Przesieka, 12–14 May 2023

INTERDISCIPLINARY DOCTORAL SYMPOSIUM

BOOK OF ABSTRACTS

RADA DOKTORANTÓW
Politechniki Wrocławskiej

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of Science and Technology

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New Energy Storage Systems: Exploring Lithium Oxygen Cells and Cathode Materials

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One of the problems that the modern world is facing is the constantly increasing demand for energy storage capacity. This ever-growing need is closely related to the expansion of the electric vehicles sector, as well as the pursuit of efficient technology for the industrial energy storage applications (e.g., storage of energy from renewable sources). Lithium oxygen cells (Li-O_2) are proposed as a possible solution to the aforementioned issues, due to their extremely high specific energy (~3500 Wh kg^{-1}) and light weight, which result from the unique semi-open system in which Li-O_2 cells operate and the reaction taking place during discharging/charging (ORR/OER). However, these factors put specific requirements toward cathode materials, such as large specific surface, appropriate porous structure, high electrical conductivity, and catalytical activity in ORR/OER. This work will shortly introduce the basic information regarding the operation of Li-O_2 cells and crucial requirements towards cathode materials. In addition, the importance of the development of new energy storage technologies and the key advantages of lithium-oxygen cells will be discussed.

Keywords: lithium oxygen cells, energy storage, cathode materials, carbon nanomaterials

The method of selection of the type and construction of anchor bolts for diversified geological-mining conditions of copper ore mines of KGHM Polska Miedź S.A. in the LGOM area

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The presentation outlined the work entitled "The method of selection of the type and construction of anchor bolts for diversified geological-mining conditions of copper ore mines of KGHM Polska Miedź S.A. in the LGOM area" carried out by the author as an implementation doctoral programme. A brief description is given of all tests carried out for this purpose, including load-bearing capacity tests of expansion anchor bolt in underground conditions, strength tests of rock samples and numerical analysis of cooperation of bolts with rock mass. The author compared results of load-bearing capacity tests and identified ways in which specific types of expansion anchor bolt can cooperate with various types of rock mass.

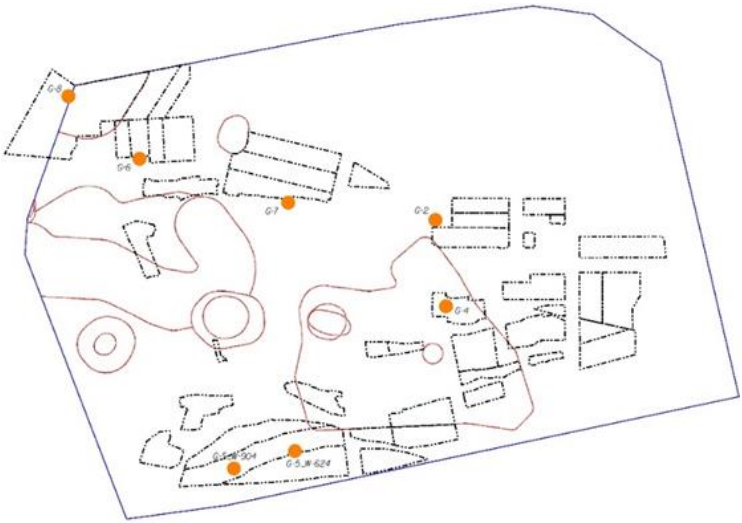

Fig. 1. Map of research testing grounds (orange points) in Lubin Mine

Keywords: rock bolting, expansion anchor bolts, rock bolting selection, roof bolting, underground mine

Microbial fuel cell able to produce biosurfactants during electricity generation

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Microbial fuel cells (MFCs) have been recognised as systems capable of degrading many types of pollutants, as well as converting some organic compounds to valuable products [1]. One of the possible directions of MFC development is the synthesis of biosurfactants from food industry waste. Biosurfactants are surface active compounds of microbial origin that can reduce surface/interfacial tension and have many advantages over chemically synthesised surfactants. In our work, we investigate the production of biosurfactants in microbial fuel cells from waste vegetable oil during electricity generation and assess the possibility of using biosurfactants to increase MFC performance. Thorough approach to solving problems with the degradation of hydrophobic oil substrates in the MFC, an optimal structure of the cell printed in 3D technology was designed and the content of one of the most important components of the medium was optimised. Furthermore, our research has shown for the first time that the biosynthesis process is a direct response to electricity generation [2].

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Keywords: MFC, biosurfactants, bioelectrochemical synthesis, sustainable development, renewable energy

Laser rangefinder module for machining industry

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Computer Numeric Controlled (CNC) machining centers, like all precision equipment, require periodic calibrations to maintain the quality of machining at the same level. Accurate measurements of a machine's geometry are required to perform such calibrations, and laser interferometers are usually used for these tasks. Unfortunately, they have quite a few disadvantages. The main ones are the high production price and the need for experienced personnel to operate them, as well as the time-consuming process of preparing such a system for operation. The biggest problem, however, is the need to take measurements relative to the starting point, and the laser beam cannot be interrupted while moving the reflector to the point to be measured.

In response to these problems, we present a prototype (Fig. 1) of a laser rangefinder that has sufficient measurement accuracy to calibrate CNC machines. Although there are already rangefinders based on the Time of Flight method that are suitable for such measurements [1], their production cost is still too high to commercialize such a solution. Our approach uses the phase difference measurement method and commonly available radio communication electronics circuits to optimize production costs and to be able to bring the device to market.

