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Preface

On behalf of the NFA 2023 Organizing Committees, we introduce with pleasure these proceedings devoted to contributions from the 7th NFA Novel Materials Fundamentals and Applications conference held in Štrbské pleso, High Tatras, Slovakia. The conference is organized by the Faculty of Science Pavol Jozef Šafárik Uninversity in Košice and Slovak Chemical Society. The conference program provides an opportunity for researchers interested in various applications of nanomaterials to discuss their latest results and exchange ideas on the new trends. The main objective of the conference umbrella is to encourage discussion on a broad range of related topics and to stimulate new collaborations among the participants.

The proceedings contain all papers of both: oral and poster presentations. We hope that these proceedings will give readers an excellent overview of important and diversity topics discussed at the conference. We thank all authors for submitting their latest work, thus contributing to the excellent technical contents of the Conference. Especially, we would like to thank the organizators that worked diligently to make this conference a success, and to the recenzents for the thorough and careful review of the papers.

We wish all attendees of NFA 2023 an enjoyable scientific gathering in High Tatras, Slovakia. I wish all participants enjoy this scientific meeting to collect new information form nanoscience.

Ivana Šišoláková

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Invited Lectures

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Alkaline Membrane Water Electrolysis Challenges Connected with the Individual Cell and Stack Components

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The water electrolysis process stands in the core of the set of technologies foreseen to enable reduction and in the final step elimination of the carbon dioxide emissions cause by industrial activities of industrially devellped economies. Currently three main types of water electrolysis are developed: (i) alkaline, (ii) PEM and (iii) solid oxides electrolysis. Solid oxides electrolysis represents the process on the lowest TRL level. On the other hand, alkaline process was commercialized more than 120 year ago and is fully matured. PEM technology stays between these two. It is currently considered as the most suitable one to be connected with the renewable electric energy sources and thus to provide hydrogen with carbon emission close to zero. Despite excellent properties (flexibility, efficiency, energy density etc.) and despite significant effort invested into related research, one important issue remains unresolved for this technology. This concerns primarily material demands, especially precious metals and fluorine chemistry based polymer electrolyte. Thus, during last decade, the attention of the community turned, at least partly, back to the alkaline version of the process.

Alkaline water electrolysis opens broad variety of new opportunities. Significantly broader range of the materials is available withstanding the conditions of the operating alkaline water electrolyser. At the same time, however, electrodes reaction mechanism changes and knowledge generated during previous research of the PEM water electrolysis in the field of the electrocatalysis is only partly transferable to the alkaline system.

The primary task of the research in the field of alkaline water electrolysis is focused on increasing process efficiency, flexibility and enhancement of the energy density. Besides optimising electrode reactions catalysts and porous electrode compartments separator properties, attention turned also to the development of an innovative version of the process. It is targeted to be, in an ideal case, able to mimic PEM water electrolysis in most of the aspects, but the expensive materials used. This is not the fully new idea. Situation differs, however, to the past trials. It is mainly given by the progress achieved in the field of polymer electrolytes chemistry. Number of novel materials appeared claiming to possess required properties, especially ionic conductivity and chemical stability. Two types of polymers are reported for this application: (i) anion selective and (ii) solvating ones. The availability of new polymer electrolysis (AMWE) having ultimate target in developing process using, similarly to the PEM water electrolysis, demineralised water as a circulating liquid medium.

Replacement of the porous separator by the polymer electrolyte in the electrolysis cell has several consequences. The most important ones include option for the reduction of the circulating KOH solution concentration. This is caused by the fact, the ionic contact between the electrodes is ensured by the polymeric electrolyte. At least into the certain degree. As it will be, however, shown, new phenomena occur due to this system modification to be considered during the process design. Also mechanism of the electrode reaction catalysis is changing with corresponding consequences regarding the electrocatalytic materials proposed for the alkaline process so far. Another aspect represent construction materials, especially in the case of electrodes. With reduced pH of the circulating medium, stability of the metallic components changes. Last, but not least, reduced pH and electrolyte temperature have consequences for the produced gasses solubility in the circulating medium and thus for the safety of the process. The above mentioned aspects will be briefly touched in this contribution, including a broader perspective of the water electrolysis process within the framework of the hydrogen economy scheme.

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Smart functionalities for Li-ion batteries

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The increasing dependence on batteries demands more precise and consistent design and monitoring of the battery's health, and state of safety to increase its reliability and lifetime. Li-ion cells are prone to different degradation mechanisms. One of the pending problems which have not been completely solved is the continuous degradation of metallic lithium. Different solutions have been proposed to address those problems. Modified nanocrystalline cellulose offers processability in solvents compatible with metallic lithium.[1,2] Use of cellulose and its modifications are considered a sustainable approach that can be applied on the surface of the metal anode using classical laydown methodology. Few micron-thick layers of cellulose, where interspace voids are filled with additives, effectively prevent constant exposure of metallic lithium towards electrolyte and anisotropy of cellulose fibres stops dendrite growth. The beneficial influence of the protective layer based on cellulose composite was confirmed with long-term lithium stripping and deposition, long-term cycling in carbonate and ether-based electrolytes, ex-situ focused ion-beam scanning electron microscope (FIB-SEM), operando ATR-IR spectroscopy and impedance spectroscopy.

Although the preventive steps incorporated within the battery cell (autonomous self-healing) can prolong the lifetime of the cell, a step forward would be enabled by the sensing system that allows the collection of different information during battery functioning. The sensing technologies should be designed in a way of monitoring the most detrimental process for the battery cell. Recently we have developed an electrochemical sensor that reliably detects manganese ions in the early stages of manganese dissolution. [3,4] The sensor printed on the battery separator is located in a key position inside the cell. The used approach can be extended in numerous ways by changing the electrodes and/or the sensing composite compounds and the geometry. Most importantly, we proved that printed electronics can be used for sensing inside the battery cell without affecting the battery operation itself.

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Energy materials from footwear waste

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During last year, 34 billion pairs of shoes have been manufactured worldwide, one-third being made of leather. Leather is based on a collageneous biopolymer used in the production of many everyday articles. Large quantities of leather waste are generated in the footwear manufacture and also after the customer stops wearing the shoes. The conversion of such waste to useful material is thus highly desirable from the environmental point of view.

The molecular structure of the skin is based on collagen protein, rich in nitrogen. Solid products of pyrolysis in an inert atmosphere, so-called biochars, are conducting nitrogen-containing carbons. Leather is commonly tanned with chromium compounds and the presence of chromium atoms in the char affects a fibrous one-dimensional morphology that is of benefit for the electrical conduction. Carbonized leather has a number of practical applications in energy storage, solid fuels, composite fillers, electromagnetic interference shielding, pollutant adsorption, catalysis, etc. [1]



Figure 1 Carbonized leather waste application.

In the present research, we have focused on finding the possibility to use waste from shoe manufacturing based on pigskin leather for the preparation of energy materials. Four types of leather carbonization and activation have been carried out: simple carbonization, two-step carbonization/activation, direct activation, and excess activation [2]. A pyrolysis temperature of 800 °C was selected after the preliminary study [3] and potassium hydroxide solution was used for the activation. All products had similar conductivity of the order of tenths to units S cm-1, which

approximately corresponds to the conductivity of conducting polymers, such as polypyrrole [2]. The products, however, highly differed in the specific surface area.



Figure 2 Chromium-pleated pigskin leather with organic dyes.

The properties of the carbonized and activated samples allowed for the preparation of batteries on a semi-operational experimental line. Positive electrodes for Li-ion batteries type CR 2032 were prepared and tested. The charge/discharge capacity of 400 mAh g-1 after 50 charging cycles was reduced by approximately about 20%.



Figure 3 Semi-production line for batteries preparation.

The results demonstrate that the carbonized leather waste could contribute to the solution of two major problems: the first, the reuse of harmful chromium-tanned leather waste, and the second, the replacement of some strategic energy materials.



Figure 4 Carbonized chromium-tanned leather for battery components production.

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15

Abstracts

16

InoHub Energy. Organic electrolytes

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Human development has brought about advancements in technology, healthcare, and human rights, contributing to an improved quality of life. However, this progress has also led to certain challenges, such as the ever-increasing demand for resources. To address the energy demand, the utilization of renewable energy sources has emerged as a clear solution, offering eco-friendly and virtually unlimited energy options. Solar and wind energy are among the most developed renewable energy sources. However, the intermittent nature of wind and solar power poses a significant challenge.

Energy storage has become crucial to store surplus energy generated by renewable sources for later use. Electrochemical Energy Storage (EES), particularly Redox Flow Batteries, have emerged as a versatile solution for energy storage, ranging from domestic applications to large-scale storage. VRFB represents the state of the art due to the reasonable price of Vanadium electrolyte (5-10 \$/L), high voltage (1.26 V), high solubility (>1.6 M) and the capacity of rebalancing the electrolytes excluding the effect of the crossover. But this technology presents some important inconvenient such as the volatile price of the vanadium electrolyte, scarce availability (85 % Vanadium is located in China, Australia and Rusia) and use expensive membranes. A plausible solution could be the replacement of Vanadium electrolyte for organic electrolytes based on earth-abundant materials that can be entirely produced in Europe.

InoHub Energy is a Slovak company specializing in the development of energy storge solutions based on Redox Flow Batteries (RFB) to integrate renewable energies into the grid and facilitate grid balancing and peak shaving. InoHub Energy has been successfully notified in 2021 by European Commission at the level of IPCEI (Important Project of Common European Interest) fo the design of an Energy Center (EC) based on flow concept. In this sense InoHub R&D team are researching about different technologies such as VRFB and AORFB trying to find a plausible candidate that can replace Vanadium electrolyte proving the same or better performance.



Figure 1 Designing and optimization of new organic electrolytes.

Development of an innovative corrosion resistant coating for bipolar plates for energy

conversion devices

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The global increase in energy demand has fuelled the critical need for sustainable solutions to offset carbon emissions and fossil fuel dependence. One of the ways to achieve decarbonization of the economy is the use of green hydrogen as an energy carrier. The chemical energy of hydrogen can be converted into electrical energy in the traditional way of a heat source, or with the using of fuel cells. Current fuel cell technology has already reached a high technological level. However, the basic obstacle to their mass distribution is production costs.

The basic component of fuel cells, bipolar plates (BPs), rely mainly on carbon composites with polymer binders. This material exhibits not entirely suitable mechanical properties, weight limitations, limited electrical conductivity and significant production costs. An alternative solution uses steel foils known for their malleability, enabling economical shaping by mechanical pressing. This approach significantly increases production capacity and subsequently reduces costs. However, a fundamental problem arises in securing the steel foil against corrosion in the operating environment of the fuel cells.

This study presents a pioneering approach to enhance the performance of bipolar plates (BPPs) in fuel cells (PEMs) through the development of a specialized polymer composite coating containing conductive particles. By integrating an epoxy resin designed for the harsh PEM environment with conductive particles, this composite exhibits remarkable stability and electrical conductivity. An innovative technique is used to organise structurally the electron conductive filler particles and thus to achieve increased levels of conductivity at reduced particle content, resulting in significant cost reductions while maintaining optimal BPP performance. The experimental findings confirm the good electrical properties and durability of the composite coating and confirm its potential as a solution for electrochemical devices, especially in PEM applications. This research contributes to the ongoing efforts in optimizing materials for sustainable and efficient energy conversion technologies.

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How to use DNA as an innovative nanomaterial for electronic devices

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DNA is a fundamental molecule storing essential information about every living creature. Although the biological function and necessity of DNA in terms of preserving life are evident, however, DNA also serves as an exceptional substrate for molecular computation (also known as natural computing), data encryption, intelligent control and even in data flow logic operation. During the last decade, DNA is one of the most promising biological molecules for both molecular nanotechnology and nanoelectronics.

Since the discovery of the structure of DNA by James Watson and Francis Crick in 1953, an enormous amount of new potential of this molecule has been explored. One of the newest fields to emerge is DNA nanoelectronics, which aims to utilize unique properties of DNA, such as its ability to self-assemble into specific structures (DNA macrame/DNA origami [1]), for constructing nanoscale electronic devices, and circuits. The advantage of using DNA is precise base-pairing properties that can be exploited to create nanoscale templates for the precise placement of other nanomaterials such as nanoparticles and nanowires, enabling the design of new types of sensors, transistors, and other functional devices. On the other hand, DNA nanoelectronics can be used to study DNA and its properties at unprecedented resolution. Nanoscale probes and devices can be used to manipulate and analyze single DNA molecules, unravelling intricate details of their structure, dynamics, and interactions. Additionally, DNA molecules exhibit tremendous flexibility, and they can conduct electric charges over distances of several tens of nanometers [2], making them appropriate substrate for biosensor development. Another attractive electronic property can be observed in the study of DNA linked to carbon-based polymers such as graphene or nanocellulose [3], where nucleotide processing enzymes can be boosted by electrical or optical signals for substrate switching and controlling their activities [3,4].

In the presented work [5], we are exploring the intriguing electronic properties of DNA and outlining concepts of new electronic polymers including semiconductive nanocellulose and green electronics, graphene-augmented DNA sensors and electronic devices enhanced by DNA wires, as well as DNA and RNA-based aptamers and DNA-integrated field-effect transistors, which have great potential for development the next-generation technology.

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Electrocatalyst Based on NiCoP for Water Splitting: Part (I) Preparation

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Hydrogen produced from renewable sources and used in fuel cells (for both mobile and stationary applications) constitutes a very promising energy carrier in the energy transition and it is likely to play a key role in decarbonization of industry. It seems that the concept of Power-to-Gas used in hydrogen supply chains might play an important role in the future energy system worldwide [1]. The, main goal of this work is the development of alternative low cost electrocatalysts in order to increase the efficiency of hydrogen production by water electrolysis and reduce the energy consumption in the process. This work is devoted to the study of NiCoP phosphides in the form of polycrystalline microfibers as new non-precious electrocatalysts for water decomposition suitable for alkaline as well as acidic environments. The fibrous structure was achieved using needleless electrospinning technology (NLE) as a viable method for large scale production of fibers from polymer solution [2, 3] (Figure 1). NLE or electrospinning of free liquid surfaces can simultaneously generate several streams from the polymer solution surface, thus increasing the number of fibers prepared per unit of time by an order of magnitude. The prepared precursor fibers by NLE underwent heat treatment in air resulting in an oxidized form of the precursor fibers and subsequent reduction in a combined Ar/H₂ atmosphere to the final form of phosphide fibers. It turned out that the key factor, which affected the final morphology, structure and electrochemical performance, was finding optimal heat treatment temperatures in both sintering environments and optimized the spinning procedures. In the first step, the composition of polymeric solution used for spinning was optimized by choosing the appropriate polymers for preservation the fibrous structure after heat treatment process. Subsequently, the heat treatment setting was optimized according to the TG/DSC analysis in accordance with final NiCoP fibrous structure. The electrochemical performance was investigated and compared with the commercial Pt/C for HER and IrO₂ for OER catalysts.



Figure 1 The schematic illustration of NLE technology with SEM image of NiCoP fibres.

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Modification of Surface Energy by Changing of Adhesion on Circulating Tumour Cell with Different Chemicals

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One of the most common causes of death is cancer. Cancer cells create tumours locally but they can spread to distinct parts of the human body. Secondary tumours, that are known as metastases, are more lethal than original tumours, because they are more aggressive and they can invade almost every organ, tissue or bone. The malignant phase of cancer is in most cases almost unstoppable and patients with this stage of cancer have high risk of recurrence. For different types of cancer we know a lot of drugs nowadays. However it is not so simple to cure this dangerous disease. Every patient is in some way different. They have various ages, health conditions, bad habits, etc. And every type of cancer is somehow different, too. So it is very difficult to find a universal remedy. Unfortunately, in a lot of cases we cannot help patients to survive and recover. Many scientists try to find new methods to help oncologic patients. Many types of cancer do not have metastatic potential, but that can change in a matter of time. Or some patients could have malignant tumours, but metastases still do not occur in other parts of their bodies. Creation of metastasis is a complex process. It has many steps, which can be blocked or slowed down. Very important role in this process has adhesion. This attribute of cells and cancer cells too is connected with several physical quantities. The most important of them is supposedly surface energy [1]. Every cell interacts with its surroundings (extracellular matrix, other cells). Surface of every eukaryotic cell of animal type is formed by cytoplasmic membrane. That contains many components, in the process of adhesion are most important receptors and ligands. Every receptor interacts only with specific ligands. Healthy cells or common cancer cells create adhesion connections with surrounding cells. However, this connection can be blocked with various chemicals that can bind to specific receptors. When these chemicals interrupt adhesion forces, cells cannot interact with different cells, so cells do not create clusters and lonely cells can be eliminated by the immune system. This is very useful information according to the process of tumorigenesis. During creation of metastases is one (circulating tumor cell = CTC) or a group of cells detached from the original tumour. They invade the bloodstream and travel to distinct places in the body. These cells need to attach to endothelial cells of blood vessels. However we can interrupt this process with chemical blocators. They adhere to this cell and block the process of adhesion to endothelium. When some chemicals attach to cells, surface energy is changed, too. This physical quantity can be used as identificator, because cells communicate with other ones thanks to the value of their surface energy. If this value changes, they do not recognize it. Every type of cancer has different receptors. So we need to find chemicals that are specific for them. It is not quite a simple task. Fortunately, we can create mixtures of chemicals that can strengthen their effect, or nanoparticles formed from different molecules.



Figure 1 Synthesis of anti-adhesive and anti-cancer nanoparticles from ursolic acid, chitosan and folate acid [2].

In our study we work with ursolic acid and as amplifiers we use folate acid. Both are organic and natural molecules. Ursolic acid [3] has on its own a very promising effect on adhesion, but it is used mostly as chemopreventive drugs in case of occurrence of colon cancer or breast cancer. Folate acid also known as vitamin B9 has only weak antiadhesive effects, but it can bind to specific folate receptors. As amplifiers we can also use several more chemicals/drugs, for example aspirin or chitosan. Every type of cell can survive only specific concentrations of these drugs, higher values are toxic for them. However, there is an optimal concentration for best results, too. Fortunately, we know many more chemicals and thanks to their combination we can find something interesting in the future. Many chemopreventive drugs are used in medicine. They can help to prolong patients' lives or can be used as degradable biomaterials during surgeries. Because human bodies are weakened after this difficult intervention weakened and their immune system cannot protect them against possible CTCs.



Figure 2 Interaction of circulating tumour cell with its surroundings in blood stream [4].

