model.

Results

Results will be shown for the realizable k- ϵ turbulence model because it only gives very similar flow simulation and parameters for realistic situation at HPP Dubrovnik. RNG turbulence model has also very good results but streamlines for PL are not showing such strong deflection to right side of draft tube.

Operational points \mathbf{PL} BEP HLVolume flow (m³/s) 29.50 45 51.50 Net Head (m) Experiment 288.84 273.774 273.13 CFD 285.66 280.85 268.82 2.58 Difference (%) -1.10-1.57

Table 7.2.2: CFD prediction of Net Head.

The turbine net head is calculated for prescribed flow rate and the corresponding guide vane opening A_0 . All the terms in the turbine net head are the result of mass averaging of the total pressure.

For all turbulence model there is opposite directions of the swirl at part-load and high-load; the direction of swirl at part load is the same as the direction of runner rotation. Opposite direction is clearly shown at [1]. Tab. 7.2.2 is proof of simulation quality. It is obvious that the CFD results fall short to experimental results. For BEP CFD over predicts net head and for two other cases there less than experimental.

Efficiency is shown in Fig. 7.2.6 where all lines underachieve experimental results from Turboinštitut laboratory [3]. An exception is HL for CFD 21.5 million volumes. All lines are constructed for Realizable k- ϵ turbulence model.

In Fig. 7.2.7 it is obvious that strong vortex is present from runner outlet to draft tube elbow where strong deflection is presented. In continuation it will be shown solutions for "breaking the vortex". Fig. 7.2.9 shows comparison of all turbulence models.

Uniformity of flow at the entrance to runner is shown in Fig. 7.2.8. Uniformity is crucial for having really balanced runner inlet conditions. Francis turbines and other water turbines are especially sensitive to some imperfections of water stream which is coming to runner blades.



Figure 7.2.7: Streamlines for PL; $\dot{V} = 29.5 \text{ m}^3/\text{s}$.



Figure 7.2.8: Flow uniformity at spiral casing.





Figure 7.2.9: Comparison of efficiency for different RANS models.

After net head, power is calculated for every test case. At Tab. 7.2.3 results are shown. Very small differences are present.

For efficiency results there is characteristic curve with peak at BEP. Difference between CFD results and experimental results is around 2.5 %.

Operational points Volume flow (m ³ /s)	PL 29.50	вер 45	нь 51.50
Turbulence model	Ро	ower (MV	V)
Standard k-ε	72.09	113.72	120.70
Realisable k-ε	72.39	114.40	120.67
RNG	72.63	114.40	120.70
Standard k-ω	72.50	114.34	120.67

 Table 7.2.3: Comparison of power for every turbulence model.

Standard k- ε turbulence model has unrealistic curve type for Francis turbine efficiency diagram. All other three curves are realistic but Realisable k- ε curve show best results at BEP and for HL.

For improvement of flow in draft tube for PL in continuation in Fig. 7.2.10 are shown two solutions. One is investigated (right) at [1] and do not give better results.



Figure 7.2.10: Draft tube parameterization.

Conclusion

At this paper results for steady state operation points are shown. Comparison of different turbulence models is shown, and best turbulence model for this case is selected. In future it is needed to fine mesh more and try with other RANS turbulence models or other approach like LES. Transient simulations will be done to show transient moments when turbine starts or change its power. Also solutions for draft tube parameterization are shown.

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7.3 A possibility to obtain Al₂O₃ - Cu - Ni composites via slip casting method

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KEYWORDS: ceramic-metal composites, slip casting, $Al_2O_3 - Cu - Ni$ system.

Abstract

This paper presents a study on the possibility of developing a method to produce hybrid composites from ternary system $Al_2O_3 - Cu - Ni$. The composites were prepared using slip casting method. Experimental results indicate that the slip casting method allows to obtain the hybrid composites. An analysis of the obtained results allows to acquaint with the correlation between forming and sintering conditions, and the basic properties of hybrid composites.

Introduction

Ceramic is a group of material known for the mankind for decades. It is solid, inorganic material containing metal, nonmetal or metalloid atoms held in ionic or covalent bond. Due to its high abrasion and corrosion resistance, good hardness and constant properties at high temperatures ceramics find numerous applications in many technical fields. It is used in production of e.g. thermal barriers, chemical filters, anode material for solid oxide fuel cells or fireproof materials [1–4]. Despite its many advantages, ceramic has also some disadvantages like brittleness and poor tensile strength, which effectively exclude it from several application as construction materials [5,6].

Continuous development of technology brings the need of creation new solutions, both technological and material. For this reason ceramic metal composites are gaining more and more attention in technological applications. Ceramic metal composites are formed as a combination of two different kinds of materials – ceramic and metal, which are characterized by different properties. Combination of materials with extremely different chemical structure, atomic bonds character and properties, leads to the creation of completely new composite material with wide range of properties and possible applications [7].

There are many possible methods for ceramic metal composites production, including infiltration technique [8,9], in-situ methods [10,11], powder metallurgy

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[12–14] and others [15–17]. One of the simplest and cheapest method is slip casting technique [18–22]. In this particular method we use ceramic and metallic powders with plasticizers and solvent to create the slurry. After mixing and homogenization processes, the slurry is cast into the porous molds. Solid green bodies are obtained due to the capillary force affecting the slurry in porous molds. After casting, samples are dried and then sintered. Whole process leads to obtain composite ceramic metal samples [5,7,23].

The aim of this study was to obtain ceramic metal composite from ternary $Al_2O_3 - Cu - Ni$ system. Due to the high contact angle between Al_2O_3 and Cu and low melting temperature of copper, Cu could come out from composite samples during sintering [24–26]. It is believed that addition of the second metallic phase, as a result of the reaction between metallic components during sintering, can reduce copper loss in the samples.

Alumina matrix composites with copper and nickel particles and the influence of nickel addition on primary characteristics of this composite were investigated in this paper.

Materials and methods

The following powders were used: α -Al₂O₃ Almatis with average particle size 66 ± 20 nm, Cu powder from Sigma Aldrich with average particle size 63 ± 30 µm and density 8.94 g/cm³ and Ni powder from Bimo Tech with average particle size 25±15µm and density 8.9 g/cm³. The data characterizing the powders were given by the producers.

SEM micrograph analysis (Fig. 7.3.1) showed that the morphology of the powders applied in the study was significantly diversified. The ceramic α -Al₂O₃ powder particles can be characterized by irregular shape. Among metal powders, Cu particles can be characterized by spherical morphology and Ni particles are characterized by dendritic shape of particles. It was found that both ceramic α -Al₂O₃ powder and metal Ni powder were firmly agglomerated. In addition, in Fig. 7.3.1 individual powder diffraction pattern are shown. They confirmed the single-phase structure of the powders used.

In the present investigation the samples were fabricated via slip casting technique. In the experimental part ceramic water-based slurries with 50 %vol solid content and 15 %vol metal powders with respect to the total solid volume were prepared. Metal phase in the composite specimens made from $Al_2O_3 - Cu - Ni$ system included 80 %vol of Cu and 20 %vol of Ni, with respect to the total metal volume content in the slurry. Additionally two reference sample series were prepared for comparison purposes: Al_2O_3 and $Al_2O_3 - Cu$ samples with 50 %vol of solid content, and 15 %vol of Cu particles, in case of composite series.

Duramax D3005 were used as a dispersant in the ceramic metal slurries. Slurries contained 1.5 %wt of the dispersant with respect to the total solid content



Figure 7.3.1: Morphology and XRD diffraction of initial powders: $a - Al_2O_3$, b - Cu, c - Ni.

weight. Ceramic suspensions were prepared with deionized water. Dispersants were added to water followed by alumina, nickel and copper powders. The slurries were mixed and then degassed in THINKY ARE-250 mixer. Slurries were mixed for 8 minutes at 2000 rpm and degassed for 2 minutes at 1000 rpm. The suspensions were degassed up to remove bubbles (> 1 μ m). The resulting suspensions were cast into porous gypsum molds, then dried and sintered in the reducing atmosphere (N₂/H₂) at 1400 °C. Scheme for the preparation of the composites is shown in Fig. 7.3.2.

The selected physical properties of the sintered composites were measured by the Archimedes method.



Figure 7.3.2: Diagram of the manufacturing process.

X-ray diffraction (XRD) was used to identify the phase composition in obtained samples. The measurements were carried out with Rigaku Miniflex II for 2θ values from 20 °C to 100 °C with CuK_{α} radiation and λ = 1.54178 Å. The analysis was done at the cross-sections of samples.

The microstructures of the sintered composite samples were obtained on theirs cross-section surfaces via scanning electron microscope HITACHI TM-1000. The samples were ground and then polished with the diamond paste of $3 \,\mu m$ to $1 \,\mu m$.

Results and discussion

The typical examples of obtained green bodies and sintered specimens are illustrated in Fig. 7.3.3. Preliminary macroscopic observations of obtained composite samples revealed no visible cracks, pores or other defects on the surface area of the specimens. Surface of all samples can be characterized by homogenous structure.

The relative density and volume shrinkage of the sintered specimens measured using Archimedes method are presented in Fig. 7.3.4. It can be noticed that the relative density of $Al_2O_3 - Cu - Ni$ composite was 83.2 ± 0.92 %. While, it was found that for reference samples $Al_2O_3 - Cu$ and Al_2O_3 the relative density measured were 88.3 ± 0.31 % and 89.7 ± 1.24 %, respectively. Based on the results of measurements of selected physical properties, it can be concluded that the addition of metallic phase in the ceramic matrix causes decrease in its relative density. It was also observed that measured values of volume shrinkage decreased

with the addition of metal phase in the composite. Volume shrinkage measured for $Al_2O_3 - Cu - Ni$ composite was $21.3 \pm 1.2\%$, and for reference samples $Al_2O_3 - Cu$ and Al_2O_3 were $25.7 \pm 0.4\%$ and $29.2 \pm 1.7\%$, respectively.



Figure 7.3.3: Examples of green bodies and sintered specimens of all series: 1.1., 1.2. $-Al_2O_3$; 2.1., 2.2. $-Al_2O_3 - Cu$; 3.1., 3.2. $-Al_2O_3 - Cu - Ni$.



Figure 7.3.4: The relative density and volume shrinkage of the obtained specimens.

SEM micrographs with phase analysis of the sintered samples are presented in Fig. 7.3.5. The XRD patterns of $Al_2O_3 - Cu$ samples after sintering at 1400 °C show that the composites consist of two phases: Al_2O_3 and Cu (Fig. 7.3.5.b). The reductive atmosphere used during the sintering permitted avoiding the formation of the new phases in references samples: Al_2O_3 and $Al_2O_3 - Cu$. It was found that the diffraction peaks obtained for the reference samples (Fig. 7.3.5.a and b) were found to coincide with the diffraction peaks gained for $Al_2O_3 - Cu - Ni$ composites (Fig. 7.3.5.c). It can be noticed, based on XRD analysis, that in composite specimens from $Al_2O_3 - Cu - Ni$ system new phase, i.e. CuNi, was present. The presence of a new phase of CuNi may be observed due to the reaction between Cu and Ni during the sintering process. Additionally, the X-ray diffraction pattern showed reflections such as α - Al_2O_3 and Ni phases in obtained composites $Al_2O_3 - Cu - Ni$.



Figure 7.3.5: SEM micrographs with XRD patterns of sintered specimens: a: AI_2O_3 , b: $AI_2O_3 - Cu$, c: $AI_2O_3 - Cu - Ni$.

Based on the macroscopic observations, it can be concluded that the samples obtained were characterized by homogenous distribution of metal particles in ceramic matrix. No visible defects (e.g. cracks, pores) were detected. Addition of nickel particles in the metal reinforcement caused change in the particles character in the ceramic metal microstructure. In composite with copper reinforcement, metal particles can be characterized by spherical morphology. Nickel is causing appearance of metal particles with more irregular morphology than it can be observed in the reference sample.

Conclusion

This study reports the fabrication and characterization of novel hybrid alumina matrix composites. It was found that the slip technique enables the manufacturing of ceramic metal composites from the ternary $Al_2O_3 - Cu - Ni$ system. Based on the presented xRD results, it was concluded that obtained $Al_2O_3 - Cu - Ni$ composites consist of three phases: Al_2O_3 , Ni and CuNi. Fabricated specimens were characterized by homogeneous distribution of metal particles in the ceramic matrix. Addition of the metal phase to the ceramic matrix caused the decrease of relative density and volume shrinkage in the examined specimens. Nickel addition also contributed to the change in metal phase morphology in the structure. Presented results have preliminary character and need to be expanded in the future. The research team plans to carry out other studies involving this type of hybrid composites in the future. Planned studies will include a mechanical tests such as hardness, fracture toughness.

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7.4 Ferritic stainless steel modified with Gd₂O₃ nanoparticles and its oxidation resistance and electrical properties

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KEYWORDS: SOFC, ferritic stainless steel, gadolinium oxide, interconnect.

Abstract

The aim of this study was to evaluate the effect of modifying the surface of a commercial ferritic steel containing 16.28 wt% of Cr with Gd_2O_3 nanoparticles deposited using either dip-coating or electrolysis on the oxidation resistance and electrical properties of this material. The samples were oxidized for 100 h in air at 1023 K. A significant improvement in corrosion resistance and electrical properties was observed after surface modification performed by dip-coating the material three times.

Introduction

Devices which can directly convert the chemical energy in fuel into electrical energy are the most promising energy storage technology. Such devices include planar solid oxide fuel cells (SOFCS) [1–3]. The main advantages of these systems include low manufacturing costs, a simple production process, possibility of automation, very high power outputs per unit area (up to 2000 W cm⁻²), and their mobility [4–9].

A single cell with a planar construction is built of three main parts: the electrolyte (yttrium-stabilized zirconia), an anode (nickel cermet), and a cathode (material with a perovskite structure) [4]. Due to the fact that a single cell produces very little power, they are assembled into stacks using interconnects, which ensure electrical contact and also provide gas separation within cells [4,10].

The most common material used to manufacture interconnects for planar sorcs is ferritic stainless steel, which is relatively inexpensive and provides better thermal and electrical conductivity than ceramics. However, metallic interconnects are also susceptible to high-temperature oxidation and the subsequent formation of scales built mainly of Cr_2O_3 , which is characterized by low electrical conductivity. As the scale grows thicker over time, the metallic interconnect

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is affected by a gradual increase in area specific resistance (ASR). This is accompanied by an increase in the internal resistance of the cell and a drop in its power output [4–10]. The electrical conductivity of steel depends on factors such as the thickness of the scale layer and its adhesion to the surface. One of the methods which can be used to improve the aforementioned properties is the addition of a small amount of active elements such as Y, La, Gd, or their oxides [4]. Active elements improve the adhesion of the scale to the metallic phase, and in the case of the Cr_2O_3 scale also decrease its growth rate. It is therefore to be expected that as the thickness of the compact chromia scale decreases, so does the electrical resistance of the steel/scale system.

The aim of the presented study was to modify the surface of the commercially available Nirosta 4016/1.4016 ferritic steel containing 16.28 wt% of Cr with Gd_2O_3 nanoparticles deposited using either dip-coating (performed one or three times) or electrolysis, and to evaluate the effect of these modifications on the oxidation resistance and electrical properties.

Materials and methods

Sample preparation The substrate used in the present work was the commercially available Nirosta 4016/1.4016 ferritic steel with a 16.28 wt% Cr content and certain amounts of other elements (Mn - 0.34 wt%, Si - 0.36 wt%, Ni - 0.35 wt%, C - 0.05 wt%, P - 0.02 wt%). Steel coupons in the shape of a rectangle with dimensions of 20×10×1 mm were prepared by polishing and degreasing with acetone in an ultrasonic bath.

Four types of samples were used. The first sample was unmodified steel (designated as Ns). The other three types were modified with Gd_2O_3 nanoparticles in one of three different ways. In the case of the sample denoted as NsGd, the surface of the samples was modified via electrolysis with a gadolinium nitrate solution at a concentration of 0.01 M. For the other two types of modified samples, the coatings were deposited by means of dip-coating, which included immersing the samples for 30 s in a bath with the same gadolinium nitrate concentration as in the case of electrolysis. The immersion was performed once for samples designated as NsGdZ and three times for those marked Ns3GdZ. All modified samples were heated at 673 K for 30 min in order to thermally decompose the hydroxides and nitrates. During this process, gadolinium oxide nanoparticles formed on the surface of the steel. An EDS map of the distribution of gadolinium and oxygen showed that it was uniform across the entire surface of the steel.

Research methods All studied samples were oxidized for 100 h in air at 1023 K. To measure the oxidation kinetics, at hermogravimetric apparatus with an MK2-G5 Vacuum Head Microbalance (CI Electronics Ltd., UK) with a sensitivity of 10^{-6} g were used.

Morphological observations of the surface and cross-section of the scales and the analyses of their chemical composition were performed by means of the Nova Nano SEM 200 (FEI Europe) scanning electron microscope coupled with an energy-dispersive X-ray spectroscopic (EDAX) analyzer. To obtain cross-sections, the samples were cut in half, embedded in resin and then polished.

The phase composition of the samples was evaluated using X-ray diffraction (Philips X'Pert Pro diffractometer). The HighScore Plus application coupled with the X'Pert diffractometer software, the PCPDFWIN database (v. 2.3), and ICSD identification cards were used to identify phases.

Electrical resistance measurements of the studied samples were conducted by means of a dc 2-probe 4-point method using an outer source of current; this parameter was measured in laboratory air at 1023 K, using a current intensity of 0.01 A. Detailed descriptions of the apparatus, the methodology of area-specific resistance (ASR), and sample preparation can be found in [11].

Results and discussion

Fig. 7.4.1 shows the oxidation kinetics curve recorded for the Ns3GdZ sample (obtained via dip-coating the steel three times) after 100 h of oxidation in air at 1023K. It can be noticed that this process approximately obeys the parabolic rate law, which means that the slowest partial process that determines the oxidation rate is the diffusion of reagents in the scale [10].



Figure 7.4.1: Oxidation kinetics of ferritic steel modified with Gd nanoparticles by three rounds of dip-coating and oxidized for 100 h in air at 1023 K.

Fig. 7.4.2 shows the mass gain per unit area of each sample, determined after 100 h of oxidation in air at 1023 K. The highest mass gain was observed in the case of the Ns sample, which proved that all performed modifications improved the oxidation resistance of the steel, as expected. Of the modified samples, Ns3GdZ (obtained after three rounds of dip-coating) exhibited the highest corrosion resistance, while the NsGdZ sample (modified via one round of dipcoating) was characterized by the lowest one, which suggests that in the case of the latter the embedded layer was too thin to adequately protect the steel from rapid oxidation.



Figure 7.4.2: Mass gain per unit area of different ferritic steel samples after 100 h of oxidation in air at 1023 K.

Fig. 7.4.3 shows the surface morphology of the oxide scales formed on unmodified Fe-16Cr steel and the steel modified with Gd_2O_3 using either dip-coating or electrolytic deposition after 100 h of oxidation in air at 1023 K.

The X-ray examination of the surface of the oxidized samples revealed that the corrosion product layer consisted mainly of chromia (Cr_2O_3) and manganese chromium spinel ($MnCr_2O_4$). The scale which had grown on the surface of unmodified steel consisted of grains that formed numerous agglomerates with a size of ca. 0.1–0.5 µm (Fig. 7.4.3a), while the surface of the steel which had undergone modification was covered with fine, isolated grains with a $MnCr_2O_4$ spinel structure and a size ranging from ca. 0.2 to ca. 1.6 µm (Fig. 7.4.3b, c and d). In the case of the Ns3GdZ sample, scratches made by polishing can be seen, which suggests that the scale formed on this steel sample was very thin (Fig. 7.4.3c). Similar

observations were made for the NsGd sample, with one significant difference; in this case, large groups of agglomerates of grains enriched with gadolinium oxide were found in the outer part of the scale (Fig. 7.4.3d). The presence of Gd_2O_3 was confirmed via EDs analysis performed for the respective areas.



Figure 7.4.3: SEM micrographs of the surface morphology of scales formed after 100 h of oxidation in air at 1023 K on: a) Ns sample, b) NsGdZ sample, c) Ns3GdZ sample and d) NsGd sample.

Fig. 7.4.4 shows the SEM micrograph of a polished cross-section of oxide scales formed on unmodified Fe-16Cr steel and steel modified with Gd_2O_3 via three rounds of dip-coating, both oxidized for 100 h in air at 1023 K.

As can be seen, the scales were characterized by good adhesion to the substrate; this was also true for the remaining samples (NsGdZ and NsGd). However, the scales formed on the modified samples were significantly thinner than the one formed on unmodified steel.

This fact was reflected in the values of electrical resistance measured at 1023 K for the scale/steel and scale/ Gd_2O_3 /steel systems. Table 7.4.1 lists the full set of

values of area-specific resistance of each of the systems obtained after the oxidation of unmodified and surface-modified steels in air at 1023 K.

The lowest ASR was exhibited by the Ns3GdZ sample, while the unmodified steel (Ns) was characterized by the highest value of this parameter. The ASR of systems based on two of the investigated samples, namely Ns3GdZ and NsGd, was well below the acceptable level for SOFC interconnects $0.1 \Omega \text{ cm}^{-2}$.



Figure 7.4.4: SEM micrographs of the cross-section of scales formed after 100 h of oxidation in air at 1023 K on: a) Ns sample and b) Ns3GdZ sample.

Table 7.4.1: Area-specific resistance (ASR) measured at 1023 K for the scale/steel systems formed by the investigated samples after 100 h of oxidation in air at 1023 K.

Sample	ASR $(\Omega \text{ cm}^{-2})$
Ns	0.17
NsGdZ	0.13
Ns3GdZ	0.03
NsGd	0.05

Conclusions

The investigations concerning the oxidation of unmodified Nirosta steel as well as samples of this steel modified with Gd_2O_3 showed that the applied modifications reduced the mass gain. The highest mass gain was observed in the case of unmodified steel, while the sample modified via three rounds of dip-coating was characterized the best result. A similar tendency was observed for the measured area-specific resistance values. The lowest ASR was observed for the sample obtained after three rounds of dip-coating. Consequently, this modification, which is both effective and inexpensive, was concluded to be the most suitable one with regard to potential application as SOFC interconnect material.
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7.5 Selective Catalytic Reduction of NO with NH₃ at low temperature over Cu-promoted-N-modified activated carbon

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KEYWORDS: SCR, activated carbon, copper oxides, DeNO_x, urea.

Abstract

Catalytic properties of activated carbons oxidized, treated with N-compounds and promoted with copper were studied in selective catalytic reduction NO_x by ammonia (NH₃-scR). The modification of the catalysts was consisting of a series of steps (pre-oxidation of activated carbon, impregnation with urea, impregnation with copper). The physiochemical properties of the obtained samples were determined using X-ray diffraction, FT-IR spectroscopy and low-temperature N₂ sorption. The modification with copper led to an increase in NO conversion (98 % of NO conversion at 300 °C).

Introduction

Selective catalytic reduction of NO_x with NH₃ is one of the most effective ways to eliminate NO_x emissions from stationary sources [1,2]. Some effective catalysts, such as V₂O₅–WO₃/TiO₂, have been developed and successfully commercialized due to their high activities. However, some problems appeared by using the commercialized catalysts. In coal-fired power plants, the sCR reactor is installed upstream of the electrostatic precipitator and flue-gas desulfurization scrubber, so the catalyst suffers from deactivation due to dust accumulation and chemical poisoning from sulfur. To solve these problems, the sCR reactor should be set downstream of the electrostatic precipitator and flue gas desulfurization scrubber. However, the temperature of flue gas is only approximately 200 °C. For the commercial sCR catalysts, such as the V₂O₅–WO₃/TiO₂ catalyst the optimum operation temperature is usually approximately 350 to 400 °C [3]. Therefore, there is a need to develop low-temperature sCR catalysts, so the catalyst bed can be located at the end of the installation, where the flue gas has already been cleaned of fly ash and most of the sulfur dioxide.

In recent years, carbonaceous materials have been recognized for the multifunctional roles that they perform as an adsorbent, a catalyst and support of the

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metal catalysts [4,5]. Examples of the superiority of carbon-based materials over other supports include high surface area and well-developed pore structures. Additional advantage is, that activated carbons (AC) are also relatively cheap material. Hence, AC becomes a good candidate for use as a support for catalysts in the low-temperature NH_3 -SCR reaction.

Modification of carbonaceuos material with N-compounds is beneficial for enhancing NO_x sorption and increasing SCR activity according to the findings of Grzybek et al. [6] who demonstrated that the carbon modified with urea showed a much higher activity than the untreated one. In addition, Matzner and Boehm [7] compared CO_2 formation of the N-modified activated carbons with the untreated carbon and proved that N-modification is important for stability.

Many types of active metals supported on Ac were proposed as $DeNO_x$ catalyst. The most frequently studied active materials were oxides/hydroxides of vanadium [8], manganese [9], iron [10] and copper [11,12]. Cu-modified Ac (Cu/Ac) catalyst exhibited high activity compared to unpromoted carbon, and titania supported catalyst at low-temperature range 150–250 °C. That was proved previously by Singoredjo et al. [12]. Moreover, Cu/Ac showed higher activity compared to Fe/Ac, according to Teng et al. [13]. Although the results of numerous studies of the reduction of NO on carbon-based catalysts have been reported, relatively few studies have been concerned with the triple modification technique: (oxidation, modification with N-groups, and active metal doping). The triple modification was carried out only by Samojeden [10] and Grzybek [14], who studied N-modified Ac promoted with Mn (Mn/N-Ac) and Fe (Fe/N-Ac) as sCR catalysts. Their results showed improvement in activity and selectivity of the studied catalysts. Therefore, further investigations are needed to evaluate the possibility of applying the triple modification by using other metals.

This work focuses on activity, selectivity and thermal stability of the prepared catalysts.

Catalyst preparation

Commercial activated carbon (AC) (Gryfskand, Hajnówka, Poland) was oxidized by concentrated HNO₃ (15 ml HNO₃ per 1 g Ac) at 90 °C for 2 hours, followed by filtration, washing with distilled water (to neutral pH) and drying at 110 °C for 24 hours. The introduction of N-groups was carried out by the incipient wetness impregnation with the urea solution (5 wt. %), followed by drying at 110 °C for 24 hours. Subsequently, thermal treatment was conducted in the flow of O₂/He (2.25 %), at a rate of 100 cm³/min, at 350 °C, for 2 hours. The obtained samples were ground and sieved to obtain 0.25–1 mm fraction.

AC was ready at the end of this step for the active phase deposition. Copper was deposited by incipient wetness impregnation with a solution of $Cu(NO_3)_2$, using various concentrations of the Cu^{2+} to obtain 1 wt%, 5 wt% or 10 wt% Cu

loading. Finally, Cu doped AC was dried and calcined in He stream for 1 hour at 250 °C.

Tab. 7.5.1 summarizes the procedures of the triple modification to obtain a series of copper promoted activated carbon catalysts which followed by characterization and catalytic test.

	Preparation procedures				
Sample	Oxidation	Modification	Impregnation	Calcination	
AC-ox	10 M HNO ₃ , 90 °C, 2 h	-	-	-	
10U		5 wt % urea, calcination 350 °C, 2 h, 100 cm ³ / min (O ₂ /He)	-	250 °C, 1 h, 100 cm ³ / min (O ₂ /He)	
10U1Cu			1 wt. %Cu		
10U5Cu			5 wt. %Cu		
10U10Cu			10 wt. %Cu		

Table 7.5.1: The list of the obtained catalysts.

Catalyst characterization

Low-temperature sorption of nitrogen $(-196 \,^{\circ}\text{C})$ was used to determine textural parameters (specific surface area, pore volume, size of pores) of the prepared catalyst by a GeminiV2.00 model 2380 apparatus (Micromeritics). Before the measurements, the samples were degassed at 150 $^{\circ}\text{C}$ for 2 hours.

X-ray powder diffraction measurements (xRD) were carried out by PANalytical-Empyrean diffractometer. The measurement range was $2\theta = 5-90^{\circ}$ with a step of 0.02°/min. The xRD patterns were obtained at room temperature. The phases identification of each diffraction pattern was performed by using PANalytical HighScore Plus v.4.0-4.7a software.