Fig. 1. Laser rangefinder prototype

Literature

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Keywords: metrology, lasers, algorithms, electronics, signal processing

Integrated GNSS tomography in meteorological applications

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The increasing number of GNSS observations, not originally intended as a source of meteorological information, are seen as valuable tools for future weather forecasting. Among the currently available data sources, where weather stations and radiosondes play the main role, GNSS stands out as an unbiased, reliable, and less costly substitute.

Most current studies on GNSS tomography focus on the use of GNSS ground receivers. However, these are difficult to deploy in high mountain or marine areas. Because of the low spatial resolution, tomographic reconstruction is difficult to apply for operational forecasting. A possible solution to these difficulties could be another type of GNSS observation. Radio occultations – signals crossing the atmosphere from GPS to LEO satellites – appear as a complement to classical observations independent of the terrain. However, combining two types of observations in one tomography model has never been done. The challenge here is to find a common way for simulating the radio occultations and ground-based GNSS signals with a common strategy for uncertainty estimation.

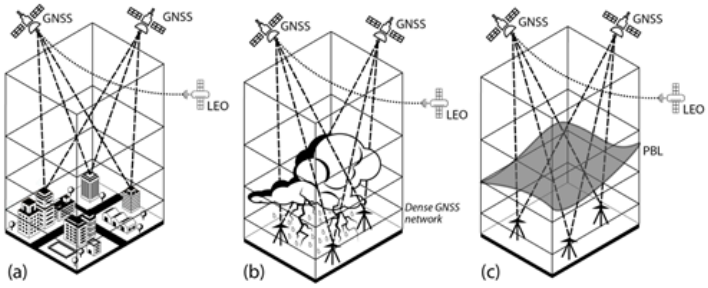

Fig. 1. Applications of GNSS tomography model in:
a) urban weather, b) severe weather, c) PBL detection and monitoring

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[2] Moller G., Landskron D., *Atmospheric bending effects in GNSS tomography*, Atmospheric Measurement Techniques, 2019, 12(1), 23–34.
[3] Rohm W., Bosy J., *The verification of GNSS tropospheric tomography model in a mountainous area*, Advances in Space Research, 2011, 1721–1730.

Keywords: meteorology, GNSS tomography, numerical weather model, ray-tracing, radio occultations

Synthesis and characterization of heteroatom-doped graphene materials for electrochemical energy storage

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The world's electricity consumption has increased significantly in recent decades, from 10 000 TWh in 1990 to 25 000 TWh in 2021. Although the global economy is still dependent on fossil fuels, harvesting energy from renewable sources is gaining importance. This calls for intensive research on methods for storing energy in the form of electricity, especially from renewable sources. The supercapacitor is an energy storage device that is widely investigated due to its high power density, fast charge and discharge rate, and remarkable stability during long-term cycling. Regardless of the energy storage mechanism (electrochemical double-layer capacitors or pseudocapacitors), the selected electrode material is crucial to its performance [1]. In recent years, graphene has become a promising replacement for activated carbon as an electric double layer capacitor (EDLC) electrode due to its outstanding properties (e.g., high specific surface area, good electronic conductivity, and mechanical robustness). The electrochemical performance of EDLCs can be enhanced by applying carbon electrodes with high specific surface areas and preferable pore-size distributions. Additional heteroatom modification of graphene materials is advantageous for boosting their capacitive performance [1, 2]. Various heteroatoms, such as nitrogen, oxygen, phosphorus, or sulfur, have been extensively studied as dopants of carbon-based materials. The oxygen or phosphorus incorporated within the graphene structure increases the wettability and improves electrolyte ions' transport at the electrode surface. Furthermore, the introduction of a heteroatom results in more defects on the graphene surface and leads to an increased number of reaction sites. Heteroatom doping also expands the operating potential window of a supercapacitor operating in an aqueous electrolyte beyond the theoretical potential of water decomposition (1.23 V). This directly contributes to achieving the goal of high energy density values [2].

Literature

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Keywords: heteroatom-doped reduced graphene oxide, hydrothermal synthesis, symmetric supercapacitor, aqueous electrolyte, electrochemical energy storage

Flow-aware multi-topology adaptive routing as a solution for network congestion

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Flow-Aware Multi-Topology Adaptive Routing (FAMTAR) is a new approach to routing in IP networks which enables automatic use of alternative paths when the primary ones become congested. In per-packet routing, due to loop prevention constraints, only a subset of disjoint paths existing between selected nodes can be used. Adaptive routing is also impossible, as the dynamic alteration of link costs leads to instability which ultimately deteriorates network performance.

FAMTAR was developed to answer the aforementioned problems by making the use of flow-based approach. It can overcome limitations of per-packet routing by maintaining separate per-flow forwarding entries. In an uncongested network, all transmissions between endpoints use shortest paths. When a shortest path becomes congested, all new flows are pushed to alternative paths, while already active flows remain on their primary paths. As a result, flows between the same endpoints can follow any number of alternative paths without the risk of loops [1]. Furthermore, paths for subsequent flows can be chosen with the current or a predicted network load in mind, effectively resulting not only in the multipath routing, but also in the adaptive routing [2]. Such an approach also ensures a better stability, as only new flows are redirected to new paths during a congestion [3].