Acknowledgements

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Preparation of Binary Zn-Ag Alloys by Powder Metallurgy and Their Surface Properties

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In recent years, the development and application of metallic biodegradable implants have been widely explored and studied *in vitro* and *in vivo*. An ideal biodegradable metallic implant should have suitable biocompatibility *in vivo* and provide proper mechanical support during the tissue repair process, as well as undergo gradual degradation in the body and be completely absorbed by the body within 1-2 years, depending on its intended function [1]. These conditions are met by three types of metals, namely magnesium, iron, zinc, and their alloys. Zinc has limited clinical applicability due to its low mechanical strength and hence the need for alloying with other metals with adequate biocompatibility and the ability to improve its mechanical properties, such as Fe, Mg, Cu, Li, Al, Sr, Ti, Ag [2]. Currently, zinc-alloys are considered a new generation of implant materials that have the potential to be used as a biodegradable material for the human body due to their high biocompatibility and excellent bone defects restoration abilities, which help to stimulate new bone development [3].

In this work, three binary alloys with composition: 98 wt.% of Zn and 2 wt.% of Ag (Zn-2Ag), 96 wt.% of Zn and 4 wt.% of Ag (Zn-4Ag), 94 wt.% of Zn and 6 wt.% of Ag (Zn-6Ag) and pure Zn were prepared using powder metallurgy technique. The Zn and Ag powders in the appropriate ratio were manually mixed to prepare a mixture with evenly distributed particles. Then 2 g of the mixture was pressed into a cylindrical shape (12 mm Ø) using hydraulic press with a pressure of 600 MPa and sintered at a temperature of 350°C for 60 minutes using a ceramic furnace in the argon atmosphere. Ag was chosen as an alloying element since it enhances the strength and ductility of Zn, along with providing antimicrobial properties and low cytotoxicity. The microstructure of the samples was observed (Figure 1 A) using the scanning electron microscopy (SEM).

From the surface properties of Zn-Ag alloys, the contact angles were measured in this study. Cell adhesion, proliferation, differentiation, and protein adsorption are key factors to be considered for the proper usage of artificial implants and their acceptance *in vivo*. These factors are closely related to the wettability of the surface and the correct function of the implant depends on whether the surface of the given material is hydrophobic or hydrophilic, that is, on the contact angle of the studied material. Studies have shown that cell adsorption, which is crucial for appropriate osseointegration, is stimulated in the range of a contact angle value of $60-80^\circ$, which corresponds to moderately hydrophilic surfaces [4]. Contact angle measurement was performed by dropping a $6 \ \mu$ L of water droplet onto the sample surface. The contact angle values of prepared Zn-Ag samples are shown in Figure 1 B). The contact angle values of all samples are in a narrow range of 65° to 73° , indicating that the surface of prepared samples is moderately hydrophilic.



Figure 1 A) SEM pictures and B) contact angle values of the prepared Zn-Ag samples.

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Synergistic Effect of Hybrid Carbon Fillers on the Electrical and Thermal Conductivity of Rubber Composites

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Carbon-based fillers are extensively used in the design of target polymer composites with desired properties by considering the intended use of the application and the environmental conditions. The most utilized fillers are carbon black (CB) and graphene nanoplatelets (GnPs), graphite, and carbon nanotubes (CNTs) [1,2] due to their exceptionally low density and high conductivity properties. Carbon-based filler materials are inclined to easily aggregate, and it is difficult for them to disperse in the polymer matrix because of the strong intrinsic van der Waals attraction force, resulting in the weakening of the thermal and electrical conductivity. To address this problem, the synergistic effect created by the combination of carbon fillers with various dimensions can improved composite conductivity [3,4]. The addition of different kinds of fillers is advantageous to cost reduction and obtaining a balanced conductivity mechanism of polymer composites. An optimum content between various constituent fillers is used to improve the thermal and electrical conductivities [5]. Hybrid carbon-based fillers consisting of graphite intercalation compounds, especially CB and GnPs, could be cost-effective solutions for improving elastomer composites exhibiting superior properties [4].

This study deals with the electrical and thermal properties of ethylene propylene diene monomer (EPDM)-based composites containing hybrid nanofillers (carbon black (CB, 20 and 50 phr) and graphene nanoplatelets (GnPs, 1-15 phr)). The nanocomposites were prepared by melt mixing in Brabender Plasticorder PLE 331 internal mixer (Brabender GmbH, Germany) with 30 ml mixing chamber at 100 °C for 7 min of total mixing time at 50 rpm of mixing speed. The samples for the measurements were vulcanized using compression molding by using a hot press (Fontijne 200, Fontijne, The Netherlands) at 160 °C without pressure for 30 sec and under pressure (5 MPa) for 10 min. Broadband dielectric spectroscopy (BDS) measurements were conducted using a Novocontrol Concept 40 instrument with an Alpha dielectric spectrometer supplied by Novocontrol Technologies GmbH (Germany). The thermal diffusivity of the samples was measured by the photothermal radiometry technique (PTR) which is a non-destructive characterization method based on the detection of an infrared (IR) signal, called the photothermal signal, emitted after a change of the sample's temperature [6].

Figure 1a shows the electrical conductivity of hybrid composites. In the case of the EPDM-based composites with a single CB, the electrical conductivity increases from 4.4×10^{-15} S/cm to 4.8×10^{-6} S/cm from 20 phr to 50 phr of CB. The enhancement in the electrical conductivity is attributed to an increase in the number of contacts between CB particles. This leads to more conductive pathways and improves electrical conductivity [7]. The formed filler-filler interaction pathway facilities electron transfer through the matrix [8]. The addition of GnPs into EPDM composites with CB has a slight effect on the electrical conductivity. It can be concluded that the synergistic effect.



Figure 1 a) Electrical conductivity and relative thermal conductivities of EPDM/CB/GnPs composites (ke: thermal conductivity composites, km: thermal conductivity matrix, σ: electrical conductivity).

of GnPs and CB on the electrical properties of samples is negligible for the EPDM-based hybrid composites with 20 phr of CB. For hybrid composites containing 50 phr CB, the change in the electrical conductivity is marginal with increasing GnP content, due to the accomplishment of the conductive network architecture of both fillers.

Figure 1b displays the relative thermal conductivity of the hybrid composite reinforced as a function of GnPs phr content. The EPDM/CB20 and EPDM/CB50 samples exhibited thermal conductivities of 0.277 and 0.298 W/mK, which are 47 % and 59 % higher than that of the pure EPDM matrix (0.19 W/mK). Despite the high k of GnPs and CB, the k of the EPDM composites increases less than anticipated. The reason is the high interfacial thermal boundary resistance (TBR) between the EPDM matrix and filler materials, which leads to lower thermal conductivity by playing a significant role in hindering phonon conduction between the matrix and the carbon fillers [9].

The combination of CB and GnPs exhibits both positive and negative effects influencing thermal conductivity. Compared with the thermal conductivity of the EPDM/CB composites, it has been determined that a negative effect occurs by adding up to 5 phr GnPs nanoplatelets to hybrid composites. This decrease in thermal conductivity is probably because the content of GnP is not sufficient to provide good dispersion and form a conductive path between GnP and CB fillers. The high TBR is due to higher phonon scattering between the GnP fillers and the EPDM matrix and thus leads to a decrease in thermal conductivity [9, 10]. The positive synergistic effect emerges at 7 phr GnPs and higher content for both EPDM/CB50/GnPs and EPDM/CB20/GnPs composites. The thermal conductivity reaches the maximum values for the EPDM/CB 50 phr/7 phr GnPs and EPDM/CB 20 phr/15 phr GnPs composites, which are 0.332 and 0.334 W/mK, respectively. The samples of EPDM/CB50 containing 7 phr GnPs and EPDM/CB20 containing 15 phr GnPs have 75 % and 76 % higher *k* than that of the EPDM matrix, respectively. Considering the composites with single GnPs, conductive networks are formed due to the contact between nanoplatelets. With the hybridization of CB with GnPs, both fillers can also act as spacers and can reduce the agglomeration of CB fillers to form a more conductive network [4].

The use of hybrid carbon fillers has promising and strategic importance for developing conductive polymer composites. Composites containing 50 phr CB and 7 phr GnP have improved electrical and thermal conductivity, and they could potentially be evaluated in cable engineering, electromagnetic radiation shielding and actuators.

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The Preparation of Zinc Biodegradable Material Coated with Electrospun PLA Fibers

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Introduction

Absorbable metals such as zinc, iron, or magnesium may serve as temporary orthopedic scaffolds [1]. Among them, zinc is considered to have an appropriate degradation rate under physiological conditions and beneficial biological properties [2]. To tailor the corrosion rate and also to enhance the biological response of such materials, polymer coatings are often used [3,4]. Polylactic acid (PLA) is a bio-based polymer that has gained significant attention in recent years due to its biological and degradation properties [5]. Electrospinning is a scalable, commonly used method for fiber production from various materials including PLA. Nanofibers due to the high surface area and specific 3D macrostructure perfectly mimic the extracellular matrix and thus may serve as a guide for cell proliferation in tissue engineering and implant surface modification. This is why biopolymers like PLA in the form of electrospun nanofibers compared to similar thin film coatings have several advantages such as higher biocompatibility, improved degradability, and drug-loading capacity when applied with implantable biomaterials, making them highly suitable for various biomedical applications.

Materials and Methods

Metallic zinc pellets were prepared by uniaxial compression via powder metallurgy from zinc powder and sintered under an inert (Ar) atmosphere to obtain the matrix material, followed by the polishing by automatic polishing machine Tegramin 40 from Struers. The efficiency and reproducibility of the polishing process and the roughness of the surface were controlled by confocal microscopy (Sensofar Plu Neox). PLA nanofibers were electrospun on the Zn tablets from the 5 wt.% solution of PLA (dissolved in a mixture of chloroform and dimethylformamide) by Nanospider NSLab200 machine by needleless electrospinning from the rod electrode at 70 kV of applied voltage. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) were employed to study the surface morphology of the prepared samples.

Results and Discussion

Sintered and polished zinc pellets (Fig. 1a,b) were coated with PLA electrospun fibers (Fig. 1c-e). The metallic surface was examined by confocal microscopy (Fig. 1a). Long, thin scratches on the entire surface of the Zn samples resulting from the sample preparation were observed. The AFM method was used to study the subgrain microstructure of zinc samples (Fig. 1b). The average surface roughness of polished zinc sample (R_a) observed from the AFM was 11.4 nm. Morphology and the distribution of the electrospun PLA fibers were observed via SEM (Fig. 1c,d). Fig. 1e shows the detail of the PLA fiber surface. No pores were formed along the electrospun fibers, regardless of their thickness which ranged from approximately 0.15 µm to 1 µm. Successful fiber deposition was carried out suggesting the preparation of the promising coating for zinc biomaterials with a potential to be further doped with additional components (e.g. antibiotics)



Figure 1 (a) Confocal microscopy micrograph and (b) AFM micrograph of the pure polished zinc. (c-e) The detailed SEM micrographs of the electrospun PLA fibers at 200×, 2 000× and 10 000× magnification, respectively.

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Electrochemical Corrosion Behaviour of Fe-Cu Biodegradable Materials in Hank's Solution

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Nowadays, biomaterials are widely used in medicine or in medical engineering. Biomaterials can consist of various materials, including polymers and metals. However, the use of metallic biomaterials for practical clinical applications including orthopaedic surgery is favoured over polymeric materials due to their better mechanical properties. The main properties of biomaterials are biocompatibility and biodegradability. In general, biocompatible materials can provide an appropriate host response under specific conditions. Biodegradable metals should be prepared from essential metallic elements (iron, zinc, copper, magnesium, e.g.) naturally occurring in the human body[1–3]. Iron is a biogenic metal found in the haemoglobin structure of human erythrocytes. The copper is an essential element which plays an irreplaceable role in several metabolic processes [4] and has antimicrobial properties. Therefore, the iron-copper material was prepared as potential degradable biomaterial and its corrosion properties was studied in Hank's solution. Four different types of samples on based on iron and copper were studied. The composition of the prepared samples was pure iron (Fe 1x, Fe 2x), and iron-copper bimetallic samples (Fe+3.3Cu 1x and Fe+3.3Cu 2x) where 1x and 2x indicates the number of the sintering cycles and 3.3 indicates the weight percentage of the used copper powder. Corrosion rate was studied via linear polarization in Hanks'solution (pH = 7.4 ± 0.2) at temperature of $37 \pm 2^{\circ}$ C (Figure 1).



Figure 1 Potentiodynamic polarization curves of Fe 1x, Fe 2x, Fe+3.3Cu 1x and Fe+3.3Cu 2x measured in Hanks' solution at 37 ± 2 °C.

Before the corrosion tests, an open circuit potential (OCP) measurement was performed. The corrosion potential of the prepared samples was calculated according to Tafel extrapolation (Table 1). The main parameter obtained was the corrosion potential, E_{corr} , which expresses the thermodynamic stability of the prepared samples. However, the determining parameter for the corrosion rate is the value of the corrosion current, j_{corr} . The value of corrosion current

(124.47 μ A), and corrosion rate (1.657 mmpy) was highest for Fe 1x sample followed by Fe+3.3Cu 2x, Fe+3.3Cu 1x and Fe 2x samples.

Sample	Ecorr [V]	jcorr [µA/cm²]	icorr [µA]	Corrosion rate [mm/year]	Polarization resistance [Ω]
Fe 1x	-0.654	124.47	124.47	1.657	697.6
Fe 2x	-0.626	83.841	83.841	1.125	749.1
Fe + 3.3 Cu 1x	-0.589	82.269	84.269	1.135	544.8
Fe + 3.3 Cu 2x	-0.595	84.789	84.789	1.138	1174.0

Table 1 Electrochemical parameters obtained from the measurements in Hanks' solution at 37 ± 2 °C.

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Porous, Large Surface Area Bimetallic Nickel-Iron Foams for Efficient Hydrogen Production via Water Splitting

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The ever-increasing requirements for clean energy are a result of rapid fossil fuel consumption and its impact on the environment [1]. This demand might be accommodated by use of hydrogen which has high energy density and near zero carbon dioxide emissions provided environmentally friendly energy source [2]. One of the outstanding methods for hydrogen production is electrochemical water splitting, however to be feasible for industrial-scale production it is necessary to develop electrocatalyst that would suficiently promote both half reactions- hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) [3].

Bimetallic nickel-iron foams were prepared by accesible method- replication of polyurethane foam. Prepared catalytic samples were subjected to phosphorization process allowing incorporation of phosphorus which is reported to improve catalytic activity.



Figure 1 SEM images and EDX analysis of NiFeP foam catalyst.

To study structure and morphology, scanning electron microscopy was used, together with EDX analysis to provide elemental composition. SEM images show visible porous structure. EDX analysis cofirmed presence of phosphorus and corroborated on nearly 1:1 ratio of nickel (45.1%) and iron (47.1%).

Electrocatalytic activity and stability were evaluated in alkaline environment (1mol.dm⁻³ KOH). Since NiFeP foams show exceptional performance as catalysts for HER as well as OER, for this testing they were used as bifunctional catalysts and deployed directly as cathode and anode to simulate electrolyser set up. Bifunctional catalytic activity was reviewed by recording polarization curves in potential range from 0.0 V-2.0 V with scan rate 1 mV.s⁻¹.



Figure 2 Polarization curves of simulated electrolyser set-up and long-term stability for NiFeP catalyst.

As it is clear from Fig 2 a), NiFeP foams electrolyser imitation setup only needed 1.67 V to achieve current density 10 mA.cm⁻² and 1.86 V to achieve 20 mA.cm⁻². Long term stability was visualized using chronopotentiometry at 10 mA.cm⁻², E-t curve is shown in Fig 2 b). Foams exhibited excellent stability during whole measurement.



Figure 3 SEM images of NiFeP foams used as cathode and anode after long-term stability measurements.
Since long term stability is key factor in real life industrial application of any catalyst, SEM images of cathode and anode (Fig. 3) were provided to show that even 22-hour use did not cause structural deterioration, in fact samples were remarkably durable and both cathode and anode remained unchanged.



Figure 4 Suggested design of electrolyser with incorporation of NiFeP foams as catalytic layers.

Considering significant activity and moreover outstanding stability in alkaline media, prepared NiFeP catalysts seem to be fitting choice for practical use directly in electrolysers, the suggested design of which is depicted in Fig. 4. Therefore, next steps shall include experimental analysis of NiFeP foams in alkaline electrolysers with emphasis on meeting aspects of applicability on industrial level.

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Morphology of Nickel-Chitosan nanoparticles

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Chitosan is a polysaccharide and derivate of chitin. From a chemical viewpoint, is a linear copolymer composed of randomly distributed $\beta(1-4)$ N-acetyl glucosamine [1]. It dissolves only under acidic conditions because of its pKa value (6.5) [2]. It is widely used in pharmaceutical and biomedical applications because of its unique properties, such as biocompatibility, biodegradability, antibacterial activity, and non-toxicity [3].

Chitosan nanoparticles (CSNPs) can be prepared by various techniques such as emulsion cross linking, reverse micellar method, linking spray drying, and ion-gelation method [3]. Ion-gelation method is based on electrostatic interactions between positive and negative charges [4]. Chitosan is a cationic polymer that can stabilize anionic substances under acidic conditions. In this case, the negative charge of polyanion - sodium tripolyphosphate (TPP) was used [5]. TPP was continuously dropped to the chitosan solution (pH = 4.8) and stirred for 30 minutes. Thereafter, two opposite charges will combine based on physical crosslinking to chitosan nanocarriers. Prepared chitosan nanoparticles were modified with solution of 0.06 M NiCl₂. 6 H₂O. Nickel solution (200 μ L) was slowly dropped into the colloidal system of chitosan nanoparticles. The prepared colloidal system was centrifugated at 10 000 rpm for 15 minutes.

Chitosan nanoparticles modified with nickel (Ni-CSNPs) have potential applications in electrochemical insulin sensors. Based on previous research, nickel or nickel oxide nanoparticles could be considered great candidates for electrochemical insulin sensors [6]. Nickel shows catalytic activity at alkaline pH by creating the specific electrocatalytic anion NiOOH⁻. The presence of NiOOH⁻ anions is essential for direct and rapid electrochemical insulin oxidation [7].

The morphology of the prepared Ni-CSNPs was studied using scanning electron microscopy (SEM) and transmission electron microscopy (TEM). Based on the obtained results, spherical structures were observed with the average size of 158 nm calculated from the TEM image (Fig. 1B). Size of CSNPs based on TEM images is shown in histogram (Fig. 1D). TEM image shows black dost, which indicates that nickel have been attached to the surface of chitosan nanoparticles. The EDX analysis (Fig. 1C) obtained from the red area of the SEM image (Fig. 1A) indicated 7.24 wt. % nickel, 29.1 wt% of carbon, 36.3 wt.% of oxygen and less than 1 wt.% of chlorine. The presence of chlorine is caused by the addition of nickel chloride to the already-formed chitosan nanoparticles. Based on results of the microscopic methods and EDX analysis, the surfaces of the chitosan nanoparticles were successfully modified by nickel.