Fourier-transform infrared spectroscopy (FTIR) analysis was performed for Cu - N/Ac by Perkin Elmer Frontier FT-IR spectrometer. Sixty scans were taken for each spectrum for wave numbers from 4000 to 400 cm⁻¹, registered with a resolution of 4 cm⁻¹ by using KBr pellets at 1:300 ratio.

Catalytic performance

The NO reduction with NH_3 was performed at atmospheric pressure in a fixedbed flow reactor. The bed consisted of 0.2 g of catalyst particles. Reactant gases (800 ppm NO, 800 ppm NH_3 , and 3.5 vol % O₂ and He to balance) were fed to the reactor through mass flow controllers, and helium was added to make up a total flow rate of 100 cm³/min. Prior to entering the catalyst bed, the gas mixture passed a zone filled with glass beads for preheating and thorough mixing. The NO reduction experiments were conducted at temperatures ranging from 140 to 300 °C. NO conversion was calculated according to the equation:

$$x(\text{NO}) = \frac{\text{NO}_{in} - \text{NO}_{out}}{\text{NO}_{in}} \cdot 100\%$$
(7.5.1)

where NO_{in} is the inlet NO concentration, NO_{out} is the outlet NO concentration.

Results and discussion

Low-temperature sorption of nitrogen In Fig. 7.5.1 the nitrogen sorption isotherms for the prepared catalysts are presented. According to the IUPAC classification, the obtained catalysts represent isotherm type IV, indicating that carbon support materials have mesoporous structure. The shape of the hysteresis loop may be classified as H4 type, which corresponds to the presence of homogeneous slit-shaped pores [16].



Figure 7.5.1: Nitrogen sorption isotherm for the obtained catalysts.

In Tab. 7.5.2 the textural parameters for the studied samples; specific surface area, micropore volume and pore width.

Sample	Specific surface area (m ² /g)	Micropore volume (cm ³ /g)	Pore width (nm)
AC	722	0.36	2.00
AC-ox	829	0.41	1.96
10U	670	0.32	1.96
10U1Cu	754	0.37	1.96
10U5Cu	563	0.27	1.96
10U10Cu	540	0.26	1.97

Table 7.5.2: Textural parameters of carbon supported catalysts

The freshly activated carbon (AC) exhibited specific surface area S_{BET} over 700 m²/g; its pore volume was equal to 0.36 cm³/g. The specific surface area and the micropore volume increased after oxidation with nitric acid for the sample (10AC) but, the reduction of both the surface area and pore volume of the AC are shown after urea impregnation and Cu impregnation. This indicates that a portion of the pore volume was clogged with the impregnating metals.

X-ray diffraction XRD patterns for the obtained catalysts are presented in Fig. 7.5.2. Three diffraction reflections are seen for the sample 10U at ca $2\theta = 25$ and 43 and 77°. They can be correlated to (002), (101) and (110) planes, respectively, of the graphite phase of carbon [01-075-1621].



Figure 7.5.2: XRD patterns of functionalized activated carbon doped with Cu

In sample with 1 wt % of copper the graphite phase was found at circa $2\theta = 25$ and 43 and 77°. The diffraction pattern of 10U1Cu is similar to that of 10U. Thus, it may be concluded that Cu oxide in 10U1Cu is most probably either very well dispersed over the surface or is present in the amorphous form [17]. The 5 wt % addition of copper resulted in the appearance of the reflections at 2θ ca 42.2°. It can be ascribed to the (200) plane of Cu₂O [01-078-2076]. The reduced copper oxide was the most abundant crystalline phase in the 10U5Cu sample. Further, increase in copper content to 10 wt. % resulted in more crystalline copper containing phases [17]. The reflections at 2θ ca 36.5, 42.2 and 73.5° can be ascribed to the (111), (200) and (311) planes of Cu₂O, respectively; whereas, the reflections at 2θ ca 38.5° arise from the (111) plane of CuO [00-045-0937]. Pure copper also was also found in the 10U10Cu sample with the reflections at 2θ ca 50.4° corresponding to the (200) plane of the face center cubic crystal structure of copper Cu [01-070-3039].



Figure 7.5.3: FT-IR spectra of functionalized activated carbons doped with Cu

FT-IR spectroscopy The presence of the functional groups in the obtained carbon materials was examined by FTIR spectroscopy and is illustrated in Fig. 7.5.3. For all samples, peaks at ca. 1120, 1560, 1715, 2900 and 3430 cm⁻¹ could be distinguished. These peaks correspond to amines, non-aromatic carboxylic groups, alkenes and water, respectively. The peak at 1120 cm^{-1} represents C – N (aliphatic) or N – H groups. The peak at 1560 cm^{-1} is ascribed to the stretching mode of carboxylic group; the peak at 2900 cm^{-1} is typical to the carbonyl stretching of carboxylic group; the peak at 2900 cm^{-1} is ascribed to the C – H interaction with the surface of the carbon [17]. Whereas the peak at 3430 cm^{-1} can be attributed to absorbed water [18,19]. For the samples with a larger content of 5 wt% and 10 wt% Cu, an increase in the water bands were observed. The increase in the

water band could be attributed that the increase in copper percentage making the carbon surface more hydrophilic.

scr for Cu doped functionalized activated carbon In Fig. 7.5.4 NO conversion of the studied catalysts at low-temperature window 140-300 °C were compared. All copper promoted samples (10U1Cu, 10U5Cu, 10U10Cu) reached about 95 % of NO conversion at 220 °C, while 10U reached 35 % of NO conversion at the same temperature. At 300 °C 10U reached 50 % of NO conversion and 10U5Cu reached 98 %. The conversion decreased with the increase of temperature over 300 °C. One of the reasons can be copper oxide accelerating the combustion of the support. Another reasons could be oxidation of ammonia, which would lead to the amount of NH₃ not sufficient to support the main reaction. NO conversion formed a sequence: 10U5Cu > 10U1Cu > 10U10Cu > 10U. It can be concluded that the impregnated quantity affects NO conversion. The efficiency of scr reached the highest value when AC is impregnated with 5 wt % Cu. This result indicates that the surface area and the pore volume are not the determining factors to improve catalytic activity in SCR, but surface chemistry has the major role. The concentration of N_2O was relatively high but below 200 ppm for all the prepared samples. 10U5Cu presented 55 ppm at 300 °C and 10U presented 65 ppm at 220 °C; while 10U10Cu presented 140 ppm N₂O.

There is another positive effect of the smaller amounts of active metals. The selectivity to N₂ of 10U5Cu was higher than 10U10Cu. The smaller amount of active material can lead to the formation of smaller aggregates and thus decrease the tendency to the formation of undesired N₂O. Similar effect was observed by Grzybek et al. [14]. Since the carbonaceous material can be oxidized under oxygen-containing atmosphere, the stability of the functionalized carbon samples the CO₂ formation was also examined as presented in Fig. 7.5.4. For the catalysts with higher copper concentration, fast combustion of functionalized Ac was observed. CO₂ concentration increased by increasing copper loading percentage in the sequence: 10U < 10U1Cu < 10U5Cu < 10U10Cu. The most interesting temperature region for Ac-based catalysts is, however, below 220 °C, where the stability of all samples was high and CO₂ concentration did not exceed 240 ppm.

Conclusions

Activated carbons were functionalized with nitric acid and ammonia, then modified with copper. Based on the low-temperature nitrogen sorption studies, an increase in specific surface area was observed after oxidation with nitric acid. However, modification with copper decreased the specific surface area.

x-ray diffraction showed that 1 wt% Cu is highly dispersed on the support surface. For 10 wt% Cu loading the formation of copper oxide phases in the catalyst structure was registered.



 $\label{eq:Figure 7.5.4: NO conversion, N_2O formation, CO_2 concentration for functionalized activated carbon treated with HNO_3 and urea doped with Cu.}$

According to the results of FT-IR, the catalyst contained amine and carboxylic groups. Moreover, the sample with 1 wt% Cu was hydrophobic and lost its hydrophobicity by loading Cu to 5 wt% and 10 wt%.

The catalytic tests exhibited high activity in the process of NH_3 -scr. The catalyst with Cu loading of 5 wt% showed maximum NO conversion. The quantity of N_2O produced for this sample was low and did not exceed 55 ppm. The triply modified carbon showed high stability below 220 °C.

Acknowlegment

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8 Abstracts

8.1 Study on oxygen absorption rate in aqueous solutions of protein in a disposable bioreactor with wave-induced agitation

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1 Faculty of Chemical and Process Engineering, Warsaw University of Technology, Poland Keywords: single-use bioreactor, wave-type agitation, absorption rate, bovine serum albumin.

Disposable (i.e. single-use) bioreactors supported with wave-type agitation provide favorable conditions for performance of aerobic cultures of animal or plant cells, as well as microorganisms. Application of oscillating movements to polymer-based culture bags induces waves intensifying the mass transfer between liquid and gas phases inside the culture bag. Waves generated inside the culture bag allow to gently renewing interfacial surface between two contacting phases, what significantly limits the level of hydrodynamic shear stress negatively influencing on the maintained cells. A volumetric mass transfer coefficient (k_{La}) is the crucial parameter characterizing the oxygen absorption rate from the gas phase inside the liquid phase in such devices.

ReadyToProcess WAVETM25 bioreactor system (WAVE 25; GE Healthcare, Sweden), equipped with 2 dm³ polymer-based culture bag (CellbagTM, GE Healthcare), has been used for studying the quantitative influence of protein concentration on oxygen absorption rate in agitated aqueous phase. Purified bovine serum albumin (BSA) and commercially available fetal bovine serum (FBS) were independently applied as sources of protein in samples of distilled water, as well as DMEM medium. The rate of oxygen absorption was measured using gassing-out method, and the values of k_{La} coefficient have been determined. Furthermore, all examined solutions of protein-enriched water and DMEM were analyzed for the impact of protein concentration on kinematic viscosity.

The results revealed that in the case of both distilled water and DMEM medium, the oxygen absorption rate in the liquid phase, as well as the kinematic viscosity are functions of protein concentration characterizing the aqueous phase. Furthermore, the applicability of the wave-induced agitation performed in disposable bioreactor platform for proceeding the submerged culture of animal cells has been confirmed.

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8.2 Optimization of SiAIOC glasses coatings formation by means of structural and microstructural investigation

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KEYWORDS: SiAlOC glasses, coatings, dip-coating, SEM.

Silicon Aluminum Oxycarbide glasses belong to a very interesting group of materials – Polymer Derived Ceramics (PDCs). These Si-based ceramics from the quaternary SiAlOC system exhibit a range of prominent properties such as excellent thermomechanical stability, chemical durability or even electrical conductivity. The combination of aforementioned features of SiAlOC glasses allows to propose the possible application in the form anti-corrosive coatings on a range of metallic substrates.

As far as the formation of SiAlOC coatings is concerned, sol-gel method and dip-coating technique seem to be very suitable. However, during their application it is crucial to investigate the working procedure, which should provide with the highest quality of coatings.

The main objective of this work was to evaluate the influence of both substrates' surface preparation (grinding/polishing) and withdrawal speed (5, 15, 30 cm/min) parameters on coatings structure and microstructure.

Microstructural studies (SEM with EDS, Confocal) showed that coatings deposited with the lowest speed on the ground substrate, possessed the highest tightness and homogeneity, and the lowest roughness resulting from the lowest thickness. Additionally, structural investigation (XRD, XPS, Raman) revealed the formation of the additional inner layer of Mn - Cr spinel and the partial release of the carbon anions in the near-surface area due to the presence of Al^{3+} cations.

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8.3 Oxidation studies of coatings based on SiAlOC glasses

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KEYWORDS: protective coatings, black glasses, isothermal oxidation.

The sol-gel method possesses the number of advantages i.e. the possibility of the well-planned material's formation, giving the chance to tailor its final composition, microstructure and resultant properties. The very interesting group of materials commonly obtained by means of this method includes so-called black glasses (named due to their color) based on silicon oxycarbide (SiOC). During the formation process, it is possible to easily modify the glasses' structure via the cationic substitution, where Al³⁺ cations replace Si⁴⁺ ones. It results in the enhancement of the already high thermal stability of the material which is also characterized with outstanding heat and creep resistance. The possible application of SiAIOC glasses may assume the protective coating material for interconnects in Solid Oxide Fuel Cells made of the ferritic stainless steel Crofer 22APU.

The investigation of the oxidation resistance of SiAlOC glasses in the form of coatings on the steel substrate was the main aim of this study.

Coatings were produced via the sol-gel method and dip-coating technique on both ground and polished steel samples. Two repetitions of a deposition with 15 minutes break and 5 cm/min withdrawal speed were applied. The subsequent two-stage thermal treatment provided with the formation of black glasses coatings, proved by the number of structural (XRD, MIR, NMR) studies. Obtained samples were used for thermogravimetric analyses (TGA) in isothermal conditions within 100 h in the air atmosphere. The combination of structural (XRD, Raman) and microstructural (SEM with EDS) studies of the surface and cross section of oxidized samples revealed a considerable improvement in the corrosion resistance of the steel in comparison to the bare substrate and the slight enhancement contradistinctively to SiOC glasses coatings.

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8.4 Graphene oxide-based materials as supports for catalyst nanoparticles

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Keywords: low-temperature fuel cells, carbon nanomaterial, molybdenum disulfide, hydrogen evolution reaction.

The world is struggling with the problem of depletion of energy resources. The main sources of energy are not renewable, and their use produces a lot of pollution of the environment. There is also a large fear of using nuclear energy, hence alternative energy sources are sought. One of the possible solutions of the above problems might be fuel cells, which convert chemical energy directly into electricity, with high efficiency and low emission of pollutants. In order to improve the catalytic efficiency, increase the surface area and decrease the price of the catalysts, various types of support materials are used for catalyst nanoparticles for fuel cells. The most common supports are carbon materials, such as graphene oxide (GO) or reduced graphene oxide (rGO).

The aim of the presented research was testing different carbon supports (such as GO, GO modified with ammonia GO-NH₃ and rGO) for catalysts used in a proton exchange membrane fuel cell (PEMFC). Palladium, platinum, nickel and iron catalysts deposited on various carbon supports were produced and used for the oxygen reduction reaction (ORR). Modification of graphene oxide with ammonia solution resulted in an enrichment of the GO structure with nitrogen (up to 1.86 wt%). Reduction of graphene oxide leads to a partial removal of oxygen groups from GO (the percentage content of oxygen in GO was 44.2%, in GO-NH₃ was 38.67% and in rGO was 14.96%). The structure and chemical composition of the prepared catalysts were analysed by TGA, XRD, SEM and XRF. Activity and catalytic stability tests of the prepared catalysts were carried out in the prototype direct formic acid fuel cell (DFAFC). The obtained results allowed to state that the enrichment of the graphene oxide structure with nitrogen causes a significant increase in the catalytic activity and allows the use of cheaper metals in catalysts used in PEMFC.

The obtained results show that carbon materials enriched with nitrogen might be also used as a support for photocatalysts based on molybdenum disulphide MoS_2 for hydrogen evolution reaction HER. Hydrogen produced in this reaction can be further used as a fuel in PEMFC.

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8.5 Modelling dynamics of polymer chains grafted to a surface of a separative membrane

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Keywords: numerical modelling, molecular dynamics, polymer brushes, anti-fouling properties, membrane separation.

The development of the membrane technology has increased significantly during the last years, leading to the growth of interest in the field of membrane modification methods. Interesting pH-switchable properties of grafted polyelectrolytes became a basis for a new approach for the fouling prevention. According to the known experimental data, poly(acrylic acid) grafted membranes were less affected by the fouling phenomenon and much easier to regenerate during the rinsing process, comparing to the reference material. Research presented in this paper describes dynamics of polymer brushes grafted to the surface of a separative membrane.

The numerical model of dynamics of polymer brush is based on coarsegrained molecular dynamics. In order to simulate grafted chains, the bead-spring model was applied. The segments of the polymers are in permanent motion due to the repulsive interaction between dissociated side groups, restoring force (representing the bounds between polymer segments) and stochastic force arising from the Brownian motion. During filtration process, the segments of the grafted chains collide with an approaching towards the membrane particles of the filtrated suspension. Due to the multiple collisions, a repulsive force occurs leading to an improvement of membrane antifouling properties. The purpose of the research was to establish the qualitative description of the polymers-particle interaction, according to the pH value of the feed.

The simulations confirmed that the increase of such parameters as grafting density, pH value and Debye length (parameter defining the range of electrostatic interactions in a solution) favours the chains transition into the highly-stretched and elongated form ("brush" regime). Thus, the increase of the mentioned parameters leads to the growth of the polymers-particle repulsive interaction and subsequently to the improvement of the membrane antifouling properties. The type of the interaction was successfully established – the force occurring between the polymers and the repelled particle is a power function of the pH value. The model also confirms the effectiveness of the pH-responsive, grafted polymers as a method of fouling prevention.

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8.6 Manufacturing of polylactide substitutes for spongy bone with increased hydrophilicity – preliminary investigation and optimization of the process

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KEYWORDS: porous implant, polylactide, Eudragit®, freeze-extraction method.

The aim of the study was to obtain polylactide spongy bone implant with a mass impregnability that enables inserting a greater volume of the platelet-rich plasma into its interior. However, polylactide is not hydrophilic enough for optimal regeneration of bone tissue. The hydrophilicity of polylactide bone implant can be increased by application of factors with increased hydrophilicity which modify the implant's surface. It was decided to incorporate a methyl methacrylate, dimethylaminoethyl methacrylate, n-butyl methacrylate copolymer under trade name Eudragit®E100 into implant's structure. The proposed method of production allows obtaining an implant with increased hydrophilicity, and thus potentially better osteogenic properties. As a method of preparing spongy bone implants, the phase inversion method with freeze-extraction variant was used.

A method for the preparation of the poly-L-lactide bone implants with an increased impregnability was developed. The process was successfully optimized with the aid of design of experiments (DOE). The mathematical models describing the influence of input variables: Eudragit®E100/PLLA weight ratio and volume ratio of methanol (porophore) to PLLA solution in dioxane on the open porosity and the mass absorbability of obtained implants, were calculated. The process for preparation of polylactide spongy bone implants was optimized to obtain a scaffold with the maximal mass absorbability at the open porosity of more than 90 %.

Developed process enabled the preparation of implants with high open porosity exceeding 93 % and mass absorbability up to 1840 %. Both obtained regression equations are adequate, which is confirmed by the fact that the differences between the results and the calculated values are small. The first model enables the control over polylactide implant open porosity. The second model enables the control over implant mass absorbability.

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8.7 Development of a force field for the simulation of liquid diiodomethane

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KEYWORDS: diiodomethane, force field, molecular dynamics.

Diiodomethane (CH_2I_2) is a liquid which is a iodine derivative of the methane. Because of its high density, diiodomethane is used in the determination of the density of mineral and other solid samples. It can also be used as an optical contact liquid for determining the refractive index of certain gemstones. First and foremost, it is used it is used as a one of testing liquid during wettability and surface free energy measurements.

Computer simulation is an important tool enabling the modelling of physicochemical properties of materials, surfaces and interfaces. However, computer "experiment" requires a reasonable force field as an input in order to be effective. Although numerous and accurate force fields for various systems (especially biological systems) are available, there are still many chemical compounds which don't have assigned forcefields and their parameters. Diiodomethane is one of these substances.

In this work a new force field for computer simulations of bulk liquid diiodomethane is proposed. Three-site model of diiodomethane molecule based on OPLS-UA (*Optimized Potentials for Liquid Simulations – United Atom*) force field and one of modification of OPLS-AA force field (W.L. Jorgensen and P. Schyman, *J. Chem. Theory Comput.*, 8 (10), 2012, 3895–3901) was developed. The molecular dynamic simulation was carried out by the LAMMPS package in NVT ensemble at 298 K. The density of liquid phase, dipole moment and radial distribution function were determined in order to compare obtained results with experimental data.

The developed parameters may be used in the future to simulations of adsorption or wetting in systems containing diiodomethane.

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8.8 Wetting of silicon (100) surface by diiodomethane

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Keywords: diiodomethane, wetting, silicon.

Wetting is the ability of a liquid to maintain contact with a solid surface, resulting from intermolecular interactions when the two are brought together. Wettability studies usually involve the measurement of contact angles as the primary data, which indicates the degree of wetting when a solid and liquid interact. The contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions: liquidvapor, solid-vapor, and solid-liquid interfacial tensions, describing by Young's equation.

The Young equation assumes a perfectly flat surface. Even in such a smooth surface a drop will assume contact angle hysteresis. The equilibrium contact angle can be calculated from advancing and receding contact angle as was shown theoretically by Tadmor and confirmed experimentally.

Advancing and receding contact angle were measured at 25 °C using sessile drop technique in order to calculate equilibrium contact angle. Measurements were made as follows: $6\,\mu L$ diiodomethane droplet was settled on the examined surface and advancing contact angle was measured, then $2\,\mu L$ of liquid was sucked from the droplet into the syringe and receding contact angle was measured.

It was found that equilibrium (Tadmor's) diiodomethane contact angle on the silicon (100) surface is equal 40.73 ± 3.50 degrees.

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8.9 Selection of solution blow spinning process parameters for the fabrication of controlled-alignment tissue engineering scaffolds

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KEYWORDS: solution blow spinning, polycaprolactone, process parameter selection, submicron fibers.

Damage to human nervous tissue commonly leads to irreversible functional impairment and loss in quality of life. Some degree of success in its restoration has been achieved using biodegradable polymeric scaffolds with aligned fibrous structure. The solution blow spinning method is proposed as a safer and potentially more effective alternative to commonly used electrospinning in the fabrication of fibrous mats with controlled morphology.

The study was aimed to investigate the influence of process parameters on fibrous sample morphology and mechanical properties, creating a basis for their selection in the fabrication of controlled-morphology tissue engineering scaffold design. Polymer concentration and rotational speed of the cylindrical sample collector were chosen as parameters with the highest suspected influence on polymer solution spinnability, fiber diameter, and degree of alignment.

Poly- ε -caprolactone was chosen as a biodegradable and biocompatible polymeric material with suitable mechanical and chemical properties. Trifluoroethanol was used as a solvent. Sample morphology was determined using scanning electron microscopy and digital image analysis. Mechanical properties of the samples were determined in directions parallel and perpendicular to the mandrel axis using static yield testing.

Fibers had average diameters in the submicron range (136-459 nm) and moderate to high degree of fiber alignment, expressed as percentage (20 to 50 %) of fibers oriented in the range of 10° and 20° from the solution feed direction. Average tensile moduli of the mats were in the range of 2.5 to 3.6 MPa and determined suitable for tissue engineering. Relations between process parameters, sample morphology and mechanical properties of the fibrous mats were analyzed and explained.

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8.10 Application of polymer-graphene fibrous nanocomposites in tissue engineering

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KEYWORDS: polymer nanofibers, graphene, tissue engineering, graphene composites.

The field of tissue engineering has been rapidly expanding during the last two decades, employing yet newer materials and manufacturing methods coming from different areas of research. Fibrous polymer materials are already commonly developed to structurally and functionally mimic natural extracellular matrix of lost human and non-human animal tissue. First attempts have been made to include graphene, hailed the groundbreaking material of the 21st century, in the implantable scaffolds and devices of regenerative medicine.

This paper presents a review of the recent advancements in the fabrication and use of fibrous polymer-graphene nanocomposites in the field of tissue engineering. Manufacturing methods used to employ the addition of graphene to polymer fibers were reviewed along with reported structural changes in respect to the pure material. An overview of the changes in material properties and in vitro cellular response after the addition of graphene in different chemical and structural forms has also been presented.

Presented summary highlights the most relevant emerging directions in the applications of polymer-graphene nanocomposites in the field of tissue engineering. An attempt to determine potential vital setbacks in the development of the field and highlight the most promising solutions has been made as a conclusion.

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8.11 Controlling the growth of bacterial biofilm on electroactive surfaces

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KEYWORDS: conducting polymer, poly(3,4-ethylene-1,4-dioxythiophene), tetracycline, bacteria, biofilm.

When forming a biofilm, bacteria have the ability to interact and communicate with each other, which makes them extremely powerful and difficult to remove. It has been shown that electrical impulses affect bacteria and can be used to modulate their behavior. Therefore, it is possible that electroactive materials, such as conducting polymers, will be a suitable matrix to control their growth.

In this work, the electroactive matrix based on poly(3,4-ethylene-1,4-dioxythiophene) (PEDOT) was obtained via electropolymerization process, and was further biofunctionalized by immobilizing drug (tetracycline) into its structure. The matrices were examined using electrochemical, spectroscopic (UV-Vis, IR) and microscopic (SEM) methods. To assess biological properties materials were tested by culturing E.coli on their surfaces. Analysis of bacterial growth was carried out by SEM microscopy, LIVE/DEAD assay and BCA (Bicinchoninic acid) protein test.

The results allowed for the correlation between physicochemical and biological properties of the surfaces, as well as confirmed the antibacterial activity of the materials in relation to the polymer, platinum and glass.

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8.12 Ionic liquids with tryptophanate anion as active ingredients prolonging vase-life of cut flowers

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KEYWORDS: ionic liquids, tryptophan, auxins, synthesis, biological activity.

All over the world, both in gardens and on plantations, we are struggling with the problem of too small development of the system of adventitious and lateral roots, rapid fall of fruits, leaves and flowers. As plant growth hormones, auxins, play a key role in controlling the way in which plants develop. The natural auxin found in all plants is 3-indoleacetic acid (IAA), resulting from the biosynthesis of tryptophan or the tryptophan-independent pathway. Due to the properties and great importance of tryptophan in the biosynthesis of plant hormones, it can be used in the synthesis of new ionic liquids (ILS) able to extend the life of cut flowers.

In our study we focused on the development of synthesis methodology of ionic liquids with tryptophanate anion and their subsequent characterization in terms of prolonging vase-life of cut flowers. We have given particular consideration to the impact of the length of alkyl chain attached to nitrogen atom in utilized cations. Structures of obtained compounds were confirmed by ¹H and ¹³C NMR spectroscopy. The solubility of the obtained ILs was tested at 25 °C in common organic solvents selected in increasing order of the value of their Snyder polarity index. In the last step of our studies we have attempted to determine the potential of application of synthesized ILS.

Ionic liquids with tryptophanate anions were obtained by a two-step reaction with high yields exceeding 90 %. Compounds containing substituents with an alkyl chain length of from 1 to 22 carbon atoms were liquids below 100 °C, which allows them to be classified in the group of ILS. All compounds were soluble in methanol, acetone, 2-propanol and DMSO and were not dissolved in ethyl acetate and hexane.

The performed studies showed that basic physicochemical properties – melting point and solubility of 1Ls, were highly dependent on the structure of the utilized cation. The vase-life of cut flowers can be extended by using solutions of the synthesized 1Ls.

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8.13 Bis-ammonium herbicidal ionic liquids comprising cinnamate anion

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KEYWORDS: ionic liquids, herbicide, new compounds, synthesis, biological activity.

Herbicidal ionic liquids (HILS) are plant protection agents that can be described as organic salts with melting points lower than 100 °C which contain at least one anion characterized by herbicidal activity. Application of herbicides provides numerous advantages, and their disadvantages can be eliminated by transformation into herbicidal ionic liquids in major perspective. Bis-ammonium HILS are known in the literature as salts comprising a cation composed of two quaternary nitrogen atoms connected together by a linker group, and one or two herbicidal anions.

An efficient method of new bis-ammonium quaternary salts with 4-chloro-2methylphenoxyacetate (MCPA) and (2*E*)-3-phenylprop-2-enate (cinnamonate) anions was developed. The selected bis-ammonium dibromide and the potassium salts of the above-mentioned anions were used for the synthesis of these compounds. In order to confirm their structures, ¹H and ¹³C NMR spectroscopy have been utilized. According to Vogel's methodology, the solubility of obtained compounds was tested in 10 representative solvents. The final element of the work was to determine the potential of application of synthesized salts. The methodology for testing herbicidal activity described in the literature was used for this purpose.