Despite recent technological advancements, the number of simultaneous flows in networks still overwhelms the capacities of switch flow tables. Solution is to focus on dynamically identified elephant flows. This can significantly reduce the number of flow entries, while simultaneously keeping most traffic covered by TE [4].

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Keywords: routing, traffic engineering, multipath, elephant flow

Management of brewing waste according to the concept of sustainable brewing

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Beer production has been known for ages around the world and it is currently reaching over 33 billion litres per year in Europe. Such a remarkable production rate is inevitably connected with large amounts of by-products, including brewers' spent grain (BSG) and spent hops. Brewing waste is still rich in valuable substances which can be reused for many purposes. Spent grain, which consists of malt which already underwent the mashing process (brewing step applied to derive sugars which can be further fermented by yeast) can be treated as a source of carbohydrates and proteins. Residues from hopping – spent hop pellets and cones – are rich in essential oils and a variety of compounds known to positively impact human health – including polyphenols, the majority of which do not get extracted during hopping [1] [2]. The goal of the studies is to develop ways of deriving and re-using valuable substances from brewing waste.

Figs. 1, 2. Brewers spent grain and hops

Literature

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Keywords: brewing, brewer's spent grain, spent hops, circular economy, brewing waste

The molecular mechanism of Antimicrobial Photodynamic Therapy against bacteria

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Antimicrobial Photodynamic Therapy (APDT) is recently an intensively explored alternative to fight bacterial infections. The main motivation is the growing problem of antibiotic resistance. Chemically, APDT is based on the light activation of a chemical compound called photosensitizer (PS), and the production of reactive oxygen species through the transfer of absorbed energy (Fig. 1). From a biological point of view, it is well-known that the main consequence of photoinactivation is the widespread oxidation of biological structures, however, the exact mechanism is still unknown [1].

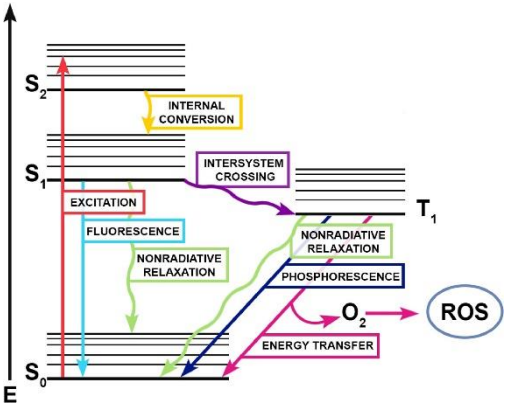

Fig. 1. Modified Jablonski diagram of chemical APDT basics. Reprinted with permission from Żak et al. [2]

The main aim of my PhD project is to describe the molecular mechanism of APDT directed against bacteria. In my research I consider the significant importance of bacterial lipids in the destruction of the cell by APDT, since the bacterial cell membrane is the first barrier to oxidative processes, and its primary component is the lipid fraction as the only one undergoing chain oxidation. Currently, through a collaboration with and Laboratoire de Chimie de l'ENS Lyon (France) I am investigating the direct effect of ADPT on giant unilamellar vesicles (GUVs) from bacterial lipid extracts as a simplified model of the bacterial cell membrane [2].

Literature

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Keywords: APDT, bacteria, GUV, oxidation, photochemistry

Optical nano-refrigators utilizing anti-Stokes cooling

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Laser cooling is a process that involves reducing the temperature of a system through interaction with light. While Doppler cooling of single atoms or dilute gases is a well-known example, a lesser-known variant of this process is anti-Stokes cooling, which utilizes phonon annihilation to lower the temperature of a solid body. This phenomenon could be used to construct optical refrigerators that are free of moving parts, reliable and can be miniaturized down to the nanoscale [1], [2].

Among the various materials proposed as optically cooling agents, rare-earth-doped nanoparticles appear to be the most promising [3]. As part of a doctoral project at the Institute of Advanced Materials, Faculty of Chemical Engineering, I am working on the production and optimization of such nanorefrigerators in an aqueous environment, which has proven to be particularly challenging [4]. In this presentation, I will briefly describe the physical mechanism responsible for the cooling process and discuss the main engineering and experimental challenges associated with this project.

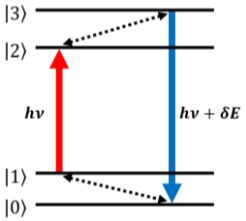

Fig. 1. Anti-Stokes cooling cycling occurring in a four-level system through red photon absorption and blue photon re-emission. The energy difference δE comes from the phonon, removed from the system

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Keywords: laser cooling, lanthanide-doped nanoparticles, Raman thermometry, optical tweezers, optical spectroscopy

Filament quality monitor for fused filament fabrication

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Additive manufacturing technologies are the basis for rapid prototyping in today's research and development process. FFF 3D printers are particularly useful, as they allow for quick and low cost production of objects on site at the research facility. It is known that uncompensated fluctuations in the material properties of the filament used for printing are the source of irregularities and defects in the manufactured elements. The discussed filament quality monitor allows for low-cost, real-time recording of filament properties such as: relative electric permeability, type of material, moisture, changes in diameter and roundness, external and internal defects, components proportions, characteristics over the length. The measurement is carried out by placing the filament between the plates of the capacitor and continuously measuring its very small capacity, which translates into the relative electrical permeability of material. In order to assign the measured value to a specific filament fragment, the device monitors the longitudinal movement of the material with a magnetic encoder. In addition, Hall sensors measure the diameter of the filament in 3 independent axes. Taking into account the changes in the filament geometry, it is possible to make corrections for the measurement of the relative electrical permeability in real-time.