Electrodes modified with Ni-CSNPs show potential as electrochemical sensors for direct and fast insulin oxidation. The development of insulin electrochemical sensors is necessary because of the worldwide increase in the number of people suffering from diabetes mellitus [6], [8].



Figure 1 SEM image of Ni-CSNPs at a scale of 50 μm (A). TEM image of Ni-CSNPs at scale of 0.5 μm; (B) and EDX spectrum of Ni-CSNPs (C) and histogram (D) of CSNPs size according to TEM image.

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Energy and economic simulation model of hybrid battery storage

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Introduction

This paper deals with the simulation of the intelligent control of a hybrid battery storage system based on a combination of lithium and lead-acid storage. The simulator allows to model real-world problems using mathematical and algebraic linear programming methods. The simulator can be effectively used to design the size of the battery storage. Using this simulator, a battery storage solution can be designed that is optimal with respect to its power consumption and generation profiles. The simulator is built in GAMS (General Algebraic Modeling System) environment.

GAMS

The General Algebraic Modeling System (GAMS) is used to model and analyze mixed integer, linear, and nonlinear optimization problems. It is useful for the analysis of large and complex systems.

The GAMS tool is widely used to solve various complex optimization problems of power and energy systems. It is used to develop mathematical models of power systems with concise Gebraic statements. Components (data, variables, models, sets, outputs) of any mathematical model encoded into GAMS for solving optimization problems. It provides various solvers such as LP, nonlinear programming (NLP), nonlinear mixed integer programming (MINLP) and linear mixed-integer programming (MILP). Some power quality issues such as optimal power flow and optimal load flow are solved using these GAMS solvers. In addition, optimization of fuel supply, optimization of production costs, load management optimization, planning of integrated transmission systems and modeling of optimally distributed energy systems can also be done using GAMS [1].

Language for modelling

GAMS provides its own declarative language for modelling mathematical problems. This language allows users to describe and formally define various types of mathematical problems, including linear programming (LP), nonlinear programming (NLP), integer programming (MIP), and others [2,3].

Outputs and analysis

GAMS allows users to analyze the outputs of their models, including sensitivity analysis, statistical analysis, and visualization of results.

Energy

GAMS has historically been used quite frequently in the power industry mainly to solve "unit commitment" and "grid congestion" problems

Simulation input data

Consumption profiles - 15 min average measured power. Ideal period of several months or years, size of maximum reserved and reserved capacity in kW. Size of the power generation resource in case of PV, in case of other resource its historical or planned profile at 15 min resolution. Definition of the characteristics and constraints of the model, the maximum reserved capacity - the maximum power that can be supplied to the customer from the distribution system, reserved capacity - the maximum capacity that can be supplied to a customer from the distribution system and is specified in the contract with the distribution company, charges for reserved capacity, distribution charges.

Charge and discharge efficiency - by default this value is approximated to 92%. However, this is a complicated function dependent on a number of parameters (temperature, charge/discharge rate).

Number of cycles allowed in one year - this figure varies based on the characteristics of the specific battery, the size of the power source - this can be a cogeneration unit, a photovoltaic plant or a hydroelectric plant.

Maximum depth of discharge of the battery - this value also depends on the specific battery, the specific capacity, capacity and price of the battery.

The possibility to run the calculation in a more complex mathematical mode, which must be activated if the purchase price of the energy is at any time higher than the purchase price including distribution charges. This can happen especially if a fixed purchase price is agreed and the purchase is linked to spot prices.

Consumption profiles from the customer, electricity price for the last annual period

The output of the photovoltaic panels - with respect to the location for one year because more electricity is produced in the Bratislava area than e.g. in Poprad

The following table shows the input menu of the simulation program.

Calculator input	Value
Reserved cacapcity RK (kW)	165
Maximal reserved cacapcity MRK (kW)	165
Cost of RK per kW per year (Eur)	55
Distribution fee per kWh (Eur)	0,07
Charging efficiency	0,95
Discharging efficiency	0,95
Number of annually allowed cycles	800
Solar size in kWp	0,83
Battery life (years)	10
DOD	0,9
Precision of imbalance prediction (%)	85
Use of MIP? (1-YES, 0-NO)	1
Do you have spec. battery size? (1-YES, 0-NO)	1
Inverter power (kW)*	100
Battery capacity (kWh)	200
Do you have spec. battery price? (1-YES, 0-NO)	1
Battery price (Eur)	104 000

Table 1 Example of input data.

The calculation process

The simulator optimizes the yield of battery storage on the reduction of the facility's reserved capacity while price arrbitration on the electricity purchase and power purchase side. The objective function looks like this:

 $Z = Power_cost + storage_cost + sum(t, energy_cost(t)) - sum(t, energy_income(t))$

(1)

where,

Power_cost - price for reserved capacity in EUR

Storage_cost - battery down payment in EUR

Energy_cost - price for the purchase of electricity including distribution charges in EUR

Energy_income - revenue from the sale of electricity in EUR

All boundary conditions are defined by additional equations, which are translated by the GAMS solver. The GAMS MIP solver uses various techniques to speed up the solution process, including:

- Heuristics to find good initial estimates
- Branching strategies to branch the solution tree
- Auxiliary methods to solve subproblems

In this more complex case, the NLP model is used or Nonlinear programming solver is a software tool for solving nonlinear programming problems. The NLP solver is based on the Newton-Raphson method. This method works by successively approximating the objective function or constraints to a linear function. GAMS NLP solver uses various techniques to speed up the solving process such as:

- Heuristics to find good initial estimates
- Linear optimization
- Global methods

Simulation results

The following section shows the simulation results of a hybrid storage system with a lithium and lead-acid battery. Table 2 shows the calculated parameters of the battery hybrid storage. The simulation program calculates the summed energy from both types of storage, i.e. from both lead acid and lithium battery.

Calculator output	Value
Battery in kW	77.55411
Battery in kWh	182.11214
Battery price in EUR	101214
Solar PV size x100kWp	1.00000
Charging (%):	0.95000
Discharging (%):	0.95000
Maximal possible peak load (MRK)	250.00000
Peak load charged (reserved capacity - RK)	65.00000
Theoretical peak load without battery	87.98400
New peak load with battery	65.00000
Peak load charges without battery with original RK in EUR:	4225.00000
Peak load charges for the whole calculated time interval in EUR:	4225.00000
Consumed energy w/o battery (kWh)	312604.39701
Consumed energy w battery (kWh)	326762.76913
Back feeded solar energy w/o battery (kWh)	13059.28048
Back feeded total energy w battery (kWh)	18246.23344
Price arbitrage income (EUR):	798
Theoretical_imbalance income (EUR)	16370

Table 2 Output data from simulation.

The following figure shows the charging and discharging pattern of the hybrid storage as a function of load, electricity prices and time of day.



Figure 1 Output waveforms of hybrid energy storage model.

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Prediction models for renewable energy sources with hybrid battery storage systems

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Introduction

This paper describes a method for predicting electricity consumption in a household or business and electricity generation from renewable energy sources. Prediction models currently form the basis for Energy Management Systems (EMS) level control systems, which are used for the application of renewable energy sources in cooperation with battery storage in distribution networks. In particular, the need for accurate prediction models in the field of energy storage should be highlighted, since an accurate prediction model of the behavior of electricity consumption and generation is the basis for the efficient use of a battery storage system throughout its lifetime. Moreover, in the application of hybrid lithium-lead energy storage, the prediction models need to be modified in accordance with the characteristics of the storage system.

Prediction of electricity consumption and generation from time series

It is possible to find a pattern in the measured electricity consumption data for a household or a manufacturing company - e.g. on a certain day of the week or time of the day there is an abnormal consumption of electricity, which is due to the fact that people in households have developed certain habits for electricity consumption. In the case of production companies, this is a phenomenon that is mainly caused by the rotation of shifts, the process or technology of production itself and the way the company is managed. On the basis of these consumption patterns, it is possible to predict with some accuracy the energy consumption of both households and manufacturing companies.

In the case of the prediction of electricity production from renewable energy sources (RES), it is mainly a matter of predicting the weather, (sunshine, wind, clouds), or the flow of water flows. Given that these are natural phenomena, the above prediction is rather difficult and complex. In the case of a photovoltaic source, the most appropriate way is to predict the maximum amount of electricity produced in a given location where the source is located, in 1 day.

Predictive models in time series

The most common prediction models used in the time series domain include:

- 1. ARIMA (Autoregressive-integrated moving average)
- 2. Vanilla LSTM architecture (Long-short term memory)
- 3. Stacked LSTM architecture
- 4. Bidirectional LSTM architecture
- 5. LSTM encoder decoder architecture
- 6. CNN1D BI-LSTM encoder decoder

In the case of the use of prediction models for the prediction of electricity consumption and generation, the most suitable model was found to be model 6, namely CNN1D - BI-LSTM encoder-decoder

CNN1D - BI-LSTM encoder - decoder model

The model is based on encoder - decoder architecture.

Encoder

It receives the elements of the input sequence one by one at every time step, learns the information from the input, and propagates it for further processes.

Feature vector

This is an internal and intermediate state which is responsible for holding the sequential information of the input which is helpful for the decoder to make accurate predictions.

Decoder

The decoder part of the architecture can be anLSTM model which helps the model to make predictions by decoding the outcome by the encoder again in a sequential format.

The following figure shows the Conv1D bidirectional LSTM encoder-decoder model [1,2].



Figure 1 Architecture of encoder – decoder.

Learning a CNN1D -BI-LSTM encoder-decoder prediction model

The resulting neural network has 2x1D convolutional layers, a Maxpool layer, a Bi-LSTM layer, and 2 linear layers resulting in 8.9 million adjustable parameter -weight coefficients. The model operates on data at 10 minute intervals and goes 1 day backwards in time (144 ten minute intervals) [2].

Prediction models on real applications

As part of the prediction model solution, the prediction was performed on an existing customer site where the electricity consumption was predicted as well as the electricity generation consumption on an existing PV source. The electricity consumption prediction model achieved the following parameters:

- Trained on over a year of real data from net load metering of site consumption in kW.
- The model is re-trained every two weeks on the latest data.
- A random forest regression method is used to train the model.
- Real consumption, periodicity over the year, week, and day, and meteorological variables such as temperature, precipitation, and relative humidity enter the model as features.
- Predictions are generated in windows every 15 minutes for 24 hours ahead (ID) and once a day at 10:30 a.m. for 36 hours ahead (DA).

Prediction model for electricity generation from photovoltaic source:

- Trained on more than a year of real data from measuring the net load of on-site generation from PV in kW.
- Re-train the model every two weeks on the latest data.
- A random forest regression method is used to train the model.

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Periodicity during the year, and day, and meteorological variables such as temperature, precipitation, relative humidity, atmospheric pressure, solar radiation, sunrise and sunset, cloud cover, and snow depth enter the model as features.

- Forecasts are generated in windows every 15 minutes for 24 hours ahead (ID) and once a day at 10:30 a.m. for 36 hours ahead (DA).

The following figures show the prediction waveforms and how they compare to the real data. In the case of meteorological data, these are downloaded from the supplier Solargis.



Figure 2 DA prediction of STM Dubnica consumption vs. reality (green - prediction, black - real).



Figure 3 ID consumption prediction STM Dubnica vs. reality (blue - prediction, black - real).



Figure 4 DA prediction of STM Dubnica FTV source production vs. reality (green - prediction, black - real).



Figure 5 ID consumption prediction STM Dubnica vs. reality (blue - prediction, black - real).

Conclusion

In the results presented above, the model showed very good predictive performance (errors in %): Consumption prediction DA: Mean Sq. Error = 11.932 Moving Avg. Error = 6.675 Median Abs. Error = 1.16 Consumption prediction ID: Mean Sq. Error = 10.603 Moving Avg. Error = 5.391 Median Abs. Error = 0.956 Production prediction DA: Mean Sq. Error = 7,845 Moving Avg. Error = 3.178 Median Absolute Error = 0.207 Production Prediction ID: Mean Sq. Error = 7.486 Moving Avg. Error = 3.173 Median Absolute Error = 0.216

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Preparation and characterization of Quantum Dots for Perovskite Solar Cells Application

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Perovskite quantum dots (PQDs) are a type of semiconductor nanocrystal that has attracted significant interest in recent years due to their unique properties and potential applications. PQDs have a tunable bandgap that can be controlled by the size and composition of the nanocrystals. This makes them suitable for a variety of applications, including light-emitting diodes (LEDs), solar cells, and bioimaging. PQDs have the potential to significantly improve the performance of perovskite solar cells [1, 2]. In particular, they can help to improve the efficiency of the solar cells by: expanding the range of light that the cells can absorb, passivating defects on the surface of the bulk perovskite material and promoting electron and hole transport. On the other hand, poor stability of PQDs still limits their use in optoelectronic devices.

In this contribution, we describe the preparation and effect of post-treatment procedure (purification, passivation, and ligand exchange) on the formation and stability of halide perovskite quantum dots. In addition, photophysical characterization by UV-VIS, photoluminescence spectroscopy (PL), time-resolved photoluminescence (TRPL), XPS (X-ray photoelectron spectroscopy) and TEM were studied. CsPbBr₃ QDs were synthesized by the conventional hot-injection method using cesium oleate, PbBr₂ and oleic acid (OA)/oleylamine (OAm) as ligands [3]. Purification and post-synthetic treatment were studied to improve the power conversion efficiency of perovskite solar cells. It is well-known, that in colloidal QDs, the surface defects arising from the removal of ligands and surface halides during purification steps, so the precise purification and surface passivation with appropriate ligand is important for high photoluminescence quantum yield. It was showed, that purification procedure – number of centrifugation steps, rpm, ratio of solvent and antisolvent, addition of small amount of ligand during centrifugation step etc, affected the stability of QDs colloidal solution. Moreover, the effect of various organic ligands (hexadecyltrimethylammonium bromide (CTAB), benzyltriethylammonium chloride (BTEAC) and didodecyldimethylammonium bromide (DDAB)) on long-term stability and efficiency of perovskite QDs were examined. According to SEM image (Fig.1), the prepared CsPbBr₃ QDs present relatively monodisperse cubic structure with average size about 10-15 nm.



Figure 1 TEM images of cubic-shaped CsPbBr3 quantum dots.

XPS analysis of CsPbBr₃ QDs shows Cs 3d peaks at 724 and 738 eV, Pb 4f peaks at 138 and 143 eV, and Br 3d peaks at 68 eV. The above experimental results confirmed the successful synthesis of the CsPbBr₃ QDs. From the series of selected ligands, perovskite QDs passivated with didodecyldimethylammonium bromide (DDAB) show most significant increase in PL along with higher stability during UV irradiation (Fig. 2). The DDA cation had long been known as efficient surfactant for preparation of hydrophobic monolayers and their charged state is pH independent (unlike OAm).



Figure 2 UV spectra of CsPbBr₃ QDs passivated with various ligands a) DDAB, b) OA/OAm.

Photoluminescence of CsPbBr₃ QDs with the surfactant OA/OAm and DDAB for solar cell applications was studied on ITO substrate. For this purpose, ITO/PQDs samples as well as ITO/PQDs/MAPI perovskite samples were prepared and the effect of surfactant and plasma treatment were analysed (Fig. 3). All depositions were performed by spin coating. O₃ plasma treatment was necessary to enable the deposition of a perovskite layer over the PQDs layer. The effect of O₃ plasma treatment of the deposited PQDs was proven with QDs - DDAB ligand and resulted in blue shift of the PQDs peak and non-monotonous change of the amplitude of the surface states peak. For OA/OAm ligand O₃ exposition did not cause any shift of the PQDs peak.

Obtained results show that photoluminescence properties of halide PQDs are influenced by post-treatment procedure, mainly by purification technique as well as subsequent ligand exchange reaction. Surface passivation by various ligands were studied in detail. Furthermore, photophysical properties of PQDs with the surfactant OA/OAm and DDAB for solar cell applications were studied on ITO substrate.



Figure 3 PL spectra of a) PQD (DDAB)+MAPI perovskite double layer and b) PQDs passivated with DDAB and OA/OAm ligands upon plasma treatment.

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Therapy of Extensive Chronic Skin Defects after a Traumatic Injury due to Microbial Contamination using a Surface Implant Made of a Biocompatible Polycaprolactone –A

Pilot Case Study

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This case study describes the use of a biodegradable polymer material, polycaprolactone (PCL), in the therapy of extensive contaminated skin defects caused by a traumatic injury. It relates to two different patients that exhibited signs of an extensive traumatic injury in the distal part of the pelvic limb, spreading from the metatarsal region to the heel joint. The surface of the wound was mechanically cleared off contaminants. Samples were collected for microbial culture tests with an antibiogram. Bacteriological cultivation tests confirmed the presence of methicillin-resistant Staphylococcus aureus (MRSA) and Staphylococcus haemolyticus. The antibiotic therapy included a combination of amoxicillin and clavulanic acid (Synulox, Zoetis, Czech Republic) in dose 20 mg/ kg two times per day for 28 days and enrofloxacinum (Enroxil, Krka, Slovenia) in dose 7 mg/ kg one time per day for 21 days. The wound was rinsed with a lavage solution Betadine 0,5% (Braunol, B. Braun, Germany), and the edges of the skin defects were refreshed by excochleation with surgical instruments. The external treatment of the wound was carried out using a antibiotic ointments - zinc complex bacitracine and neomycini sulphate (Baneocin, Sandoz GmbH, Austria). The implantation of the PCL scaffold was indicated after surface contaminants, eschars, and desiccated parts were cleaned off the wound. The PCL implant was attached directly with suture material polydioxanone (Polydox 2 EP, Chirana, Czech Republic) to the surface of the damaged structures. After the procedure, the wound was covered with a surface dressing. As early as in the first week after the application of the PCL, the formation of a new granulation bed and epithelisation of the wound edges were observed. Over the following weeks, defect edges exhibited gradual contraction; this was accompanied by gradual detachment of the temporary implant. In both patients, the average healing time after the scaffold implantation was 68 days of the therapy initiation. The implantation of a scaffold, used as the external dressing, represents a appropriate alternative application for a chronic defect, where it was impossible to apply a skin flap or close the defect directly. Such an implantation structure, together with tissue regeneration, facilitated achieving a similar effect and accelerated the healing of the extensive skin defect.

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Effective Young's Modulus of Fe-Based Cellular Material

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Introduction

One of the problems associated with using metal orthopaedic implants is the "stress shielding" by the implant. The discrepancy between the Young's modulus of bone (10–30GPa) and compact metal materials (110–230GPa) causes most of the load acting on the bone-implant system to be borne by the implant. This leads to a gradual thinning of the unloaded bone tissue, which can eventually result in damage to this tissue or the release of the implant [1,2]. One way to address these issues is to reduce the modulus of elasticity of the used metal materials by introducing pores. A promising alternative is to manufacture implants for orthopaedic surgery from metallic cellular materials [3].