As a result, 15 novel bis-ammonium HILS were obtained with high efficiency by a two-step reaction. HILS containing three structurally different linkers and five different lengths of aliphatic chains, had melting points below 100 °C. All HILS were soluble in water, methanol, chloroform, however, they had no affinity towards acetonitrile, ethyl acetate, toluene and hexane. The herbicidal efficacy of all synthesized ILS was higher in comparison to commercial formulations.

In the framework of our research new ionic liquids with the bis-ammonium cation and anions such as MCPA and cinnamonate have been proposed as the new potential herbicides. Physicochemical properties and biological activity were closely dependent on the structure of the cation.

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8.14 Synthesis of new, axial and central chiral (thio)squaramides, and their application as organocatalysts in enantioselective reactions

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Keywords: organocatalysis, cinchona, catalyst recovery, asymmetric reaction.

After the tragical story of the drug called Contergan in the 1950s only the enantiopure active pharmaceutical ingredient (API) could be used as a drug component. The enantiopure API could be produced by enantioselective synthesis. In our research group during enantioselective reactions, asymmetric organocatalysts provide the necessary chiral environment. The term organocatalysis means a non metal-based catalysis using small organic molecules. In my research work I aimed to produce new axially, and central chiral, bifunctional, binaphthyl-cinchona-(thio)squaramide organocatalysts (4a, 4b, see Figure 8.14.1).



Figure 8.14.1: Synthesis of new (thio)squramide organocatalyst

The catalytic activity of the prepared organocatalysts (4ab) was studied in enantioselective *Michael* addition which can be widely used as a C-C coupling step in the synthesis of many drug intermediates (eg. prostaglandin E1, baclophen, or oseltamivir). With the benefit of the basic character of catalysts, we would like to recycle them by a simple aqueous extraction after salt formation.

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8.15 Development and application possibilities of new, hydrogen bond donor organocatalysts

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Keywords: organocatalysis, hydrogen bond donor, (thio)squaramide, (thio)deltamide, enantioselective reactions.

The importance of hydrogen donor scaffolds is increased during the past decade. They can be used in many fields of chemistry, for instance, as recognition motifs in anion receptors, or as a subunit in organocatalysts. Their activities are directly related to their hydrogen bond donation capability which is correlated with the acidity of the NH groups. The first, dual hydrogen bond donor unit was the widely known urea. During the evolution of hydrogen bond donors many other strained ring structure were discovered, which have even higher acidity of NH groups (Figure 8.15.1).



Figure 8.15.1: Synthesis of new (thio)squramide organocatalyst

During our work new cinchona-deltamide and (thio)squaramide derivatives were synthesized. These organocatalysts were applied in Michael addition of 1,3-dioxo compounds to β -nitrostyrene with excellent enantiomeric excesses (up to 99 % ee). It is important to note that this was the first preparation and organocatalytic application of the deltamide skeleton in asymmetric reactions.

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8.16 Microwave reactors for hydro- and solvothermal synthesis. Measurements problems and scale up possibility

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KEYWORDS: microwave, reactor, zinc oxide, hydroxyapatite, nanopowder.

Microwave solvothermal synthesis (MSS) is the great example of microwave assisted wet chemical synthesis process. In today's world it is counted as one of the most popular chemical methods of obtaining nanopowders, like HAP, ZnO, ZrO₂, doped materials and other. Microwave heating enables a better control of the reaction time, fast heating and reducing the thermal gradients. The morphology, grain size and specific surface area of the nanopowder can be controlled by the microwave reactor and the high pressure consolidation technology for ceramic materials, this also results in a better crystallinity comparing to the precipitation process.

At the Laboratory of Nanostructures, IHPP PAS, we have been developing new type microwave reactors for nanomaterials synthesis for more than 10 years. The use of the microwave radiation and the unique design of the reactor permit precise pressure control during the quick synthesis processes, controlled with the accuracy of even one second. The reactor also presents a control system which allows for an automatic operation in the stop flow mode or use the batch (closed vessel) mode in bigger production scale than in other commercial equipment. Temperature measurements of the suspension are quite difficult, thermocouples can be burned out by sparking and also generate errors, strongly absorbing materials inside the reactor can also misjudge the IR sensor and showing not reliable temperature. Better way in that situation (ionic liquids inside) is using fiber-optic sensors, which are in contact with reaction mixture.

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8.17 Verification of separation effectiveness of filters applied for diesel fuel dewatering

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KEYWORDS: cellulose filters, hydrophobicity, water separator, diesel dewatering.

In order to reach quality requirements for diesel fuel, new separation materials are continuously being developed. The common diesel fuel filtration method is a single stage separation using hydrophobic material which constitutes a barrier for dispersed water droplets, but enables the oil to pass through its pores. A desired filtration material for good filtration products should be characterized by a low pressure drop and long operation time. To meet these objectives the hydrophobic separators should be characterized by self-cleaning properties and low adhesion of both solids and water to the surface.

Presented work concerns verification of separation effectiveness of different filters in water separation experiments. For this purpose filters in a form of standard pleated elements were constructed. The structure purchased from Ahlstrom was used as a base material (untreated used as a reference). The material was modified to increase its hydrophobicity using the octadecytrichlorosilane (OTS). Due to its self-assembling properties the coating formed on the surface enabled to obtain highly hydrophobic surface in a relatively simple procedure, and did not block the pores. Additionally, commercial separators offered to vehicle fuel system were examined under the same process conditions - this provided a reference and enabled benchmarking of our in-house developed filter media. To characterize the obtained separation materials, the measurements of static contact angle (CA) and sliding angle for water droplets were carried out. These parameters define the ability of the filter material to repel water by capillary forces, and thus prevent its accumulation on the surface due to high mobility. Moreover, the structure of materials surface was verified for uniformity of coating using Scanning Electron Microscopy.

The conducted research shows that surface modification with ors is an effective method to improve filter material applied for diesel fuel dewatering. The experiments also confirmed that water separators are very sensitive to addition bio-compounds and presence of various additives (quality improvement agents). These compounds stabilize the emulsion and hinder the coalescence process, thus making the standard filters ineffective for water removal from the diesel fuel.

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8.18 Synthesis and properties of 1,7-disubstituted perylene diimides

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Keywords: perylene, diimide, hydroxylamine.

Perylene diimides (PDI) are an interesting material for photovoltaic applications due to their chemical, thermal and photochemical stability as well as intense light absorption in thevisible range and high quantum yield of fluorescence. They can replace fullerenes in polymer solar cells, acting as an electron acceptor. PDIs are also used in optoelectronics and OLED diodes. Quite good solubility is an important feature of this group of compounds. Solubility improvement is obtained by condensation of perylene dianhydride with appropriate amines.

PDIS were obtained in the condensation reaction. Hydroxylamines with short chains and perylene dianhydride were used for those PDIS synthesis. The presence of a hydroxyl group at the end of the chain allows for its' further modification. Brominated perylene diimides and various aromatic substituents boron esters were coupled using the Suzuki method. Each product was made in fewsteps synthesis.

Products were purified by column chromatography. The purity and structures of obtained compounds were confirmed by ¹H and ¹³C NMR spectroscopy. UV-Vis absorption spectra reveal some differences in spectrum range and intensity. These compounds may be suitable for photovoltaics, but the protection of the hydroxyl group is required.

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8.19 Synthesis and application of a cinchona squaramide organocatalyst immobilized on poly(glycidyl methacrylate)

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Keywords: organocatalysis, cinchona alkaloids, poly(glycidyl methacrylate), immobilized catalyst, Michael addition.

Nowadays, organocatalysts have wide application in asymmetric reactions, and their recovery is essential for their economical application. the immobilization on a polymer support can mean a promising solution. During this work, a cinchona squaramide enantioselective organocatalyst was synthesized from quinine (1, Figure 8.19.1) using published synthetic methods.

Poly(glycidyl methacrylate) (PGMA) was chosen for the part of the polymer support in the light of its modifiable reactive epoxide functional groups. The cinchona squaramide catalyst was successfully immobilized on this polymer.

The activity of the immobilized organocatalyst (2, Figure 8.19.1) was examined in different solvents (ethyl acetate, dichloromethane) in enantioselective *Michael* addition of 1,3-dioxo compounds to β -nitrostyrene. The immobilized catalyst was recovered from the reaction mixture 4 times by centrifugation, and successfully reused.



Figure 8.19.1: Quinine (1) and the immobilized organocatalyst (2).

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8.20 PDMS – coated Particle Track Membrane for microfluidics – fabrication and application

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KEYWORDS: solid membrane, microfluidics, polydimethylsiloxane, particle track membrane.

Polydimethylsiloxane (PDMS) is widely used in microfluidic devices due to its properties: gas permeability, biocompatibility, clearness and easy processability. Many analytical microsystems include PDMs membranes as a gas-liquid contactor. However, the preparation of applicable PDMs membrane is problematic due to difficultness in membrane separation from the matrix and effortless placement in proper device.

The aim of the research was obtaining PDMS/Particle Track Membrane (PDMS/PTM) membrane for oxygen saturation level measurements in microfluidic device. Membranes were developed using two methods and *Sylgard 184* kit which consists of silicone elastomer and curing agent. *Elcometer 3570* – micrometric film applicator was used to coat PTM membrane by liquid elastomer layer. The second approach required a mixture consisted of elastomer, curing agent and hexane. This mixture was dosed directly to the water surface in Petri's dish. Curing process temperature was different for every method. In the first one, hybrid membrane was heated at 180 °C for 15 minutes. The second method required room temperature and 2 days for complete evaporation of hexane from PDMs coating. Structure and thickness were measured using scanning electron microscope (SEM).

Several membranes with the thickness in the range of $19.42-124.46 \,\mu m$ were obtained. Membranes obtained using the second method were characterized by a significantly lower standard deviation of thickness in its different places than those made using an applicator. All membranes were effectively used to gas solubility measurement in a microfluidic device.

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8.21 Analysis of influence of aggregate structure on its behaviour in non-newtonian fluid

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Keywords: fractal aggregates, CFD, computational fluid dynamics, non-Newtonian fluid, mucus.

Fractal aggregates are complex structures made of primary particles. They are organized in branched forms. Aggregates occur as a constitution of medical formulations or pollution. Modelling of those structures is important for the prediction of their transport properties (e.g. diffusion coefficient).

The research was conducted in non-newtonian fluid (carboxymethyl cellulose dissolved in water) with parameters similar to human bronchial mucus. Applying computational fluid dynamics (CFD) hydrodynamic correction factor was calculated for various types of aggregates, which were made of different number of primary particles. Then received values were implemented to the Moskal-Payatakes model, which allows to determine falling velocity of aggregates and their trajectory in 3D system. In addition, another theoretical model called equivalent sphere approach was used. It is based on approximation of complicated aggregates structures with a single sphere with volume equal to the sum of volumes of primary particles in examined object. Both theoretical models were compared with the experimental results. Comparing parameter was aggregates falling velocity in steady state conditions.

Received results indicate large impact of the particle morphology on the behavior and properties of aggregate. It is suggested to continue research on this issue to obtain a model, which will enable to forecast aggregates motion and influent factors more precisely. In the next research, it is also worthy to focus on the durability of aggregates.

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8.22 Modification of black glasses layers properties for medical applications

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Keywords: silicon oxycarbide, sol-gel, coatings, bioceramics, biocompatibility.

Silicon oxycarbide based materials (SiOC) are very often cold black glasses. They might be obtained with multiple methods but one which guarantees to obtain homogenous amorphous materials is ceramization of preceramic precursors. With this method, it is also possible to modify the material with chosen ions to enhance its properties or add new ones suitable for the selected applications.

In this work, hermetic layers on metallic substrates based on amorphous silicon oxycarbide doped with phosphorus and cerium ions were presented. The phosphorus ions were applied to improve the biocompatibility, while modification with cerium ions is proposed to enhance bioactivity and the corrosion resistance and add antibacterial and antioxidant properties. The preceramic precursors in the form of ladder-like silsesquioxanes were obtained via the sol-gel method, modified and deposited on the metal substrate with the use of the dipcoating technique.

Infrared spectroscopy confirmed the preparation of the material of the desired structure and composition. It also depicted that dopants caused the increase in the amount of non-bridging oxygens in the glass network, which might cause a drop in mechanical properties. However, the surface state (roughness, morphology, wettability and surface free energy) analysis, corrosion resistance alongside the in vitro bioactivity and biocompatibility tests results showed nontoxicity, suitable and stable properties appropriate for the medical application.

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8.23 The influence of doping ions on the sol-gel synthesis of SiOC preceramic precursors

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KEYWORDS: silicon oxycarbide, sol-gel, preceramic precursors, spectroscopy.

SiOC (silicon oxycarbide) based amorphous materials are simply called black glasses. The most efficient path of their preparation is via ceramization of the proper polymeric precursors. In this work, ladder-like silsesquioxanes obtained by the sol-gel method were proposed. This route is highly effective and enables modification with various ions or nanoparticles. In this way, the properties of this bioactive and corrosion resistant material might be enhanced or some novel might be added.

The modifications with phosphorus and cerium ions were proposed to alter the silicon oxycarbide based materials. Phosphorus ions might be introduced to the glass network to enhance the biocompatibility of the black glasses, however, they may also have a slightly negative influence on the corrosion resistance. On the other hand, cerium ions and oxide as the additive elevates bioactivity and corrosion resistance of the basal ceramic material. Moreover, they possess bacteriostatic and antimicrobial properties.

This work is focused on the structural studies of the phosphorus and cerium modified materials. Sols, xerogels, bulk black glasses and layers were examined using numerous of spectroscopic and microscopic methods: middle infrared spectroscopy (FTIR), Raman spectroscopy, energy dispersive spectroscopy (EDS) and X-ray photoelectron spectroscopy. It was possible to specify how dopants changed the sol-gel process, the structure of the preceramic precursors as well as the materials in the bulk or final layered form.

It was depicted organophosphorus compounds are volatile and inactive and it was difficult to bond into the polymeric precursor structure. On the contrary, cerium is very active ion occurring in two oxidation states and altered initial silses-quioxanes strongly and the chelation process was necessary. However, these did not have an impact on the final materials and the modified black glasses of desired structure and composition were obtained.

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8.24 Burn rate measurements and thermal analysis of gasless pyrotechnic compositions on the example of a Fe – BaO₂ system

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KEYWORDS: combustion, burn rate measurement, delay detonators.

Pyrotechnic compositions are commonly used in time-delay detonators. They enable the creation of blasting networks, where explosives are initiated in a sequential manner. The intervals between the firing of individual explosives directly affect the amount of excavated minerals what show the optimal degree of fragmentation. For time-delay detonators it is very important to use special pyrotechnic compositions, which are insensitive to both external and internal factors, such as minor quantitative composition changes, moisture content, pressing load and pressure.

The following work presents the results of burn rate measurements conducted for a composition based on carbonyl iron and barium peroxide. These compositions create less than 10 litres of gaseous products per 1 g of burned composition. The results of thermogravimetric studies, conducted in inert atmosphere, indicate that the combustion of iron and barium peroxide mixture occurs in the solid state, as the temperature of thermal decomposition of barium peroxide is greater, than the temperature of the ignition. Burn rates in the range of 4-36 mm/s were found for compositions with an iron content between 15% and 50%. Compositions containing more than 50% iron could not be initiated by a black powder fuse. As such they cannot find broad use in geotechnical applications as a delay composition. On the basis of X-ray diffraction analyses it has been found that iron-barium spinels and unreacted iron are the main combustion products.

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8.25 New explosives precursors: investigation of the possibility of obtaining pyrotechnic mixtures and explosives using substances not covered by European regulations

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Keywords: explosives, precursors, detonation, DDT.

The regulation (EU) No 98/2013 of the European Parliament and of The Council of 15 January 2013 on the marketing and use of explosives precursors lists highrisk substances which can be misused for illicit manufacture of explosives. These substances are either not provided to the members of the general public at all or their purchase is subjected to notification, when at concentrations exceeding the specified values. The list of substances in European regulation includes the most popular explosives precursors which have been used in the past for the illegal production of explosive charges. However, the list of "high risk" substances is not exhaustive, as it does not include numerous substances, which are widely used in spectacular and technical pyrotechnics. In spite of ongoing legislative work, numerous strong oxidants and reducing agents, such as potassium manganite (VII), percarbonates and perborates, iron powders, silicon powders and Mg – Al alloy powders remain outside of control, which can serve the abovementioned illegal activities.

The main purpose of the following work was to analyse the possibility of using compounds, such as percarbonates, perborates and peroxides, for the synthesis of organic peroxy compounds, such as urotropin peroxide or acetone peroxide. Determination of both the qualitative and quantitative composition of synthesized substances was performed using NMR technique. The progress of the reaction was determined using the manganometric method. The studies have also been carried out for mixtures of fine-grained or highly porous components: strong oxidising agents and porous silicon or various metal powders. The assessment of the possibility of illegal use of the prepared mixtures was made on the basis of the ability of the mixture to do work (using ballistic pendulum).

Research results indicate the possibility of using sodium percarbonate, sodium perborate and barium peroxide to synthesize HMTD and TCAP, which is accompanied however by a slight decrease in reaction efficiency (by ca. 10 %) and longer reaction time, compared to the synthesis using oxygen peroxide.

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8.26 Electro-synthesis and investigation of indole and carbazole "copolymers" with 3-hexylthiophene

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Keywords: conjugated polymers, electrochemical polymerisation, poly(3-hexylthiophene), polyindole, polycarbazole.

Polymers with π -conjugated electronic structures find application in organic light emitting diodes, photovoltaic cells and electrochromic windows. In our study, we attempted to produce poly(indole-co-3-hexylthiophene) and poly(carbazole-co-3-hexylthiophene) using electrochemical polymerisation.

In our work, at first we synthesized polyindole, polycarbazole and poly(3-hexylthiophene) via cyclic voltammetry, to use them as reference materials. After that, we tried to obtain their copolymers. For that purpose, we attempted polymerization using several co-monomer ratios (from 1:5 to 5:1) and various applied potential ranges.

Received compounds were investigated by IR spectroscopy; the ¹H NMR spectrum of polyindole was recorded but suffered from poor signal/noise ratio due to the low concentration of the polymer. We examined the electrochemical properties of all produced systems using cyclic voltammetry.

The results show that electrochemical copolymerization was not successful. Instead, we obtained polyindole and polycarbazole N-substituted with 3-hexyl-thiophene.

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8.27 Optimal parameters of the SiC-based suspension for the slip casting method

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KEYWORDS: silicon carbide, dispersion, stabilization, viscosity, rheology.

There are very few reported papers on the dispersion of silicon carbide (SiC) powders into water. Moreover, a small number of researchers have used ammonia or sodium hydroxide solutions to adjust the pH of their suspensions. In both cases the aim was to maximize the zeta potential of the SiC particles in aqueous suspension. Good quality ceramic materials and products made from these materials for specifically responsible applications can be achieved by optimizing the manufacturing technology already at the stage of preparation of the powder suspension.

In the present work, the dispersion of silicon carbide powder in aqueous media was studied in terms of surface characterization, the particle stability as well as rheological behavior, etc. The suspensions were prepared from submicron SiC powder (UF10, H.C. Starck) with a specific surface area of $10 \text{ m}^2/\text{g}$ ($d_{BET} \sim 0.5 \mu\text{m}$). The suspensions were stabilized with various amounts of NaOH, i.e.; 0.2, 0.4, 0.6, 0.8 and 1.0 wt.%. Mixture of sintering activators ($10 \% \text{ Al}_2\text{O}_3$ and Y_2O_3 powder, mass ratio 3:2) was added to the slips. The mass of activators was calculated with respect to the SiC powder. Rheological studies concerned relation between viscosity of the suspensions and amount of the slip agent, sintering activators and binder. Improved rheological properties of the suspensions confirmed by high value of the zeta potential were achieved at pH 10. The suspensions showed pseudoplastic behavior which recommended them for application in slip casting method. It was found, that rheological properties of the SiC suspensions depended on many factors such as solid phase content and particle size distribution.

The results showed that well dispersed SiC suspensions can be developed at a constant load of 40 vol% using 0.4 wt.% of NaOH as dispersingagent and binder, allows to get a homogeneous green body.

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8.28 Dispersing of submicrometric SiC powders and improving its rheological behavior

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KEYWORDS: silicon carbide, stabilization, TMAH, dispersion.

Silicon carbide has got many unique properties (such as high hardness, high resistance to frictional wear, high thermal conductivity, high resistance to oxidation), which initiate a wide interest of the SiC products in various industries. One of the important aspect in the production of ceramics materials, including SiC, is the process of obtaining a slurry (slip) with optimal/effective rheological properties in order to achieve high and homogeneous compaction of the final products. In this case it is important to find an appropriate way of dispersing of ceramic powders, i.e. preparation of the suspensions with the highest possible fraction of a dispersed phase and low viscosity.

The results of the research concern stabilization of the silicon carbide aqueous suspensions using a slip agent. There were conducted rheological studies of SiC aqueous suspensions made of submicron SiC powder UF10 (H.C. Starck) with a specific surface area of 10 m^2 /g. Thanks to application of tetramethylammonium hydroxide (TMAH) satisfying low viscosity and high solid phase volume fraction in the suspension (30 and 40 vol.%) were obtained.

The work presents results of investigations on aqueous suspensions of the submicrometer silicon carbide powder with high solid loading (40 vol.%). Knowledge of an ability of particles to form stable suspensions is essential when products are formed by slip casting method. The optimum amount of TMAH (0.4–0.6 wt %) was determined which was necessary to stabilize suspensions made from the SiC powder. All suspensions were stable when pH was higher than 10, what has been determined by zeta potential measurements. Changes on the SiC particles surface caused by the dispersants were identifiable by xPs method.

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8.29 Structure of aluminum-iron phosphate glasses by theoretical and experimental studies

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Keywords: iron phosphate glass, glass network, molecular dynamics, Raman spectroscopy, Mössbauer spectroscopy.

Phosphate glasses are technologically important materials. Their high thermalexpansion coefficients and low liquidus temperatures make them attractive for hermetic sealing to metals. Ca phosphate glasses can be biocompatible. Rare earth phosphate glasses are high potential materials for laser and optoelectronics industry. They can maintain proton carriers at intermediate temperatures what makes them promising materials as solid electrolytes for fuel cells. Phosphate glasses could also be used as host materials for fertilizers of controlled dissolution. The above properties are strongly related to their structural features.

The subject of the studies is $62 P_2 O_5 - 19 Fe_2 O_3 - 19 Al_2 O_3$ glass which structural properties have been determined using experimental methods like FTIR, Raman, and Mössbauer spectroscopy. The experimental results were compared to theoretical investigations with the application of classical (MD) and quantum molecular dynamics (CPMD).

Based on the conducted investigations the glass is built of short phosphate chains which are joined together by iron or aluminum oxygen polyhedra. The iron ions are present mostly in the ferric state in coordination to oxygen from 4 to 6. The similar coordination numbers were also taken by aluminum ions. The CPMD calculations showed the possibility of formation of a weak metallic interaction between iron ions which can be a driving force of observed iron clustering. The experimental and theoretical studies confirmed a dual role of iron as the glass network former or modifier.

The combination of theoretical and experimental studies can give a new insight into phosphate glass network studies.

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8.30 Molecular dynamics simulations and spectroscopic studies of sodium-iron phosphate glasses

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KEYWORDS: Raman spectroscopy, molecular dynamics, computer simulations, iron phosphate glass.

Iron phosphate glasses have been intensively studied as materials for immobilization of radioactive wastes. These glasses are particularly attractive due to their ability to accommodate large amounts of metal oxides and sulphur compounds and their high chemical durability. Also, have low melting temperature what is important to avoid excess radionuclide volatilisation. The glass is built of $[PO_4]$ tetrahedra connected with each other by bridging oxygens and one double bound (P = O) is formed due to pentavalency of phosphorus. Iron in these glasses is present in II and III oxidation state. Both Fe(II) and Fe(III) can take coordination numbers to oxygen from 4 to 6.

The subject of the studies were glasses with a formal composition of $xNa_2O(100-x)(0.23 Fe_2O_3 - 0.11 FeO - 0.66 P_2O_5)$ mol.% where x = 0, 5, 10, 15, ..., 50. The classical molecular dynamics (MD) was used to determine the structural changes caused by the increasing amount of sodium. The glasses were also investigated experimentally using FTIR and Raman spectroscopy. The theoretical investigations were compared to experimental results.

The obtained results from MD simulations are in a good agreement with the experiment and the current state of knowledge. Increasing content of Na causes depolymerization of the glass network. The glasses with high sodium content are mainly built of Q^0 and Q^1 structural units as well as short [PO₄] chains. Also, in these glasses were observed separated iron oxide clusters. The sodium is a glass network modifier. The increase in the sodium content causes an increase of Na coordination number to oxygen. The Na – O distance is independent of Na content.

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8.31 Studies on the fire protection properties of the wood adhesives

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KEYWORDS: fire protection, wood, adhesives, polyvinyl acetate.

Adhesives generally find their application in the gluing of materials. Although, new application methods are being developed. Materials which are used in the construction industry, need to be fireproofed. Wood, commonly used in buildings constructions, is a good example of a material that requires fireproof properties. Adequate modification of the adhesive may give it fireproof properties but also ensure a fire protection of wood, while maintaining its adhesive features.

The results of the research concerning the development of an adhesive formula with a reduced flammability for bonding wood and wood-based elements were presented. Influence of different fire retardants and ceramic fillers e.g. phosphates, oxides, fibers on the polyvinyl acetate adhesive were studied. Thermal analysis (DSC-TG), strength tests, rheology, pH and flammability measurements were made.

The results have shown that the addition of the ceramic retardants and fillers into the adhesive dispersion could improve its thermal and flammability properties. For instance, kaolin causes movement of the third (and last) decomposition steps of PVAc (char degradation to CO_2) towards higher temperatures. Moreover, the addition of kaolin in the combination with other compounds such as melamine phosphate, glass fibers, aluminum oxide and silica (total 21 wt%) could contribute to the achievement of better properties of the adhesive.

The studies revealed that some of prepared adhesives compositions could have potential application as a fireproof adhesive in the future.

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8.32 Impact of modified halloysite on intumescent properties of protective ceramic coatings

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KEYWORDS: fire protection, intumescent coatings, halloysite.

The intumescent coating mainly consists of a dehydrating agent, carbonizing substance and foam producing a substance. During the fire, the intumescent layer is charred, forming a rigid pumice-like structure, which acts as a thermal insulation. Softening, evaporation, decomposition etc. draw heat from the environment, whereas the pumice structure insulates the material against excessive temperature rise. In effect, the protected material can stay for a longer time under the fire without changing its properties.

Substances that were used to formulation of the intumescent coating include epoxy resin, melamine, pentaerythritol and ammonium polyphosphate. To achieve better properties of intumescent, other compounds such as halloysite and graphite were also applied. Unmodified halloysite and modified (with acid or base) halloysite were used. The influence of the type of halloysite on the intumescent size as well as its compactness and adhesion of the coating to the substrate were compared. Suitable fire tests and thermal analysis (TG/DSC) were done. MIR and SEM analysis helped to described the intumescent mechanism.

The results indicate a better effect of modified halloysite than comparing to the unmodified. The coating with the addition of modified halloysite was compact, well adhered to the substrate and was 3 times more intumescent (the swelling size was 50 times of the initial thickness of the coating). Moreover, SEM images of char have indicated a homogeneous, porous and compact structure.

The research has shown that appropriate modification of halloysite could have a positive impact on intumescent properties of protective ceramic coatings.

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8.33 Highly sensitive AdSV determination of iron in presence of azo compound on renewable mercury film electrode

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KEYWORDS: iron, adsorptive stripping voltammetry, renewable mercury film electrode.

When we consider elements that built our planet, iron is one of the most important metals, which helps to sustain life on Earth. It can be found in earth crust, mostly in a form of minerals but it is also a part of chemical compounds that built living organisms and regulates processes crucial for their life. This is the reason why methods for iron determination might be applied in different fields, e.g. medicine, geology or environmental studies. Literature reveal wide spectrum of methods, among which the most frequently mentioned are inductively coupled plasma mass spectrometry (ICP-MS), atomic absorption spectrometry (AAS) and spectrophotometry.