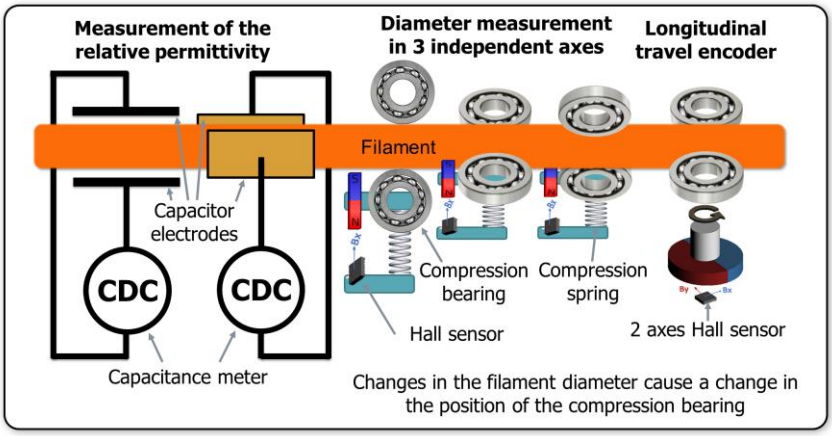

Fig. 1. Filament Quality Monitor Schema

Keywords: electronics, additive manufacturing, filament metrology

Effect of repeated non-thermal plasma treatment on virulence characteristics of phytopathogenic fungi

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Food loss is a serious problem worldwide, especially considering the growing global population and the fact that about one-third of all food produced for human consumption is lost or wasted [1]. Diseases caused by phytopathogenic fungi cause the loss of up to 30% of the world's crop yields, enough to feed 600 million people annually [2]. It is widely believed that low-temperature plasma can overcome many of the limitations of traditional fungicides and is considered one of the most promising sterilization method. A reduction in the pathogenicity of fungi subjected to repeated plasma treatment was observed, which is reflected in an increase in the percentage of germinating seeds, as well as the weight and length of plant parts artificially infected with the tested fungi after the 5th, 10th and 15th plasma treatment. The reduction in the negative effects of pathogens on host tissues under the influence of multiple plasma treatments indicates that this technique can be considered as a method for controlling plant pathogens in agriculture and food processing.

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Keywords: phytopathogenic fungi, cold plasma, virulence, sterilization, crop loss

Investigation of bending process parameters of anisotropic materials on the geometric, mechanical, and fatigue properties the product

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Sheet metal bending is widely used in numerous branches of manufacturing. Bent parts are frequently used in responsible roles, such as hangers or brackets, which impose strict requirements on technological quality and durability, including fatigue strength. It is known that the bending process influences the material structure in the bending zone. Cracking due to overbending always starts on the grain edges [1, 2], which is similar to the fatigue crack forming mechanism that also begins on grain edges [3]. Although the current literature does not describe the influence of bending process parameters on the fatigue life of a product, given the similar crack initiation mechanism and microstructure influence on fatigue strength, it can be assumed that a correlation between process parameters and fatigue life expectancy exists and can be described. An analysis of this issue will be conducted both numerically and experimentally. FEM analyses of anisotropic materials' bending processes using Barlat's and Hill's anisotropic plasticity models will be conducted. Anisotropic plasticity parameters were obtained using a biaxial tensile test with DIC strain measurement. Experimental tests will be conducted in an industrial environment with a commercial brake press and tools. The main objective of this work is to elaborate on the universal guidelines for choosing bending process parameters of anisotropic materials in terms of achieving the optimal technological quality and fatigue strength of the finished product.

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Keywords: anisotropic materials, sheet metal bending, fatigue life, FEM analysis

The potential application of biochar in agriculture and environmental protection in the context of the circular economy

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Due to the continuous growth of the population and increasing consumption, the amount of waste generated and the need for its valorization are increasing. Nowadays, the management of food/plant waste (such as peels, leaves, straw, freshwater and marine algae) is necessary. Waste plant biomass and food waste can be used as a feedstock in a various thermal processes resulting in valuable bio-based products. The pyrolysis/co-pyrolysis process is one of the thermal processes that convert waste/biowaste into usable products including biochar, biooil, and biogas. Depending on the conditions of this process (temperature, time, modification etc.) and the raw material, the obtained products will differ in durability, content of elements, aromaticity, etc.

The conducted research is aimed at checking the possibility of using waste biomass to produce biochar, which will be use in wastewater treatment and agriculture. Due to the porous structure, high specific surface area, and many functional groups, biochar will be used to remove organic and inorganic pollutants from wastewater. In order to apply the concept of a circular economy, after biochar removes ions of biogenic elements (such as nitrogen and phosphorus) from wastewater, enriched biochar can be used as a soil additive. Additionally, good sorption properties of biochar also allow it to immobilize pollutants in the soil, which will reduce their bioavailability for plants.