Direct measurement of the elastic properties of quasi-homogeneous samples prepared solely from cellular materials is usually complicated and sometimes even impossible. When using static methods, the detectable response of the sample is commonly accompanied by plastic deformation of the material; when using dynamic methods, the cellular sample acts as an oscillator with a very low quality factor (Q-factor) [4]. To avoid these complications, we must use more sophisticated methods and approaches.

In this contribution, we describe the determination of the effective modulus of a cellular material using the flexural vibrations of a three-layer sample, the middle layer of which is made up of the tested material. When the rod performs flexural vibrations, the maximum deformation occurs near the surfaces of the rod that are perpendicular to the plane of bending. Near the centre of the rod, the deformation is much smaller. Hence, if the cellular material is placed in the centre of the rod, it should be protected from plastic deformation. Moreover, the use of compact surface layers also eliminates the influence of other properties of cellular solids that are unsuitable for precise measurement (such as high damping of vibrations, low moment of inertia, etc.).

Preparation of samples and measurement of their properties

Fe-based cellular materials were prepared by the following procedure. Hollow iron oxide particles, which are a waste product from the industrial pickling of wires, served as the starting material (precursor). The precursors were reduced to metallic iron in a $90\%N_2 - 10\%H_2$ atmosphere at a temperature of 950°C for 180 minutes.

The powder composed of such hollow iron particles and a traditional Fe powder consisting of solid particles (Höganäs, ASC 100.29) were used to prepare sandwich samples. It was a three-layer structure, where the inner layer (core) was made of cellular material formed from hollow spherical iron particles of various sizes. Four fractions of hollow balls with diameters of 0.7-0.8 mm, 0.8-0.9 mm, 1.0-1.3 mm and 1.4-1.7 mm were used. The edge layers were made of traditional Fe powders consisting of solid particles. The samples were pressed at a pressure of 100 MPa and sintered for 60 minutes at a temperature of 1120°C in a hydrogen atmosphere. To measure the elastic response of such distinctly anisotropic samples and subsequently determine the properties of the materials from which they were created, we used a dynamic resonance method [5]. Geometric characteristics of individual layers were determined by metallographic methods.

Theory

The dimensions of the cells of the cellular material are much smaller than the dimensions of individual layers or the entire sample. In analyzing the macroscopic response of the sample, the cellular material can therefore be considered as an effectively homogeneous continuous medium and the corresponding mathematical apparatus can be used. A

modification of the classical Bernoulli-Euler theory of vibration for long thin rods made it possible to express the dependence of the frequency of bending vibrations of layered samples on the elastic and geometric properties of individual layers and to determine the relationship between these frequencies and the bending stiffness of rod B_{\parallel} and B_{\perp} for bending in the plane of layers and perpendicular to this plane. The bending stiffness - to - area moment of inertia of the rod cross section ratio is termed as the apparent modulus of elasticity E_{\parallel} or E_{\perp} . For symmetrical three-layer rods, these findings lead to expressions [6]:

$$E_{||} = E_p + (E_s - E_p)w_s \tag{1a}$$

$$E_{\perp} = E_p + \left(E_s - E_p\right) w_s^3 \tag{1b}$$

 E_p is the Young's modulus of the surface layer material, E_s is the Young's modulus of the middle layer material, and w_s is the volume fraction of the middle layer. By measuring E_{\parallel} and E_{\perp} and adjusting the equations, the modulus of elasticity of the middle layer material E_s can be expressed either as:

$$E_{S} = E_{||} + \frac{E_{||} - E_{\perp}}{w_{S}(1 + w_{S})'},$$
(2a)

when the volume fraction of the middle layer, w_s , is known, or as:

$$E_{S} = E_{p} + sign(E_{||} - E_{\perp}) \frac{E_{||} - E_{p}}{E_{\perp} - E_{p}} \sqrt{(E_{||} - E_{p})(E_{\perp} - E_{p})},$$
(2b)

when the Young's modulus of the surface layer material is known.

Discussion

Since the Young's modulus of the surface layer material is higher than the modulus of elasticity of the core, the measured apparent moduli E_{\perp} were higher than E_{\parallel} for all three-layer samples with a cellular core, which is consistent with the theory [5]. Theseapparent moduli were measured for samples with varying thicknesses of the middle layer, i.e., with different volume fractions of the middle layer, w_s . Subsequently, the modulus of the material of the middle layer, E_s , was determined using equation (2a). The obtained values are in Table 1.

 Table 1 Effective Young's modulus of cellular materials made from hollow iron particles of various diameters.

Diameter of the used hollow particles [mm]	E_s [GPa]
0.7 - 0.8	25.6 ± 0.8
0.8 – 0.9	23.1 ± 0.6
1.0 – 1.3	18.7 ± 1.1
1.4 – 1.7	16.9 ± 1.2

Conclusion

In this contribution, we have demonstrated that a three-layer sample with a core made of cellular material and surface layers made of traditional iron powders can be used for the indirect measurement of the modulus of elasticity of the cellular material, which is usually very difficult to measure directly. The study of the influence of various microstructure parameters on the moduli of elasticity of cellular materials continues.

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Novel Sulfur-based cathode materials used in Li-S batteries

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Introduction

Lithium-sulfur batteries (LSB) have recently become one of the most promising types in the new era of battery technology. Li-S batteries have advantages of low cost and high safety. Also, they are environmentally friendly, which is important for the development of the renewable clean energy sources. The practical applications can be found in portable devices, electric vehicles, and medical equipment.

Lithium–sulfur batteries (lithium metal and sulfur are the anode and cathode, respectively) are one of the most valuable secondary batteries because of their high theoretical energy density ($\sim 2600 \text{ Wh kg}^{-1}$).

Sulfur naturally forms ring shaped molecules of 8 sulfur atoms, and the reaction with lithium can be therefore written as:

 $16\text{Li} + \text{S}_8 \rightarrow 8\text{Li}_2\text{S}$

However, the intrinsic conductivity of sulfur cathode materials is poor, and the lithium polysulfide formed during lithiation dissolves easily. Also, the volumetric expansion during charging and discharging affects the LSB electrochemical performance, e.g. the rate performance, cycle life, and coulombic efficiency. In attempts to improve the LSB electrochemical performance, various sulfur composites have been prepared by using carbon materials, metallic oxides, and conductive polymers, and also various composite cathode materials for applications [1].

LSB advantages and hindrances

Although the implementation of sulphur seem to be promising in a number of applications ranging from portable electronics to electric vehicles, there are also some limitations. Li/S are the low operating voltage of around 2.15 V during discharge, there is the isolating property of both sulfur and Li₂S, the volume change of approximately 79 % based on full transformation of sulfur to Li₂S, safety problems can occur due to the lithium metal anode and a polysulfide shuttle mechanism. The electrical insulating nature of sulfur and the high solubility of lithium polysulfides as intermediate products generated during the discharge process in traditional organic electrolyte have resulted in very poor cycle life [2]. From the recent research many attempts for improvement have been tried. A storage system based on lithium/sulfur might be the most promising candidate for the next generation lithium batteries. Li/S battery has a theoretical capacity of 1672 mAh/g and a theoretical energy density of 2600 Wh/kg, which is about five times higher than that of the LiCoO₂/graphite and LiFePO₄/C systems [3]. Sulphur is abundant in nature, cheap and environmental friendly. Promising results have been achieved by modifying the cathode in the Li/S battery with carbon or polymer coating. Also by evenly distributing sulphur in the composite cathode material consisting of conductive matrix, enhancing the cyclability and performance of the composite cathode, and stabilizing the retention of polysulfides. With the use of silicon instead of metal lithium anodesulfur and solid polymer electrolyte can the sulphur based cathode batteries be better applied also in the commercial world.

(1)



Figure 1 High-resolution SEM images of Li-S cathode material surface.



Figure 2 Measurement of cylic voltametry of Li-S cathode.

Conclusion

New scientific advances in understanding the reactions occurring in the cells, and most importantly the use of new materials are key to overcoming all mentioned drawbacks. With the increasing research in the past years and the development of novel nanocomposite materials with smart engineering design, electrolytes and cell configurations will positively impact the research and applications of LSB.

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Determination of Texture Characteristics of Layered Materials.

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Porous substances occur in many areas of chemical technology, most often as catalysts, membranes, adsorbents. Layered materials can also be considered porous materials and therefore the knowledge of textural properties is one of the important characteristics of these materials. One of the large groups of layered materials are clays. Clay materials are divided into several groups, which differ in their structure and also have different textural properties. Therefore, the knowledge of the basic textural characteristics of these substances, such as the shape, width, pores volume and classification, porosity, specific surface area (S_{BET}), true and apparent density, as well as the appropriate methods for their determination are necessary for the processing and use of clay materials. The methods for examining porous materials vary according to the size of the pores. The adsorption methods are preferably used for micro and mesoporous materials, while the Hg-porosimetry for macroporous materials. The methods of studying the structure of solids are mostly based on adsorption phenomenon. The goal of all adsorption theories is to predict the amount of adsorbate needed to covering the surface with the monolayer of gas molecules and to determine the area required to the adsorption of one molecule of adsorbate. From the number of theories the "BET" isotherm is currently used to the S_{BET} calculation. As the example of clays characterization, the determination of structural characteristics of kaolinite, bentonite, montmorillonite and rehydroxylated kaolinites using the adsorption methods. The adsorption isotherms were measured on an ASAP 2020 and 3Flex surface analysers (Micromeritics, Norcross, GA, USA) using the gas sorption technique (N₂ at 77 K). These adsorption isotherms were fitted according the Brunauer-Emmett-Teller (S_{BET}) method and t-plot method (St-plot) for specific surface area, the micropore volume by the t-plot method and the poresize distribution by the Barrett-Joyner-Halenda (BJH) method and Density Functional Theory (DFT) method. In addition, the scanning adsorption isotherms of all the mentioned samples were measured.



Figure 1 Scanning adsorption-desorption isotherms of Bentonite.

Scanning isotherms provide important information about the pore network geometry, including its connectivity and pore size distribution, which cannot be revealed from the main adsorption and desorption isotherms (Figure 1). In this study, results concerning complex clay textural analysis were obtained. In conclusion, although there is a wide variety

of methods applicable to the clay texture characterization, each method has the limitations, which must be taken into account when evaluating the results.

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Synthesis of novel polyimides and their applicability in the preparation of membranes for gas separation

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Introduction

Biogas is the gas mixture produced by the anaerobic decomposition of organic matter with the majority of CH_4 and CO_2 . Biomethane, which is a possible substitute for natural gas, can be obtained by removing CO_2 from biogas. Membrane separation of CO_2 from biogas is a rapidly developing process and offers a cheaper and more eco-friendly alternative to water/organic scrubbing in biomethane preparation. The crucial component of the membrane separation unit is the membrane module containing the separation membrane. The separation efficiency of the membrane influences the economy of the separation process. The development of new effective membrane materials has been the focus of scientific interest over the past decades. Polyimides are the most commonly used membrane material for CO_2 separation due to their low initial cost and high thermal, mechanical, and chemical resistance. Current research of polyimide-based membranes focuses mainly on improving separation properties by increasing CO_2 permeability and CO_2/CH_4 selectivity. Developing new polyimide materials is one option. This work focuses on the synthesis of novel polyimides and testing their applicability in membrane gas separation.

Experimental

The polyimide synthesis was realized using a classic two-step polymerization method. In the first step, the diamine and the dianhydride(s) were reacted in a molar ratio 1:1 in N-methylpyrrolidone under a nitrogen atmosphere to obtain the polyamic acid solution (PAA). The second step was the imidization of the PAA through thermal annealing. The different temperatures in the range from 210 °C to 250 °C were tested.

In this work, the 18 different polyimides based on dianhydrides: 4,4'-(hexafluorisopropylidene)diphthalic anhydride (6FDA), 4,4'-carbonyldiphthalic anhydride (BTDA) and 3,3',4,4'-Biphenyltetracarboxylic dianhydride (BPDA); diamines: 2,2-bis(3-amino-4-hydroxyphenyl)hexafluoropropane (bisAPAF), 4,4'-(1,4-Phenylenediisopropylidene) bisaniline (bisP), 2,4,6-trimethyl-m-phenyldiamine (DAM), 3,5-diaminobenzoic acid (DABA) and 4,4'-Oxybis(3-(trifluoromethyl)aniline) (oxybis) were synthesized.

The solution casting method has been applied for membrane preparation. Two different approaches were used. In the first case, the PAA solution as casting solution was used, and the imidization was carried out with a prepared membrane. In the second one, the PAA was firstly precipitated in the water to produce the flakes which were imidized. After imidization, the flakes were dissolved to prepare the casting solution.

For all prepared membranes that showed sufficient resistance to overpressure of 8 bar were determined separation characteristics by the Wicke-Kallenbach method in a laboratory-scale module using a pressure-rise permeation apparatus. The set-up scheme is presented elsewhere [1]. Separation measurements were performed for the binary CO₂/CH₄ input mixture with different composition (molar ratio CO₂: CH₄ 1:3, 1:1, 3:1) and overpressure on the retentate side (2, 4, 6 a 8 bar). Helium was used as sweep gas. The outlet mixture composition was analyzed using GC equipped with methanizer and FID detector

The degree of imidization was determined by infrared spectroscopy (FTIR), thermal stability was determined by thermogravimetric analysis (TGA), and membrane surface morphology was observed by scanning electron microscopy (SEM).

Results and discussion

The optimization of the whole membrane preparation procedure as well as testing different methods for the imidization step of polyimide synthesis (thermal, chemical and azeotropic imidization) were carried out. It has been found that the method of imidization and the synthesis conditions have an impact on the solubility of polyimides and consequently on the preparation of membranes and their separation properties.

Effect of used imidization method.

Chemical imidization, representing one of the possibilities of converting PAA to polyimide, was used in the imidization of five polyimides (6FDA-bisAPAF, TDA-bisAPAF, BPDA-bisAPAF, BPDA-bisP and BPDA-DAM), but only polyimides based on the bisAPAF diamine were successfully imidized .During chemical imidization by acetic anhydride and pyridine the modification of the polyimide chain occurs. An acetate chain is attached to the place of the hydroxyl groups that diamine bisAPAF contains. Chemically imidized polyimides were soluble in solvents suitable for the preparation of membranes by solution casting (chloroform and THF), but the membrane could only be prepared from polyimide 6FDA-bisAPAF.

The azeotropic imidization method was successful only in the case of polyimide 6FDA-bisAPAF, the polyimide was soluble in suitable solvents, but the membrane could not be prepared.

The third tested thermal imidization method was successfully applied to all prepared polyimides. It was found that the polyimides 6FDA-bisAPAF, 6FDA-DABA, BTDA-bisAPAF and BPDA-bisAPAF can be thermally imidized even at a temperature of 190 °C, which is a lower temperature than commonly reported in the available literature. This finding was important for the polyimides 6FDA-bisAPAF and 6FDA-DABA, which were soluble in suitable solvents for membrane preparation only if their imidization temperature was lowered. However, the membranes prepared from these materials were too fragile and it was not possible to measure their separation properties. For the remaining polyimides, it was necessary to use an imidization temperature of 250 °C. Polyimide 6FDA-oxybis also belongs to this group, from which it was possible to prepare a membrane by the casting method. The solubility of prepared polyimides is summarized in figure 1.



Figure 1 Solubility of prepared polyimides.

Separation efficiency of membranes

The list of successfully prepared membranes including the method of preparation is summarized in table 1.

Membrane ID	Polyimide	Type of imidization	Method of membrane preparation
M1	6FDA-bisAPAF	Thermal imidization	MPAA, MPI
M2		Chemical imidization	MPI
M3	6FDA-oxybis	Thermal imidization	MPI
M4	BTDA-bisAPAF	Thermal imidization	MPAA
M5	BTDA-bisP	Thermal imidization	MPAA
M6	BTDA-oxybis	Thermal imidization	MPAA
M7	BPDA-bisP	Thermal imidization	MPAA
M8	BPDA-DABA	Thermal imidization	MPAA
M9	BPDA-oxybis	Thermal imidization	MPAA

 Table 1 List of prepared membranes (MPAA –solution casting from PAA, MPI – solution casting from dissolved polyimide].

The membranes prepared from polyimide based on 6FDA dianhydride show higher CO_2 permeability values than membranes from polyimides based on BTDA and BPDA, as they contain bulky perfluorinated groups $-CF_3$, but on the other hand, they show several times lower CO_2/CH_4 selectivity values than membranes from polyimides based on BTDA and BPDA. It can be expected that the arrangement of polymer chains based on 6FDA, due to the presence of a pair of $-CF_3$ groups bound to one carbon, will not be as tight in the membrane as in the case of polymers with BTDA and BPDA, which will lead to a larger internal free volume and thus greater permeability of the components. An increase in the internal free volume therefore has a negative consequence in reducing selectivity, as the transport of the second unwanted component (CH₄) also increases at the same time. The example of comparison of membrane separation efficiency for feed mixture CO_2/CH_4 1:1 is demonstrated on figure 2.

For membranes based on BTDA and BPDA, it would be appropriate to consider the preparation of mixed matrix membranes (MMM) that would allow an increase in CO_2 permeability by adding a suitable selective membrane filler based on MOF, e.g. ZIF-8 or UiO-66.



Figure 2 Comparison of separation efficiency of membranes based on diamine oxybis.

The figure 3 compares the separation properties of the polyimide membranes prepared in this work (the composition of the input mixture CO_2 : $CH_4 = 1:1$ and a pressure of 2 bar). As can be seen at first glance, none of the prepared membranes exceeded the upper limit of the Robeson diagram [2, 3], however, they are around the average values and exceed in their properties some membranes that are currently used in industry. Promising candidates for further processing are the membranes M2 (chemically imidized 6FDA-bisAPAF) and M9 (BPDA-oxybis), both showing relatively good CO_2/CH_4 selectivity values. Membrane M2 achieved a CO_2 permeability of 23.26 Barrer and a CO_2/CH_4 selectivity of 31.32. The M9 membrane achieved a CO_2 permeability of 5.89 Barrer and a CO_2/CH_4 selectivity of 59.91. Another remarkable membrane was the M6 membrane (BTDA-oxybis), which at a pressure of 2 bar and excess methane presents the CO_2/CH_4 selectivity up to 113.76 together with CO_2 permeability of 3.77 Barrer. CO_2 permeability values could be further increased by adding a membrane filler as already mentioned above.



Figure 3 Robeson diagram with polyimide membranes prepared in this work.