In the following work we proposed adsorptive stripping voltammetry as a highly sensitive method for iron determination. Measurements were conducted in a typical three-electrode quartz cell, whereas homemade renewable mercury film electrode Hg(Ag)FE was used as the working electrode. In order to improve sensitivity, azo compound was used as a ligand. Instrumental parameters for the procedure of iron (III) determination were optimized. The influence of type, concentration and pH of supporting electrolyte, the concentration of azo compound and the surface area of working electrode were investigated. The optimal conditions have been achieved in acetate buffer pH 5.6 while the stripping step was carried out at the potential –400 mV for 20 s. Obtained detection limit was 1.7 nM. Experiments conducted based on developed procedure were compared using controlled growth mercury drop electrode (CGMDE).

Developed method was successfully applied in sensitive determination of iron (III) in environmental samples.

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8.34 Metformin determination on modified GC electrodes using AdSV

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Keywords: metformin, diabetes mellitus, adsorptive stripping voltammetry, modified glassy carbon electrode.

Diabetes mellitus is a metabolic disorder characterized by increased sugar level in blood. Two main types might be distinguished – type 1 and type 2. Statistics show that 90 % of patients suffering from diabetes have type 2 diabetes. In type 2 body's cells do not react to insulin, the hormone which is responsible for decreasing sugar level in blood. That is why other medications instead of insulin must be used in treatment of type 2 diabetes. One of the substances available on the market is metformin, which belongs to the group of biguanides. The main effect caused by metformin in patient's body is decreasing the glucose production in the liver. Moreover, it makes body tissues more sensitive to insulin. That is why it is successfully used in diabetes therapy as a first-line agent.

The most common solutions for metformin determination are the ones from the group of spectrophotometric and chromatographic methods. Unfortunately, they might be often characterized by low sensitivity, long retention time and complicated sample preparation process. Therefore, voltammetry is a good alternative due to its high sensitivity, simple procedure of sample preparation and relatively low cost of single analysis.

In the following work we proposed adsorptive stripping voltammetry with modified glassy carbon electrode for sensitive metformin determination. Different types of surface modifications were tested. Instrumental parameters like sampling and waiting time, pulse amplitude, step potential, preconcentration time were optimized. Measurements were conducted in acetate buffer as supporting electrolyte.

Developed method was successfully applied in sensitive metformin determination in pharmaceuticals products.

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8.35 Transfer of the static MTMS-based aerogel fibrous filter modification method to a flow system

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KEYWORDS: fibrous filter modification, MTMS-aerogel, oil mist filtration.

Purification of oil mist contaminated gas streams is a problem which troubles many branches of industry. High purity requirements introduce the need to perform modification of commonly used fibrous filters in order to improve their efficiency, lifetime, etc. Presented sol-gel method allows for the synthesis of methyltrimetoxysilane (MTMS)-based aerogel directly on the fibers. Modified material is more hydrophobic, oleophilic and also characterised by larger specific surface area, thus increasing oil sorption capacity and filtration efficiency.

The modification of fibrous filters with MTMs-based aerogel in batch mode has been previously developed by our team and reported elsewhere. The following study focuses on transfer of modification method from a static to a flow system, while obtaining the most advantageous morphology of modified filter.



Figure 8.35.1: Comparison of filter modifications in static and flow systems.

Influence of process parameters, such as solvents volume ratios, catalysts (oxalic acid and ammonia solutions) concentrations and ammonia flow rate, on aerogel structure and its deposition on the filter fibres were discussed.

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8.36 Hydrodynamical water purification

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Keywords: water, purification, restoration, alternative water cleaning ways.

Our world faces the problem of acute shortage of pure water, which is suitable and useful for daily use, and the usual methods of its purification by mechanical ways, chlorination and fluoridation are obsolete and have a lot of disadvantages. In order to invent new alternative methods of water purification, the works about alternative cleaning types were studied out. An analysis of the literature reports on hydrodynamic water treatment was carried out and it was found that experiments of hydrodynamic water purification were not carried out.

For our experimental research, a sample of contaminated water from a natural open source was selected. This sample was divided into three parts: the first one was not exposed to any external influences, in the second sample vortical motion of the liquid was created using a stirrer, in the third one an aerator was installed to saturate the sample with air. All samples were subjected to initial and periodic control of chemical oxygen demand and total microbial numbers.

According to the obtained data, the starting points of the study were obtained, and successively selected samples showed that the changes in the two samples, to which external influence was applied, differ from original sample. These changes indicate dynamics of the hydrodynamic method of water purification.

In order to check the effectivity of hydrodynamic water treatment, our scientific research will be held for longer time to have clearer dynamic of results and will be also transferred to the experimental apparatus. It is expected to obtain more clear results, which will show more active changes in key indicators that will demonstrate greater feasibility of using our machine for alternative water treatment.

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8.37 Effect of changing chalcogen atom on electron delocalization on benzochalcogendiazoles radical anions

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KEYWORDS: organic electronics, electron paramagnetic resonance, computational chemistry, electron delocalization.

Benzochalcogendiazoles (BChDA) are strong electron acceptor compounds that are widely investigated in the field of organic photovoltaics (OPV) and organic field effect transistors (OFET). In combination with electron donor unit BChDA are part of a lot of low and high molecular weight ambipolar compound, that can be reversibly both p- and n-doped.

Subject of our research was group of three model donor-acceptor-donor molecules that differing in chalcogen atom in central benzochalcogendiazole unit. Experimentally have been determined current-voltage characteristic and quantitatively delocalisation of unpaired electron on electrochemically generated radical anions of investigated compounds series, measured by electron paramagnetic resonance. This results were compared with ab initio quantum chemical calculated electron densities, B3LVP level of theory were used with 6-311G(d,p) basis set.

We have received compliance between an experimental and a computational results, they show that, the heavier chalcogen atom, the spin density localize more at molecule center. Electron delocalization, adjustable by chalcogen atom change, influence the charge separation and the charge trapping effects in opvs.

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8.38 Immobilization of gelatin on electrospun polyesters nanofibers to enhance biological response

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KEYWORDS: polymers, aminolysis, surface modification, tissue engineering.

Polyester nanofiber scaffolds are attractive from the perspective of tissue regeneration due to appropriate morphology mimicking the fibrous structure of extracellular matrix, as well as suitable porosity and mechanical performance. However, undesirable hydrophobicity and the lack of biological cues limit their effective interaction with cells. Surface modification of electrospun polymer nanofibers is essential method to enhance biological response.

In this research, poly(caprolactone), poly(lactide) and poly(lactide-co-caprolactone) nanofibers were obtained via electrospinning process and subjected to the surface modification. First step was aminolysis with usage of 6 % w/v ethylenediamine in isopropanol solution at different conditions. Then, aminolyzed samples were chemically activated with 1% w/v solution of glutaraldehyde in water for 2.5 h at room temperature, which was necessary for further immobilization of gelatin via covalent bonding. Morphology, amount of amino groups, wettability, mechanical properties and cell response were characterized for all modified polyester nanofibers.

Chosen conditions of surface modification allowed to maintain original morphology of all types of polyester nanofibers. Ninhydrin test confirmed effectiveness of aminolysis conditions for poly(lactide) and poly(lactide-co-caprolactone) nanofibers. Additionally, differences in impact on mechanical properties were observed. All samples were completely hydrophilic after gelatin immobilization and improvement of cell response was observed.

This study shows that this type of surface modification is relatively effective way to improve cell adhesion and growth on the fibers surface and there is perspective of further optimization of process in the aspect of cell response and scaffold properties.

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8.39 Reconstruction of particle size distribution based on a finite number of distribution's moments in the Matlab environment

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KEYWORDS: reconstruction, moments, distribution, Matlab.

The moment method is very effective and convenient for solving the population balance, however its disadvantage is the lack of knowledge about the statistical distribution of particle size. This inconvenience poses a challenge to reconstruct these distributions, which is the goal of the work.

Over the years, various attempts have been made to deal with this issue. This work focuses on the analysis of reconstruction based on predetermined formulas of statistical functions, and at a later stage on the reconstruction based on the "statistically most likely" [1] function and a new function. For this purpose, the Matlab environment and the numerical procedures in it were used.

Based on the calculations made, interesting conclusions about the use, advantages and limitations of the above methods were obtained. It was found that simple statistical relationships are useful only in a narrow group of distributions of a simple character, while distributions of more complex shape should be solved on the basis of more complex relationships. The method "statistically most likely" and new function were compared. The first method better maps the distribution of variability in the linear scale, while the second method in the logarithmic scale. The methods also differ in that the "statistically most likely" method is less sensitive to the initial parameters in the numerical procedure, but more sensitive to the integration range, while the new function is almost insensitive to the integration range, but sensitive to the initial values. During the calculations, it was decided to focus on adjusting the logarithms of the differences in moments. Based on the experience, it was found that the most universal numerical procedure was the "Levenberg-Marquardt" algorithm.

In summary, the numerical procedures used have the potential to be used in CFD programs as an extension to population balance settlement procedures. The procedures created would help to assess the process in terms of particle size, which can be particularly useful in the powder industry.

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8.40 Design and calibration of Young's interferometer with piezoelectric adjuster

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KEYWORDS: interferometry, piezoelectricity, phase shift, Young experiment.

Interferometry is a common technique used in various applications for characterization of wavelength, angle, phase shift, displacement, shape and many other. It is a non-invasive method, which basically uses an interference of two waves to extract investigated information. There are many types of interferometers and each has its own advantages, disadvantages and applications. If the phase shift of light is changing fast, the acquisition must be done with high precision in time. In this case, camera-based interferometry has to small sampling rate, and detector-based interferometry have only one measurement point.

In this work we proposed interferometer based on the principle of Young's double-slit experiment with a spatial control of fringe pattern and possibility to control the distance between two light beams. Our setup consists of Helium-Neon laser with wavelength $\lambda = 633$ nm as a source of light and two-channel photodetector placed in a Fourier plane. To induce a phase shift in the system, we have implemented a piezoelectric adjuster in one arm of the interferometer. We described essential parameters of proposed setup and investigated the impact of the distance between two beams on the performance of our device. The comparison of a theoretical model and obtained phase modulation caused by piezoelectric element is presented and discussed.

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8.41 The depolarization properties of nematic liquid crystal

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KEYWORDS: nematic, liquid crystal, depolarization measurement.

Depolarizers are used to randomly vary the polarization state of incident light. They are often used in many optical devices to minimalize errors caused by polarization effects. There are different types of depolarizes such as Lyot depolarizers, Wedge depolarizers, Faraday rotators, fiber optic depolarizers or Liquid Crystals (LCs). Among all LCs have the advantage that they can be electrically controlled and switched, and are inexpensive and low weight.

In this work, we investigate depolarizing properties of Nematic Liquid Crystal (NLC). For characterization of tested material we have measured a Degree of Polarization (DOP) for six different states of polarization of input light as a function of voltage applied to cell filled with LC. When the electric field is applied to LC, the molecules change their orientation and for certain voltage values the direction of switching is random, therefore the depolarization effect occurs. Texture of LC, when the value of DOP is low, shows a discontinuity of the director and forms a Schlieren texture. The investigation of stability of DOP and texture formation in time will be performed. Our device could be implemented as a depolarizing element in systems, which does not require certain state of input polarization.

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8.42 Voltammetric testing of the degree of aluminum release from tea leaves

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Keywords: aluminum content in tea, determination of Aldetermination of aluminum, voltammetry, tea infusions.

Tea plants (*Camellia sinensis*) are known to be Al (III) hyper-accumulator and it is an important, second after water, beverage in the world. Drinking tea over a prolonged period of time may make more than double of an intake of aluminum. It has been claimed that Alzheimer's disease is linked with Al content in the human brain. Other diseases in which aluminum also plays a significant role in Parkinson's dementia, encephalopathy, osteomalacy, osteodistrophy, anemia, gastrointestinal symptoms, possible cardiotoxicity features, dialysis encephalopathy syndrome. Aluminum is clearly a powerful neurotoxic agent, so it is very important to detect and determine the aluminum content in food and other materials to be able to reduce exposure to this hazardous element and eliminate products in which the aluminum content is high.

The aim of the work was to check whether the aluminum present in the tea leaves is released into the infusion and whether its concentration increases after the addition of lemon juice. As samples, 4 types of tea were used: black, green, red and white tea. All kinds of tea originated from China and came from one producer the Mayo company. To examine the concentration of aluminum in tea leaves and the percentage of aluminum that is released into the solution, two kinds of samples were prepared: tea leaves and tea infusions. Measurements were performed using differential pulse voltammetry (DPV). The highest concentration of aluminum was observed in the case of red tea (0.133 % of the leaves weight), and the lowest in the case of white tea (0.041 % of the leaves weight). The highest concentration of aluminum was also recorded in the infusion of red tea – about 8 mg/L. After the addition of lemon juice, the aluminum concentration increased in all infusions.

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8.43 Development of an electrochemical procedure for the determination of aluminum in tea samples

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Keywords: DP voltammetry, electrochemical procedures, determination of aluminum, tea, Hg(Ag)FE.

Voltammetry as an analytical research method has many advantages. To be able to determine concentrations, new procedures are required to determine the trace amounts of analytes in real samples with a complex matrix.

This work presents, DPV methodology of indirect aluminum determination in tea leaves and infusions using the renewable silver amalgam electrode -Hg(Ag)FE. This electrode is mercury free and has a huge analytical potential for applications. It was also recently applied in many works. The composition of the supporting electrolyte was: 0.1 M ammonia buffer, 0.01 M potassium bromate, 0.25 µM calcium, 0.1 µM ethylenediaminetetraacetic acid (EDTA) and 42.5 µM alizarin S. A self-referencing strategy was proposed which relies on alternate voltammetric curves registration with and without conditioning of the electrode surface. The developed procedure utilizing formation of aluminum-alizarin S complex shows linearity in the range of $2-50 \ \mu g L^{-1}$ of Al (III) concentration, with r > 0.997. In the case of the electrode conditioning LOD is $0.2 \,\mu g \, L^{-1}$ and repeatability expressed by cv is 1–2 %. Introducing an additional operation i.e. electrode activation results in decrease of sensitivity from 0.0162 to 0.0043 μ A/ μ gL⁻¹. The method was verified using CRM (tea leaves). Due to the wide variety of tea origin, types and producers, four most popular sorts (black, green, red and white) were chosen, made by one manufacturer. It was demonstrated that the proposed methodology may be applied in Al (III) determination in tea leaves and infusions.

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8.44 Verification of regression equations describing the effect of process parameters on the fiber diameter and the beads size

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KEYWORDS: electrospinning, fibers, bead-on-string, factorial design.

Polymeric mats obtained by the electrospinning process are being extensively investigated paying special attention to their applications in drug delivery systems like: wound healing, inhalation therapy, cancer therapy or tissue engineering. Optimization of this process would allow to reduce the time of research and the number of experiments.

The work presents verification of regression equations, which describe the influence of process parameters (electrical voltage, flow rate and dynamic viscosity of polymer solution) on the fiber diameter (without and with bead-on-string structures) and on the size of beads. Regression equations were established by a 2^3 factorial design. To determine the significance of the mathematical equation coefficients, the analysis of variance and the *t*-test were used. On the other hand, the F test was used to test the adequacy of equations.

The conducted analysis proved that the electrical voltage has the most significant influence on the diameter of fibers without beads, while the dynamic viscosity of the polymer solution has the greatest impact on the diameter of the beaded fibers. On the other hand, the both factors (voltage and viscosity) have the most significant influence on the size of beads. The flow rate of the polymer solution and the correlation between the parameters have no significant effect on the size of the fibers and beads.

The proposed method can be used as a tool to optimize the electrospinning process by determining the process factors of the highest statistical significance in the regression equations and selecting their values that will allow to obtain electrospun mats with the desired structure.

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8.45 Adsorption of volatile organic compounds on activated tyre pyrolysis char

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KEYWORDS: adsorption isotherm, char, end-of-life tyres, pyrolysis.

Every year in Europe the number of end-of-life tyres (ELTS) increases by 2.5 million tonnes. The direct disposal of ELTS in landfills is banned in Europe. One of the possible ways of recovering materials from ELTS is pyrolysis. The products of pyrolysis are: char, oil, gas and metal.

This work concerns adsorption of a model volatile organic compound (voc) on CO_2 -activated tyre pyrolysis chars. The results of this work are adsorption isotherms obtained at different temperatures.

The physical activation of the tyre pyrolysis char were carried out in a thermobalance TG 209 F1 Libra (Netzsch, Germany) equipped with a micro furnace and a precise ultra-microbalance. Surface area of the activated chars as well as adsorption isotherms were determined using the 3Flex Surface Characterization Analyzer (Micromeritics, USA).

Before the main experiment, the nitrogen adsorption-desorption isotherms were determined for granular activated carbon (GAC), non-activated and activated chars at different temperatures. They are presented below.



Figure 8.45.1: Nitrogen adsorption/desorption isotherms for GAC and the non-activated and activated chars at 77 K.

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8.46 Thermal oxidation of boron carbide edges

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KEYWORDS: boron carbide, thermal oxidation, boron oxide.

Boron carbide (B_4C) is one of the hardest material behind cubic boron nitride and diamond and covalent material used in personal and vehicle armor, abrasives, neutron absorber in nuclear reactors and metal matrix composites. Among several methods for the synthesis of boron carbide most commonly used method is the carbothermal reduction of boron compounds: boron, boric acid (H_3BO_3), or directly boron oxide (B_2O_3) by carbon. The source of carbon is usually fine crystalline graphite or coke oil. The reaction is carried out in a protective atmosphere at temperatures in the range of 1700–2000 °C. The product, formed in these conditions is coarse and strongly agglomerated, which requires intensive crushing and grinding before continuing its usage. The goal of this paper is thermal oxidation of boron carbide edges. The dimensions of the resulting powders can be controlled by the temperature and duration.

In this research used two types of boron carbide: commercial below 1 μ m and boron carbide synthesized by our research team. The powders were subjected to thermal treatment in the air by recording both the thermal effects (DTA) and mass changes (TG) to determine the temperature of the edge oxidation temperature. All powders were placed in crucibles and then heat-treated at a temperature from 600 to 800 °C with different time.

All obtained powders were characterized by the X-ray diffraction (XRD). We conducted a morphological examination of powders by scanning electron microscopy (SEM) with X-ray energy dispersive spectroscopy (EDS). The crystallite sizes were determined on the basis of the half-width reflex (021) by the Scherrer method. As a result of thermal pickling, in most cases, the boron carbide content in the samples was reduced. By carrying out this process, the dimensions of the boron carbide grains were changed, resulting in a powder with nanometric sizes of individual particles. It can be seen that the morphology modification strongly depends on the temperature of the thermal etching. The best results for commercial and synthesized boron carbide were obtained at different process temperatures. It is therefore important to choose the temperature of the thermal etching to the specific powder.

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8.47 Chemical etching of boron carbide edges with the removal of excess carbon after synthesis

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KEYWORDS: boron carbide, chemical etching, sodium hydroxide, aqua regia, saccharides.

Boron carbide (B_4C) has many features such as the highest hardness (it is the third hardest material, after the diamond and cubic boron nitride), superior thermal stability, low density (2.52 g/cc), lightweight, chemically resistant, large absorption of neutrons and high melting point (~ 2300 °C). In the literature, there are many various synthesized method of synthesized boron carbide such as carbothermal reduction (CTR) [5–8], sol-gel method [9], the SHS method (self-propagating high-temperature synthesis) [10], magnesiothermic reduction, chemical vapor deposition (CVD), mechanochemical synthesis. The goal of this paper is synthesis pure nanopowders of boron carbide and compare with commercial boron carbide and chemical etching of its edges with the removal of excess carbon after synthesis.

In this research used two types of boron carbide: commercial below 1 μ m and boron carbide synthesized by our research team. Three solutions with different properties were selected as pickling reagents: maximally concentrated NaOH solution, royal water and Murakami solution – suitable for pickling covalent materials. The digestion process was aided with ultrasounds to prevent secondary agglomeration of crystallites for one day.

All obtained powders were characterized by the X-ray diffraction (XRD). We conducted a morphological examination of powders by scanning electron microscopy (SEM) with X-ray energy dispersive spectroscopy (EDS). Based on the results of the conducted research, it can be concluded that chemical etching is an appropriate method of morphology modification of boron carbide powder. Chemical etching in each of the used etching agents caused a decrease in the size of crystallites of boron carbide powders. The size of the crystallites of the starting, synthesized powder is about 3 times smaller than their size in the starting commercial powder. The best results are used as a digestive agent of the Murakami solution.

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8.48 Synthesis and application of cinchona-based, enlarged organocatalysts

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Keywords: organocatalyst, catalyst enlargement, C_3 -symmetry, asymmetric synthesis.

Organic solvent nanofiltration is a membrane separation technique based on a membrane which has different permeability to different compounds. The rejection depends mainly on the size of the molecules – hence compounds with higher molecular weight have higher rejection. Therefore catalyst enlargement can help to overcome the separation bottleneck. In my research work I managed to carry out more ways of enlarging cinchona alkaloid derivatives by attaching them to a central core.

During the first strategy commercially available hydroquinine was demethylated and then attached to 1,3,5-*tris*(bromomethyl)benzene. The reaction gave the product catalyst 1 with proper yield (65 %). The other methodology was carried out by click reaction. 1,3,5-*tris*(Azidomethyl)benzene was used as a central unit and the triple bond was formed on quinine in a two step (bromine addition, hydrogen bromide elimination) reaction. The synthesized catalyst 2 can be easily modified with further hydrogen bond donor units like squaramide or thiourea.

The enlarged organocatalysts were tested in *Michael* addition reactions. The asymmetric organocatalysis was successfully demonstrated and allowed pretty high yields (up to 90%) and enantioselectivities (up to 97% ee). The concept of size-enlarged cinchona-based organocatalysts presented herein enables new possibilities for fine chemical manufacturing, and further boosts growth in the exciting new era of organocatalysis.

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8.49 Characteristic of antifreeze proteins produced by psychrophilic yeast from *Glaciozyma martini* species

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KEYWORDS: antifreeze protein, yeast, psychrophiles, freezing, ice.

The development of transplantology has led to the search for ways to extend the life of cells, tissues, organs as well as protect them from the harmful effects of the freezing process. The use of chemical substances for cryoprotection is associated with the possibility of damage to the biological material, which is why attention has been paid to natural materials such as peptides or proteins. Research is currently being conducted on proteins derived from psychrophilic organisms that allow them to survive under harsh temperature conditions $(0-4 \,^\circ\text{C})$. Antifreeze proteins (AFP) are designed to increase the thermal hysteresis of water and the inhibition of ice recrystallization.

The collection of microorganisms of the Institute of Technical Biochemistry of the Lodz University of Technology includes many strains originating from areas where the temperature seasonally or constantly does not exceed 5 °C. After culturing in 4 °C on a medium containing glucose, bactopeptone, yeast extract and sodium chloride, the yeast from *Glaciozyma martini* species was indicated as the producer of these proteins. The protein was purified by means of ice affinity chromatography. The apparatus used in the laboratory was created by hand. After obtaining a homogeneous formulation, a test for thermal hysteresis activity was performed using a differential scanning calorimeter (DSC).

After the above tests, the yeast of *Glaciozyma martini* proved to be the producer of these proteins. They synthesize a secreted, glycosylated protein with a mass of ~ 27 kDa with thermal hysteresis activity. The recent studies aim to isolate the AFP protein gene from total RNA for subsequent expression in the yeast expression system.

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8.50 Computational fluid dynamic simulations of high shear mixers

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KEYWORDS: mixing, impeller, dispersing, CFD.

In processing industry dispersion process is commonly realized in stirring tanks with an impeller. In order to obtain desirable final properties of a product, these devices must meet a number of requirements. They have to generate shear stress sufficient for splitting solid particles suspended in liquid, generate circulation which provides constant suspension of particles and directs them toward the impeller and prevent formation of dead volumes, which cause low homogeneity of a final product. This study considers simulated flow generated with various geometry of sawtooth impellers, investigate power consumption, mixing time and energy dissipation rate. Set of these parameters allows to define the efficiency of a process.

During the research, computational fluid dynamic methods were used. Simulations were conducted in turbulent regime, therefore k- ϵ turbulent model was used. Volume of fluid model was applied to inspect liquid surface curvature during the process. Power draw and mixing time were observed in order to measure the energy consumption. Near impeller flow stream and higher energy dissipation rates volume were established to measure particle splitting ability of the impellers. Liquid velocity distribution was examined to check whether the dead volumes are formed.

As a result of the described research, one geometry of an impeller was chosen, due to its best breakage ability, according to power consumption. Using this geometry of an impeller allows to obtain specific product properties with lower energy expenditure, what is caused by high circulations generated by the impeller, and to achieve high homogeneity value.

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8.51 Apatite inducing ability of titanium after direct laser interference lithography

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KEYWORDS: titanium, direct laser interference lithography, simulated body fluid, XPS.

The main aim of this study was to analyze the kinetics of the apatite layers formation process after immersion in sBF on laser-modified titanium surface. We propose direct laser interference lithography technique in order to obtain the surface with periodic and hierarchical patterns on Ti grade 2 sheets after shot peening and acid etching. The method presented in this study was developed in order to locally functionalize the surface of prefabricated elements with the original roughness. The fabrication of the multimodal topography can be used to take the advantage of favourable micro- and nano-roughness and to mimic the bone hierarchical surface structure after the remodelling process.

The titanium surface was characterized in terms of the shape, roughness and chemical composition. In order to obtain a set of information, the numerous research methods have been used: scanning electron microscopy, optical profilometry, atomic force microscopy and X-ray photoelectron spectroscopy. The process of apatite formation on the patterned titanium surface in a simulated body fluid was thoroughly investigated by correlating the SEM observations as well as X-ray photoelectron spectroscopy (KPS) and Fourier-transform infrared spectroscopy (FT-IR) measurements.

The formation of biomimetic apatite layers was accelerated on titanium surface structures after DLIL modification. Periodic titanium patterns induce faster apatite growth at the early immersion stages. This effect is mainly connected to the surface properties DLIL surface, such as presence of higher amount of hydroxyl groups, larger surface area and negatively charge of the surface.

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8.52 Microstructure and mechanical analysis of laser structured titanium grade 2 for biomedical applications

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KEYWORDS: titanium, microstructure, mechanical properties, laser patterning.

A suitable technique which can be used for modification of the titanium with the initial, not flat topography is Direct Laser Interference Lithography (DLIL). The technique presented in this study, can generate complex types of textures with high resolution, resulting in micrometer size patterns in one step. Expect for modifying the surface topography, laser irradiation, with the specific thermal characteristic, may induce microstructure changes below the free surface including grain refinement. What is more, the dissolution of the light elements, such as oxygen or nitrogen, strongly depends on the interactions between the laser, substrate and used atmosphere.

In this study we performed a careful cross-section microstructure analysis by combining complementary methods such as focus ion beam (FIB), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and scanning transmission electron microscopy (STEM) on different scales to elucidate the microstructure and surface chemistry after laser-patterning and the correlation with phase composition (GI-XRD).

A cross-section microstructural analysis revealed that all the modifications caused grain refinement. DLIL texturing results in the formation a thin (1–1.5 μ m), continuous layer with lath-like grains. The GI-XRD analysis showed no changes in phase composition, what indicates that the formation of layer with small lamellar grains is a result of the high cooling rate from the β -stability region or higher temperatures. The gained results are important with regard to the evaluation of laser patterned surfaces in the biomedical applications. The description of the microstructure and chemical composition of the DLIL modified titanium samples, can be useful when understanding and characterizing the processes on the bone/implant interface.

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8.53 c-cvd synthesis of helical carbon nanotubes as a potential energy storage nanomaterials

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KEYWORDS: carbon nanotubes (CNTs), helical CNTs, c-CVD synthesis, energy storage.