Keywords: waste biomass, pyrolysis, biochar, biosorption, agriculture

Analysis of the influence of geometrical and technological parameters of the anisotropic aluminum sheet punching process on tool wear

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Current research in stamping processes is focused on identifying tool wear mechanisms. Predicting wear is challenging due to the complicated phenomena in the cutting zone, including large contact forces and multiple wear mechanisms occurring simultaneously. Damage to the cutting edge leads to a deterioration of the cut edge quality, particularly in burr height. Punch wear rate and type depend on many factors such as material type, punch geometry, and friction conditions [1]. Punching clearance is also important [2]. While greater clearance reduces wear, it also negatively affects product quality. In industrial practice, tool wear is mainly assessed based on cut edge quality evaluation, without distinguishing between wear mechanisms. This approach is not optimal for cutting anisotropic materials where different edges wear faster. Specially designed tool geometry can reduce this phenomenon and ensure longer tool change intervals, reducing manufacturing costs. Tool wear mechanisms in stamping processes can be classified as abrasive, adhesive, plastic, and fatigue [3]. The aim of this work is to determine the factors that influence the dominant wear type depending on process parameters to ensure maximum possible service intervals. This could result in creating innovative punching tool geometries. Considerations will be carried out using FEM analyses and experimental methods in an industrial environment.

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Keywords: anisotropic materials, blanking, punch wear, FEM analysis, aluminum alloys

Water in beer brewing

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Beer is a popular drink across the world. There are four basic ingredients needed for beer production: water, malt, hops and yeasts. Water content in beer is above 90%. Water is composed of various minerals, such as calcium, magnesium, and sulfates, which can affect the flavor and character of beer. The mineral content of water can vary depending on the source, and different regions may have water with varying mineral profiles. Water treatment methods can be used to modify the mineral content and pH level of water to achieve the desired brewing water profile. Methods such as reverse osmosis, deionization, and acidification can be used to adjust the water's mineral content and pH level to the desired levels. Different brewing styles may require different water profiles to achieve the desired flavour and characteristics. For example, certain beer styles, such as pilsners or lagers, may require water with low mineral content, while others, such as stouts or porters, may benefit from water with higher levels of minerals [1]–[3].

To sum up water is a critical component in the brewing process and can have a significant impact on the quality and flavor of beer. Brewers must consider the mineral content and pH level of their brewing water to achieve the desired characteristics and flavours in their finished product.

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Keywords: beer, water, brewing, fermentation, water treatment

Characterization of a Co-based alloy with high glass forming ability

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This work involves extending the knowledge about the group of cobalt-based alloys with a high glass-forming ability with the aim of developing an amorphous structure. In this work gas-atomized powder Fig. 1a, casted plates Fig. 1b and bulk samples by selective laser meting Fig. 1c are presented. Powder and bulk samples were successfully fully amorphous, while the plate exhibits presents of some microscopic crystals inside the amorphous matrix.

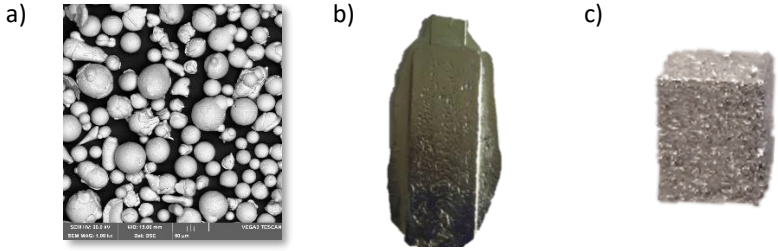

Fig. 1. Co47.6B21.9Fe20.4Si5.1Nb5 alloy developed by: a) gas atomization, b) casting, and c) SLM

The amorphous structure of those alloys allows to obtain a very high elastic limit, higher than that of commonly used steels. At the same time, amorphous alloys exhibit a very high hardness combined with brittle structure, especially cobalt-based alloys that are in the field of interest. The characterization of $Co_{47.6}B_{21.9}Fe_{20.4}Si_{5.1}Nb_5$ in this work involves nanohardness analyses of developed samples. The highest hardness was observed for crystals observed in the plate – 25.5 GPa, while the matrix has still very high 14.3 GPa. The powder and bulk sample had a hardness on the level of 14.6 GPa. Future research concerns the development of composites with an amorphous metal matrix and the ductile phase as a reinforce. In the future, these types of composites can ensure both a very high elastic limit and resistance to critical cracking.

Keywords: amorphous metals, additive manufacturing, bulk metallic glasses composites, rapid solidification processes

Technology of fertilizers with amino acids obtained from high-protein raw materials