Conclusions

In this work the synthesis procedures of novel polyimides were optimized and these polymers were successfully used for membrane preparation. The membranes separation efficiency was evaluated in the binary CO₂/CH₄ mixture under different conditions. The membranes showed average separation efficiency. But still there is the possibility to increase CO₂ permeability by preparation of MMMs. Also the other alternative would be the preparation of a membrane from 6FDA-BTDA-oxybis or 6FDA-BPDA-oxybis polyimides, since polyimide materials based on 6FDA dianhydride show relatively high CO₂ permeability values.

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XPS Study of Solid Electrolyte Interphase Layer in Silicon-Graphite Anodes

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Li-ion batteries are one of the most cost-effective solutions for energy storage and dominate the market nowadays for high-energy demanding applications such as electric vehicles (EVs) and plug-in hybrid electric vehicles (PHEVs).

The operation of Li-ion batteries is based on the intercalation of Li-ions into the layered materials as graphite during charging and then Li-ions are stored in the layered oxide cathode materials during discharging. Present Li-ion batteries use graphite anodes that exhibit excellent cycling performance. In order to increase relatively low discharge capacity (372 mA h g⁻¹ for LiC₆) of graphite anodes different alloying-type anode materials are being studied. Silicon is one of the most promising candidates for powering future batteries due to its high theoretical specific capacity (4200 mA h g⁻¹)[1]. Another advantage of silicon is its low-cost and that it is environmentally friendly. Disadvantage of silicon-based anodes are low electrical conductivity (~10⁻³ S cm⁻¹) and Li diffusion coefficient (10⁻¹⁴- 10⁻¹³ cm²s⁻¹), huge volume expansion (ΔV ~300%) during lithiation/delithiation and unstable solid-electrolyte-interphase (SEI) layer which results in capacity fade and degradation of the Si-based anodes [2]. To overcome the negative aspects of the uncontrolled growth of the SEI, the strategies as the use of electrolyte additives and the application of protective surface coating by ZnO layer.

To understand the evolution of the surface chemistry of the Si/Gr electrodes, XPS analysis was carried out before and after electrochemical measurements for the Si/Gr electrodes (pristine and 20 ALD cycles ZnO coated electrodes. We have performed also Depth profile XPS analysis to evaluate the structure of SEI layer. The electrodes after electrochemical cycling showed the presence of LiPF₆/Li_xPO_yF_z (from the electrolyte 1 M LiPF₆ in EC: DMC) on the surface which is confirmed by the F1s peak at 687.4 eV, P2p peak at 137.2 eV and approximately matching in both cases the PF₆⁻ stoichiometry F1s(LiPF₆)/P2p(LiPF₆) = 5.5–5.7. The higher amount of Li₂CO₃ and lower signal of silicon indicate a thicker SEI layer in the case of an unprotected pristine electrode. The ZnO protected Si/Gr electrode minimized the amount of carbonate formation during cell cycling. The presence of a stable SEI layer was confirmed by these results.

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Different types of matrices for encapsulation of sulfur in Li-S battery

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Portable electronic devices and electromobiles are experiencing popularization and high demands are placed on them, especially on the secondary battery system. The priority is mainly on high energy density. A modern trend nowadays is the technology of electrochemical energy storage in battery systems [1]. Requirements for high-performance energy storage are constantly growing, furthermore this has motivated researchers to develop new types of batteries that have high energy density, long life, and low cost. Lithium sulfur (Li-S) batteries are among the most auspicious nominees for achievement these requirements due to their capacity (1675 mAh.g⁻¹) and energy density (2600 Wh.kg⁻¹) [2]. However, the development and commercial use of Li-S batteries is obstructed by restrictions such as low conductivity of sulfur, volume expansion, polysufide shuttle effect and Li dendrite formation. The solution is to modify the sulfur cathode using different methods. The most common method is to encapsulate sulfur in its structure. Thus, volume changes during lithiation and delithiation would be effectively dampened [3].

In this work were used three different types of matrices (graphene oxide, polypyrrole and metal-organic framework) for encapsulation of sulfur to their structures. These matrices were further used not only as encapsulation matrices but as a one the additives for preparation of cathode material in Li-S battery. Composition of individual electrodes were for S/C/GO/PVDF (64:13:13:10 wt.%); S/C/ppy/PVDF (54:23:13:10 wt.%) and S/C/STAM-1/PVDF (60:15:15:10).



Figure 1 SEM images of A) S/C/GO/PVDF; B) S/C/ppy/PVDF; S/C/STAM-1/PVDF electrodes and ilustrating image of real electrode.

To examine the morphology and structure of the prepared electrode's surface scanning electron microscopy (SEM) was used. Prepared electrodes was examined with electrochemical impedance spectroscopy, cyclic volatmmetry and galvanostatic cycling for electrochemical characterisation. The cycling took place in the range of potentials from 1,8 V - 2,8 V. The initial discharge capacity of the prepared electrodes at 0.1 C were around 654 mAh g^{-1} for S/C/GO/PVDF; 861 mAh g^{-1} for S/C/ppy/PVDF and 481 mAh g^{-1} .



Figure 2 Initial charge and discharge cycles of prepred electrodes and schematic ilustration of electrochemical cell used for electrochemical measurements.

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Surface Active Biodegradable Polymeric-metallic Bone Substitutes with Antithrombotic Properties

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Biodegradable orthopaedic implants and fixation devices are attractive materials to avoid post-operations and the need for removal after the new tissue grows. Biodegradable metals (BMs), such as zinc (Zn), iron (Fe) and magnesium (Mg) are often used metals [1] and their combination with degradable polymers can extend their biological interactions with living tissue. The coating of biodegradable polymers, such as poly-lactic acid, chitosan and collagen embedded with conductive nanoparticles can enhance the cellular interactions of BMs [2]. Carbon nanotubes (CNTs), gold (Au), and ruthenium (Ru) nanoparticles are compatible materials with biodegradable polymers to obtain conductive polymeric matrix on BMs. Finally, coating their surface to avoid blood thrombus formation and inflammation risks is essential. Marine-sourced fucoidan is a good candidate to avoid thrombus formation with a combination of fluoroquinolones to reduce the risk of infection [3,4]. In this study, the polymeric matrix was blended with Au and Ru NPs and to optimize the conductivity. Fucoidan was immobilized onto the surface via carbodiimide chemistry after plasma activation using radio-frequency plasma under vacuum. Electrochemical impedance spectroscopy (EIS) was used as a tool for the conductivity determination of NPs embedded samples. The electrical conductivity was extracted from the impedance data by taking the reciprocal of the resistance values at different frequencies (Fig.1). The values of ~ 0.0042 S for the ruthenium sample and ~ 0.0014 S for the gold (Au) samples were observed suggesting their potential in tissue engineering applications.



Figure 1 Nyquist diagrams of Au and Ru samples with equivalent circuit used for fitting.

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The Effect of Carbon Substrate Selection on Catalytic Activity of Transition Metal-based Catalyst for Hydrogen Evolution Reaction

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Global energy demand and consumption are constantly increasing, with the most of energy coming from fossil fuels [1]. However, massive combustion of these fossil fuels poses a severe environmental threat to the world [2].

Therefore, renewable energy sources and ways of storing excess of this energy have recently drawn a great deal of attention. One of the promising strategies for excess energy storage consist in conversion of this energy into stable chemical fuel-hydrogen by water electrolysis [3]. However, pursuing an efficient and cheap alternative catalyst to substitute state-of-the-art platinum-group electrocatalysts remains a prerequisite for the commercialization of this technology [4].

Therefore, this work deals with the preparation and testing of the electrocatalytic activity of the catalysts for hydrogen evolution reaction (HER) based on carbon and transition metals. In the present study, catalysts were fabricated by electrodeposition of nanoparticles containing nickel, cobalt, phosphorus and oxygen on four different carbon substrates using the cyclic voltammetry method. Carbon fibers prepared by needle-less electrospinning technology (CF-NLES), commercial carbon fibers (CF), carbon cloth (CC) and 3D carbon substrate prepared from corn cob (3D-CS) (Fig. 1) were used as substrates and electrodeposition of nanoparticles on all substrates was performed in three-electrode electrochemical system under the same conditions. The electrolyte used for electrodeposition was composed of Co(NO₃)₂, (CH₃COO)₂Ni, NaH₂PO₂ and CH₃COONa.



Figure 1 Carbon substrates used in the preparation of catalysts: A) carbon fibers prepared by needle-less electrospinning technology, B) commercial carbon fibers, C) carbon cloth and D) 3D carbon substrate prepared from corn cob.

The surface morphology and elemental composition of prepared catalysts were characterized by scanning electron microscope (SEM) with EDX elemental analysis. SEM images of catalysts together with EDX analysis confirmed the presence of nanoparticles containing phosphorus, nickel, cobalt and oxygen in all studied catalysts (Tab. 1, Fig. 2). These elements came from the electrolyte used for electrodeposition. EDX analysis also identified the presence of carbon from substrate and shown that catalysts differ in their elemental composition. Furthermore, SEM images show that nanoparticles deposited on various carbon substrates have different sizes.
Studied catalyst	Content of C [wt%]	Content of O [wt%]	Content of P [wt%]	Content of Co [wt%]	Content of Ni [wt%]
CF-NLES 3c	5.66	20.88	4.52	32.15	36.79
CF 3c	8.77	19.18	0.88	31.48	39.68
CC 3c	32.90	19.05	0.59	20.58	26.87
3D-CS 3c	14.10	17.25	1.37	29.42	37.86

Table 1 Elemental composition of prepared catalysts determined by EDX analysis.



Figure 2 SEM images of catalysts based on: A) carbon fibers prepared by needle-less electrospinning technology, B) commercial carbon fibers, C) carbon cloth and D) 3D carbon substrate prepared from corn cob.



Figure 3 A) Current-potential curves of studied catalysts and B) long-term stability measurement for the most active catalyst CF-NLES 3c in 1 mol·dm⁻³ NaOH.

Potential electrocatalytic activity of prepared samples towards HER was investigated in alkaline environment (1 mol.dm⁻³ NaOH) by the linear sweep voltammetry method. Measured current was normalized to the electrochemically active surface area (ECSA) of prepared catalysts. ECSA was estimated from the double layer capacitance via cyclic voltammetry measurement. Current-potential curves obtained for individual catalysts are shown in Figure 3A. Even though all carbon substrates were modified the same way, obtained current-potential curves clearly shows that these catalysts differ in their HER activity. Catalyst based on carbon fibers prepared by needle-less electrospinning technology (CF-NLES 3c) was identified as the most electrocatalytically active (Fig. 3A) and was further subjected to the long-term chronoamperometric stability test at 300 mV vs RHE. As can be seen from the Fig. 3B this catalyst exhibited outstanding stability during whole measurement.

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The Influence of the Gentamicine-loaded Ceramic Coating on the Degradation of Ironbased Biodegradable Materials

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Orthopaedic implants for stabilization and repair of complex bone fractures are usually made of stable, bioinert alloys, such as stainless steel, titanium, aluminum, or chromium. [1]. Biodegradable materials have become a trend in recent years. Their advantage is controlled resorption directly in the patient's body, which eliminates the need for repeated surgical interventions.

Surface treatments of biodegradable metal materials can improve their biocompatibility by increasing the activity of the implant surface in living tissue as well as degradation properties. Calcium phosphate (CaP) ceramic coatings on metal biodegradable implants are a good example of combining different biomaterials in order to design an implant with better properties. The combination of good mechanical properties of biodegradable metal such as iron or zinc with the bioactivity of CaP coatings is suitable for various orthopedic applications [2].

In this work, the iron-based samples were prepared from carbonyl iron powder by cold pressing into pellets at 600 MPa and sintered in a tube furnace at 1120 °C in a reducing atmosphere for 1 hour (Figure 1a). Electrochemical deposition of the CaP layer was carried out using an Autolab PGSTAT 302N potentiostat. Cathodic deposition was performed at a current density of 0.85 mA/cm^2 for 40 min. The coated samples were soaked in a 1 mol/l NaOH solution at a temperature of 65 °C for 2 hours, washed in distilled water and dried at a temperature of 80 °C for 2 hours - Fe-CaP samples (Figure 1b). In the case of Fe-CaP+Ge samples, gentamicin sulphate – Ge (300mg/50ml) was added to the electrolyte solution of the same composition as in the previous case, and the coated samples were dried at a temperature of 37°C for 2 hours (Figure 1c).



Figure 1 Macroscopic images of prepared samples a) Fe, b) Fe-CaP, c) Fe-CaP+Ge (magnification 20x).

Dynamic degradation testing was performed using the Autolab PGSTAT 302 N potentiostat in a three-electrode circuit. The potential range \pm 200 mV from OCP potential at speed 0,1 mV/s. During the test, the samples were immersed in Hanks' solution with pH 7,4 \pm 0,2 and thermostated to 37 \pm 2 °C. The samples were immersed in 50 ml of Hanks' solution during all measurements.



Figure 2 SEM images of prepared samples before degradation a) Fe, b) Fe-CaP, c) Fe-CaP+Ge (magnification 500x).

Macroscopic images of the prepared materials are shown in Figure 1. In the case of the iron sample (Figure 1a), scratches were visible on the surface due to the roughening of the sample surface by abrasive papers. In Figures 1b and 1c, uniform surface coverage was observed after electrodeposition of the CaP ceramic layer (Figure 1b) as well as the drug-doped CaP coating (Figure 1c). The surface morphology of the prepared materials was also studied by scanning electron microscopy (SEM) (Figure 2). SEM micrographs of the prepared samples revealed irregular ceramic coatings obtained by electrodeposition (Figures 2b, 2c). For the CaP-coated sample (Figure 2b), microstructures with different dimensions formed by thin plates and growths as well as unevenly distributed rod-like microstructures were observed. For the Fe-CaP+Ge sample, flower features typically around 500-700 µm in size were observed completely covering the substrate surface as seen in Figure 1c.

The OCP potential was registered for 60 minutes. After about 40 minutes, the OCP values stabilised in the range from -0.42 to -0.53 V for each sample. Lower OCP values were observed for the coated samples (Fe-CaP and Fe-CaP+Ge). This indicates decreased tendency to corrosion in the coated samples as compared to uncoated one. To determine the corrosion rate (*CR*), dynamic polarization tests were performed in Hanks' solution at 37 ± 1 °C.



Figure 3 Potentiodynamic polarization curves of Fe, Fe-CaP and Fe-CaP+Ge samples after electrochemical degradation in Hank's solution.

Values of corrosion potential (E_{corr}), corrosion current density (j_{corr}) and *CR* values were determined by the Tafel extrapolation method from the potentiodynamic polarization curves (Figure 2). A potential shift to a more positive value was observed for both coated samples with the CaP coating and the CaP coating containing gentamicine. This indicates a higher resistance to corrosion compared to the uncoated Fe samples. In the sample with CaP coating doped with gentamicin, a slight shift to more negative potential values was observed compared to the Fe-CaP sample, which indicates better corrosion properties in the samples with the addition of the antibiotic, which was also demonstrated by the obtained *CR* values. The highest corrosion rate was achieved by the sample of pure iron – 0.523 mmpy. Lower values were obtained for both coated samples – 0.347 mmpy for the Fe-CaP sample and 0.363 mmpy for the Fe-CaP+Ge sample compared to the uncoated sample.

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Indentation size effect in the hardness measurements of high entropy carbides

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In the context of hardness measurement, indentation size plays a significant role in determining the hardness of a material. Hardness is a material property that quantifies its resistance to deformation, and it can be measured using various methods, with one of the most common being the indentation method, which includes techniques like the, Vickers, Brinell and Rockwell hardness tests. Indentation size effect (ISE), in general, is observed in shallow indentation tests, which is manifested as an increase (NISE) or decrease (RISE) in hardness with penetration depth decreases [1]. In our case, the ISE was investigated during hardness testing of high entropy carbides with different hardness, applying indentation loads from 50 mN to 10 N. The experimental systems were recently developed (Hf-Ta-Zr-Nb-Ti)C and (Mo-Nb-Ta-V-W)C high-entropy carbides

Α., (1	Hf	Та	Zr	(Hf-Ta-Zr-	Nb-Ti)C
				Elements	At.%
				С	63.6
•	<u>25 μm</u>	<u>25 μm</u>	<u>25 μm</u>	Hf	8.2
	Nb	Ti	C	Та	8.1
	Sales Frank	1748/19		Zr	6.1
	Berlin and	Carl and		Nb	6.3
10 μn	25 μm	25 µm	25 µm	Ті	7.7
В	Мо	Nb	V	(Mo-Nb-T	a-V-W)C
В	Мо	Nb	V	(Mo-Nb-T	a-V-W)C At. %
B	Мо	Nb		(Mo-Nb-T Elements C	a-V-W)C At. % 63.8
В	Мо 2 <u>5 µ</u> m	Nb 25 µm	Υ 2 <u>5 μm</u>	(Mo-Nb-T Elements C Mo	a-V-W)C At. % 63.8 6.4
B	Μο 2 <u>5 μm</u> Τa	Nb 2 <u>5 µ</u> m W	V 2 <u>5 µm</u> С	(Mo-Nb-T Elements C Mo Nb	a-V-W)C At. % 63.8 6.4 6.3
B	Mo 2 <u>5 μm</u> Ta	Nb 2 <u>5 μm</u> W	V 2 <u>5 µm</u> C	(Mo-Nb-To Elements C Mo Nb Ta	a-V-W)C At. % 63.8 6.4 6.3 8.0
В	Мо 2 <u>5 µ</u> т Та	Nb 2 <u>5 µ</u> m W	V 2 <u>5 µm</u> С	(Mo-Nb-T Elements C Mo Nb Ta V	a-V-W)C At. % 63.8 6.4 6.3 8.0 7.0

Figure 1 SEM images and EDX maps of HEC.

The load dependence of hardness was analysed using the traditional Meyer's law, the proportional specimen resistance model and the modified proportional specimen resistance model. The best correlation (R2 > 0.99) between the measured values and the used models was achieved using the modified proportional specimen resistance model. This resulted in the so-called load-independent hardness of (Hf-Ta-Zr-Nb-Ti)C and (Mo-Nb-Ta-V-W)C systems 21.96 and 14.81 GPa in the case of analyses for 50 mN - 10 N load range and 25.42 GPa and 14.13 GPa in the case of 50 mN - 1 N load range, respectively. The different deformation and damage mechanisms detected as a potential reason for the origin of the load-size effect were microcracks at grain boundaries during the micro/macro-indentation and plastic deformation/nanocrack formation at the indents during nano/micro-indentation.

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DFT Calculations of Molybdenum Phosphide as an Electrocatalyst for the Hydrogen Evolution Reaction

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One of the primary building blocks used in many chemical industries, such as the production of ammonia or oil refinery, is hydrogen. It has since been seen as an essential green alternative fuel with zero emissions. Currently, steam reforming is used to manufacture roughly 95% of the hydrogen, which also produces greenhouse gas emissions.