Carbon nanotubes (CNTS) since their discovery were found as an intriguing and useful nanomaterials in many fields from materials science to engineering to biomedicine due to their extraordinary properties. Those characteristics include excellent electrical/thermal conductivity and high mechanical performance accompanied by the energy storage capability. CNTS are cylindrical quasi-one-dimensional macromolecular architectures with diameters in the range of few nanometers and length of micrometers to hundreds of millimeters. Moreover, they have been observed in various geometries like straight, toroid, coiled, branched or helical, which strongly affect their properties.

Herein, we propose the synthesis of helical CNTS (h-CNTS) using catalytic chemical vapour deposition (c-CVD) method using different catalyst nanoparticles (iron, cobalt, copper and molybdenum) and different carbon sources (mixture of xylenes and toluene). The main goal of the study is to optimize the conditions of the c-CVD synthesis and the catalyst type to obtain various geometries of CNTS, with the focus on h-CNTS. As-obtained nanomaterials will be characterized using SEM, TEM, XRD and Raman spectroscopy to correlated conditions with the final CNT geometries.

We expect to demonstrate that the appropriate selection of the precursors of the catalyst nanoparticles as well as carbon feedstock will enable design of the CNT geometries. As the future studies, CNTS of various geometries will be dispersed in ionic liquids and examined how their morphologies and dispersion quality influence on the energy storage properties.

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8.54 The impact of purification and characteristics of carbon nanotubes onto their dispersibility in ionic liquids

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KEYWORDS: carbon nanotubes, ionic liquids, dispersion, purification, properties.

Carbon nanotubes (CNTS) are carbon allotropes of the tubular 1D-structure. Since discovery, they have found interest in many fields due to their unique combination of excellent physicochemical properties like electrical conductivity, strength, flexibility and thermal conductivity. Between the individual CNTS there are weak but abundant interactions, i.e. van der Waals forces, hence, CNTS tend to agglomerate. Moreover, due to their intrinsically hydrophobic nature, they are difficult to disperse in organic solvents and water.

In this study, we discuss the influence of CNTS properties on their dispersibility in different ionic liquids (ILS), which molecular structure was pre-designed on the imidazole core. Particularly, we demonstrate how geometry, aspect ratio and purity affect dispersibility of various in given ILS. ILS were selected as the dispersing media due to their frequently minimal toxicity, capability of recycle and overall eco-friendliness. Among various classes of ILS, the most frequently used are the ones containing *N*-heterocyclic cations – also employed here in our studies due to economy and well-defined physicochemical properties.

As the outcome of our research, we will prepare a mini-library of 1L-dispersions of CNTS of different morphology, geometry, type and level of contamination. The dispersing media will be in-house synthesized 1Ls. The quality of dispersions will be quantified spectrophotometrically, and also using optical microscopy and further cryo-TEM imaging.

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8.55 All-solid-state Ca²⁺-selective electrodes with TCNQ and KTCNQ crystals as internal layer

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KEYWORDS: ion-selective electrode, all-solid-state, calcium, TCNQ crystals.

The work concerns the potentiometric sensors, which are commonly used in environmental and clinical analysis. In recent years the major development of one group of potentiometric sensors called an ion-selective electrodes was observed. This paper presents the impact of organic molecular crystals (TCNQ) that were used as mediation layers on the analytical parameters of solid-contact Ca^{2+} -selective electrodes.

Calcium ions' concentration and its fluctuation plays an important role in human organisms and environment. In human organisms 99 % of calcium is found in bones and teeth as a key element of their structure and only 1 % of calcium (in form of calcium ions) is responsible for metabolism. However, the ionic form is crucial for initiating physiological processes such as vasoconstriction, blood coagulation, muscle contraction or nerves transmission. Because of the widespread occurrence and their significance, the selective, accurate and reliable recognition of calcium ions is crucial. Mass Spectrometry, Chromatography or Atomic Absorption Spectrometry could be applied for the calcium analysis although they are usually expensive, complicated and time-consuming. Potentiometry method is not only inexpensive and fast in response but also allows to determine the ionic form of calcium which is essential in clinical analysis.

The research covered preparation of electrodes with ion selective membranes and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its potassium radical salt (KTCNQ) internal layers as well as determination of their parameters. Prepared calcium-selective electrodes showed a near-Nernstian slope, short time of response and repeatable and reproducible values of standard potential. Application of the TCNQ and KTCNQ crystals as an internal layer reduces the membrane resistance and improves stability of the potential compared to electrodes without such layers due to the presence of material which exhibits both electronic and ionic transduction. Moreover, TCNQ-KTCNQ in calcium-selective electrodes improves their selectivity toward to interfering cations and lowers the detection limit.

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8.56 The influence of sodium-selective membrane composition on analytical parameters of TCNQ-based potentiometric sensors

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KEYWORDS: ion-selective membrane, solid-contact, TCNQ crystals.

An essential element of ion-selective electrodes is an ion-selective membrane. For liquid membranes the most commonly used compound is PVC with an addiction of plasticizer, lipophilic salt and ionophore. All presented components play a specific role in the membrane, therefore their content must be properly selected to ensure the expected selectivity and sensitivity of the electrodes.

The conventional electrodes are rapidly being replaced by so called all-solidstate electrodes obtained by removing the internal solution from electrode's construction. The replacement of liquid contact by a solid contact (sc) layer and the creation of all-solid-state ion-selective electrodes (ASS-ISES) have created a new field in potentiometry method.

In this work some investigations concern influence of the ion-selective membrane composition on sodium-selective electrodes properties are presented. The sodium-selective electrodes were prepared with the use of sodium ionophore III as ionophore and 7,7,8,8-tetracyanoquinodimethane (TCNQ) and its sodium radical salt (NaTCNQ) as transducer layer. All kinds of prepared electrodes were tested using potentiometric and chronopotentiometric studies and significant impact of membrane composition on electrode parameters was observed. Among investigated sensors, TCNQ/NaTCNQ-contacted all-solid-state electrodes exhibited the best analytical and electrical performance due to the presence of the intermediate layer, which simplifies the ion-to-electron transduction process between the ion-sensing membrane and the glassy carbon electrode. Exemplary, these electrodes with sodium ionophore III had a close-to-Nernstian slope (58.63 mV/pNa) in the range from $10^{-5}-10^{-1}$ M NaCl and revealed detection limit of $10^{-5.2}$ M. The highest capacitance was observed for electrodes based on TCNQ/NaTCNQ as intermediate layer (139 µF).

The developed sensors have been successfully used in the determination of sodium in natural waters with the results obtained being in very good agreement with those of flame photometric experiments, confirming the potential of the developed ISES for the fast analysis of sodium ions in water.

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8.57 Simulation of cascade LNG liquefaction process in Aspen Plus

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KEYWORDS: liquefaction process, Liquefied Natural Gas, numerical simulation, Aspen Plus.

Liquefied natural gas (LNG) is produced in the liquefaction process of natural gas. In the condensation process LNG is cooled to approx. -162 °C. There are three basic methods of condensation: *i*) classic cascade cycle, *ii*) cascade cycle with mixed refrigerant and *iii*) turbo-expander decompression cycle.

In this paper the simulation results of natural gas liquefaction in the cascade cycle are presented. The composition of LNG used in the simulation was as follows: 92.4% methane, 5.6% ethane, 1.9% propane, 0.1% n-butane.

Numerical simulations were carried out in the Aspen Plus process simulator using the PENG-ROB method which is based on the gas equation of state developed by Peng and Robinson in 1976. The refrigerants in the individual cascade were methane, ethane and propane.

Based on the analysis of the obtained results it was found that with increasing mass flow rate of the refrigerant in the tested cascade, the amount of liquefied LNG also increased. The larger the mass streams of the refrigerants, the higher values of the received heat stream from natural gas were noted in simulation results. Moreover, increase of energy consumption of the compressor with increasing refrigerant streams were also observed.



Figure 8.57.1: System of the cascade LNG liquefaction process.

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8.58 Determination of Vitamin K2 by differential pulse voltammetry with bi-disc glassy carbon electrode

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Keywords: glassy carbon electrode, Vitamin K2 (menaquinone), voltammetric determination, stripping voltammetry.

In the recent years a lot of interest is placed in vitamin κ_2 (menaquinone), which may be synthesized by some bacterial species both directly in the human digestive tract as well as beyond, in the process of food fermentation. Vitamin κ_2 encompasses several different homologues which differ from each other by chemical structure. The ring structure of 2-methyl-1,4-naphthoquinone is characteristic of all forms of this vitamin, they differ by the length of the side chains composed of unsaturated isoprenoid units, which may count from n = 1 to n = 13.

This paper presents a novel, high sensitive analytical method for electrochemical determination of vitamin K2 at bi-disc glassy carbon electrode using differential pulse voltammetry. Preliminary research included optimization of the composition, concentration and pH of the supporting electrolyte and instrumental parameters of stripping cyclic voltammograms (DP Asv and DP csv). The highest analytical DPV response of VK2 was obtained in supporting electrolyte containing 40 % of ethanol and 0.04 mol L⁻¹ Britton-Robinson buffer (pH 11.0). In the range from -0.2 to -0.8 V well-shaped cathodic and anodic peaks current were registered with accumulation time of 10 s. Under optimized experimental conditions, a linear calibration curve in the vK2 concentration range of 0.06–0.55 mg L⁻¹ with the 0.017 mg L⁻¹ limit of detection was achieved.

The obtained results indicate that the developed method is analytically useful for the determination of vitamin κ_2 in various samples.

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8.59 The study of voltammetric determination of Vitamin K2 with the application of carbon and mercury electrodes

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Keywords: glassy carbon electrode, mercury electrode, Vitamin K2 (menaquinone), voltammetric determination.

The purpose of this work is to shows the possibility of voltammetric determination of Vitamin κ_2 using mercury and carbon electrodes. Vitamin κ is a group of chemical compounds which, in the construction of the structure is distinguished by a ring of 2-methyl-1,4-naphthoquinone with lipophilic side chain attached at the position c₃. Vitamins κ include natural occurring vitamins κ_1 and κ_2 and synthetic derivatives such as κ_3 . Particularly noteworthy is vitamin κ_2 and its homology $M\kappa$ -n, n – number of unsaturated isoprenoid residues ($1 \le n \le 13$). Its source is some food products, especially fermented (e.g. sauerkraut, pickles, etc.), but it is mainly produced by saprophytic bacterial flora.

This paper, discusses the results of research on the possibilities of vitamin κ_2 determination in food products and several dietary supplements using a controlled growth mercury drop electrode (CGMDE) and glassy carbon electrode (GCE) using differential pulse voltammetry (DPV). Initial tests included optimization of the composition, concentration and pH of the supporting electrolyte and instrumental parameters of DP Asv and DP Csv voltammograms. The results achieved are the linear range of the method: 2–100 µg L⁻¹ (r = 0.988, CGMDE) and 80–400 µg L⁻¹ (r = 0.986, GCE); the limit of quantification: 0.5 µg L⁻¹ (CGMDE) and 20 µg L⁻¹ (GCE); sensitivity: 6 nA L µg⁻¹ (CGMDE) and 1.3 nA L µg⁻¹ (GCE); Relative RSD standard deviation: 1.3 % (CGMDE) and 6.2 % (GCE).

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8.60 Influence of composition changes on rheological properties of clay-cement binders

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Keywords: clay-cement binder, rheological properties, thixotropy, clay minerals, cement.

Clay-cement mixed binders are used in many areas especially in the construction and renovation of flood protection. The rheological parameters in the liquid state belong to the main criteria for their usefulness, which determine their application properties, i.e. the possibility of submerging to the ground and proper crosslinking.

In this paper, the results of rheological studies are shown concerning claycement binders based on Belchatów clay (contained beidellite) and Koc kaolin (contained kaolinite), Portland cement and water glass as a modifying additive. The flow curves, values of elastic modulus G', loss modulus G'' and time of the "crossover" phenomenon were compared. The effects of composition changes on the rheological properties of the binders in the liquid state in terms of their performance were determined.

These studies showed that rheological properties of clay-cement binders depend on type of clay mineral. Belchatów clay slows down the crosslinking effect of the binder. In the binder gel structures are formed that can be successively rarefied with shear in the entire volume. Kaolinite makes grain aggregates with greater mechanical strength. During shearing, they may break down into smaller aggregates while maintaining the plastic properties of the binder.

In general, rheological properties of clay-cement binders depend on type of clay mineral. In case of their application, measurements of flow curves, viscosity and elasticity modulus should be carried out.

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8.61 Viscoelastic properties of clay-cement binders

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Keywords: clay-cement sealing binder, viscoelastic properties, flow curve, cement, clay minerals.

Clay-cement sealing binders are used in many areas especially in the construction and renovation of flood protection. Modernization of flood embankments, often located in inaccessible area, requires the transport of finished binder over considerable distances. The most common solution is to create a portable base in which the binder is produced in the form of a suspension, and then it is transported using pipelines to the place of work. The viscoelastic properties in the liquid state belong to the main criteria for their usefulness (i.e. the possibility of submerging to the ground and expected crosslinking afterwards).

This work presents the results of studies concerning freshly prepared claycement binders based on Bełchatów polymineral clay and Koc kaolin, Portland cement with the addition of water glass as the initiator of the hydration process. The flow curves, values of elastic modulus G', loss modulus G'' and time of the "crossover" phenomenon were compared. The influence of composition changes on viscoelastic properties of liquid state binders in the aspect of functional properties was determined.

These studies confirmed that viscoelastic properties of clay-cement binders depends on type of clay minerals. In case of their application, measurements of viscosity and elasticity modulus should be carried out. Belchatów clay (contained beidellite) slows down the crosslinking effect of the binder. The ratio of G''/G', modulus at low shear rates is less than 1, which indicates their liquid properties. Kaolin Koc (contained kaolinite) makes grain aggregates with greater mechanical strength. The ratio of G''/G' modulus at low shear rates is greater than 1, which indicates a greater share of elastic properties of such binders.

To sum up, sealing binders based on kaolin koc exhibit different viscoelastic properties than binders based on Belchatów clay. Their properties inhibit possibility of their application.

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8.62 High temperature interactions between refractory raw materials and copper slags

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KEYWORDS: copper slag, corrosion, powder test, raw material, XRD.

Copper is one of the most important non-ferrous metals. It is produced during high temperature processes from copper-poor ores but at the end of those operations its purity reaches even 99,99 %. At first ore must be extracted and enriched using e.g. a flotation method. Then it is subjected a heat treatment in shaft kiln, a two-step converter process and fire refining. Another step is electrolytic refining and at the end it is casted into different shapes.

The most challenging issue for the refractory materials used in this field of industry are the high temperature processes occurred between refractory linings and copper slag. Copper slag which is formed in this thermal device and during converter process is very destructive for refractory linings. It is build of oxides such as CuO, PbO, SiO₂ or As_2O_3 which are aggressive and form low melting phases. Depending on the stage of copper process, a chemical composition of a slag can be different and hence the phase composition is changing. In the first stage of converter process it contains a lot of lead oxide but in the second stage a high concentration copper oxide is observed.

The main purpose of this work was to investigate the influence of copper slag from different stages of converter process on different refractory raw materials. The research was conducted on powder samples of refractory raw materials and slags and heated up to the temperature of 1300 °C. The main physicochemical properties were tested. The phase composition of the samples was evaluated using XRD method. Characteristic temperatures were determined using a hot stage microscopy method. The microstructure was observed using scanning electron microscopy with analysis in micro-areas (SEM/EDS).

Refractory raw materials which contained chromium oxide in their composition showed higher corrosion resistance compared to those without the presence of this component.

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8.63 Corrosion resistance of modified magnesia refractory material in contact with copper slag

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KEYWORDS: copper slag, corrosion, contact corrosion test, XRD.

Production of copper is one of the most effective process among all non-ferrous industries – the final product which the purity reaches 99,95–99,99 % is produced from the ore with a few percent copper content.

Refractory materials used in this field of industry should withstand not only the thermal stresses. They are in continuous contact with the feedstock so they are also subjected to mechanical stresses. The last and the worst issue is the corrosion caused by the formation of copper slag. Components of the slag react with refractory linings and shorten their lifetime. Combination of these factors enforces the use of high-quality refractory materials which should be characterized by high densification, extremely high corrosion resistance and also high thermomechanical properties. Nowadays commonly used refractory materials in this field of industry are magnesia-chromite refractories but due to the toxicity of chromium still new product are developed.

The main purpose of this work was to investigate an influence of copper slag from first stage of converter process on a modified magnesia material. Magnesia refractory material was modified by using a few percent of calcium zirconate, $CaZrO_3$ and spinel, $MgAl_2O_4$. The research was conducted on powder samples mixed together and heated up to the temperature 1300 °C. Also the contact corrosion test was carried out at mentioned temperature. The main physicochemical properties were tested. The phase composition of the samples was evaluated using XRD method. Characteristic temperatures were determined using hot stage microscopy method. The microstructure was observed using scanning electron microscopy with analysis in micro-areas (SEM/EDS).

The results were analyzed and the interaction between refractory product and copper slag was assessed.

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8.64 Determination of β-cyclodextrin/surfactants complexes formation by surface tension measurements

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KEYWORDS: surface tension, surfactants, cyclodextrins, inclusion complexes.

Cyclodextrins are naturally occuring oligosaccharides. They have very characteristic structure, which allows them to include variety of different compounds inside their inner torus. β -cyclodextrin (β -CD) consist of seven subunits of D-glucose. The addition of cyclodextrins to the surfactant solutions can help to achieve better properties, for example to overcome the negative influence of the surfactants on the human organism. It is especially important in the cosmetic and pharmaceutical formulations.

The purpose of presented research was to investigate the influence of β -CD addition on the surface tension of water surfactant solutions. The surfactants used in the presented research were as follows: anionic (SDS), cationic (CTAB) and non-ionic (Triton®X). The optical tensiometer of KSV Instruments was used to perform these studies.

The obtained results are shown in the form of graphs presenting the surface tension of surfactant solutions versus concentration in the presence and the absence of β -cyclodextrin. Based on the results, we can assume that addition of β -cyclodextrin to the water solutions of cationic and non-ionic surfactants has an influence on the surface tension of these solutions. In case of anionic surfactant (sDs) there was no influence of β -cyclodextrin addition on the surface tension values. The increase of the surface tension value is the result of the creation of inclusion complexes between cyclodextrins and surfactant molecules. The anionic sDs doesn't create inclusion complexes with β -cyclodextrin. The presented research may find many practical applications in different branches of industry e.g. pharmaceuticals and cosmetics.

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8.65 Influence of surfactants on the adsorption of alginic acid on the alumina surface

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KEYWORDS: adsorption, surfactants, alginic acid, alumina.

Adsorption of polymers is an important issue in many branches of industry. This process is complicated and its final outcome depends on many factors such as type of the polymer and its molecular weight, type of used adsorbent, temperature and pH. The addition of surfactants to such system may change its properties as well, due to the formation of the polymer-surfactant complexes. In this case, the adsorption of such complex may be higher or lower than the pure polymer itself. The information is necessary to describe for example stability of the studied systems.

The aim of this study was to investigate the influence of ionic (CTAB; SDS) and non-ionic (TX-100; TX-165 and TX-405) surfactants as well as pH of the solution on the adsorption of alginic acid (AA) on alumina. To determine the adsorption of alginic acid the colorimetric method was used.

Surface tension measurements together with the adsorption data show that the macromolecules of alginic acid are able to form complexes with CTAB, however, they compete for the adsorption centers on the metal oxide surface with SDS. Non-ionic surfactants do not affect alginic acid adsorption. It should be emphasized that the alginic acid/surfactants/alumina system has not been studied before, which confines its possible applications in the field of functionalized materials.

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8.66 Validation of the RANS turbulence model for CFD simulations of the Francis turbine

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Keywords: Francis turbine, power, k- ε , k- ω , vortex rope.

CFD simulations in present time are most important part of designing of turbine components, and also become very powerful tool to reduce product development cycle. Flow through high head Francis turbine installed in Hydro Power Plant (HPP) Dubrovnik (Croatia) is considered. In this paper validation of experimental results for efficiency and power was made. Two Francis turbines with 126 MW power each are installed in HPP Dubrovnik.

Geometry of the spiral casing, guide and stay vanes, runner and draft tube are reconstructed using 3D CAD software Solidworks. Simulation was done for three different operational points PL (Partial Load), BEP (Best Efficiency Point), and HL (High Load) using the experimental results from laboratory. In this paper results are compared for three different k- ε variants (Standard, RNG, Realisable), and standard k- ω for the same computational set up. Simulation is made for full scale model with frozen rotor approach with approx. 24 million finite volumes.

The CFD results for the turbine power and efficiency confirmed the experimental ones at design flow and off-design conditions as well. Realizable k- ϵ had best results for this kind of flow and computational set up. For PL is shown flow deflection in one side of draft tube, and vortex rope. For HL vortex direction at the draft tube inlet is different than for PL. The opinion and one solution for possible flow improvements in the draft tube has been given. Recommendations and guidelines for next simulations has been given.

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8.67 Factorial design of the electrospun polymeric mat structures as a tool for selection of electrospinning process parameters

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KEYWORDS: electrospinning, factorial design, polymer fiber, bead-on-string structure.

Electrospun polymeric mats are a promising material in the fields of controlled drug delivery and cell cultures for tissue engineering. The electrospinning process is one of the techniques used to manufacture such mats because it is rather easy to employ and cost-efficient. Current research on the electrospinning method is concentrated on the conditions of the process, fiber characteristics and their potential application. As of today, there are several studies regarding the influence of process conditions as they relate to the properties of the obtained product.

In the work, experimental factorial design was carried out to determine the effect of selected electrospinning process parameters on the diameter of the uniform and heterogeneous fibers (with spheroidal structures) and the size of the spheroidal fragments (beads) which were obtained in this process. Factorial design enables one to determine the influence of the analyzed factors on the system response (polymeric structure sizes) and the mathematical relationship between them and the response with a minimum number of experiments.

The analysis considered such process variables as: electrical voltage (U), dynamic viscosity (μ) and flow rate (Q) of electrospun poly(vinylpyrrolidone) ethanol solution. Both beaded and bead-less fibers were obtained during the electrospinning process. Scanning electron microscopy was used to determine the sizes and structure of obtained product.

As a result of the research it was found that the greatest effect on the size of the beaded fibers and beads was observed for the solution viscosity whereas the voltage had the greatest effect on the diameter of the bead-free fiber. The described method can be used as a tool for the selection of values of process parameters which allow to obtain the electrospun mats with desired structures.

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8.68 Investigation of the effect of cinchona organocatalyst's quinuclidine substituent on enantioselectivity in *Michael* reactions

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Keywords: organocatalysis, cinchona alkaloids, organocatalyst recovery, enantioselective reactions.

The cinchona-based organocatalysts have wide application according to the literature. They are applied in asymmetric reactions (*Michael* addition, *Morita-Baylis-Hillman* and *Diels-Alder* reactions) with high yields and enantiomeric excesses. They are used with different saturation on the quinuclidine substituent, but it was not determined, whether it has any effect on the catalytic cycle. During this work, this effect was investigated.

Cinchona-based organocatalysts were synthesized with three differently saturated quinuclidine substituent (ethyl, vinyl, ethynyl), and with four different catalytic units (hydroxyl, amine, thiourea, squaramide, Figure 8.68.1).



R = ethyl, vinyl, ethynyl

Figure 8.68.1: Structure of new cinchona-based organocatalyst with different hydrogen-bond units.

For the investigation of the effect of quinucludine substituent, the pK_a values of these twelve catalysts were measured using UV pH titration, and they were applied successfully in asymmetric *Michael* addition (up to 99 % yield, and 91 % ee). Furthermore, theoretical calculations helped to corroborate the experimental results.

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8.69 Industrial approach to membrane functionalization in biomedical applications

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Keywords: upscaling, membrane modification, polyvinylidene difluoride, extracellular vesicles.

Over the last few decades, membrane technology has become of major importance in biomedical applications, since it is simple to use, robust, cost-effective and scalable. Advanced functional polymer membranes have generated high interest due to their novel functions in various applications such as drug delivery, coatings for medical and life science devices etc. The aim of this work is to develop an industrial approach with scientific and business point-of-view for membrane functionalization to satisfy the requirements of the market.

In this work, an example of upscaling from laboratory to industrial scale has been demonstrated for functionalizing membranes with a hydrophilic coating with the goal of extracellular vesicle (EV) filtration. The idea is to isolate and fractionate EVs by using functionalized membranes in order to use them as biomarkers for diagnostic tests of tumor derived EVs or to monitor the progress of disease and the efficacy of treatments. A thorough analysis and evaluation of technical feasibility, cost estimation and chemical safety for upscaling was carried out in addition to the scientific research to develop a sustainable and strategic industrial model to bridge the gap between industry and academic research for advanced functional polymer membranes.

For this purpose, polyvinylpyrrolidone (PVP) and acrylic acid (AA) were used as a starting point to functionalize polyvinylidene difluoride (PVDF) membrane material using radical polymerization. The process parameters and reaction conditions were identified in the lab scale and then scaled up for industrial production. First results have shown that PVP & AA were successfully coated at the industrial scale. In the next step integrity of the coating was evaluated along with characterization of the functionalized membrane. In conclusion, polymer membranes were successfully functionalized at industrial scale and the results have shown great potential to upscale novel functionalization for various applications.

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8.70 Dependence of preparation conditions on quality and strength of binder made of Tetraethyl orthosilicate and 1,2-Bis(triethoxysilyl)ethane

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KEYWORDS: amorphous steel, binding, tensile strength.

As we are living in the 21st century, electricity is something obvious in our live. In order to reduce the price of electricity, research according to transformer efficiency is still evolving. An amorphous steel is a new material dedicated to the magnetic transformer core production. Previous work presents that application of the binder to this material can successfully increases the efficiency of the magnetic core.

During the presented examination, a sol binder was tested on Metglas 2605 foil. Used binder consists of two sols based on two different precursors: tetraethoxysilane (TEOS) or dipodal 1,2-Bis(triethoxysilyl)ethane (BTSE), and various application configurations were tested. The first option was a stepwise process with two separate sols, and the second with a binder made of 1:1 volume of TEOS and BTSE sols. All amorphous steel samples covered with various binders were examined according to the quality and binding properties. Optical microscopy, confocal microscopy, scanning electron microscopy and Raman spectroscopy were used to confirm the quality of received samples. In the second step, binding properties were tested with tensile strength measurements.

Received results indicate the best application way to obtain good quality binder with high binding properties. Moreover, performed examination indicates differences depended on preparation conditions which strongly influence on the successful application process.

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8.71 Kinetic of drying process of sol solutions based on Tetraethyl orthosilicate and 1,2-Bis(triethoxysilyl)ethane

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KEYWORDS: kinetic, drying process, silanes, rheometry.

Silanes are compounds that possess unique properties. These are caused by functional groups, where some of them are hydrolyzable and others can be organo-functional. Hydrolyzable groups make silanes perfect candidates to couple with the metallic surface as they can create useful metal-oxane bonding (M - O - Si).

Presented poster contains results of kinetic of the drying process of two sol solutions. Both solutions are made of anhydrous alcohol, acidified water and silanes: tetraethoxysilane (TEOS) or dipodal 1,2-Bis(triethoxysilyl)ethane (BTSE). In order to determine how the drying process proceeds two methods were used, namely infrared spectroscopy in attenuated total reflection technique (ATR) and rheometry. In both cases samples were tested at selected temperatures between room temperature and 200 °C, maintaining drying procedure.

Received results show which temperature is responsible for every step during consolidation process of prepared sols. Used examination points out the border between liquid and solid form of tested samples. It allows adjusting drying procedure to desired properties of a final sample like caused stresses or elasticity, what is a very important knowledge from an application point of view.

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8.72 The use of Rutin Hydrate pickering particles to combat lipid oxidation in food emulsion

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KEYWORDS: emulsions, food, antioxidants, lipid oxidation.

Lipid oxidation (LO) is a major concern in the food industry, as it can lead to numerous negative effects including: formation of unwanted compounds, loss of nutritional value, as well as changes to taste, texture and appearance of foods. The increased usage of unsaturated fats in foods to help combat major health issues such as obesity and heart disease does, for all its benefits, make food more susceptible to LO. The problem of LO is further amplified when using Oil-in-Water (O/w) emulsions in foods due to the fact that LO is a process which is accelerated by reactions taking place at the surface of oil droplets; the formulation of O/w emulsions sees a tremendous increase in the interfacial area of the oil phase, and this provides more sites upon which LO reactions can take place.