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Synthetic nitrogen fertilizer production is responsible for 2.4% of global greenhouse gas emissions. The production and use of fertilizers also affects on the environment by contributing to greenhouse gas emissions, the consumption of non-renewable raw materials and the environmental dispersion of fertilizer components, resulting in eutrophication. This situation, along with other problems of modern agriculture (the necessity to increase production for an increasing number of people, environmental degradation), leads to the exploration of renewable sources of fertilizer components and other forms of plant growth stimulation. There are currently 126 agricultural biogas plants registered in Poland with a total production capacity of 599 million m^3/year. Due to their qualification as Renewable Energy Sources, the energy transformation policy and the current political situation, we can expect a further increase in their quantity. Therefore, the management and rational use of digestate will be an important issue in the near future. Currently, this residue is spread on fields or used in agriculture as a fertilizer. Due to its low nitrogen content, this is only economically reasonable in the nearest surroundings of the biogas plant. This form of fertilization when applied in large quantities (20–50 t/ha) will increase the nitrogen content, but may lead to changes in the soil rhizosphere. In the face of this, the primary purpose of fertilization – to increase yield – is not guaranteed. They are not the only problems related to the use of digestate as a fertilizer. Biological activity is responsible for the emission of methane into the atmosphere. The liquid form can also be problematic, both in terms of transport (need for special containers) and subsequent operation (single, rapid release of nutrients, potential for run-off into surface water). In view of these challenges, it is necessary to: develop new fertilizer formulations for agriculture together with the production technology, developing waste-free management technology for selected residues, reduce the negative effects of agriculture on the environment through controlled release of fertilizer components.

The study was funded by Horizon2020. Grant no: 696356.

Keywords: fertilizers, waste valorization, nutrient recovery, amino acids

Hydrogen combustion system for spark ignition engine

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The so-called hydrogen knock phenomenon may have two mechanisms of formation, thus we are talking about heavy or light knock [1]. Since heavy knock formation is related mostly with compression ratio being a geometrical feature, the system is designed to improve the combustion parameters of the hydrogen-air mixture in the area of light knock. The use of an active prechamber integrated with the engine head should enable the use of leaner mixture degree than in the case of chambers screwed into the spark plug seating. Presented solution should ensure greater heat transmission from the combustion process and allow for even flame propagation due to orifices installed in the prechamber necking area. The main advantage of the discussed system should be a higher compression ratio while maintaining pressure pulsation below the light knock limit.

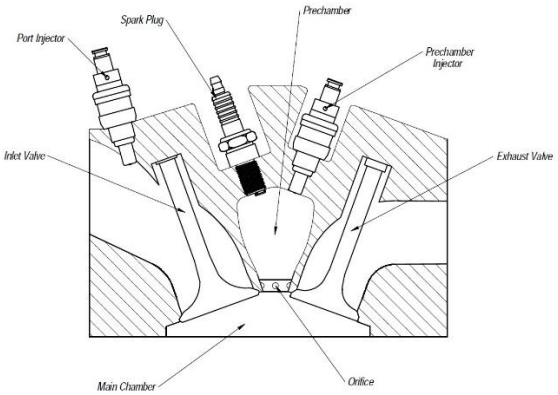

Fig. 1. Simplified scheme of hydrogen combustion prechamber system [2]

Literature

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Keywords: hydrogen combustion, hydrogen knock, prechamber, H2ICE, combustion engine

Deep Learning Methods in Reinforcement Learning: Continual Learning and Explainable AI in Robotics Applications

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Reinforcement Learning allows learning by using feedback from the environment or labeler in terms of rewards. It is used successfully as part of Natural Language Processing algorithms such as ChatGPT3.5 and can also be applied in robotics applications for learning manipulation or locomotion tasks; however, a few problems need to be solved. In this presentation, I will briefly introduce a few of them and show current approaches.

The first is the problem of Continual Learning [1], which means learning a few consecutive tasks using the same model to have a universal algorithm that can handle many tasks. Another one is explaining the decisions the algorithms make. Deep Neural Networks, which are used as a backbone of modern AI algorithms, are a black-box approach, which limits their applications in real-life such as in autonomous driving, due to the high risk of damage. However, some methods, such as SHAP [2], show what inputs are problematic and help to get insight into AI decision logic. After having a reliable model trained in a simulator, the final phase is to transfer it to a physical device, which is the last problem I want to describe.

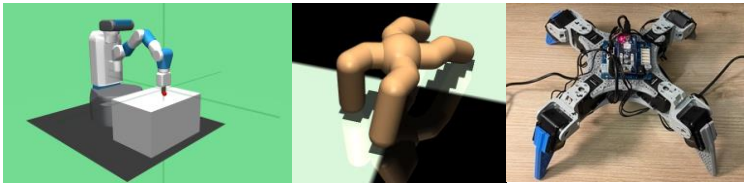

Fig. 1. Example of a fetch-reach manipulation task and a locomotion model transfer from simulator to a quadruped robot.

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Keywords: Reinforcement Learning, Deep Learning, Continual Learning, Explainable AI, sim2real

Average entanglement entropy of midspectrum eigenstates of quantum-chaotic interacting Hamiltonians

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How to describe a chaotic system? That question has gained notable attention due to its connection to the real world depiction. Being macroscopic, in this case chaos is described within a set of deterministic laws that can lead to not necessarily predictable results as the entry constraints are set. Therefore, it is not impossible to say that even a tiny alteration in the initial conditions may have devastating consequences for the whole system. This way, a butterfly flapping its wings may even cause a tornado in Texas [1].

How to define chaos when the system is no longer macroscopic and quantum effects have to be considered? It turns out that the answer to this question is not straightforward. As of our understanding, the best description of quantum chaotic systems is given when one treats it as effectively defined by purely random matrices [2]. One way to indicate quantum chaos may be to verify how much does a part of the system in highly energetic states know about its rest. There exists a standard measure that quantifies such knowledge, namely the entanglement entropy. In other words, we check the agreement between the prediction for purely random states and the entanglement of quantum chaotic interacting Hamiltonians. We find indications that, in the middle of the spectrum (in the high temperature regime), the magnitude of the negative corrections to the random states prediction is only slightly greater than zero, yet nonvanishing.