Water electrolysis, which may be driven by green electricity from renewable sources (such as photovoltaics, wind turbines, etc.), is a far more ecologically safe way for producing vast amounts of extremely pure hydrogen. The hydrogen evolution process (HER) and the oxygen evolution reaction (OER) are the two half-cell reactions that enable electrochemical water splitting. The performance of both the cathode (the catalyst for HER) and the anode (the catalyst for OER) materials must be optimized if the efficiency of the entire process needs to be raised.

The most dominant strategy for accelerating the kinetics of water electrolysis is the development of highly active and long-term stable catalysts. Recently, a lot of research is focused on the utilization of metal phosphides supported on various forms of graphene, providing promising overpotentials for HER and OER reactions. The high stability and good catalytic and bifunctional characteristics of transition metal phosphides (TMPs) make them desirable water splitting catalysts [1-4].

Deeper details about the water electrolysis process using phosphide-based catalysts can be provided by the density functional theory method, which can be used to determine the activation energy, Gibbs free energy, individual transition states, or reaction steps of the process. Therefore, our research focused on DFT calculations of hydrogen behavior on optimized MoP surface which were performed with the use of Quantum ESPRESSO code. MoP hexagonal unit cell was optimized with lattice constants a = 3.345 Å, c = 3,448 Å, $\alpha = \beta = 90^{\circ}$ and $\gamma = 120^{\circ}$. Based on these results and XRD results the MoP(101) surface was optimized. Hydrogen adsorption was studied on Bridge, Top and Hollow sites of the MoP(101) surface and led to the results of free energy 0.16 eV for Hollow site and -0.74 eV for Bridge site.

Provided results will be used for determination of transition states and consequently compared with theoretical calculations of hydrogen atom behaviour on other type of metal phosphides such as FeP or FeMoP. These theoretical results will also serve to supplement our experimental investigations of MoP, FeP and FeMoP catalysts in HER process.

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Fe-Cu materials as a promising biodegradable implant

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Introduction

Biodegradable (absorbable/resorbable) materials are being applied to the human body and after a certain period of the time in the healing process, naturally degrade and leave the system as part of the body's biological fluids. On the other hand, bioinert metal materials are still often used for production of implants in orthopedic surgery. They stand out in good mechanical strength, resistance to wear and corrosion, but are prone to various chronic inflammatory reactions and physical irritation [1]. All these facts can lead to various health problems and repeated surgical procedures to remove or replace the implant. For this reason, the research and development of biodegradable metal materials based on magnesium (Mg), iron (Fe) and zinc (Zn) began. The most studied are biodegradable materials based on magnesium. Iron is a biogenic element very important for the human body. It is a trace element found in the human body with a content of about 4 g. Iron in the body can also be found in membrane enzymes that participate in oxidation processes in the human body. Its deficiency causes problems in the formation of red blood cells, resulting in lower production of erythrocytes [2]. Copper is one of the essential elements not only for humans but also for other higher organisms. It plays an important role in metabolic pathways because it allows many enzymes to function properly. Copper is also necessary in the formation of hemoglobin, myelin and melanin, has antioxidant effects and maintains the strength of the skin and blood vessels. In the body, it binds to albumin and is transported to the liver [3]. So, materials based on Fe and Cu offer an interesting option for the development of biodegradable materials.

Experiment

The experimental part of this work is focused on monitoring the corrosion properties of iron (Fe) and iron-copper (Fe-Cu) samples prepared by the powder metallurgy method. The influence of the chemical composition and preparation method (number of sintering cycles) on the degradation behaviour of the prepared materials was studied. The experimental conditions were created to resemble and meet the conditions of the human body as much as possible. The electrolyte used to monitor corrosion properties was Hanks' solution, which contains inorganic and organic components present in the human body. The ambient temperature was kept constant at 37°C using a flow thermostat and the pH of the solution was 7.4.

Water-atomized iron powder (ASC 100.29 Höganäs AB) with a particle size of 63 µm to 180 µm and iron powder with the addition of copper Fe+3.3 wt.% Cu were used to prepare the samples. Samples Fe+3.3 wt. % Cu were formed by electrolytic deposition of copper from an aqueous solution of copper sulphate (0.06 M CuSO₄.5H₂O) and sodium citrate (0.06 M CuSO₄.5H₂O) onto the surface of atomized iron powder particles (30 g). The electrolysis lasted 30 minutes at a current intensity of 1A and took place galvanostatically (in a two-electrode connection) in the electrolyser.

Discussion

The particles of Fe(ASC) iron powder and Fe+3.3 wt.% Cu powder formed by galvanic plating differed not only in chemical composition but also in surface structure. In the images (Fig. 1), the smooth surface of Fe(ASC) iron powder particles is visible, while the copper-plated particles are covered with grains and show a rougher surface.



Figure 1 SEM images of iron powder Fe (ASC) (A), and with copper particles Fe+3.3 hm.% Cu (B). Scale 20 μm.

The experiment also included monitoring the surface of individual samples before and after corrosion. The images show the view of the samples before corrosion (Fig. 2) at different magnifications. On the samples after corrosion, it was possible to see a change in the surface caused by the corrosion reactions that took place. This change is visible as a layer of corrosion products on the surface of the samples. Expected iron corrosion products include oxides and hydroxides. Most often, during corrosion processes of iron, a black coating of iron oxide (Fe₂O₃) or iron-iron oxide (Fe₃O₄), a blue-green product of iron hydroxide (Fe(OH)₂) or a reddish-brown iron hydroxide (Fe(OH)₃) are formed. Copper corrosion is accompanied by the formation of products such as red-colored copper oxide (Cu₂O) and black-colored copper oxide (CuO).





Figure 2 Images of Fe(ASC) sintered 1x (1. line), Fe(ASC) sintered 2x (2. line), Fe+3.3 hm.% Cu sintered 1x (3. line), Fe+3.3 hm.% Cu sintered 2x (4. line) with magnification 20 (A), 50 (B), 150 (C), 200 (D) before corrosion.

One of the most important obtained parameters is the E_{cor} - corrosion potential expressing the thermodynamic stability of the material. However, the determining parameter for the corrosion rate is the value of the corrosion current, j_{cor} . Measured values are listed in the Table 1. Even though the corrosion potential of the 1x sintered Fe sample was more negative compared to the 2x sintered sample, the value of the corrosion current was higher (124.47 μ A), thus a higher corrosion rate was also observed. During the sintering of pure iron, the porosity of the material may decrease, or the nature of the pores may change, which results in a slower course of corrosion. Based on the measurements of the obtained corrosion parameters, it follows that the fastest corrosion processes took place on the 1x sintered Fe(ASC) sample, whose corrosion current value was the highest. The course of corrosion was somewhat slower on the 2x sintered Fe+3.3 wt.% Cu sample. With a small difference, the 1x sintered sample Fe+3.3 wt.% Cu also corroded with the same rate. Corrosion was the slowest on the 2x sintered Fe(ASC) sample, which had the lowest corrosion current value.

Sample	Sintering	Ecor [V]	jcor[µA.cm ²]	icor[µA]	Corrosion rate CR [mm/year]	Polarisation resistance PR [Ω]
Fe(ASC)	1	-0.654	124.47	124.47	1.657	697.6
re(ASC)	2	-0.626	83.841	83.841	1.125	749.1
Fe+3 3Cu	1	-0.589	84.269	84.269	1.135	544.8
1°C+5.5Cu	2	-0.595	84.789	84.789	1.138	1174

Table 1 Values of corrosion parameters for samples Fe(ASC) and Fe+3.3hm% Cu.

The experimental results show that the most suitable candidate for the preparation of medical implants from the studied iron (Fe) and iron-copper (Fe-Cu) materials is the 1x sintered Fe(ASC) sample due to its corrosion rate of 1.657 mm/year, which was the highest among the studied samples. In the next phase of research, it is necessary to increase the corrosion rate of Fe-Cu materials, as they are expected to exhibit better biological properties compared to pure Fe.

Acknowledgements

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Effect of glycerol-citrate polymer addition on microstructure, mechanical strength, and invitro cellular properties of hydroxyapatite bone cement

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Composite materials combining calcium phosphate cements (CPCs) and biopolymers have attracted more attention in recent years due to the option to efficiently improve the physico-chemical properties, such as moldability, setting time, injectability, biodegradation rate as well as mechanical properties of CPCs [1-3]. Although many attends have been conducted on the incorporation of natural and synthetic thermoplastics into CPC structure, however, studies oriented towards the addition of thermosetting counterparts, like polyol citrates have rarely been reported [4].

Therefore, the present work aimed to develop composite bone cement consisting of the tetracalcium phosphatemonetite cement mixture (C) and glycerol-citrate polymer (GCA), which was efficiently coated on the cement powder surface in an amount of 2.5wt% by simple infiltration in ethanol solution. The composite powders were first cured at temperatures of 105 and 170°C, and then cement samples were prepared by mixing the powders with the 2 wt% of NaH₂PO4 liquid phase to produce two composite cements denoted as GCA/C105 and GCA/C170, while the pure cement C without polymer addition was taken as the blank sample. The influence of GCA addition on phase change, microstructure, mechanical, and in-vitro cellular properties of the CPC was thoroughly investigated. The results demonstrated that the GCA coating did not alter significantly the microstructure and phase composition of the cements, plate and needle-like hydroxyapatite crystals were formed in all samples after the transformation of the original phases. The setting time of cements decreased slightly with the polymer addition from 13 min in original C cement to 12 and 10 min in GCA/C170 and GCA/C105 cements, respectively. However, considerable strengthening and an increase of the mechanical properties were achieved by the incorporation of GCA into the CPC matrix. The highest compressive strength (CST= 57±3.7 MPa) was measured in GCA/C105 composite, which was significantly higher than that of the pure C cement (CST= 33±2.9 MPa). The addition of GCA increased also both the macro- and microhardness and the highest values were found for the GCA/C105 cement (H= 362±20 MPa and 540±130 MPa, respectively). The enhancement of macrohardness was about 50% compared to the pure C cement ($H=233\pm19$ MPa) in agreement with the trend of compressive strength data. The Young's modulus of all three samples was similar with values of 15-17 GPa.

The in-vitro cytotoxicity tests showed high proliferation activity of the osteoblastic cells in all cement extracts providing useful information for developing new composites for potential use in regenerative medicine.

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Electrochemical Testing of Redox-Flow Batteries with Novel Design

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Abstract

Redox flow batteries, often simply referred to as flow batteries, are a type of electrochemical energy storage device used for storing and releasing electrical energy. They are particularly suited for applications requiring long-duration energy storage and have gained attention in the renewable energy and grid management sectors. Redox flow batteries operate on the principle of redox (reduction-oxidation) reactions, where chemical species in solution undergo electron transfer to store or release energy [1].

Flow batteries consist of two separate electrolyte tanks, each containing a different chemical solution. These solutions are called the "positive electrolyte" and the "negative electrolyte." They are usually composed of different redoxactive materials as vanadium, which can be organic or inorganic compounds dissolved in water. Between the two electrolyte tanks, there is an electrochemical cell stack. This stack consists of multiple individual cells, with each cell containing a positive and negative electrode separated by an ion-selective membrane. The membrane allows ions to pass through while preventing the mixing of the two electrolyte solutions. During the charging process, electrical energy from an external source is used to drive an electrochemical reaction in the positive electrolyte, causing it to become oxidized (lose electrons), while the negative electrolyte undergoes a reduction reaction, gaining electrons. The electrolyte solutions. The energy is stored in the form of electrochemical potential energy in the redox-active species within the electrolyte solutions. The extent of the reaction in each electrolyte determines the amount of energy stored. When the battery is discharged, the stored energy is released as the redox reactions in the electrolytes are reversed. Electrons flow from the negative electrode through an external circuit to the positive electrolytes are reversed.

Results and discussion

The Inohub cell was assembled consisting of the following parts:

Membrane (membrane area 50 cm ²)	
Flow frames	Produced by TUKE
AVcarb graphite felts	SIGRACELL TF6
Sealings (0.5 mm thick, EPDM)	TRELLEBORG
Copper current collectors	Produced by TUKE
Distribution plates	Produced by TUKE
Inohub battery Assembling process:	



Graphite felt electrode and flow frame installation.



Membrane installation.



Figure 1 Fully assembled Inohub cell before the cycling experiments.

For the measurements, a 1.64 M vanadium-electrolyte solution from Pinflow was used. The pump rate was set to 80 RPM. The cell was allowed to equilibrate with the electrolyte prior to testing in order to monitor any electrolyte leakage. No leakage was observed.

Impedance measurements

Before cycling, impedance measurements were performed on the Inohub cell battery. The cell resistance was found to be 27 mOhm, equivalent to 1.35 Ohm/cm². The Pinflow cell's resistance with untreated felt was previously studied and found to be between 0.8-1.0 Ohm/cm² [2]. However, it is not possible to directly compare the obtained values due to differences in materials (Membrane, Graphite felts supplier and treatment) and measurement conditions (State of Charge). The membrane used in the Inohub cell measurements was previously tested, which may have affected the overall cell resistance. Moreover, one copper electrode is affected by small amounts of pitting corrosion spots after contact with electrolyte from previous measurements with leakage. Despite this fact, the EIS results are in accordance with published and expected results.

Thus, for the proper comparison future impedance measurements for the Inohub and Pinflow cell are required.



Figure 2 Impedance graphs of the Inohub cell before the cycling.

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Electrocatalyst Based on NiCoP for Water Splitting: Part (II) Electrochemical Characterization

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The electrochemical activity of NiCoP fibres prepared by Needle-less electrospinning technology was studied by voltammetry methods. The new types of electrocatalysts were investigated in both alkali and acidic environment for hydrogen as well as oxygen reactions. The alkaline environment was represented by 1M KOH and acidic by 0.5M H_2SO_4 . The NiCoP electrocatalysis were sintered in air atmosphere at different temperatures: F7 - 700°C, F8 - 800°C, F9 - 900°C, F10 - 1000°C, F11 - 1100°C. Sintering in air was followed by sintering in a reducing atmosphere, where the fibers underwent transformation from the oxide phase to the phosphide phase. All fibrous samples (F7-F11) were compared with commercial 20wt% Pt/C and bare PIGE working electrode. Moreover, HER LSV curve of NiCoP particles, noted as P9 was also compared with hydrogen catalytic activities of fibrous NiCoP materials.

The electrochemical measurements were provided on Vionic potentiostat/galvanostat (Metrohm, Switzerland). Calculation of potential with respect to reversible hydrogen electrode was applied according to Evs. RHE = Evs. Ag/AgCl + EAg/AgCl + 0.0591 × pH. The Cdl values were tested by cyclic voltammetry (CV) method at scan rates 10, 20, 50, 100, 150, 200, 250, 400 mV/s. The electrochemically active surface area (ECSA) of samples was estimated by use (CV) method. The ECSA of a catalyst sample was calculated from the double layer capacitance Cdl according to ECSA=Cdl/Cs. However, solving for the exact surface area of our material was difficult due to the unknown capacitive behavior (Cs) of our specific catalysts. But we can safely estimate relative surface areas, as the double layer capacitance is estimated by plotting the Δj around OCP against the scan rate and calculated as $\Delta j = ja - jc$.

Electrochemical results showed that the NiCoP fibers prepared by this methodology operate for HER in alkaline solution at overpotentials E_{-10} (-0.141V) and E_{-20} (-0.230V) vs. RHE and low value of Tafel slope (66 mV/dec), while in acidic media the corresponding values are E_{-10} (-0.146V) and E_{-20} (-0.265V) with Tafel slope of 77 mV/dec. Moreover, this fibrous material exhibited low charge transfer resistance and the largest ECSA of these materials series. The NiCoP F9 endured to work for 22 hours without any microscopic degradation.



Figure 1 LSV curves of NiCoP fibres measured in 1M KOH (HER and OER) and 0.5M H₂SO₄ (HER). Acknowledgements

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Nanostructured Nonequilibrium Oxides and Their Magnetism

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The interplay of magnetism and structural disorder in nanostructured complex oxides is a fascinating subject of recent interest [1,2]. The present work reviews a one-step mechanochemical synthesis and magnetic properties of magnetoceramics with a variety of structure types (cubic spinel, orthorhombic olivine, perovskite, hexagonal structure, double perovskite). The case studies are presented, focusing on recent progress in a fundamental understanding of the structural disorder–magnetism relationships in "interface-controlled" complex oxides prepared by mechanochemical routes. The far-from-equilibrium structural disorder in iron containing magnetic nanomaterials is studied by means of ⁵⁷Fe Mössbauer nuclear probe spectroscopy. The functional behavior of mechanochemically synthesized oxides is characterized by SQUID measurements. Selected examples of the separation of interfacial/surface effects from bulk effects in oxide nanoparticles are presented. It is demonstrated that interfacial effects in the mechanochemically synthesized ceramics may result either in an enhancement of magnetic behavior or in its degradation, *i.e.*, in a desired or undesired magnetic property modification, when compared to magnetism of their bulk counterparts prepared by a conventional ceramic method.

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Novel Electrochemical Sensor for Ciprofloxacin Determination

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The primary role of antibiotics is to inhibit the growth of bacteria and destroy them. Ciprofloxacin is a secondgeneration quinolone, broad-spectrum antibiotic. Ciprofloxacin exhibits enhanced Gram-negative and Gram-positive bacteria like Salmonella spp., Escherichia coli or Staphylococcus aureus. It is used to treat and prevent numerous infections (urinary tract, skin, and lower respiratory infections) [1,2]. These days, many different methods are used for antibiotic detection, including colorimetric, fluorescent, and electrochemical methods. In contrast, electrochemical techniques can be considered as the most suitable method due to their analytical properties, and rapid response time [3,4]. Screen-printed carbon electrode (SPCE) represented an excellent way for the new electrochemical sensor for antibiotics determination because of the miniaturization of the system and low price [5].

In this work nickel screen-printed carbon electrodes (SPCE) were used for ciprofloxacin determination (CIP) due to its low price and simple use. The morphology of SPCE was studied using scanning electron microscopy (SEM), and the elemental composition of the surface of non-modified SPCE was studied by EDX analysis. SPCE at 1000x (Fig. 1A) and 5000x magnification (Fig. 1B) is shown in Fig. 1. The surface is not completely smooth because of the process of preparation. The EDX analysis showed 99,9 % of carbon. The active surface area of SPCE was determined in a solution consisting of 5 mM K₄[Fe(CN)₆]/5 mM K₃[Fe(CN)₆] and 1 M KCl via the cyclic voltammetry, and calculate via Randles-Sevcik equation. Active surface area of non-modified SPCE was 0.18 cm². Stability of the electrode was tested in 5 mM K₄[Fe(CN)₆]/5 mM K₃[Fe(CN)₆] when the current decrease after 50 measurements was only 4.78%. The long-term stability and study of the storage conditions proved that the SPCE can be considered as the suitable diagnostics tool for ciprofloxacin determination.