The use of Rutin Hydrate (RH), a natural and potent antioxidant compound, as Pickering particles for the stabilisation of o/w emulsions provides a potential solution to this problem. This compound was investigated for its ability to both provide o/w emulsions with physical stability, through its ability to act as a Pickering particle, as well as oxidative stability, through using a variety of antioxidant mechanisms to combat LO.

Results have shown that RH can be used to produce o/w emulsions (with average D[3,2] droplet diameters of ~ 11 μ m) which were stable throughout the duration of study (14 days). RH stabilised emulsions were also shown to be significantly more effective at combatting LO than Polysorbate 20, a conventional emulsifier. Emulsion droplet size was found to be a significant factor in determining the rate, and extent of LO in formulated emulsions. It was also found that the location of Rutin Hydrate, be it at the interface of O/w emulsions or in the continuous phase, had no significant impact on LO.

This study shows promising results for the use of ${\tt RH}$ as an emulsifier for ${\rm O}/{\rm w}$ food emulsions.

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8.73 Influence of MTMS-based aerogel structure on properties of modified filter

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KEYWORDS: filter modification, MTMS-aerogel, oil mist filtration.

Purification of oil mist contaminated gas streams is widely carried on common fibrous filters. Unfortunately, most of which do not meet the gas purification requirements, so the filter modification is needed. This work focuses on applying methyltrimetoxysilane (MTMS)-based aerogel synthesis into modification method of polypropylene fibrous filters (produced by melt-blown technology). Due to the deposition of aerogel structure on filter fibres, surface phenomena are intensified, thus oil filtration efficiency is improved.

Structure of deposited aerogel can be controlled via numerous synthesis parameters. By adjusting the size of primary particles, structure of silica network, porosity and aerogel layer thickness, the properties of modified fibrous filter can be controlled.



Figure 8.73.1: Examples of aerogel structures obtained on filter fibers

Macroporous aerogel layer (A) gives fibres highly developed contact area resulting in increased separation efficiency and oil sorption capacity. On the other hand such structure has relatively low mechanical stability and causes increased pressure drop during the filtration. Highly cross-linked microporous aerogel structure layer (B) results in lower oil sorption capacity (compared to structure A), but also in decrease of pressure drop.

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8.74 Oil mist filtration dynamics of fibrous filters modified with MTMS-based aerogel structure

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Keywords: filtration dynamics, MTMS-aerogel, oil mist filtration.

Filtration of air contaminated with dispersed oil phase is a problem that occurs in many branches of industry. Filtering materials dedicated to oil mist filtration should meet certain requirements, like: high separation efficiency, good oil sorption capacity, long lifetime and relatively small pressure drop. To enhance material properties, modification with highly porous, hydrophobic and oleophilic methyltrimetoxysilane (MTMS)-based aerogel is proposed.

Native and aerogel modified fibrous filters were investigated on oil mist filtration test bench, produced by PALAS GmbH, with diethylhexylsebacate (DEHS) as test oil. Changes in fractional separation efficiency (in respect to droplets diameter $0.2-10 \,\mu$ m) and pressure drop were measured together with an increasing amount of oil deposited on fibers during the test. Influence of the modification on filter lifetime and oil resuspension in steady-state filtration (full saturation) were investigated.

Studies showed that filters modified with MTMS-based aerogel are characterized by higher oil mist separation efficiency and enhanced oil sorption capacity than native materials. While loaded with the same amount of oil, modified filters exhibit significantly higher retention than native ones. On the other hand highly developed, thick aerogel layer creates a barrier for airflow and cause an increase of pressure drop.

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8.75 Determination of biocides in environmental samples using LC-MS/MS

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Keywords: liquid chromatography, mass spectrometry, personal care products, environment pollution.

Cosmetics, pharmaceuticals and detergents require protection in the form of additives against the growth of microorganisms. The most commonly used preservatives include compounds from the isothiazolinone group such as chloromethylisothiazolinone (CMI), benzisothiazolinone (BIT) and methylisothiazolinone (MIT). An extensive use of biocides is a serious threat to the environment. Currently, sewage treatment plants are not able to effectively eliminate pollutants entering the sewage in the form of organic compounds, which results in their penetration into surface waters. Moreover, a big threat is posed by the fact that popular biocides, such as MIT, are leached from the paints used to cover facades and roofs of buildings by rainfall and can be brought into the soil or discharged into surface waters.

Liquid chromatography coupled with mass spectrometry is a dynamically developing combined technique, which is widely used in the qualitative and quantitative analysis of complex biological and environmental samples.

The aim of this study was the development of new, sensitive analytical methods, which allow detection and determination of chemical compounds even at lower concentrations.

Water and soil samples were taken from areas that may have been exposed to contamination with compounds from the PCPS (Personal Care Products) group. In the next step, the samples were extracted and analyzed with the use of LC-MS/MS. The developed analytical method enabled the determination of environmental concentrations of the tested compounds. The obtained results indicate large pollution of the natural environment by biocides.

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8.76 The use of LC-MS/MS in the analysis the role of cytochrome P-450 in the PCPS elimination by fungi of the genus *Basidiomycetes*

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Keywords: liquid chromatography, mass spectrometry, personal care products, cytochrome *P-450, biodegration.*

Personal care products (PCPs) are a wide group of compounds commonly used as additives in soaps, shampoos, toothpastes etc. They can be applied as preservatives, disinfectants, antibacterials, repellents, UV filters and fragrances. PCPs are intended for the external use and are not subjected to metabolic changes within the human body, which allows their penetration into the natural environment in an unchanged form.

White rot fungi, belonging to the *Basidiomycetes* family are characterized by the ability to decompose contaminants. Their extracellular enzymes such as lignin peroxidase, manganese peroxidase and intracellular systems including cytochrome P-450 can participate in the degradation of compounds such as phenols, dyes, chlorinated insecticides, pesticides, polychlorinated biphenyls and many others.

Liquid chromatography coupled with mass spectrometry is a dynamically developing combined technique, which is widely applied in the qualitative and quantitative analysis of complex biological and environmental samples. It is one of the most important methods used in the assessment of biodegradation of xenobiotics by microorganisms.

The aim of this study was to explain the role of cytochrome P-450 in xenobiotics elimination by filamentous fungi. In the conducted research, the process of elimination was analyzed using liquid chromatography tandem mass spectrometry in 48 h cultures with the addition of cytochrome inhibitors: 1-aminobenzotriazole, metyrapone and proadifen.

It was observed that the addition of three different inhibitors CYP-450 in 0 h of incubation did not stop the elimination process. The obtained results showed that cytochrome P-450 was not involved in the process of substrate bioconversion.

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8.77 Elimination of acetamiprid by Metarhizium sp.

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Keywords: Metarhizium sp., acetamiprid, liquid chromatography, mass spectrometry, elimination.

Neonicotinoids are a relatively new group of compounds classified as neurotoxic synthetic insecticides. They are divided into 3 main classes: chloropyridinyl, chlorothiazolyl and tetrahydrofuryl compounds. Acetamiprid belongs to first group. Every year, as a result of human activity, considerable amounts of them are introduced to the environment contravening the ecological balance and having a negative impact on the microorganisms living in the soil. In order to limit the use of synthetic insecticides, safer ways to protect plants require a development, e.g. bioinsecticides. Entomopathogenic fungi are applied as biopesticides in regulation of arthropods in natural environment. The main representatives are fungi from the genus *Metarhizium*, commonly found in soil.

The aim of the research was to check the elimination capability of genus *Metarhizium*. In our research, *M. anisopliae* ARSEF7487, *M. brunneum* ARSEF2107, *M. robertsii* ARSEF727, *M. lepidiotae* ARSEF7412, *M. globosum* ARSEF2596, *M. robertsii* IM6519 and *M. robertsii* IM2358 were used. Precultures (after 1 day of incubation) were transferred to Czapek-Dox medium at a 1:9 ratio. The concentration of acetamiprid in the tested samples was 5 mg L⁻¹ Stock solution was prepared in acetonitrile (10 mg L⁻¹). The abiotic samples were also prepared. The samples were incubated on a rotary shaker (160 rpm) at 28 °C. After 7 days of incubation, the extraction by the QUECHERS method was carried out and samples for liquid chromatography coupled with mass spectrometry analysis were prepared.

The highest decrease of acetamiprid compared to the abiotic control was determined for *M. robertsii* 1M2358, *M. lepidiotae* ARSEF7412 and *M. brunneum* ARSEF2107 (22.6 %, 16.7 % and 13 % loss of substrate, respectively, with reference to their control) (P < 0.05). Other *Metarhizium* sp. do not have ability to eliminate acetamiprid from the culture medium (P > 0.05). Moreover, no metabolites derived from the degradation of acetamiprid were detected.

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8.78 Effect of acetamiprid on fungal biomass of Metarhizium sp.

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KEYWORDS: Metarhizium sp., acetamiprid, fungal biomass, toxicity.

Entomopathogenic fungi, commonly found in soils, are parasites arthropods and regulate their populations in the natural environment. These fungi are applied as biopesticides in pest control in organic farming as an alternative to the use of chemical plant protection products, i.e. insecticides. Neonicotinoids can be distinguished from many groups of insecticides. They are a relatively new group of compounds having a strong neurotoxic effect. Acetamiprid is widely used as plant protection product worldwide, adversely affecting on human and animal health and disturbing the balance of the natural environment due to its persistent in soil and water systems. In recent years, its undesirable effects on bee populations have been discovered.

The aim of the study was to determine the effect of acetamiprid on fungal biomass for fungi of genus *Metarhizium*. In our research, *M. anisopliae* ARSEF7487, *M. brunneum* ARSEF2107, *M. acridum* ARSEF7486, *M. robertsii* IM6519 and *M. robertsii* IM727 were used. The fungal cultures were established in Czapek-Dox medium with density 10^6 spores mL⁻¹. The concentration of acetamiprid in the tested samples was 5 mg L^{-1} . Stock solution was prepared in acetonitrile at a concentration of 10 mg mL^{-1} . The biotic samples were prepared without toxic substrate. The samples were incubated on a rotary shaker (160 rpm) at 28 °C. For fungal biomass estimation mycelia were filtrated by Whatman 1 filter paper and drying at 105 °C to reach a constant weight.

The growth inhibition in the presence of a toxic substrate was demonstrated for *M. robertsii* 1M727 (41 % with reference to its control) (P < 0.05). In other cases, differences between fungal biomass in biotic controls and tested samples are not statistically significant (P > 0.05). It has been proven that acetamiprid added to cultures at a concentration of 5 mg L⁻¹ did not inhibit growth in *M. anisopliae* ARSEF7487, *M. brunneum* ARSEF2107, *M. acridum* ARSEF7486, *M. robertsii* 1M6519.

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8.79 Synthesis of imidazole ionic liquids as dispersing media of carbon nanotubes

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Keywords: ionic liquids, synthesis, green solvent.

Many solutions are based on organic solvents as: benzene, halides, alcohols, amides, which are environmentally dangerous, i.e. toxic to flora, fauna and humans. From the technological point of view, solubility of the reactants and products can cause difficulties in the isolation from the post-reaction mixtures and hence the overall production. The quest for the alternatives to the most toxic solvents has become a major concern and priority to both industry and academia. One of the possible solutions is the application of ionic liquids (ILS) – "molten salts". They have many advantages over conventional solvents such as: wide range of temperatures of liquid state and the excellent ability to solve variety of substances. Moreover, they are known as dispersants for carbon nanoallotropes toward a variety of applications, including thermal engineering.



Figure 8.79.1: Method of the herein proposed synthesis of ILS.

The purpose of the study is to synthesize the imidazole-based ILs with linear or branched alkyl substituent (R_1 and R_2) and the organic anion (X^- = acetate, thiocyanate).

The structure of the ILS will be confirmed using ¹H, ¹³C NMR spectroscopy and ESI-MS. Additionally, the received ILS can be used as a dispersants for carbon nanotubes in the future research.

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8.80 Investigation of the potential of lactic acid fermentation in bio-remediation of whey

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KEYWORDS: whey, lactic acid fermentation, valorization.

Whey is the main by-product of cheese making, its annual production worldwide exceeds 200 million tonnes. Its environmentally conscious and cost effective management poses a challenge for the dairy industry. The substance itself is the aqueous solution of lactose, whey proteins and small amounts of various milk-derived components. Whey proteins are nutritionally beneficial, thus they are usually separated and sold as dietary supplements. Valorization of lactose in whey can be achieved by various biotechnological conversions.

This study investigates the potential of carrying out lactic acid fermentation on deproteinized whey (DPW) in order to create a whey-derived drink. Nine lactic acid bacteria (LAB) strains belonging to the *Lactobacillus* and *Lactococcus* genera were screened for their ability to ferment DPW.

Our results indicate that all LAB strains require nitrogen supplementation for the sufficient fermentation of DPW. Growth of strains was most supported by the addition of high-molecular weight whey proteins, whereas lactose utilization was the most pronounced when DPW was supplemented with pre-hydrolyzed soy- or casein peptones. The observed difference in growth and fermentation characteristics is presumably associated with the varying protease activities of the strains.

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8.81 Problems associated with hydrogen storage

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KEYWORDS: hydrogen storage, hydrogen storage technologies, hydrogen economy.

In recent times, the demand for energy has increased significantly, however, the deposits of natural resources are being depleted. This created the need to search for new energy sources. For a long time hydrogen has been processed as a new ecological source of energy. Hydrogen is the most commonly promoted primary at room temperature in gaseous form. In relation to other energy carriers such as methane, methanol, or octane (which is the main component of gasoline) has the lowest density and the largest heat of combustion per 1 kg of mass. However due to hydrogen properties, mainly low density, there is a problem with its storage.

The most common is the storage of hydrogen in the gas phase, but this method requires very high pressures and despite this, a small amount of energy is accumulated in large volumes of tanks. In the case of storage of hydrogen in the liquid state, it is necessary to use very low temperatures of about 20 K, which leads to an increase in costs, there is also a loss of hydrogen by the evaporation and this method of storage is not suitable for applications where hydrogen is not collected continuously. Another approach widely studied recently is possible to store hydrogen in solids, research concerns both pure alloys and intermetal-lic compounds. Metal hydrides are solid materials characterized by a reversible method hydrogen storage. In the case of metal hydrides, hydrogen is absorbed directly to the material. Large amounts of hydrogen in this form they can be stored in small volumes under low pressure and at a temperature close to room temperature, this solution is not yet commercially used.

Each of the hydrogen storage methods is not free from problems or defects, therefore there are still ongoing studies to create warehouses with a large hydrogen capacity, however, with a small volume of tank.

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8.82 Chitosan hydrogels based on the pyrimidine nucleoside (UMP)

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Keywords: chitosan, hydrogels, pyrimidine nucleoside, structural properties.

Over the last decade, there has been an increased development of research conducted in domestic and foreign scientific institutes on the development of biomaterials which could be used in biomedical engineering. Particularly intense work is devoted to hydrogels, which, compared to other biomaterials, have physical properties similar to living tissue due to the relatively high-water content, softness and plasticity. Hydrogels can be used for the controlled release of bioactive molecules and as scaffolds in tissue engineering.

The aim of the research is to create a new generation of thermosensitive chitosan hydrogels intended for injectable scaffolds for nerve regeneration.

Chitosan from crab shells, lactic and hydrochloric acid at a concentration of 0.1 M were used for preparation of hydrogels. Uridine 5'-monophoshate was used as a neutralizing and buffering agent. This substance, which in addition to allowing the phase transition of the sol into a gel, additionally a regenerative effect on the components of the nervous system by improving the neurotransmission. UMP influences the formation of new synapses between neurons. The structure of hydrogels was investigated by FT-IR spectroscopy. The crystallinity of gel structure was determined by X-ray diffraction analysis (XRD). In addition, micro-images were made using SEM microscopy.

The obtained diffraction patterns show that the chitosan lactate and chloride hydrogels contain crystalline phases. In turn, based on SEM images, it can be concluded that the hydrogel structure is highly porous, which provides a suitable environment for cell multiplication.

All analyzed systems exhibit thermogel features for which the increase of temperature initiates the sol-gel phase transformation. Moreover, the future potential of chitosan hydrogels in the biomedical applications is very promising both for therapeutic and diagnosis.

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8.83 Hydrogels enriched with nanostructured carbon materials for use in bone tissue engineering

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KEYWORDS: chitosan, hydrogels, graphene oxide (GO), biomedical engineering.

The beginning of the 21st century has resulted in an intensive growth of research conducted in the field of nanomedicine, focused on the implementation of nanoscale materials in clinical practice. The use of graphene oxide seems to be particularly promising. It is an oxidised form of graphene that has carboxyl, hydroxyl and epoxy functional groups in its structure.

The aim of the research is creation the thermosensitive chitosan hydrogels containing graphene oxide for biomedical applications, for example for damage regeneration bone tissue. Chitosan from crab shells with low viscosity of a degree of deacetylation $SD \sim 79.5\%$ and molecular weight of 86 kDa, lactic acid, hydrochloric and graphene oxide with an atomic ratio of C/O = 2.2 were used for preparation of gels. Sodium β -glycerophosphate was used as a neutralizing and buffering agent. The structural characteristics of hydrogels were based on the analysis of X-ray diffraction (XRD) and FT-IR spectra. Within biological tests there has been an evaluation of survival of osteoblast cells the Saos-2 line.

Based on the FT-IR analysis, changes in the wide asymmetric band range for the 3300 cm⁻¹ wave number and bands for the 1080 and 980 cm⁻¹ wave numbers with a small arm for 970 cm⁻¹ were observed. In turn, the biological research has shown that osteoblast cultures on the carrier with GO were characterized by a significantly higher number of viable cells than in the case of a pure hydrogel.

Thermosensitive chitosan gels formed at physiological body temperature can contain nano-ingredients in their structure. Based on the results of the biological study, it was found that chitosan hydrogels with GO can be a potential material used as injectable scaffolds for the regeneration of bone tissue.

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8.84 A possibility to obtain an Al₂O₃ - Cu - Ni composites via slip casting method

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Keywords: $Al_2O_3 - Cu - Ni$ system, slip casting, ceramic-metal composites.

The ceramic-metal composites are the group of materials that have properties of both ceramic and metal. Among the different types of ceramic-metal composites we can distinguish the hybrid composites. The components of hybrid composites are substrates that during the consolidation process e.g. sintering at high temperature react with each other and this influences the final phase composition of the material.

This paper presents a study on the possibility of developing a method to produce hybrid composites from ternary system based on the Al_2O_3 – Cu system with the addition of nickel particles. The composites were prepared using slip casting method. The following powders were used: α -Al₂O₃ Almatis with average particle size 66 ± 20 nm, Cu powder from Sigma Aldrich with average particle size 63 ± 30 µm, Ni powder from Bimo Tech with average particle size $25 \pm 15 \mu$ m. Ceramic water-based slurries with 50 vol.% solid content were prepared with 15 vol.% metal powder with respect to the total solid volume.

The selected physical properties of the sintered specimens were measured by the Archimedes method (according to the norm PN-76/6-06307). The phase composition of the sintered samples was investigated. Scanning electron microscope (SEM) analysis of the obtained sinters was also performed.

Experimental results indicate that the slip casting method allows to obtain the hybrid composites. An analysis of the obtained results allows to acquaint with the correlation between forming and sintering conditions, and the basic properties of hybrid composites.

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8.85 Properties of 3Y-TZP/Al₂O₃ composite as a solid electrolyte material for a new generation of electrochemical devices

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KEYWORDS: electrolyte, tetragonal zirconia, solid oxide fuel cells.

Solid oxide fuel cells are currently the most efficient devices used for the conversion of chemical fuels directly into electrical power. To achieve a high-power output of a single cell, the ohmic losses in the layer placed between the cathode and the anode should be minimized. Hence, electrolyte materials that ensure fast oxide ion transport must be used. Furthermore, high strength and durability are also desirable properties for such materials, especially when the planar cell configuration is used. One of the ways in which such properties may be achieved is the application of partially-stabilized tetragonal zirconia polycrystals containing 3 mol% of Y_2O_3 . This material has been selected because of its high electrical conductivity and good mechanical strength, which can be improved further by adding Al_2O_3 in amounts which exceed its solubility limit in 3y-tzp.

The objective of the study was to obtain 3Y-TZP composite sinters with 1, 5, 10 and 15 mol% of Al_2O_3 from a 3-YSZ powder synthesized using the citrate process, and to examine the way in which the phase composition and microstructure of the obtained samples affects their electrical and mechanical properties. Two types of samples were prepared. In the case of the first type, aluminum was introduced during the chemical synthesis of the 3-YSZ powder. To obtain the second type of sample, the 3-YSZ powder was impregnated with an alcohol solution of aluminum nitrate (v) at the appropriate concentration. Both types of powders underwent 2 h of thermal treatment at 600 °C followed by isostatic pressing. They were then subsequently sintered for 2 h in air at 1500 °C.

Morphological observations and chemical and phase composition studies were performed via X-ray diffraction (xrd) and scanning electron microscopy combined with energy-dispersive spectroscopy (SEM-EDS). The electrical conductivity of the samples was measured by means of electrochemical impedance spectroscopy (EIS).

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8.86 Ferritic stainless steel modified with Gd₂O₃ nanoparticles and its oxidation resistance and electrical properties

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KEYWORDS: SOFC, ferritic stainless steel, gadolinium oxide, interconnect.

Devices which can directly convert chemical energy in fuel into electric power are the most promising energy storage technology. Such devices include solid oxide fuel cells (soFcs), which offer a considerable number of advantages. The cells are joined into stacks using so-called interconnects, which ensure electrical contact and also provide gas separation within cells. The most common material used to manufacture interconnects for planar soFcs is ferritic stainless steel, which is relatively inexpensive and provides better thermal and electrical conductivity than ceramic interconnects. However, metallic interconnects are also susceptible to high-temperature oxidation and the subsequent formation of scales, resulting in a gradual increase in the internal resistance of the cell and a drop in its power output. The electrical conductivity of steel depends on factors such as the thickness of the scale layer and its adhesion to the surface. One of the methods which can be used to improve the afore-mentioned properties is the addition of a small amount of active elements such as Y, La, Gd, or their oxides.

The aim of this study was to modify the surface of the commercially available Nirosta 4016/1.4016 ferritic steel containing 16.3 wt% of Cr with Gd₂O₃ nanoparticles deposited using either dip-coating or electrolysis, and to evaluate the effect of these modifications on the oxidation resistance and electrical properties. The studied specimens were oxidized for 100 hours in air at 700, 750, 800 and 850 °C and under isothermal conditions. The thermogravimetric method was used to determine the oxidation kinetics. The morphology of the samples and their chemical and phase composition were examined using XRD and SEM combined with EDS, while electrical conductivity was measured via the constant current two-strand method.

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8.87 Effect of vacuum on activated sludge

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KEYWORDS: vacuum, activated sludge, floc structure, extracellular substances.

Activated sludge technology is widely used for biological wastewater treatment. One of the critical points of the treatment is separation of activated sludge from treated wastewater. Degassing of activated sludge after the reaction zone is claimed to be helpful in this case (see European Patent Office, Patent No. 0790851). Few literature data confirm not only that degassing of activated sludge results in better sludge sedimentation but enhances the efficiency of nutrient removal. The degassing is realized via pressure decrease to app. 50 mbar. The intermittent exposure of vacuum to activated sludge have not been fully recognized yet. It is proposed that the better efficiency of nutrient removal results from increase of biomass concentration in the reaction zone. The aim of the study is to get closer to this phenomenon and recognize suspected mechanisms.

Activated sludge not treated and vacuum treated was analysed for suspended solids concentration, effluent and flocs characteristics and settling properties of activated sludge. Number of active bacteria was also encountered.

As supposed the negative pressure causes disintegration of activated sludge flocs. The flocs were cut to smaller ones and some of them disappeared. Settling properties changed after vacuum treatment. Due to the disintegration of flocs the supernatant after vacuum treatment was characterized by other turbidity and more reach in organic compounds.

Reduction of pressure for a short time causes not only degassing of activated sludge but also changes flocs size and number and detaches some organic polymeric material embedded around cells and flocs.

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8.88 Effect of vacuum on removal of nitrogen from activated sludge

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KEYWORDS: vacuum, activated sludge, nitrogen concentration.

According to Henry's Law the concentration of gases dissolved in a liquid depends on its partial pressure in the gas phase and the temperature. Based on the principle that the solubility of gases is lower at reduced pressure, a vacuum is used to remove gases from liquids and suspensions. In wastewater treatment this phenomenon is used to remove gas bubbles entrapped by activated sludge floc structure (see European Patent Office, Patent No. 0790851) that may limit the settling efficiency. It is claimed in literature that degassing of activated sludge before its inflow to secondary settling tank improves sludge settling properties and enhances biological nutrient removal. The aim of the study was to assess the extent of nitrogen removal through vacuum degassing.

The activated sludge was affected by several different values of vacuum and different durations. The tests were performed on activated sludge and the supernatant obtained by centrifugation and filtration of the activated sludge after vacuum treatment.

The relative total nitrogen concentration of activated sludge samples exposed to vacuum showed no statistically important differences. The obtained differences between vacuum treated samples and control activated sludge (not treated with vacuum) were similar to standard deviation of the analysis.

An attempt was made to estimate the amount of nitrogen that low pressure becomes less soluble in water/wastewater and can be removed in gaseous form. Thus the confirmation of the removal of nitrogen from activated sludge was not possible. The above, however, does not diminish the importance of degassing technology in removing gas bubbles and, consequently, settleability improvement.

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8.89 Vitamin B₃ determination by means of voltammetry and electrochemical impedance spectroscopy techniques

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KEYWORDS: vitamin B₃, voltammetry, impedance, charge transfer resistance.

The term *vitamins* accounts for the heterogenic group of organic compounds, which are essential for the proper and undisturbed functioning of living organisms. One of them, described as vitamin B_3 or niacin, participates in red blood cells creation and is responsible for the regulation of the cholesterol amount in the blood. It is also a key constituent of NAD and NADH coenzymes, needed for electrons and hydrogen transfer in cellular respiration. Both the deficiency as well as the excess of the vitamins in the body can lead to the various symptoms, which in case of niacin include numbness, mucositis, pellagra, hyperuricemia or changes in macula flava. Therefore, the determination of the niacin amount in dietary ingredients and pharmaceuticals is of the essence.

For that purpose, two electrochemical methods are proposed. The first one is voltammetry, in which the oxidation or reduction of an analyte is forced by an applied potential and the resulted current is measured. The deployment of different techniques allows for the minimization of the interferences' influences on the obtained results. The electrochemical spectroscopy (EIS) is a nondestructive technique, used for study and characterization of fuel cells and batteries, thin films, corrosion appearance and electron transfer kinetics.

The influence of the buffer type, its concentration and pH-value, alongside with the parameters for differential pulse adsorptive stripping voltammetry (DP AdSV) were taken into consideration for niacin determination with the use of working electrodes made from different materials. Using the cross-validation technique, the calibration curves were established and the validation parameters were calculated. The dynamic range for both methods reached up to the nanomolar amount of analyte in the sample.

The proposed method for vitamin B_3 determination are characterized by a high accuracy and low limits of quantification. Moreover, in comparison to the commonly used chromatographic procedures, they are cheaper as well as less time consuming and do not require the use of toxic chemicals.

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8.90 Electrochemical sensor for the characterization and determination of benzodiazepines

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KEYWORDS: voltammetry, sensors, benzodiazepines, drug detection.

The term *Benzodiazepines* accounts for a group of psychoactive drugs, whose main chemical structure composes of benzene and diazepine rings. They influence the g-aminobutyric acid receptors, which results in the increased ion conduction, causing antianxiety and sedative effects. Benzodiazepines are the biggest group of the abused pharmaceuticals, whose sedative effect increases strongly when they are mixed with alcohol. Moreover, they are easily available on the black market. Therefore, it is of the essence to develop fast and reliable methods for their determination in biological and environmental samples.