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Keywords: quantum chaos, entanglement, entropy, condensed matter, quantum mechanics

Metabolic signatures of mice brain reveals a changes during aging

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Metabolomics is an analytical profiling techniques which allow to analyze a small molecules, universally known as metabolites, in biological samples and investigate their changes in physiological conditions as well as under diseases [1]. Actually, one of the most commonly used techniques in metabolomic approaches is Nuclear Magnetic Resonance Spectroscopy (NMR), especially in brain metabolism research. As is well known, aging is associated with multiple changes in phenotypical, physiological, and functional states [2]. Unfortunately, little is known about how metabolic pathways change across development. To fill this knowledge gap, it is quite attractive to use metabolomic approaches (NMR) to analyze the image of nervous tissues in different age [3]. These results not only can provide new information about potential biomarkers implicated with age, but also allow one to solve complicated biochemical pathways.

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Keywords: metabolomic, nuclear magnetic resonance spectroscopy (NMR), mass spectrometry (MS), aging, neurobiology

The importance and influence of the state policy on housing construction in Wrocław, including the activity of housing cooperatives in the period of the Weimar Republic

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The starting point of the doctoral dissertation is a discussion of the housing situation after the First World War in Germany, with particular emphasis on Silesia. Housing conditions were tragic; there was a quantitative and qualitative lack of housing for the poorest class. In the first post-war years, the Weimar Republic began activities to solve the housing problem, the country made an effort to build new social housing estates, which became a model of modern housing solutions, and significant changes in the architectural form took place. Thanks to the introduction of Charles Gates Dawes' plan (foreign capital supplied the German economy), from April 1924, the phase of economic improvement began. New architectural trends spread in Germany more than in any other European country.

In 1926, the State Research Society for the Economics of Construction and Housing was established to carry out and finance research on rational development and to support model housing projects. It dealt with the internal layouts of apartments and their surface, new materials and technologies. At the beginning of the 1920s, Wrocław was perceived as a unique place on the map of Europe because of new ways of solving housing problems. Housing estate cooperatives and housing associations of general utility greatly impacted new housing estates. The research will aim to show the impact of mentioned institutions and companies on the development of modern housing. The last point is to examine the influence of the interwar period's architecture on residential architecture after the Second World War.

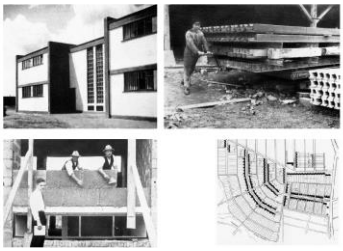

Fig. 1. Dessau, Töerten housing estate, arch. W.Gropius, 1926-1928. Bericht über die Versuchssiedlung in Dessau, Reichsforschungsgesellschaft für Wirtschaftlichkeit im Bau- und Wohnungswesen, Sonderheft 7, Vol. 2, April 1929, pp. 5, 41, 84, 137

Keywords: architecture, modernism, social architecture, housing estates

The surface modification in low-pressure cold sprayed TiO_2 coatings: effect on mechanical and photocatalytic properties

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The TiO_2 photocatalytic coatings' most important properties are durability and photocatalytic activity. Those features form a basis to determine its degree of usefulness. In this study, the self-synthesized amorphous TiO_2 powder was used to low-pressure cold spray photocatalytic coatings. Two strategies were adopted to change the surface properties, which can influence the mechanical properties of the coatings: (I) reduction of the scanning step, (II) filling the depressions in the already sprayed coating with the second layer. The coatings surface topography (measured by roughness and waviness) results showed that the first strategy makes coatings thicker, with a more uniform surface. The second strategy leads to obtaining more rough surfaces with no significant change in the thickness. The preliminary study results indicate that the first strategy was superior to the other one, both in terms of mechanical (described by cohesion and adhesion) and photocatalytic (measured by the decomposition of methylene blue under UV) properties of the coatings.

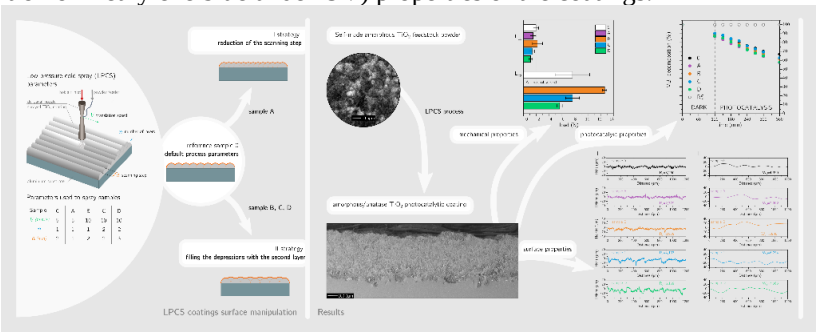

Fig. 1 Graphical abstract of the experiment and results.