Figure 1 SEM images of non-modified SPCE at 1000x (A) and 5000x(B) magnification.

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Thin Film Microstructure Optimization Chamber

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Principle

Today, energy poverty and emissions are major problems. Sustainable and green energy production is one of the most important and urgent challenges that we have to tackle [1]. The use of solar panels is spreading worldwide and is growing steadily. But, as is well known, conventional silicon-based solar cells fabrication is expensive and it's not environmentally friendly [2]. Polymer-based solar cells could be a solution, because they are cheap and environmentally friendly to produce. They have received a lot of attention because of their great properties, such as flexibility, lightweight and semi-transparency[3]. However, the production of polymer-based solar cells still presents difficulties. The energy conversion efficiency of organic solar cells is affected by the microstructure of the active layer [4]. The microstructure of the active material is strongly influenced by several factors. One such factor is the deposition/processing method of the active layer. In other words, the efficiency of the solar cell is directly affected by the deposition method of the active layer [5]. There are several types of film-forming techniques that can be used to produce optimized thin films, including inkjet printing, roll-to-toll printing, spin-coating, etc.; each method has its advantages and disadvantages [6]. Therefore, the scientific community puts a lot of attention to develop more effective deposition and processing techniques. This work presents a processing technique that can be used to improve the morphological properties of thin films.

Principle of operation

The optoelectronic properties of thin polymeric films can be tuned and enhanced by optimizing the film microstructure through the utilization of various deposition and processing techniques [7]. In order to establish precise control over the internal microstructure of the active films, we propose to employ an efficient processing technology that is based on the exposure of thin active films to solvent vapors, followed by swelling and deswelling of films in a temperature-and vapour-controlled environment.



Figure 1 Schematic representation of Thin Film Microstructure Optimization Chamber.

A device was built to be used to change the optoelectronic properties of thin films by fine-tuning of their nanostructure [8]. The device consists of an aluminium chamber with a Peltier element at the bottom; the solvent vapour flows in through a tube and it condenses on the sample. The pre-made thin films are placed in this chamber, and the changes can be viewed by a microscope through the glass window on the top, as you can see in Figure 1. This device could control the temperature by 0.01 °C. To achieve this accuracy, a high-performance Peltier element was used ensuring temperature change very precisely by fine-tuning the electric current passing through it. Another great advantage of the Peltier element consists on direction changing of the electric current, the cold and hot sides of the element are reversed, allowing very fast heating and cooling between -5 and 100 °C. A controller was used for such precise control of the electric current. The controller continuously detects the temperature of the Peltier by a thermometer sensor, and if this temperature does not correspond to the predetermined temperature, the controller increases or decreases the electric current. The controller is managed by a computer program that can change the temperature in many ways (linearly, exponentially, slowly, quickly, etc.). At the same time, with the help of a gas bubbler the amount of solvent vapours inside the chamber is precisely controlled. The evaporation rate of the solvent can be used to control the microstructure of thin films. The aforementioned Peltier element was mounted on the bottom of the isolated chamber into which vapour of organic solvent was introduced. By fine varying of the amount of solvent introduced and removed via a precise control of the film temperature, the microstructure of the thin films could be controlled. The solvent saturated environment was created by bubbling the solvent and then, by introducing the solvent vapours into the chamber through suitable tubes. When solvent precipitates on the thin film, the molecular mobility will increase. At this point, the molecules can move freely and adopt ordered conformations. As the temperature slowly increases, the solvent begins to evaporate and the molecules begin to adopt various ordered positions. This procedure would offer an unprecedented control over the solvent evaporation rate during the processing procedure, leading to highly-ordered thin film microstructure and thus to puzzling optoelectronic properties.

Conclusion

A new, simple but efficient device was built to change the morphology of thin films. With this thin film processing technique, the microstructure of polymer-based thin films can be optimized. The sample is placed in an aluminium chamber; the temperature of the chamber can be finely regulated. Organic solvent vapour is releases into the cooled down chamber; the solvent vapour condenses on the thin film, and as a consequence, the molecules can move freely in the film. The temperature of the chamber is slowly raised until the solvent evaporates; meanwhile the molecules can take a more ordered form.

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Preliminary biocompatibility assessment of zeolite-based bone implants for osteoporosis treatment

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Osteoporosis is the most commonly occurring metabolic bone disease. The characteristic features of this multifactorial illness are the appearance of progressive microarchitectural defects and a decrease in bone mass, which is clinically manifested by a decrease in bone strength and a high risk of fractures. The direct cause of osteoporosis is the lack of homeostasis between the activity of bone-forming osteoblasts and bone-resorbing osteoclasts [1]. Zeolites, belonging to the group of aluminosilicate materials, have a number of beneficial features in terms of applications in bone tissue engineering. Importantly, zeolites are characterized by biocompatibility, high specific surface area and good biodegradation in an acidic environment. In addition, they have antioxidant and anti-inflammatory properties, relatively good mechanical parameters and can be used as effective carriers of drugs [2], [3]. The aim of the research was the production of a bone implant based on synthetic and natural zeolites for potential use in the treatment of osteoporotic fractures. As part of the project, three types of biomaterials were produced using various zeolites: (1) synthetic zeolites produced according to the procedure developed by our research team: Na-A (implant marked as Mat Na-A) and Na-X (Mat Na-X), (2) natural zeolite (Mat Clinoptilolite), and (3) synthetic commercially available zeolites: type 4A (Mat 4A) and type 13X (Mat 13X). Moreover, bone implant made of hydroxyaptite (HA) was also produced and served as a control material. All bone scaffolds were manufactured according to the procedure contained in the Polish patent no. 235822. Conducted research showed that produced implantable biomaterials were characterized by a macroporous microstructure. On the basis of the MTT cytotoxicity assay performed according to the ISO 10993-5 standard, it was demonstrated that the tested biomaterials were non-toxic to mouse preosteoblasts (MC3T3-E1) (Fig. 1A) and human fetal osteoblasts (hFOB 1.19) (Fig. 1B). Interestingly, the viability of cells exposed to extracts from Mat Na-X and Mat Na-A biomaterials for 24 hours was higher compared to other biomaterials, including control Mat HA implant.



Figure 1 Evaluation of the cytotoxicity of the tested biomaterials against MC3T3-E1 and hFOB 1.19 cells using the MTT test. The cells were exposed to biomaterial extracts for 24 hours. The culture medium served as a control. (* statistically significant results compared with control cells with p-value < 0.05; one-way ANOVA followed by Tukey's test).

High biocompatibility of Mat_Na-X and Mat_Na-A bone scaffolds was also confirmed in direct contact with the cells using fluorescent Live/Dead staining. CLSM microscope images showed viable (green fluorescence) and well spread cells of the MC3T3-E1 line at high density on the surface of the tested biomaterials (Fig. 2A). Cell morphology on the surface of the scaffolds was also assessed using fluorescent staining of the cytoskeleton and CLSM observation. It was shown that mouse preosteoblasts cultured for 3 days on the surface of the biomaterials were well flattened and had normal morphology, which proved their strong adhesion to the substrate (Fig. 2B).



Figure 2 CLSM microscope images of (A) MC3T3-E1 cells cultured on the surface of zeolite-based biomaterials (Mat_Na-A and Mat_Na-X A) for 48 hours and fluorescently stained with Live/Dead kit (viable cells – green fluorescence, dead cells – red fluorescence) and (B) MC3T3-E1 cells cultured for 72 hours after cytoskeleton staining (nuclei – blue fluorescence, cytoskeleton filaments – red fluorescence).

Preliminary results of *in vitro* studies indicate that the implantable biomaterials developed on the basis of Na-A and Na-X zeolites are highly biocompatible. Nevertheless, to fully confirm biomedical potential of developed zeolite-based biomaterials it is necessary to conduct further research to assess their physico-chemical and mechanical properties.

Acknowledgements

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Biological characterization of OEGMA-based hydrogel wound dressing material with

intrinsic antibacterial activity against Pseudomonas aeruginosa

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Background

Wounds are created due to thermal or physical injury that causes a break in a continuity of the epithelial layer of the skin or mucosa [1]. Delayed and prolonged healing process of the acute wounds may lead to the chronicity and creation of non-healing wounds. Chronic wounds are characterized by elevated pH in the wound bed, high levels of proinflammatory cytokines, reactive oxygen species (ROS), and matrix metalloproteinases (MMPs). In turn, due to alkaline pH in the wound bed, chronic wounds are prone to bacterial infections [1,2]. A major pathogen that may be found in the microenvironment of infected chronic wounds is Gram-negative bacterium *Pseudomonas aeruginosa* [3].

The aim of this study was to assess biological properties of newly developed hydrogel type wound dressing material. For this purpose antibacterial activity tests against *Pseudomonas aeruginosa* and biocompatibility tests (cytotoxicity, cell adhesion and proliferation) towards human skin fibroblasts were performed.

Materials and Methods

Wound dressing material

The biomaterial was produced based on well-defined copolymer of oligo(ethylene glycol) methyl ether methacrylate (OEGMA) and 2-(dimethylamino)ethyl methacrylate (DMAEMA), utilizing quaternization with dibromohexane for hydrogel formation.

Biocompatibility tests

In vitro cell culture experiments were performed using normal human skin fibroblasts (BJ cell line, ATCC). Indirect cytotoxicity assay was conducted according to ISO 10993-5 standard using liquid material extract prepared according to ISO 10993-12. Fresh culture medium was a control. The cells were seeded into 96-multiwell plates in a complete culture medium and exposed to biomaterial extract for 24 hours. Afterwards, cell viability was determined using *Cell Counting kit-8* (WST-8 cytotoxicity test).

The cytotoxicity and cell adhesion to the wound dressing were evaluated in direct contact with the cells by confocal laser scanning microscope observation (CLSM, Olympus Fluoview equipped with FV1000). The cells were seeded directly on top surface of the biomaterial, cultured for 72 h, and then stained using *Live/Dead Double Staining Kit*. Cells cultured on polystyrene served as a control. CLSM images were taken to visualize both the cells on the biomaterial surface and fibroblasts growing next to the dressing on polystyrene well.

Fibroblast proliferation was determined indirectly using extract of the dressing prepared according to ISO 10993-12. BJ cells were seeded into 96-multiwell plates in the complete culture medium and exposed to biomaterial extract for 24, 48 and 72 hours. Afterwards, the cells were lysed and their number was determined using the LDH total assay according to the manufacturer instruction. The number of cells was calculated using a calibration curve made for known concentrations of BJ cells. Based on obtained results Doubling Time (DT) and Growth Rate (GR) were calculated using Doubling Time Computing software version 3.1.0.

Antibacterial activity against Pseudomonas aeruginosa

Antibacterial tests were performed using *P. aeruginosa* PAO1 pVLT31-eGFP. The cultures were induced for GFP (green-fluorescent protein) production using 0.4 mM isopropyl-ß-d-1-thiogalactopyranoside. To determine antibiofilm properties of the hydrogel, induced *P. aeruginosa* PAO1 pVLT31-eGFP bacteria were incubated with the biomaterial for 30 min (evaluation of bacteria adhesion) or 24 h (evaluation of mature biofilm formation) at 37 °C without shaking. Bacteria cultured in the polystyrene well of 96-multiwell plate without tested biomaterial served as control. The hydrogel and the polystyrene control were analyzed by fluorescence microscopy (Leica DMi8 inverted fluorescent microscope, Leica Microsystems CMS GmbH).

Antibacterial activity of the hydrogel was determined using *Contact Toxicity* – *Collagen Matrix Model*. For this purpose, the wells of 24-multiwell plate were coated with a collagen derived from rat tail. Then, the collagen matrix was inoculated with *P. aeruginosa* PAO1 cells and incubated for 30 min at 37 °C without agitation to allow cells to adhere. Afterwards, planktonic cells were washed and tested biomaterial (6 mm in diameter) was placed on the inoculated collagen matrix. The 24-multiwell plate was incubated for further 24 h at 37 °C and then the hydrogel sample was taken off and analyzed by fluorescence microscopy. Apart from biomaterial surface that was in contact with *P. aeruginosa*-inoculated collagen layer, the surface of *P. aeruginosa*-inoculated collagen matrix that was in the contact with tested hydrogel as well as the area next to the biomaterial-collagen matrix contact were examined by fluorescence microscopy.

Results and Discussion

Performed biological characterization of the developed hydrogel dressing material clearly proved its high biomedical potential. The biomaterial was non-cytotoxic to the human skin cells, it promoted fibroblast proliferation (Table 1) and did not allow the cells to attach to its surface. The cells growing on the biomaterial were viable (green fluorescence), but were round and not attached (Figure 1). In turn, fibroblasts cultured on the polystyrene next to the hydrogel were well spread and viable, proving non-toxicity of the tested biomaterial. It should be noted that enhanced fibroblast proliferation is desired phenomenon since it accelerates the regeneration of chronic wounds. In turn, hindered fibroblast adhesion to the dressing material ensures painless dressing exchange during healing process. These properties of the biomaterial are crucial taking into account its potential clinical applications as wound dressing.

Parameter	Control	Biomaterial
Viability (%)	100	87.5
Doubling Time (hours)	44.11	35.63
Growth Rate	0.0157	0.0195

Table 1 Quantitative results of cytotoxicity and proliferation assays.



Figure 1 CLSM images of human skin fibroblasts growing on the surface and next to the biomaterial after live/dead staining (green fluorescence = viable cells).

Synthesized novel hydrogel material showed antibiofilm activity against *P. aeruginosa* bacteria since no cells were detected on the surface of the biomaterial after 30 min (attachment phase) and after 24 hours (mature biofilm phase)

of incubation (Figure 2). In contrast, fluorescent *P. aeruginosa* bacteria were observed on the control polystyrene surface at both time intervals. It clearly proved that developed hydrogel had the ability to inhibit both the attachment of bacteria in the early biofilm stage and the maturation of typical biofilm. Antibacterial properties of the biomaterial were proven in the *Contact Toxicity – Collagen Matrix Model*. The test revealed that there were no bacteria on all investigated surfaces: (1) biomaterial surface that was in contact with *P. aeruginosa*-inoculated collagen matrix, (2) surface of *P. aeruginosa*-inoculated collagen matrix that was in the contact with tested hydrogel, and (3) surface of the *P. aeruginosa*-inoculated collagen matrix that was not in contact with the biomaterial but was located next to the hydrogel.

It was assumed that intrinsic antibacterial activity of produced hydrogel resulted from the presence of positively charged groups on its surface that served as attachment sites to lipid A in the membrane of *P. aeruginosa*, disturbing the integrity of bacterial membrane and reducing the viability of *P. aeruginosa*.



Figure 2 Transmitted-light and fluorescence microscopy images presenting lack of the growth of *P. aeruginosa* PAO1 pVLT31-eGFP on the biomaterial surface after 24 h incubation.

Conclusion

It was concluded that OEGMA-based biomaterial is a good candidate to be used as a hydrogel wound dressing for the management of chronic wounds with high risk of bacterial infection. This type of the dressing material would provide antibacterial protection and appropriate moisture and oxygenation at the wound bed, accelerating the healing process.

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The Influence of Intense Plastic Deformation on hydrogen absorption

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Introduction

Hydrogen, considered an excellent energy carrier and a secondary clean energy source, holds significant promise in various domains, including transportation, industrial fuel, and energy storage. This is due to its high calorific value and environmentally friendly attributes [1]. The advancement of the hydrogen energy sector plays a pivotal role in supporting the worldwide transition towards cleaner energy and achieving decarbonization goals [1,2].

Metal hydride, utilising a reversible chemical interaction of hydride-forming alloys, is the primary focus of the solidstate hydrogen storage community. Research on these materials have focused on the development of potential candidates with improved bulk and weight capacities, kinetics of rapid hydrogen desorption, and long-term cycling stability [3].

High entropy alloys (HEAs) is an innovative alloying approach characterized by a high concentration of multiple principal elements, are anticipated to offer hydrogen storage capabilities that align with hydrogen storage requirements. This is due to their diverse composition, customizable phase structures, and unique hydrogen-related performance, particularly the intriguing concept of single-phase HEAs, which could provide new insights into the hydrogen storage mechanism. Recent studies suggests that body-centered cubic (BCC)-structured HEAs outperform conventional alloys in terms of hydrogen storage properties, encompassing hydrogen capacity, kinetics, activation, and cyclability [4-6]. The composition design and fabrication process of these alloys also significantly influence their suitability for various hydrogen applications. While there have been several reviews on high-entropy hydrogen storage alloys, a comprehensive overview of BCC-structured HEAs for hydrogen storage remains notably absent.

High-pressure torsion (HPT) is a commonly used technique for severe plastic deformation, enabling the creation of ultrafine-grained structures with promising mechanical and functional properties. Since 2007, researchers have employed this method to enhance hydrogenation kinetics in various magnesium-based hydrogen storage materials. Recent studies have revealed that HPT is not only effective in accelerating hydrogenation kinetics but also in improving hydrogenation activity, enhancing air resistivity, and, most notably, in synthesizing new nanostructured hydrogen storage materials with high densities of lattice defects [7].

In this study, we focused on the influence of severe plastic deformation on the hydrogen storage capacity in a highentropy alloy, equimolar HfNbTiZr.

Results

The alloy was prepared through arc melting from pure elements, followed by homogenization annealing at 1200°C for 24 hours and subsequent quenching in water. High-pressure torsion (HPT) was carried out at room temperature, under a pressure of 7.5 GPa, with 5 rotations at a speed of 0.2 RPM. The maximum shear strain reached. The alloy's microstructure consists exclusively of a body-centered cubic (BCC) phase, but the grain size reaches 20-30 nm, which is approximately 10 times smaller than in conventional BCC alloys.

Measuring of hydrogen absorption capacity in the deformed bulk sample by means of electrochemical method revealed a significant difference in hydrogen absorption capacity compared to recrystallized samples, but its overall H/M value is low < 0.02.

The powder sample prepared from this alloy, measured by the volumetric method (Sievert's method), exhibited a significant increase in the overall hydrogen storage capacity, H/M > 1.45 in the alloy, see Figure 1. The current results of this study on the single-phase HfNbTiZr HEA alloy suggest that both the free surface factor and defected microstructure influence hydrogen storage of the alloy.



Figure 1 Pressure-Composition-Temperature (PCT) isotherms of highly deformed (HPT) HfNbTiZr HEA sample measured in bulk form by means of electrochemical method (blue curve) compared to volumetric measurement (Sievert's method) on pulverized sample.

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The HfNbTiZr HEA samples were prepared and deformed at Kyoto university. Volumetric absorption measurement was done at the AGH Krakow, Poland.