This paper focus on different electrochemical sensors, which can be applied in the determination of benzodiazepines. The particular attention was paid to the construction and materials used in those sensors, as well as to their basic characteristic, obtained e.g. by means of scanning electron microscopy and cyclic voltammetry. Differential Pulse or Square Wave voltammetry in conjunction with the stripping techniques were applied to determine the concentration of benzodiazepines in pharmaceuticals and Human urine.

By means of cyclic voltammetry the electrochemical behavior of benzodiazepines was investigated and as a result the information about the reaction mechanism as well as the number of electron and protons participating in the studied reaction were acquired. Based on that the structural changes, which take place during redox reactions, were elucidated. The conducted validations confirmed the described methods which utilize the electrochemical sensors comply with the requirements relating to dynamic range and low limit of detections. Unfortunately, these methods may be susceptible to interferences, therefore the proper choice of measurement conditions is of the essence.

This literature review indicates that the use of electrochemical sensor, conformable with the idea of *green chemistry*, allows for fast and reliable determination of benzodiazepines derivatives in environmental samples.

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8.91 Regeneration method of fibrous filters modified with MTMS-based aerogel dedicated for oil mist separation

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KEYWORDS: filter regeneration, oil mist filtration, MTMS-aerogel.

Oil mist separation is a problem that occurs in many branches of industry that is commonly limited by filtration utilizing non-woven filters. Modification of filters with methyltrimethoxysilane (MTMS)-based aerogel, enables material to gain hydrophobic and oleophilic properties, high oil sorption capacity and increased contact area, thus increased oil mist separation efficiency. This study focuses on determination of filter regeneration parameters and its influence on reused filter properties.

Polypropylene filters, produced in melt-blown technique, were modified by MTMS aerogel by two step acid-base method. In order to determine sorptiondesorption (s-d) capacity, modified filters were immersed in diethylhexylsebacat (DEHS) for 20 min, left for 24 h and weighted. Next, filters were regenerated by immersion in pre-selected organic solvents (isopropanol, acetone or n-hexane) for 20 min, dried for 24 h at 50 °C and weighted. s-d cycle was repeated 5 times. Solvent effect on filter structure and stability of aerogel coating was investigated by repetition of immersion in solvents and drying sequence for samples prior to oil immersion. After each cycle, Filters were characterized by SEM and water/air contact angle measurement.

s-D tests have shown, that the best filter regeneration was obtained for n-hexane and acetone, and the worst for isopropanol. Good regeneration with n-hexane, was confirmed by SEM, where unlike in case of two other solvents, no oil was observed in aerogel structure. It is worth mentioning, that oil sorption capacity for n-hexane and acetone was stable in each cycle. Although, acetone gave very similar s-D results to n-hexane, it distinctly promoted aging of polymer and weakened aerogel layer. Regeneration with n-hexane was chosen for further investigation on oil mist filtration test bench.

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8.92 Characterization of the strengthening phases in the Ni-based superalloy

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Keywords: aerospace, investment casting, carbides, gamma prime.

Ni-based superalloys are an irreplaceable group of materials in many crucial and strategic applications, including military and civil aircrafts. Among factors allowing operation in the jet engines, it can be distinguished creep resistance, high corrosion and oxidation resistance, and also stable microstructure. The main goal of this research was the comprehensive study of the phase composition, morphology and chemical composition of precipitates in the Ni-based superalloy. The material was fabricated through the investment casting and subjected to full heat treatment, namely solution + aging. Comparison of precipitates features was performed using scanning electron microscopy (SEM) equipped with Energy Dispersive X-ray spectroscopy detector and scanning-transmission electron microscopy (STEM) by the probe Cs-corrected Titan³ G2 60-300 with Chemistem system. It was stated that the irregular distribution of alloying elements during solidification of casting led to heavy segregation and despite the solution heat treatment, the microstructure did not be homogenous. The microstructural observation revealed the high volume fraction of γ' precipitates, both in the nearcubic and eutectic morphology (above 50%). In the interdendritic spaces due to segregation of alloying elements the Ta- and Hf-rich carbides were observed. It was also stated the Ta/Hf relation is strictly connected with the morphology of MC-type carbides. Blocky carbides strongly enriched in hafnium were generally located in the close vicinity of eutectic γ/γ' islands. Near or along grain boundaries were formed more complex morphology enriched in tantalum, like Chinese script or rods.

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8.93 Study of the γ/γ' misfit parameter in the Ni-based superalloy by XRD

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Keywords: XRD, aerospace, superalloy, misfit, cubic-morphology.

The γ/γ' lattice misfit and γ' volume fraction are the two most significant structural parameters of Ni-based superalloys. In this work, the lattice parameters of the $\gamma(a_{\nu})$ and $\gamma'(a_{\nu'})$ phases and subsequently the γ/γ' misfit coefficient were investigated by X-ray diffraction. It has been utilized peak deconvolution to obtain the data for the registered reflections. Ni-based superalloy in the as received condition consisted of relatively high volume fraction of γ' precipitates (above 50 %). Microstructural observation revealed that the γ' precipitates had a nearcubic morphology in dendrite cores. In the interdendritic spaces γ' occurred as a eutectic (γ/γ') islands. Obviously, the δ parameter slightly varies in a different location of superalloy due to segregation of alloying elements, but XRD technique was used to obtain an average γ/γ' misfit parameter. The γ/γ' lattice misfit was defined as $\delta = 2(a_{\gamma'} - a_{\gamma})/(a_{\gamma'} + a_{\gamma})$. The X-ray diffraction study was carried out on thin foils (thickness 50 µm and diameter 3 mm) using X-ray diffractometer Philips X'Pert Pro. The obtained results shown that the lattice parameter of disordered y matrix was lower than ordered $L1_2$ y' precipitates, and so calculated misfit parameter was positive. The mean misfit parameter was lower than 1% which indicated to a good matching of precipitates with a matrix. Lattice misfit is generally related to the morphology of precipitates and internal stresses. The misfit between the lattice parameters of the γ and γ phases was not too large, and so the interface was coherent and the interfacial energy remained low.

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8.94 Chemical modification of roving and textiles for application in prepregs

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KEYWORDS: natural fibres, roving, silanization, composites, flammability.

The bast fibres are readily used as reinforcement of composites due to the low density compared to glass fibres, kevlar, synthetic fibers, which in turn leads to a reduction in the weight of the final product. Replacing glass fibres with natural fibres in composites is beneficial from the point of view of environmental impact, especially when using natural polymer resins.

In order to increase the adhesion of the fibres to the natural epoxy resin and reduce flammability, flax products must be modified. The study concerns silanization of flax roving and textiles. This process gives possibility of using more complex reactants than simple ones used in other modification processes. To achieve the best adhesion and maximum reduction of flammability a number of parameters have been adjusted, such as concentration, pH, temperature, and reaction time.

Effectiveness of conducted processes for reducing flammability has been verified with Pyrolysis and Combustion Flow Calorimeter (PCFC). Tests have been performed according to the standard of ASTM D7309-2007. The heat release temperature (T_{max}), maximum heat release rate (HRR_{max}) and time at which HRR_{max} occurs (t_{max}) have been determined. Changes on fibre surface have been evaluated with Scanning Electron Microscope (SEM).

The improvement of fire retardant properties of natural fibres (roving, fabric) as well as the improvement of the adhesion between natural fibres and an epoxy resin have been achieved.

In the next stage of studies an innovative high-pressure process for chemical modification of flax fibres, in form of roving and fabric, with use of silanization method will be developed.

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8.95 Effect of precipitating agent on the structure, morphology and electrochemical properties of LiCoO₂ cathode material in lithium ion batteries

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KEYWORDS: lithium-ion batteries, cathode material, layered structure, cobalt oxide.

Lithium transition metal oxides with the formula $LiCoO_2$ (M = Co, Mn, Ni) have been extensively studied as cathode materials for rechargeable lithium-ion batteries due to their high output-voltage, high specific-energy and long-cycle life. Their remarkable electrochemical properties can be attributed to the layered structure which allows short diffusion paths for lithium ions.

Lithium cobalt oxide has been used as a cathode material since 1990 but it still remains the most widely used cathode material for commercial Li-Ion batteries. The most commonly used procedure of $LiCoO_2$ preparation is the solid-state method. However, a high-temperature treatment is necessary to obtain lithium cobalt oxide.

In this research work we report synthesis of LiCoO₂ by wet impregnation of Co_3O_4 with aqueous solution of LiOH \cdot H₂O. The Co_3O_4 powders were obtained by precipitation method with three different precipitating agents: NH₄(CO₃)₂, NH₃ \cdot H₂O, (NH₄)₂C₂O₄ starting from $Co(SO_4)_2 \cdot 7$ H₂O as a cobalt precursor. Structure and morphology of the synthesized powders were characterized by X-ray diffraction (xRD), scanning electron microscope (SEM) and BET surface area. The electrochemical properties of the cathode materials were examined using a coin cell with a Li foil as the anode electrode.

The analysis of the obtained results will allow us to determine how the use of different precipitating agents influences the structure, morphology and final electrochemical properties of lithium cobalt oxides.

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8.96 Post-synthesis modification of geopolymer structure

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KEYWORDS: geopolymer, dealumination, desilication, porosity.

The term "geopolymers" refers to inorganic, amorphous or partially semi-crystalline materials which can be obtained in the reaction of aluminosilicates (e.g. fly ash, metakaolin) with alkali-activator. This results in monolithic material with three-dimensional network consisting of $[SiO_4]$ and $[AIO_4]$ tetrahedra bonded together by oxygen atoms. Geopolymers are used as e.g. sustainable equivalents of cementitious materials, or heavy metal sorbents. Also, first attempts to exploit them in catalysis were made. The aim of this work was to modify the metakaolin-based geopolymers by desilication and dealumination treatments in order to obtain hierarchical mesoporosity.

The parent geopolymer was obtained by alkali-activation of metakaolin with sodium hydroxide solution at 80 °C. It was then ion-exchanged with NH_4NO_3 and this form was subjected to desilication (NaOH), dealumination (Na₂H₂EDTA), and the combination of both processes. The textural and structural characterization of the obtained materials was carried out. For this purpose, X-ray diffraction (XRD), nitrogen adsorption-desorption experiment, scanning electron microscopy (SEM), vibrational spectroscopy (FTIR and Raman) were used.

The presence of zeolite A and hydroxysodalite in parent geopolymer was confirmed. The raised background in XRD pattern indicated the formation of amorphous phase, i.e. sodium-alumino-silicate-hydrate gel (N-A-S-H). The applied modification processes resulted in the degradation of zeolite A structure, which was observed as the decrease in the intensity of a band at 560 cm⁻¹ in MIR spectra as well as its characteristic peaks in XRD patterns. The sequential dealumination and desilication treatment caused the significant increase in mesopores volume. Also, it seems to be more effective than a not-combined treatment. Therefore, such a modification can be applied to enhance geopolymer properties for catalysis and environmental protection.

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8.97 Lightweight geopolymer monoliths for methylene blue removal from wastewaters

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KEYWORDS: geopolymer, inorganic polymer, adsorption, dye.

Geopolymers are synthesized by mixing a silicon and aluminum source with an alkaline activator, which transform into hardened materials. They exhibit fire and chemical resistance as well as relatively high compressive strength. The application of geopolymers as sorbents is a relatively new area of research. One of the commonly used dyes is methylene blue, which is known to cause blindness, abdominal disorders and respiratory distress, so its removal from wastewaters is mandatory. The aim of this paper is to develop lightweight geopolymeric monoliths for the application as dyes sorbent.

Metakaolin was utilized as a source of silicon and aluminum and sodium hydroxide solution as an activator. To enhance sorption properties porosity of geopolymer was increased. Expanded glass aggregates were used for this purpose, as they have open porosity, what is advantageous in the context of adsorption. The monolithic samples were formed. The activation of the specimens was carried out at 80 $^{\circ}$ C for 24 hours.

The structural characterization of the samples was conducted by X-ray diffraction and infrared spectroscopy. Microstructure observations were carried out in a scanning electron microscope. Sorption of methylene blue from a solution with various concentrations was conducted. The remaining dye concentration in the liquid was evaluated by uv spectroscopy. The proposed monoliths can effectively remove the dye from wastewaters.

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8.98 Preparation and analysis of the surface of modified steel materials and their applications as a surface for endothelial cell culture

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KEYWORDS: stainless steel, endothelial cells, HMEC-1.

Endothelial cells are commonly used in modern laboratory research. They are widely applied in many fields of science, but they play their most important role in the biomedical engineering research. We are constantly working on the best ways to use endothelial cells to improve the properties of synthetic implants, such as biocompatibility with the patient's body.

Presented work concerns the use of 316L stainless steel materials for the cultivation of endothelial cells of HMEC-1 cell line in order to select the most appropriate parameters encouraging cells to adhere and grow. The first step in the modification of pure metal discs was to obtain the PEGDMA (polyethylene glycol dimethacrylate) layer by electropolymerization. Then carboxyl groups were attached to the polymer layer and process parameters were tested. The aim of second step was to make a reaction between the carboxyl groups from the surface of the steel discs and the amino groups from the aminoacids of the peptide with the REDV sequence that is recognized by endothelial cells as a suitable surface for adhesion and proliferation.

Modified materials were analyzed using goniometer, Fourier-transform infrared spectroscopy and bicinchoninic acid assay. Later, endothelial cells were cultured on the materials for 3 and 5 days. Then they were fixed and dyed with antibodies with fluorophore to visualize nuclei, vinculin and von Willebrand factor. The observation of visualized structures was carried out using a scanning confocal microscope. Finally, it was possible to assess the best conditions in which HMEC-1 line could anchor, develop and functionalize.

As a result of these tests, it was possible to see that endothelial cells grow better on the steel with peptide coating rather than on uncoated material. Adhesive sequences encourage cells to adhere and metabolize and higher concentration of REDV and higher parameters of carboxylation give better results of the analysis.

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8.99 Biologically active double salt ionic liquids with cations based on diglycolamine

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KEYWORDS: herbicidal ionic liquids, quaternization, synergistic activity, double-salt herbicidal ionic liquids.

The unwanted vegetation in the agricultural fields is usually neutralized by selective herbicides from the group of growth regulators (e.g. 4-chloro-2-methylphenoxyacetic acid – MCPA or 3,6-dichloro-2-methoxybenzoic acid – dicamba), however they are able to permeate to water and air. These issues have been addressed by introducing herbicidal ionic liquids (HILS). The approach has been enhanced by merging two HILS into a double salt in order to cause synergistic interactions between anions.

Since the prolonged use of a single anti-weed agent usually causes a rapid enhancement of the herbicidal resistance, we fused together two HILS comprising anions derived from synthetic auxins, MCPA and dicamba, thus creating fully selective double salt herbicidal ionic liquids (DSHILS). We applied an alkyl derivative of diglycolamine as a source of the counterion in order to maintain favorable surface activity as well as hydrophilic properties of the synthesized DSHILS. The obtained double salts, as well as their single-anion counterparts, were subsequently tested in greenhouse experiments in order to evaluate their biological activity towards dicotyledonous weeds.

Unexpectedly, DSHIL comprising the cation with the longest (hexadecyl) alkyl substituent was characterized by greater herbicidal efficacy in comparison to single-anion HILS with either MCPA or dicamba with the same cation, despite the fact, that the dose of DSHIL in the experiment was significantly lower. Moreover, every compound tested was more effective than a commercially available herbicide at the same dose. Therefore, another experiment was carried out in order to optimize the molar ratio of MCPA and dicamba anions in the structure of DSHIL.

The results confirm that only a small addition of dicamba (molar fraction lesser than 0.3) in DSHIL with diglycolamine-based cation is necessary to create a synergistic effect between the herbicidal anions.

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8.100 Synthesis and properties of chiral ionic liquids derived from mandelic acid

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KEYWORDS: ionic liquids, mandelate anion, antimicrobial activity, homologous series.

Ionic liquids (ILS) can be divided into three generations, which include salts designed for the type of dominant properties. The latest, third generation of ILS are designed for their biological activity. Numerous ILS belonging to this group are synthesized in order to obtain strong agents exhibiting antibacterial properties. Such activity results from the synergy of the amphiphilic cation and the antiseptic anion. Special attention is given to ILS comprising anions of natural origin, including mandelic acid-based ILS.

A homologous series of both (S)-mandelates and (R)-mandelates of a high enantiomeric excess was obtained. All ILs possessed a cation derived from mepiquat chloride – a biologically active piperidine derivative of low toxicity.



Compounds containing substituents with an alkyl chain length of from 4 to 10 carbon atoms were liquids at 25 °C, thus they may be referred to as room-temperature ionic liquids (RTILS). The presence of a hydroxyl group in the cation structure significantly increases the hydrophilicity of the products, which is reflected in the solubility analysis.

The minimum inhibitory concentration (MIC) and minimum bactericidal concentration (MBC) results confirm the high biological activity and synergistic effect between the cation and the anion of the obtained ILS. Furthermore, it is also observable that the extension of alkyl chain in the cation structure results in the increase of the biological activity.

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8.101 Magnesium hydrides used in hydrogen storage technology

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Keywords: magnesium hydrides, hydrogen storage, alternative energy sources, magnesiumiron hydride (Mg₂FeH₆).

Currently, three ways of storing hydrogen are known: in the gas phase (compressed hydrogen), in the liquid phase (condensed hydrogen, additionally stored at very low temperatures around 20 K) and in the solid phase (adsorption or absorption of hydrogen in solids, chemical reactions). The last of these methods is the youngest technique and constantly researched and developed, but with this technique the greatest hopes are connected because it is the most secure. The value of the pressure used in this technique is from a few to a dozen bars, and the hydrogen is strongly connected with the solid phase, that even at any leakage, it will release very slowly, which will immediately detect the threat.

Most of the materials used in this method are powders - because in this form the material is characterized by a highly developed specific surface, thanks to which hydrogen reacts with it more easily. The materials used in this technique are really many, including nickel (LaNi₅) or chromium (ZrCr₂) alloys, borohydrides (NaBH₄), carbon materials (nanotubes, fullerenes, graphene, activated carbon) but also magnesium compounds.

Due to the high hydrogen absorption capacity (up to about 7.6 % wt. in the case of MgH₂) and the reversibility of the reaction, magnesium hydrides are the most promising materials for solid phase hydrogen storage. The highest ability to absorb hydrogen among all hydrogen compounds is MgH₂, unfortunately it is characterized by slow kinetics of absorption and hydrogen release, as well as a high temperature of H₂ release (673 K). Therefore, ternary magnesium hydrides are more popular, so this work describes this material group. A very interesting material is Mg₂FeH₆. This compound is characterized by the highest hydrogen content among all known hydrogen compounds – 150 kg/m³ by volume and hydrogen content by 5.46 %. These parameters have a direct impact on the fact that it is one of the most studied compounds in the aspect of hydrogen storage.

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8.102 Selective Catalytic Reduction of NO with NH₃ at low temperature over Cu-promoted-N-modified activated carbon

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Keywords: SCR, activated carbon, copper.

The selective catalytic reduction (scr.) in the presence of O_2 remains the novel technology for controlling NO_x emissions from stationary sources. The commercial catalyst is a solution widely accepted in industrial practice, but it require high temperature window and the scr installation could be positioned upstream of electrostatic precipitator (before FGD unit). Therefore, it is significant to develop new efficient and low-temperature catalysts. Active metal oxides supported on carbon material are one of the active scr catalysts used at low temperature range. However, the development of the technique for the supported carbon for (scr.) of NO_x with ammonia is still a challenge.

For this purpose, a series of carbon-supported catalysts were prepared by: (1) oxidation with 10 M of nitric acid, and (2) modification with urea (5 wt.%) and/or (3) promotion with (1, 5 or 10 wt.%) copper. Various techniques of characterization are used to understand (i) the effect of the triple modification technique on scr activity and (ii) the specific types of surface species responsible for the catalytic activity.

The obtained catalysts were characterized by XRD, IR and N₂ low-temperature sorption. The efficiency of SCR of NO are experimental studied by testing 200 mg of the catalysts in NH₃-SCR under the following conditions: 800 ppm NH₃, 800 ppm NO, 3.5 % O₂, rest He, flow rate: $100 \text{ cm}^3/\text{min}$; temperature range: 140-300 °C.

The catalytic properties of active carbons treated with N-compounds and promoted with copper oxide were studied in scr. The modification with copper led to the increase in NO conversion. The catalyst promoted with 10 % Cu exhibited about 95 % of NO conversion at 220 °C. The sample doped with 5 % Cu represent the lowest N₂O formation at 300 °C – 55 ppm and the activated carbon oxidized with 10 M nitric acid and treated with 5 % urea represented the highest stability. The studied catalysts showed low CO₂ concentration below 220 °C.

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8.103 Analysis of heat modelling failure around contiguous micro objects

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Keywords: heat transfer, finite element methods, computational fluid dynamics, numerical analysis, approximation theory.

Some approximation methods and simulation solutions in computational fluid dynamics do not give exact results when analyzing some models. Even with the best simulation conditions (with an unlimited number of iterations and small mesh settings which requires high processor speed and takes long simulation time). The simulation quality depends on many factors such as simulation mechanism, input conditions, mesh settings and a number of numerical iterations for reducing the errors.

This paper covers a numeric approximation solutions of finite element methods (FEM) for analysis of heat modelling failure around contiguous micro objects using ANSYS software. The simulation of heat flux around disks in a semi-infinite space had been developed using ANSYS software. The simulation had been repeated many times with different conditions.

The results of the simulated heat flux had been compared with other results using exact formulas of heat flux around two and three disks. The comparison results guided to understand the heat modelling failure around contiguous micro objects to help in dealing with complicated models where there are no exact formulas to check the results.

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8.104 Dyeing techniques as markers of the hydrophobicity of the surface of contact lenses

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KEYWORDS: contact lenses, hydrophobicity, dyeing techniques.

Among those who wear contact lenses, almost half of them experience discomfort and dryness in the eyeball. These symptoms were most often noted a few hours after using the lenses. This is caused by changes in the lens surface (deposition of proteins and lipids, called biofobing) during the use of the lens.

The presence of proteins on biomaterial surfaces can be detected by selective staining using appropriate probes. Dyeing is an important biochemical technique that allows you to visually detect interesting places on the material, without isolating them. Sudan IV is a fat-soluble pigment. It is used to stain lipids, triglycerides and lipoproteins. It has the form of red-brown crystals whose melting point is 199 °C, and the maximum absorbance occurs at 520 nm. Its presence is an unambiguous marker of the hydrophobic character of a given surface.

The studies included identification of hydrophobic domains, both in hydrogel and silicone hydrogel lenses. A lipophilic dye, Sudan IV, was used for the research. Analysis of the results allowed to determine the percentage share of hydrophobic domains that are potential sites for lipid deposition and other organic contaminants on the surface of the lens material.

It has been observed that contact lenses, both hydrogel and silicone hydrogel, have hydrophobic regions in their structure. Both the basic structure of the matrix (in the two-phase system, the siloxane fragments have hydrophobic character) and the environment in which the lenses are stored have an impact on their quantity.

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8.105 Polymer matrices for controlled dosing of drugs - perspectives

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KEYWORDS: contact lenses, drugs, controlled dosing.

The problem of eye diseases is a threat of increasing intensity conditioned by the aging processes of society as well as the overcoming of environmental factors such as excessive exposure to electronic equipment.

The local administration of ophthalmic drugs directly to the eyeball in the form of eye drops is a method used to treat diseases of the anterior segment of the eyeball. It is estimated that this method of dosing the drug accounts for about 90 % of commercial contact formulations. The use of eye drops has many undeniable advantages: the ease of drug delivery to the patient, biocompatibility and low cost. Usually, however, only a small fraction of the dose administered to the patient (1–7%) is absorbed due to drug leak from the eye along with tear fluid, metabolic degradation as well as non-specific absorption.

Accordingly, there is a need for a drug delivery system that effectively and for a longer period of time provides the patient with a therapeutic dose of the substance. Attempts have been made to use contact lenses as controlled dispensing systems for ophthalmic drugs.

One-day-hydrogel lenses were used for the tests. The lenses were immersed for a period of one day in the ophthalmic drug solution. After this time, the process of drug release from the matrix using UV-VIS was investigated.

After immersion of the hydrogel lenses in the drug solutions, a release time of tens of minutes was obtained, which gives promising results for the future. A lens soaked in a solution of the drug allows for a long-lasting and stable release of the drug substance, which gives better therapeutic effects.

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8.106 Comparison of hydrotalcite-alike materials prepared by different synthesis methods

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KEYWORDS: hydrotalcite, LDH, urea synthesis, solution combustion synthesis.

Hydrotalcite is a material widely examined as a catalyst in processes such as SCR or methanation. The goal of this research was to compare the crystallinity and structure of the hydrotalcite-alike materials prepared through the different synthesis methods.

The chosen preparation techniques were: coprecipitation, urea hydrolysis method and solution combustion synthesis. Two different types of material were prepared by each of the methods. One type of samples was containing Mg - Al species in molar ratio 3:1, second Ni – Mg – Al with molar ratio 1:2:1 subsequently. The choice of preparation techniques was dictated by the simplicity of experimental procedure and further possibility of deposition of the material on the catalytic structures like monolith. Two elemental compositions were chosen to examine if the same experimental conditions lead to the same type of crystallinity. In order to obtain the information about constitution of samples, XRD and FTIR analysis were provided. In prepared samples, hydrotalcites were obtained via coprecipitation and urea method. Solution combustion synthesis usually led to oxides structures such as periclase or spinel.

Preparation of hydrotalcites via solution combustion method should be improved, probably through lowering the combustion temperature or stronger alkalization of the resulted powder.

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8.107 The barium-gallo-germanate glasses as a perfect matrix for RE ions to induce intense emission in UV, VIS and IR region

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KEYWORDS: barium-gallo-germanate glasses, glass modifiers, structural properties, optical properties.

The optoelectronic is a field of technology which uses specific light properties to acquire, collect, transmit, process and present information. The glass materials are recently widely used as a material to build devices for optoelectronic. The optical properties of mentioned materials depend on its compositions, manufacturing process and follow it structural properties. The barium-gallo-germanate glasses are the object of intensive scientific research as it is a potentially perfect candidate for light collector and transmitter.

The presented research concern optical and structural investigations on barium-gallo-germanate glasses gradually modified with specific oxides which introduce low or high phonon energy into the glass structure. The studied glass system was doped with lanthanide ions to investigate emission properties of prepared glass samples.

The investigation of prepared glass system was possible thanks to X-ray diffraction measurements (Panalytical Empyrean powder diffractometer using Cu $K\alpha$ ($\lambda K\alpha$ = 1.54186 Å), SEM/EDS (SEM-FEI NOVA 200 NanOSEM), FTIR spectra measurements (Bruker Company Vertex 70v spectrometer and Horriba Yvon Jobin Labram HR micro-Raman spectrometer) and spectrometer to generate emission spectra.

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8.108 Structural investigation on gallo-germanate glasses modified with various content of barium oxide

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KEYWORDS: gallo-germanate glasses, barium oxide modifier, refractive index.

The matrix material for the optical glass needs to possess specific optical, chemical and mechanical properties. The barium-gallo-germanate glass seems to be perfect candidate for matrix material as it possesses good mechanical properties, high corrosion resistance, good solubility of RE ions, thermal stability and relatively low phonon energy. All of mentioned properties depend on the composition of the material.

In this paper barium gallo-germanate glasses were synthesized with different molar content of barium and germanium oxide. The manipulation of molar composition is to study the obtained glass samples' properties and further its optimization. Based on the analysis of the results, the glass with the best properties was selected. The chosen glass will be doped with lanthanide ions and the emission properties will be investigated.

Following study were used to investigate the obtained glass samples: X-ray diffraction measurements, SEM/EDS, FTIR and Raman spectroscopy and refractive index measurement.

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8.109 Ultrasonic deposition of nano-hydroxyapatite layers on polymeric surfaces

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KEYWORDS: hydroxyapatite, coating, sonochemistry, nanotechnology, nanomedicine.