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Development of a potential scaffold for cartilage tissue engineering in vitro

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Introduction

Osteochondral defects (OCD) or lesions (OCL) are a significant problem causing such clinical symptoms as chronic pain, stiffness, swelling, instability, and limited functional activity [1]. Due to specific cartilage tissue structure, current conventional treatment methods have a number of constraints, making the whole process more complicated and less efficient [2]. All known techniques such as bone marrow stimulation, cartilage transplantation, subchondral bone drilling, and chondrocyte or mesenchymal cell transplantation usually temporary relief the symptoms and most often lead to the formation of fibrous repair tissue [3]. Due to the above-mentioned facts, tissue engineering and material-based approach seem to be promising solutions that can overcome conventional regeneration techniques limitations of cartilage tissue [2], [4], [5]. The aim of this work was the development of a method for the production of a potential cartilage scaffold dedicated to being used in the process of repairing cartilage tissue damage. The work focuses on the preliminary assessment of the biocompatibility and microstructural properties of the scaffold based on polymers of natural origin (chitosan and curdlan) and hydroxyapatite nanopowder.

Materials and Methods

The biomaterial production was started by dissolving 2% (w/v) chitosan in an 1% acetic acid solution. Then the obtained chitosan solution was mixed with 10% (w/v) curdlan, 10% (w/v) hydroxyapatite nanopowder, and 1% (w/v) sodium bicarbonate. Next paste was heated at 95 °C for 20 min, frozen, and lyophilized. After lyophilisation sample was immersed in PBS for 3h and dried at room temperature. The production method is detailed in the patent application (P.442450).

Cell culture test

A cytotoxicity of produced biomaterial was evaluated by WST-8 and LDH total tests in accordance with ISO-10993-5:2009 using normal human adipose-derived mesenchymal stem cells (ADSC). Scaffold cytotoxicity and cell adhesion were also estimated using direct Live/Dead staining kit.

Microstructure characterization

Top surface of the biomaterial was visualized by a scanning electron microscope, whereas areal surface roughness (S_a) was measured by 3D laser scanning microscope (confocal optical profilometer). The sample porosity was estimated by micro-computed tomography (micro-CT).

Results and Discussion

Conducted biocompatibility evaluation revealed that synthesized biomaterial was non-toxic to the ADSCs. Despite the fact that WST-8 test revealed significant decrease in cell viability comparing to the control, no statistically significant differences between sample and polystyrene control was noted in LDH total assay (Fig. 1). The obtained results can be explained by the decrease in cellular metabolism observed in WST-8 test, caused by the biomaterial extract.



Figure 1 WST-8 and LDH total cytotoxicity tests conducted according to ISO 10993-5.

Similarly, Live/Dead staining evaluation provided the results indicating non-toxicity of the produced cartilage scaffold. Only viable (green) and well attached cells with normal morphology were observed on the sample (Fig. 2).



Figure 2 Live/Dead staining of ADSC cultured on biomaterial for 3 days (green fluorescence represents viable cells, while red represents dead cells).

Microstructure characterization revealed that tested biomaterial possessed high total porosity $(39.21\% \pm 2.86)$ (Fig. 3C) and appropriate surface area roughness (44.38 μ m ± 5.36) enabling good cell attachment. Stereoscopic image presenting biomaterial structure as well as SEM analysis are presented in Figure 3.



Figure 3 A – Stereoscopic image of produced scaffold; B – SEM analysis of tested biomaterial; C – Pores size and their distribution in the structure of biomaterials analyzed by micro-CT.

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Conclusions

Produced scaffold is characterized by good biocompatibility and high porosity. Appropriate surface roughness of the evaluated sample ensures good cell adhesion and possibilities for cell pre-seeding and growth on its surface. Nevertheless, in order to fully assess the biomedical potential of the produced biomaterial, further advanced cellular and microstructural research is necessary.

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Welding of Al-Cu-Si-Mg alloys – mechanical properties and microstructure

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Introduction

An appropriate chemical composition as well as the manufacturing technology will allow to manufacture Al alloys with tensile strengths up to 300 MPa without sophisticated heat treatment. The principal advantage of these aluminium is a good combination of strength and elongation and accepted formability. However, the weldability can be Achilles' heel. The term "weldability" designates, in a given alloy, not only the ability to produce defect-free weld, but also to provide the required joint properties and quality. For aluminium alloys the following issues should be recognized:

- Gas porosity.
- Oxide inclusions and oxide filming.
- Solidification (hot) cracking or hot tearing.
- Reduced strength in the weld and HAZ.
- Lack of fusion.
- Reduced corrosion resistance.
- Reduced electrical resistance.

Therefore the proper welding technologies should be developed. The properties of the welded elements become an important issue in broader application of these material. It has higher strength than 6061 grade that are used in similar applications, however, its weldability is worse because of the higher content of alloying elements like Cu and by a high tendency to hot cracking. It has been already shown that producing high quality joints requires rigorous welding conditions that comprise such factors like the amount of heat input to the joint, preheating temperature as well as specific welding conditions.

In the paper the results of metallographic examination and mechanical properties of electron beam as well as Friction Stir Welding joints of Al alloys (Al-Cu-Si-Mg) are presented.

Experimental procedure

The Al-Cu-Si-Mg alloys were used in this study. A summary of chemical composition and mechanical properties is provided in Table 1. The electron beam welding (EBW) process as well as friction stir processing (FSW) were used to weld all specimens at the welding speed of 1.0 and m/min for EBW (in vacuum) and 0.45 m/m for FSW (without shielding gas). Before welding the surface of the specimens was chemically cleaned with acetone.

Table 1 Chemical composition of aluminium alloys.

Symbol		Chemical composition [%] Mechanical pro					nical prop	erties	
	Cu	c:	Ma	Mn	Fa	C.	R _m	Re	Α
	Cu	51	wig	IVIII	re	CI	[MPa]	[MPa]	[%]
1A	0.6	1.0	0.7	0.6	0.0	0.25	229	101	14.8
2A	0.8	1.2	0.8	0.6	0.0	0.25	250	111	14.8
3A	1.2	1.2	0.8	0.6	0.0	0.40	309	143	13.0
3B	1.4	1.2	0.8	0.6	0.0	0.40	280	128	10.4
6060 max	0.1	0.6	0.6	0.1	0.3	0.05	170	140	8
6061 max	0.4	0.8	1.2	0.15	0.7	0.35	290	240	10

Microstructural examinations were carried out by the light microscope and scanning electron microscope. The Vickers microhardness measurement across the weld and the base metal was carried out on metallographic specimens at a load of 100 G. The tensile tests of the base metal as well as of the welded joints on specimens cut off perpendicular to the joint axis, were performed at room temperature using the mechanical universal testing machine.

Results

The main goal of investigation was to study the influence of EBW and FSW on quality, mechanical properties as well as on macro- and microstructure of welded joints. The visual tests revealed that welded joints fulfil the requirements. The macrostructure of EB welded joints in Figure 1 were presented. The quality of welded joints on the cross sections was also confirmed. However, for some technological parameters the welding imperfections such as incompletely filled groove (511) was revealed.



Figure 1 The macrostructure of EB welded joints, without imperfection and with imperfection.

The transverse tensile tests acc. to EN ISO 4136 standard revealed that for all welded joints the rupture out welds were observed. The strengths of welded joints (Table 2) were higher than minimal requirements (min 65% R_m of base materials for EBW and 80% for FSW).

Process (wolding speed	R _m [MPa]					
r rocess / weiding speed	6060	6061	1A	2A	3A	
FPW 1000 mm/min	165	230	225	247	244	
	165	225	211	235	249	
EBW 2000 mm/min	162	230	225	231	258	
	164	226	221	228	261	
R_{mmin} 65% Rm of base material	110	188	151	163	197	
FSW 710 mm/min	161	-	189	203	251	

Table 1	Strongtha	of FDW	and FOW	wolded	ininta
I able 2	Strengtus		and row	weided	IOHIUS.

	162	-	190	201	251
	162	-	189	205	250
R_{mmin} 80% Rm of base material	136	-	185	200	242

The bend tests with a roller acc. EN-ISO 5173 standard were also carried out. The plasticity of welded joints was partially confirmed. For some alloys and welding speed, during tests cracks were observed. Therefore, the optimization of welding process should be carried out. It should be noted, that for all specimens the positive results of bend test have to be achieved.

Symbol	Welding speed mm/min	Diamater of mandrel [mm]	Angle, 0	Remarks
	1000	20	180	Without cracks
LDW IA	2000	20	180	Without cracks
EDW 2A	1000	25	180	3 - without cracks, 1 - crack 5 mm
LDW 2A	2000	25	180	Without cracks
	1000	30	180	3 - without cracks, 1 - crack 15 mm
EDW 3A	2000	30	180	3 - without cracks, 1 - crack 5 mm
FSW 1A	710	20	180	Without cracks
FSW 2A	710	25	180	Without cracks
FSW 3A	710	30	180	Without cracks

Table 3 Plasticity of EBW and FSW welded joints.

Microstructural observation (Fig. 2 and 3) was performed on SEM for each welded joint to determine the morphology of the precipitates. In the HAZ, Mg₂Si phases with larger sizes and rounded shapes were visible than directly in the weld made using the EBW method. The joints produced by the FSW method were characterized by a wide weld area and an irregular weld line. Analysis of the crystallographic orientation of EBSD and grain orientation spread (GOS) showed differences in the shape of grains and the degree of recrystallization process in the weld area between the FSW and EBW methods. The distribution of microhardness measurements shows a slight decrease in hardening in the HAZ (Fig. 4). It was found that in joints welded by both methods, the hardness of the welds for alloys with increased copper and chromium content is higher by approx. 5%.



Figure 2 Microstructure of EBW, 1A alloy.



Figure 3 Microstructure of FSW, 1A alloy.



Figure 4 Distribution of microhardness in a) EB and b) FSW welded joints, 1A alloy.

Conclusions

On the basis of NDT, metallographic examination, hardness measurements and mechanical tests of the base material and welded joints the following conclusions can be drawn:

- Visual tests and macroscopic examination have shown that the electron beam welded joints are fulfil the required quality level B in accordance with the EN ISO 13919-2:2021-07 standard. Only for the welded joint made of 1A alloy with a welding speed of 1000 mm/min, the quality level C was established.
- The tensile strength of the welded joints met the required criterion Rm min.>65% Rm of the base material.
- All samples taken from welded joints made of alloys 1A (1000 and 2000 mm/min), 2A (2000 mm/min), met the requirements of the bending test, reaching required bending angle 180° without scratches and cracks. On one of the set of 4 samples taken from welded joints made of alloys 2A (1000 mm/min), 3A (1000 and 2000 mm/min) revealed in the flexural test cracks longer than 3 mm.
- Based on the analysis of hardness measurements of welded, it was found that, the hardness increased in the weld material as well as HAZ.
- Visual tests and macroscopic examination have shown that FSW joints are fulfil the required quality requirements.
- mechanical properties FSW joints made of alloys numbered: 1A, 2A, 3A obtained the required tensile strength Rm min > 80% Rm base material.
- Based on the analysis of hardness measurements of FSW joints, it was found that, the hardness increased in the stir zone

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Compressive and Corrosive Behavior of Zinc Biodegradable Open-cell Foams

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Introduction

The increase in human lifespan has led to an increasing number of surgical interventions, including orthopedic implants surgeries. Two major drawbacks have been identified in using long-term metallic implants as the replacement and/or regeneration of damaged hard tissues: stress shielding and releasing toxic metal ions due to mechanical wear and corrosion [1]. Recently, there has been a demand to develop metallic biodegradable materials to use them as a hard tissue temporary replacement. These materials are intended to support the injured bone for 12-24 weeks and then gradually dissolve within the body [2]. The advantage of degradable materials is that they eliminate the need for secondary surgical intervention to remove the implant. Metallic materials such as iron, magnesium, zinc, and their alloys have shown promising mechanical and degradation properties in the human body. Porous materials have become popular in biomedical applications because they resemble human bone's structure and properties, allowing for faster tissue formation and fluid transport, thus reducing the required regeneration time. Another advantage of porous materials is that the mechanical properties can be adjusted by changing the volume fraction of the solid material in the sample. Zinc-based metal foams have recently become the focus of the research of biodegradable materials since zinc-based biodegradable materials, in particular, have excellent biocompatibility and degradation behaviour and exhibit the beneficial features of porous structure [3]. However, there are still only a few studies concentrating on developing zinc-based foams for biomedical uses and, particularly, on the influence of corrosion on their mechanical properties.

Results

In this study, the compressive properties of open-cell pure zinc foams manufactured by two different methods are investigated. First, low-density open-cell foams were produced by a modified investment casting method [3]. Foams with two different pore diameters (2.6 mm and 3.2 mm) were made, and the cell strut thickness varied (0.4 mm, 0.45 mm, and 0.55 mm average strut-thickness). The relative density, 100 times the volume fraction of the solid material in the specimens, was between 7% and 18%. Salt replication technique was also employed to investigate the performance of a higher relative density foam [4]. In this case, sintered salt particles were infiltrated under low pressure with zinc. The average pore size and the relative density of the salt replicated sample were 0.9 mm and 40%, respectively. Rectangular blocks, length of 25 mm and cross-section of 20 x 20 mm² for the investment casting sample, and 12x12x12 mm³ for the salt replicated sample were tested in compression before corrosion and after four-weeks immersion in Hanks' solution at 37 ± 2 °C. The results of the compression test are shown in Figure 1. For low relative density foams (7%) the corrosion did not affect the mechanical properties. In contrast, for investment casting foams with higher relative density, the mechanical behavior changes due to corrosion are more pronounced. Changes in the characteristics of the stress-strain curve of investment casting samples are also visible. On the contrary, the high relative density salt replicated foam exhibits higher strength after corrosion; however, the stiffness of the foam is significantly reduced. This suggests that structural parameters like pore size and strut thickness also influence the changes in the mechanical properties due to corrosion.



Figure 1 The stress-strain curve of zinc foams made by (a) investment casting method with 3.2 mm average pore size and different cell strut thicknesses (b) salt replication technique before corrosion (continuous lines) and after corrosion (dashed lines).

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Curdlan dressing enriched with silver nanoparticles for the treatment of infected wounds

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Introduction

Non-healing wounds are a significant concern for both patients and the healthcare system [1]. This type of wound develops by complications resulting in infection of both acute and surgical wounds, leading to bacterial colonization with biofilm formation [2]. For this reason, research is being undertaken to develop multifunctional bioactive wound dressings containing antibacterial agents [3]. The high prevalence of infections and the growing risk of antibiotic resistance are the reasons why potent alternatives to antibiotics are currently on the topic [2]. One of the promising wound healing practices is the use of silver ions because of their strong antimicrobial effect, which was already known in antiquity [4]. The conventional method, however, has some inherent limitations with the toxicity of the element itself, causing skin discolouration or the formation of resistance in bacteria. Threefor, new and innovative strategies for effective therapy using this precious metal are constantly being sought. One of them are nanoparticles that effectively fight microorganisms in lower concentrations than silver ions alone [5]. Currently, in regenerative medicine, a new concept of combating bacterial infections is being observed, involving the incorporation of metal nanoparticles into the polymer structure of biomaterials, limiting the survival of strains showing resistance to antibiotics [6]. The main purpose of this study was to develop a nanocomposite matrix based on a natural polymer - curdlan enriched with silver nanoparticles with potential use as a dressing dedicated to heavily infected exuding wounds.

Materials and Methods

Preparation of Ag nanoparticles

Silver nanoparticles were obtained by chemical reduction of silver nitrate (ion source) with the use of ascorbic acid reducer. The nanoparticles were then centrifuged, the supernatant was discarded, and the pellet was frozen and then lyophilized.

Characterization of Ag NPs colloid solution

To confirm the preparation of silver nanoparticles, UV-Vis spectroscopy method was used. Spectra of the nanoparticles suspension were measured using a Genesys 150 UV-Vis spectrometer, in steps of 1 nm in fine scan mode.

Preparation of polysaccharide matrix

Curdlan matrix was prepared by mixing curdlan powder and silver nanoparticles at the appropriate ratio to make suspension in deionized water. The obtained homogeneous mass was transferred to a mould, which was incubated in a water bath at 95°C. Then, the biomaterial was cooled and moved to -80°C and lyophilized. The resulting foam-like material was subjected to further testing.

Microstructure characterization

Resultant biomaterial was visualized in both dry and wet states, after soaking in phosphate-buffered saline by a stereoscopic microscope Olympus SZ61TR.

Cell culture test

The cell culture experiments were carried out using human normal skin fibroblasts (BJ) purchased from ATCC. To assess cytotoxicity of produced materials, indirect test (MTT assay) using fluid extract of the biomaterial was conducted according to ISO 10993-5 (2009). Cytotoxicity was analysed by preparing biomaterials extracts

(24-h and 48-h) from the tested dressing and then added to cells seeded to wells of the multiwell plate at a concentration of 1×10^4 cells. BJ cells were cultured for 24-h at 37°C, 5% CO₂ and then cytotoxicity was measured.

Antimicrobial activity evaluation

Antibacterial activity evaluation of developed biomaterials was assessed using direct contact test based on disk diffusion method with modification. Following bacterial strains were used: *Staphylococcus aureus*, ATCC 25923 and *Pseudomonas aeruginosa*, ATCC 27853. Samples were plated onto Mueller-Hinton agar medium inoculated with bacteria and incubated at 37°C for 24 h. Afterwards, a disk diffusion zone of inhibition has been measured.

Results and Discussion

Obtained absorption spectrum exhibited a plasmon absorption band at ~ 400 nm which is the characteristic of silver nanoparticles (Fig. 1). Foam-like biomaterial was highly absorbent and its structure changed to the gel after contact with the fluid and transferred to hydrocolloid material (Fig. 2). The biocompatibility test showed that the developed material was non-cytotoxic to human skin fibroblasts. Additionally, the assessment of growth inhibition zones confirmed that the developed material had the ability to inhibit both Gram-positive and Gram-negative pathogenic bacteria.



Figure 1 Absorption spectra of Ag nanoparticles.



Figure 2 Microstructure of produced biomaterial (scale bar = 500 µm), A) dry, B) soaked.

Conclusion

The results presented confirm the production of a biomaterial characterized by high biocompatibility. Foam-like biomaterial has the ability to transform into typical hydrocolloid dressing with superabsorbent properties after contact with fluid. Developed method allowed for effective incorporation of silver nanoparticles into the polymer matrix, which did not adversely affect its biocompatibility. It is worth noting that the developed biomaterial demonstrates the ability to kill harmful bacteria in its close surroundings. Based on the presented pilot results, it can be assumed that the developed biomaterial has great potential to be applied for infected exuding wound management.

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