Millions of bone reconstruction operations are conducted every year. In most cases, autologous bone grafts are made, which often associated with complications. A promising alternative to autologous bone grafts are individual bone scaffolds made of bioresorbable polymers. Biofunctional implants fills the defect in the tissue and carry the loads. The presence of groups with hydrophilic properties (e.g., – OH) on a biomaterial surface is preferred. For this reason, the modification of the surface of polymeric and metal materials is becoming more and more popular.

In the field of regenerative medicine, homogeneous, biocompatible, bioactive coatings stimulating the regeneration of bone or cartilage tissue. All these conditions are met by nano-hydroxyapatite layers deposited by ultrasound. Hydroxyapatite (HAP) is the main mineral component of the bone, responsible for the stiffness and mechanical strength of the bones.

This work presents the dependence of the main parameters of the hydroxyapatite ultrasonic coating process and the degree of surface coverage.

Optimization of the parameters of the ultrasonic process allowed to obtain fully reproducible nano-hydroxyapatite layers on the surface of polymer and polymer-hydroxyapatite implants. The layers of nano-hydroxyapatite deposited by this method create layers with a thickness of 150–350 nm, both on the external surface of the implants and inside porous structures, e.g. bone scaffolds. Hydroxyapatite layers increase the biocompatibility of implants and, consequently, stimulate faster bone tissue regeneration.

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8.110 Water vapour adsorption on HAP nanocrystals

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KEYWORDS: hydroxyapatite, adsorption, desorption, kinetics, BET isotherm.

Nanotechnology became a key word of public interest, with the special respect to nanomedicine applications. One of the most popular biomaterial is hydroxyapatite (HAP). Composites consisting of HAP nano-crystals and biocompatible polymers have been widely used in orthopedic and dental application. These composites can provide both ease of use and superior mechanical properties of polymers, osteoconductivity and bioactivity of HAP. Hydroxyapatite presents hydrophilic properties. Therefore the influence of water on the final properties of complex nanomaterials.

The aim of the work was to examine the speed and efficiency of water adsorption and desorption from the surface of different types of hydroxyapatite nanoparticles. The mass changes caused by water adsorption/desorption on the surface of nanopowders exposed to various humidity level of around: 26%, 38%and 60% were detected. Experiments were performed with use of HAP nanopowders produced in the Nanostructure Laboratory at the Institute of High Pressure Physics, Polish Academy of Sciences in Warsaw, signed with trade mark $GOHAP^{TM}$. Two types of $GOHAP^{TM}$ were used: type 1 and 6, with specific surface area of 50 and $200 \text{ m}^2/\text{g}$, respectively.

A strong influence of ambient relative humidity on the speed and efficiency of water adsorption by the surface of nanopowders was shown in this investigation. The results of testing of hydroxyapatite nanopowders was shown on the kinetic curves of the atmospheric water adsorption process at air humidity level of around: 26 %, 38 % and 60 % respectively. Moreover, the results shows a reduction in mass during the desorption process initiated by decreasing the level of ambient water dispersion. In addition, the BET adsorption isotherm was estimated, based on which it is possible to determine optimal operating conditions with nanohydroxyapatite.

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8.111 Kolliphor surfactants - adsorption properties

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KEYWORDS: surfactants, Kolliphor, surface tension, adsorption.

Kolliphor surfactants are fatty acid esters of polyoxyethyleneglycerol. They are commonly used in pharmaceutical formulations as solid dosage forms and lipid based delivery systems to improve the bioavailability of poorly water-soluble drugs. The most frequently used Kolliphor, Kolliphor ELP (purity form of Kolliphor EL) was used as a vehicle for solubilization of a series of hydrophobic drugs, including cyclosporin A, diazepam, paclitaxel or benzocaine. Kolliphor RH40 is used as an emulsifying agent in self-emulsifying drug delivery systems (SEDDS) in combination with other co-solubilizer or co-solvent. Therefore, it seems reasonable to study the properties of surface-active compounds that can later be used as solubilizers.

The aim of presented study was to investigate the influence of the temperature (293–318 K) and concentration of two Kolliphor surfactants, Kolliphor ELP and Kolliphor RH40 $C = 10^{-8}-10^{-2}$ M on adsorption process at the air-water interface. The measurements of static surface tension were carried out and parameters such as pC20 parameter or standard Gibbs free energy of adsorption was determined at various temperatures.

The most important conclusion is that the values of surface tension of aqueous solutions can be used for ΔG_{ad}^0 calculation on the basis of pC20 parameter. The obtained results show that Kolliphor ELP has the greatest effectiveness in reducing surface tension of water at 293, 303 and 308 K, which is confirmed by the highest values of pC20 parameter. At 293 and 308 K greater spontaneity of adsorption has Kolliphor ELP, which is confirmed in lower values of ΔG_{ad}^0 .

All of the standard free energy of adsorption values are negative, which indicates that the adsorption process at the air-water interface occurs spontaneously.

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8.112 Sweeteners in food industry

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KEYWORDS: sweeteneners, food industry, sorbitol, surfactants.

Sweeteners are food additives which replace sugar in food products. They are increasingly used as an alternative source of sweet taste for diabetics. In addition, due to the growing interest of consumers in a healthy lifestyle, energy-reduced products, i.e. these which contain sweeteners instead of sucrose, are becoming more and more popular. In Poland, the following intense sweeteners are allowed: acesulfame κ , aspartame, salt of aspartame and acesulfame, cyclamate and its sodium and calcium salts, neohespydrine DC, saccharin and its sodium, potassium and calcium salts, sucralose, thaumarin, neotame or stevia.

Key benefits of intense sweeteners include: calorie reduction, preservation of sweet taste, no effect on blood glucose and they do not create conditions for the development of caries. Thanks to the above properties, these substances may be helpful in the prevention and treatment of obesity and they can be used both in food for diabetics and in food for people who, without giving up sweet taste, would like to limit their energy intake. The benefits of using these substances in food make manufacturers use them in an increasingly wide range of products. One of the most popular sweeteners is sorbitol, for example in chewing gum.

The aim of presented study was to investigate basic properties of sorbitol, such as conductivity, viscosity, density, surface tension and pH at 293 K. The influence of the nonionic surfactant on the surface tension of sorbitol was also determined.

The main conclusion is that the aqueous sorbitol solution is slightly acidic, its surface tension is 67.23 mN/m, and the conductivity value is in the range of 2.01–3.77 μ S/cm. In the case of sorbitol solutions of low concentration, their density and viscosity do not change, whereas at higher concentrations the above mentioned values increase to the value of 1.004 g/cm³ and 1.06 mPa s at the sorbitol concentration of 10⁻¹ mol/dm³.

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8.113 Composite layer reinforced by TiC particles fabricated in situ in steel castings

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KEYWORDS: composite, in situ, TiC, hardness, MMCs.

Wear abrasive is one of the main processes of the destruction construction elements that occurs primarily on the working surfaces of details. Therefore, ones seek to design materials reinforced surface or zonal reinforcement using techniques such as laser cladding, thermal spraying, and welding (TIG) or a separate group consists in foundry methods.

The aim of this study was to produce layers of composite type TiC – Fe (titanium carbide/ferrous alloy). For this purpose, an aqueous foundry coating with the addition of substrates TiC and "binding material"- carboxymethylcellulose (CMC) was prepared. In the first stage of the structure investigation, analysis of CMC using spectroscopic technique (FTIR) was conducted. Further, a coating, on the basis of a 2 % aqueous solution of CMC, containing a powder of titanium and graphite, was prepared. The coating was characterized in terms of physicochemical and technological properties such as thermal decomposition, viscosity and contact angle. The technological process was based on covering the casting mold cavity with coatings containing substrates of the TiC formation. The temperature of the casting alloy was the factor initiating the synthesis reaction of the TiC.

As a result, the composite layer having a thickness from 1.5 to 5 mm was obtained. Composite layer characterized by a heterogeneous structure, which was related to reactive infiltration, displaying separation area by base alloy. The investigation of composite layer structure, using X-ray analysis (XRD) and the microstructure using scanning electron microscopy (SEM), show the presence of TiC ceramic phase. Using Vickers' method, the conducted hardness measurements in the area of the composite layer show a hardness of 700 HV1 cooperation, what constitutes more than two-fold increase compared to the base alloy.

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8.114 Modified bentonite-derived materials as catalyst for selective catalytic reduction of nitrogen oxides (SCR)

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KEYWORDS: pillared bentonite, acid activation, alumina, iron, copper, selective catalytic reduction, NO, ammonia.

In recent times, excessive emission of adverse nitrogen oxides (NO_x) from stationary and mobile sources is observed. Currently, the most efficient technology to convert NO_x is the selective catalytic reduction. It involves the reduction of nitrogen oxides by the reducing agent (ammonia or hydrocarbons) into harmless molecular nitrogen and water vapour. Although the industrial catalyst $V_2O_5 - TiO_2 - WO_3$ or $V_2O_5 - TiO_2 - MoO_3$ provides high NO conversion rates, it has some considerable limitations. Therefore, finding a novel and effective and economic scr catalyst is nowadays a big challenge.

Cationic layered clays, including bentonites have been investigated as potential catalysts for scr $DeNO_x$ systems. This class of materials is abundant in the nature and relatively cheap. Additionally, their modifications, e.g. acidic treatment and intercalation, result in the generation of high specific surface area and acidic and redox active sites formation. What is more, their ion-exchange properties provide incorporation of metals catalytically active in scr reaction.

For the sake of these promising catalytic properties of cationic layered clays, bentonite-derived catalysts were prepared and tested in the NH_3 -scR reaction. A series of bentonite samples was treated with 0.8 M solutions of hydrochloric and nitric acids for 2 hours. Subsequently, the samples were treated with oxalic acid for 2 hours. After drying and calcination, the samples were pillared with alumina by the ion-exchange method using an aluminium hydroxy-oligometric solution. Therefore, the materials were impregnated with iron, copper and lanthanum. The structure of the obtained catalysts were characterized by XRD and FTIR and the texture analysis was carried out by low-temperature N_2 sorption. The scR catalytic tests carried out over analyzed samples indicated high conversion rate of NO and selectivity to N_2 for all of the tested materials. Acid treatment and pillaring strongly enhanced the catalytic activity. The study over modified bentonites indicated that after certain modifications they have a strong potential as the catalysts for DeNO_x systems.

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8.115 Ionic liquids dispersions of functionalized CNTS – en route to modern energy storage materials

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KEYWORDS: carbon nanotubes, dispersion, ionic liquids.

Carbon nanotubes (CNTS) are allotropic form of carbon characterised by cylindrical nanostructure. Their discovery drew attention of many researchers of various fields of science and technology since CNTS show exceptional properties and therefore constitute a very promising material for multiple applications, e.g. in optics, electronics or thermal management.

Dispersion is a system consisting of minimum two phases out of which at least one is made of ultra-fine matter scattered in the other one; the latter one (dispersing medium) must be continuous. CNTS do not disperse easily in various solvents due to abundant interactions derived from pi-pi stacking and van der Waals forces; i.e. they tend to form agglomerates. Functionalisation of the outer CNT surface is often necessary to achieve stable dispersions, but modification of CNTS induces defects in their walls, decreases their aspect ratio (they can be cut) and, consequently, aggravates CNTS' thermal, electrical and mechanical properties. Recently, imidazolium-based ionic liquids (ILS) were found as a new class of CNT dispersants. ILS are generally defined as low-melting organic salts which are liquid below 100 $^{\circ}$ C (those with higher melting points are often called molten salts). In last years, ILS have been frequently used as "green" solvents and functional additives in the synthesis of new substances and materials.

The aim of our studies is determination of the effect of the IL anion and cation on CNT dispersion. We will use three types of CNTS: commercially available multiwall CNTS (MWCNTS) Nanocyl NC7000TM and two types of MWCNTS synthesised in our laboratory via c-CVD method. Our purpose is to change the CNTS' surface character by introducing functional groups (-OH, -COOH, -Cl and $-NH_2$). After that, dispersions of CNTS in different ILS based on imidazolium derivatives will be prepared. The quality and stability of each dispersion will be verified by optical microscopy. Our ultimate goal is to apply the IL-functionalised-CNTS systems as energy storage materials.

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8.116 Modelling of suspension grinding processes in selected industrial apparatus

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KEYWORDS: suspension grinding, stirred media mill, silica comminution, ultra-fine grinding, dissolver.

Ultra-fine grinding is a crucial process in many branches of the industry. It is commonly used in energy generation, pharmaceutical, paint, cement, pyrotechnical industries and many others. Important problem is choosing the right parameters which will allow to optimize the cost of such an operation.

Today there are various devices offered by manufacturers designed for the purpose of ultra-fine grinding. Performance of such apparatus is sometimes poor and the energy consumption rate and the breakage rate per one cycle could be vastly improved. The key aspect of the optimization is the reduction of recirculation number of product slurry. This will lead to a great reduction of energy used and to the improvement of the device efficiency.

Computational fluid dynamics software was used to model the process of ultra-fine grinding in stirred media mill apparatus. The energy was provided via shaft rotating with a given angular velocity. The turbulent flow k- ε model was used during the simulations.

For stirred media mill calculations with and without milling media were conducted. The conducted simulation included the influence of process parameters on the breaking of particles in solid-liquid suspension. Silica particles and TiO₂ (titanium oxide) suspended in water were used as a base material for the analysis.

The influence of rotational shaft speed, volume flow, apparatus geometry changes and solids concentration was calculated. The model was then compared to a laboratory scale stirred media mill based on the industrial grade one. The particle sizes were determined with the use of BeckmanCoulter DLS device. Sizes were compared with the unsteady simulation results in corresponding times.

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8.117 Characterization of ligand shell for mixed-ligand coated zinc oxide quantum dots

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KEYWORDS: quantum dot, zinc oxide, mixed-ligand shell, physicochemical properties.

The current growing interest in quantum dots (QDS) technology is stipulated by the unique optical properties of these semiconductor nanocrystals, namely their size-dependent properties and exceptional photostability. However, QDS are hybrid nanoobjects and the surface organic ligands have profound effect on modulation of different physicochemical parameters as well as toxicological impact of these nanocrystals. In this regard, an appropriate surface functionalization allows rational manipulation of key QDS properties and facilitate their further application. For instance, the possibility to obtain heterogeneous organic ligand coating could be crucial for numerous bioapplications i.e. for the design and preparation of drug-delivery systems. Therefore, there is a great challenge to develop efficient synthetic strategies affording reproducible QDS with stable mixedligand organic shells. Moreover, the adaptation of traditional analytical methods for the characterization of these nanosystems is also important and it is still a very challenging issue.

We present a novel wet organometallic processing method which yields monodispersed and high-quality ZnO-QDS coated with mixed-ligand shell. The presented method consist the synthesis of appropriate organometallic precursor, the preparation of ZnO-QDS as well as their characterization by means of scanning transmission electron microscopy (STEM), powder X-ray diffraction (PXRD), dynamic light-scattering (DLS) measurements, thermogravimetric analysis (TGA), FTIR, Raman spectroscopy (RS), UV/Vis spectrophotometry, and photoluminescence (PL) spectroscopy.

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8.118 Towards novel ZnO quantum dots coated with mixed-ligand shell

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KEYWORDS: quantum dot, zinc oxide, mixed-ligand shell, nanoparticle, nanocrystal.

Quantum dots (QDS) are nanometer-scale semiconductor nanocrystals (NCS) with dimensional similarities to biomacromolecules. The current growing interest in QD technology is stipulated by QDS unique photophysical properties, namely their size-dependent spectrum properties, high photostability, narrow light emission spectrum together with efficient light absorption spectrum. Both, the electric and optical properties of quantum dots make them a very attractive objects for the applications as a new generation of fluorescent, semiconductor devices or tools for cellular imaging.

In the last decades, the nanoworld has been dominated by cadmium-based nanostructures. However, potential utility and large-scale applications of these NCs are limited due to negative biological and environmental impacts. Zinc oxide (ZnO), as a heavy-metal-free substituent for commonly used CdX (X = S, Se, Te) QDs, is one of the most versatile systems with far-reaching perspectives.

The goal of the presented work is the design and synthesis of luminescent organic-inorganic water-soluble functional materials based on semiconducting ZnO nanoparticles as systems ready for potential biological applications. The presented results include the synthesis of organometallic precursor, its controlled transformation into ZnO Ncs as well as characterization of basic physicochemical properties of described system, i.e. size, morphology and optical properties.

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8.119 New strategy of food samples classification

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KEYWORDS: wine profiling, DPV, Ir ring electrode, ATLD trilinear decomposition.

Wines profiling nowadays is a rapidly developing branch of the wine industry. The expansion of analytical methods for quality control of wines is very important to ensure the reproducible quality of obtained beverages. Due to the difficulties in choosing such analytical techniques, it is necessary to base the quality control of the produced beverages on the tasters. The unquestionable disadvantage of the organoleptic technique in assessing the quality of the wine produced is the subjective sense of taste of each sommelier.

The analytical technique that gives hope for solving the problem of wine profiling is the differential pulse voltammetry technique with the use of metallic electrodes. The electrode which provides very good results in relation to testing of wine profiles is the iridium ring electrode.

The use of Principal Component Analysis technique for the obtained voltammograms of four wines (two white and two red) did not allow satisfactory separation of individual profiles. The expected profiling effect took place only after applying the three-linear data decomposition realized by the alternating trilinear decomposition (ATLD) algorithm Separation of the capacitive component (which is like noise and does not carry analytical information) from the faradaic component (which is important in the field of analytical chemistry) within each group of wine profiles gave the expected results of the wine distinction. The proposed approach was for the first time applied to determine the origin of objects, using the DPV curves.

The work will show the distribution of current components obtained during voltammetric measurements and their impact on data analysis.

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8.120 Voltammetric determination of anethole on carbon electrodes

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KEYWORDS: anethole, DPV, GCE, BDDE, CPE.

Anethole is the main ingredient in anise oil, but in lower concentration it also occurs in fennel oil. On the industrial scale, it is primarily used as a flavoring substance, but undoubtedly an important aspect is its bactericidal properties. An important feature of anethole is its lack of resistance to light and oxygen.

In this work, a comparison of the operation of a glassy carbon electrode, a boron-doped diamond electrode and a yttrium oxide (Y_2O_3) doped carbon paste electrode with reference to the quantitative determination of anethole under optimized conditions will be presented.

The typical optimizations of measuring parameters were carried out separately for each of the electrodes. The best parameters during optimization were obtained for the Carbon Paste Electrode doped by Y_2O_3 . The sensitivity of the method of anethole determination was $1.34 \pm 0.10 \,\mu\text{A/mgL}^{-1}$, correlation coefficient 0.9991, linearity range is from 1.4 to 7.0 mg/L and limit of detection is 1.1 mg/L. However, in the case of this electrode, the use of biological samples in the form of oils deteriorated its parameters. However, the most stable electrode was a diamond electrode doped with boron, because the greatest drop in sensitivity that was observed during the tests was only 0.22 %. The developed method was applied for the determination of anethole in biological and food samples which were Ouzo vodka, alcoholic extract from a fennel and essential anise oil.

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8.121 Poly(glycerol sebacate) as prepolymer material for biomedical applications – synthesis and purification method

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Keywords: poly(glycerol sebacate), prepolymer, synthesis, purification, optimization.

Polyesters are very interesting materials for scientists looking for biodegradable and biocompatible materials. The development of tissue engineering is related to the need for materials that build cellular scaffolds. Currently one of the newest polyesters, which could be biomaterial for tissue regeneration is poly(glycerol sebacate).

The first mention of poly(glycerol sebacate) dates back to 2002. Even then, this polymer was proposed as a new biodegradable elastomer for medical applications. Currently, interest in this material is growing year by year. The simplicity and availability of monomers makes a relatively low cost of its manufacture. Poly (glycerol sebacate) is a biocompatible, biodegradable, non-immunogenic and nontoxic material. It is postulated to use a polymer with suitable properties as follows: cell scaffold in soft tissue engineering, drug carrier, surgical sealants, and as a contact surface for biomedical sensors. Most of the works focus on the synthesis of the crosslinked polymer (no isolation of the prepolymer) adapted to perform one function. In our work, we focused on developing a synthesis and purification of a non-crosslinked product, which is called prepolymer. The material produced by us can be processed in a simple way for functionalization. This is an incredible advantage appreciated by manufacturers of medical devices.

The work received the prepolymer poly(glycerol sebacate), the synthesis method was optimized, and the method of purification was proposed. The equipment for industrial polymer production has been proposed. The material was characterized by IR spectroscopy, NMR spectroscopy and the acid and ester numbers were determined for delimitation of esterification degree.

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8.122 Preparation of copolymer of poly(glicerol sebacate) and poly(L-lactide) and using it in the electrospinning method

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Keywords: tissue engineering, prepolymer, poly(glycerol sebacate), poly(L-lactide), copolymer.

Tissue engineering is a rapidly developing field of science that aims to create, repair or replace tissues and organs with biomaterials or biologically active molecules. The main goal is to create a material that resembles the home tissue of the body as much as possible. Particular attention should be paid to polymers that can be obtained synthetically, by means of a chemical reaction, but which degrade in a biological environment and do not cause harmful products for the body. We can improve the material's properties by subjecting the material to electrospinning. New material properties, such as large specific surface area, variability of surface functions and better mechanical properties occur, when the fiber diameter falls within the nano-range.

In the research copolymers of poly(glycerol sebacate) and poly(L-lactide) with different molar ratios (1:4, 1:8, 1:16, 1:8 with cross-linked prepolymer) were received. The obtained products were analyzed for the acid number, ester number, FT-IR, GPC and ¹H NMR. Two copolymers with the highest molar mass were selected for the electrospinning process. The spinning was carried out with the addition of polycaprolactone, with a variable PCL:copolymer ratio of 3:1, 1:1, 1:3, and one PCL nonwoven fabric was produced as a reference sample. The non-woven fabric were tested using SEM (scanning electron microscopy), an apparatus measuring the angle of wetting and tensile strength.

On the basis of SEM tests, it was found that the more copolymer in the nonwoven fabric, the thinner the fibers. The improvement of wettability was noticed only for PCL nonwoven: 1:1 uncrosslinked copolymer. The strength parameters of all nonwoven fabrics have improved. The greatest improvement was observed for PCL nonwoven: a 3:1 copolymer (cross-linked).

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8.123 In vitro bioactivity evaluation of the gel-derived glasses

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KEYWORDS: bioglasses, in vitro bioactivity, tissue engineering, sol-gel method.

Bioglasses have numerous advantages, such as the ease of making modifications. In particular, their modifying with different therapeutic ions can be a promising way of obtaining new materials for medical applications.

The aim of the study was introducing ions of strontium, cerium, and zinc in the concentrations (7 and 10% mol) to the gel-derived bioglasses, dedicated for the potential applications in the engineering of different tissues, and evaluate the particular modifiers impact on their bioactive performance in vitro.

Bioglasses from the SiO₂-CaO-P₂O₅-MO system, with the SiO₂/(CaO+MO) ratio equaling 0.74 or 5 were obtained by the sol-gel method. The MO concentrations, where MO: SrO, ZnO or CeO₂, were 7 and 10 % mol. The in vitro bioactivity of the obtained glasses was assessed in a 2D composite experimental model, concerning incorporation of tested bioglass particles into the PCL (poly(ε -caprolactone)) polymer matrix. Then, samples were immersed into the simulated body fluid (SBF) solution for 3.7 and 14 days, respectively and characterized with SEM/EDS (Scanning Electron Microscopy with Energy Dispersive Spectroscopy) for surface morphology and composition, FTIR-ATR (Fourier Transform Infrared Spectroscopy Attenuated Total Reflection method) for structural analysis and ICP (Inductively Coupled Plasma Spectrometry) for rate of ionic exchange between SBF and materials analysis.

The results indicated different apatite morphology and rate of formation in accordance with the type and concentration of introduced modifier. That effect was significant especially in the results of SEM/EDS analysis. Amongst the modifiers, strontium appeared to favor apatite formation in the best result, what can be explained with its structural function in glasses. Moreover, the A2 system glasses indicated an overall higher level of *in vitro* bioactivity in comparison with the s2 ones. The ICP analysis, indicated various manners of ionic exchange with SBF, especially for the Ca²⁺ and PO₄³⁻.

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8.124 Ab initio-based kinetic Monte Carlo simulation of Cr segregation process in bcc – Fe – Cr alloys

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KEYWORDS: kinetic Monte Carlo, density functional theory, Fe-Cr alloys, grain boundaries.

Grain boundaries (GBS) are an immanent components of crystal structure of the structural materials, such as e.g. Fe – Cr steels. Moreover, they have considerable influence on the materials properties, especially on the mechanical ones. As a consequence of that, is necessary to investigate the effect of Cr segregation on the GBS in order to understand more deeply the bcc – Fe – Cr steels.

In the current study, we investigated the segregation process of Cr atoms at Fe-Cr tilt GBs. The spin-polarized density functional theory (DFT) calculations of bulk system and $\Sigma 5(310)$ tilt GB were performed. The Nudged Elastic Band method was used due to determine the migration barrier of Fe, Cr and the vacancy. The established database was used to parameterize the Atomistic Kinetic Monte Carlo model which allow to simulate the segregation phenomenon.

The fluctuation of magnetic moments, chemical potentials, formation and migration energies of point defects were studied as a function of distance from GB's plane. Moreover, the AKMC simulations were used to obtain the Langmuir-McLean segregation isotherm.

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8.125 The ab initio study of hydrogen-vacancy complexes in diamond

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KEYWORDS: Hubbard model, hydrogen-vacancy complex, diamond electronic structure.

Hydrogen plays an essential role in the growth process of artificial diamond and can easily form complexes with lattice vacancies. Despite substantial efforts to resolve the electronic structure and the ground state properties of *HV* center the final remarks are ambiguous, while the complexes of vacancy with two and more hydrogen atoms remain unexplored.

In this work, we used spin-polarized, hybrid density functional theory method to investigate the electronic structure and magneto-optical properties of various hydrogen-vacancy clusters in a diamond. Our theoretical results indicate very strong tendency toward the formation of H_nV complexes up to 4 hydrogen atoms that are mostly electrically and optically active centres. One of the investigated defects introduce highly correlated electronic states that pose a challenge for density functional theory and therefore, require the special treatment when charge- and spin-density related properties are determined. We introduced an of extended Hubbard-like model of Hamiltonian with fully ab initio provided parameters to analyse the complex electronic structure of highly correlated $H_2V(0)$ defect. The role of quantum tunnelling of hydrogen in HV centre and its impact on the hyperfine structure was discussed.

We demonstrate that experimentally observed HV(1-) centre is similar to well-known NV(1-), i.e. i) it possesses triplet ³A ground state and ³E excited state in $C_{3\nu}$ symmetry; ii) the calculated zero-phonon line is 1.71 eV (1.945 eV for NV(1-)). A detailed experimental reinvestigation based on optically detected electron paramagnetic resonance spectroscopy is suggested to verify whether the HV(1-) centre has metastable singlet shelving states between the ground and excited state triplets and as a result, whether it may exhibit a spin-selective decay to the ground state.

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8.126 Computational fluid dynamics simulations of electric storage-tank water heater

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KEYWORDS: computational fluid dynamics, water heater, heat transfer, limescale.

Hot water is an essential element in everyday human life, for example, showering, clothes washing or dish washing. The most common type of water heaters – electric storage-tank water heater has a few disadvantages like limescale, dead zones or even corrosion that worsen the work parameters, mainly heat exchange and lifetime.

The purpose of this work is to eliminate above listed drawbacks and make installation more efficient by changing the internal geometry of the storage-tank water heater. The first part of this work is focused on the simulation of work of a typical water heater to identify problems. The results showed that near enabled electric heater temperature is at least 5 times higher than the average temperature in the rest of the tank. Along with the temperature change, the pH value also changes. At high temperatures, the water is slightly acidic, which in turn accelerates the corrosion processes. Furthermore, under the influence of temperature, the water changes its physical and chemical properties causing precipitation of limescale. The phenomenon of precipitation increases with rising temperature.

Next, the authors presented possibilities of changing dosing water into the tank. It reduced maximal temperature of water and electric heater wall. That helps to prevent corrosion, reduces limescale formation and limits dead zones especially at the bottom of the tank.

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