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Keywords: 5 TiO_2, soft ceramic, low-pressure cold spray, cold gas dynamic spraying, ceramic coating, amorphous

Animal waste materials as a source of valuable nutrients for plants

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Selenium is an important micronutrient in the human organism. It is delivered with food. It is found in the greatest amounts in animal protein products, meat, including seafood, dairy products and eggs. Due to its similarity to sulphur, it is incorporated into amino acids, building important selenoproteins [1]. Slaughtering animals for food, in addition to obtaining edible products such as meat and offal, is connected with generating of inedible products such as horns, hides, hoofs, tallow, dung, bristles, gall bladder, ears, skin, and blood. Depending on the region and culture, waste may be even 40–55% of the animal's weight. With an annual worldwide production of more than 250 million tonnes of meat, a similar amount of waste is generated. These wastes are mainly proteins and fats, which contains important macro- and micronutrients. They can be returned to the agri-food cycle as fertiliser for plants [2].

Acknowledgments

This project is financed in the framework of the Polish-South African/South-African-Polish research projects, grant PL-RPA2/08/BioSeFert/2019 entitled: „Biofortification of plant biomass with selenium by utilization of biofertilizers obtained via microbiological solubilization" attributed by the National Centre for Research and Development.

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Keywords: selenium, nutrients, proteins, food, wastes

Can ‘Quantum Tea’ stay hot forever?

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As we know from everyday experience, a cup of tea left in a room will eventually reach room temperature. Then, it is impossible to know if the considered beverage was a hot tea or an iced tea. Information on the initial state of tea was lost due to its interaction with the environment (in a process called thermalization). Fortunately, due to technological development, humankind invented an insulated flask that allowed people to enjoy well-chilled ice tea for a whole day, even during increasingly common heatwaves.

A ‘Quantum Tea’, in contrast, even in the best insulation from the environment, will lose information about the initial state due to quantum processes. This irritating tendency of quantum systems to forget about their initial conditions is one of the most difficult problems to overcome in the development of a quantum computer.

However, there may exist generic quantum systems that do not thermalize and may preserve the initial state for infinitely long times. The most promising candidates are disordered systems with many-body interactions that exhibit very slow dynamics and may be important for future applications in quantum computing. Nevertheless, numerical calculations are challenging and the consensus about the stability of such systems is not reached yet, but the underlying difficulties have been identified [1, 2].

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Keywords: disordered quantum systems, ergodicity, eigenstate thermalization, many-body localization

Gear pump with radial compensation

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Today, the gear pump is one of the most commonly used displacement pumps in hydraulic drive systems, it is characterized by high efficiency [1] and the lost power is converted into heat [2]. There are many design variations depending on the application [3]. Internal gear pumps commonly used in hydraulic drives did not appear until the second half nineteenth century. As with the external gear pump, one gear acts as the drive gear. An external drive is connected to the axle of this wheel. In the rotor of the driving wheel rotation, the driven wheel with internal gearing also rotates, sometimes also called a toothed rim. The liquid is transported through the interdental grooves, and the tight separation of the suction space from the discharge space is achieved by means of an additional element, called a sickle insert. It owes its name to its characteristic appearance. The surface of this insert works closely together with the surface of the tops of the gears. Pumps of this type are designed to transport all types of liquids. The radial compensation of the sickle insert consists in obtaining two flexible tongues which, when subjected to pressure from the side of the pressing space, reduce the clearance between the insert raceway and the pinions of the gear wheel. Below is a view of the introduced patent solution No. P.431145 approved by the Patent Office of the Republic of Poland.

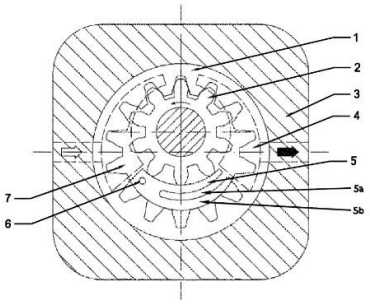

Fig. 1. Cross-section of a modified crescent insert based on patent P.431145:
1 – gear rim, 2 – gear wheel, 3 – pump body, 4 – pumping space, 5 – crescent insert, 5a – bay inside the sickle insert, 5b – flexible sickle insert, 6 – fixing pin, 7 – suction space

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Keywords: gear pump, capacity, internal gearing, sickle insert, friction resistances

Seismic vibration analysis as an environmentally friendly method of improving rail transport safety

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Based on the measurement and classification of seismic vibration signals emitted by moving animals, the research intends to develop a system for detecting and identifying animals near railroad tracks. The proposed solution is an active, non-infrastructural method that does not interfere with animal migration routes, so it will not affect the biodiversity of the environment and will reduce the barrier effect of the railroad network.

In order to detect animals' presence before a potential collision with trains, which occurs frequently in Poland, the method includes algorithms for recording and recognizing deers, moose, roe deers, and wild boars' footfall signals. The seismic signal is analysed using digital signal processing and machine learning algorithms (in a supervised approach), which can distinguish between vibrations coming from an approaching animal and those coming from other, disruptive sources like people, trains, and cars. Measurements in controlled environments (like zoos and nature reserves) are used to collect samples of animal walking signals that are afterwards validated in actual environmental conditions. The presented solution will be supporting component in various systems of deterring animals from railroad tracks. The overall concept is to increase railroad safety through an innovative, ecological, and developmental approach.

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Keywords: rail transport, railway safety, seismic vibrations, signal processing and classification, wildlife protection

Additive manufacturing of an individualized leg orthosis

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The main aim of the presented research and practical work was to design a functioning, stable and usable pair of 3D printed lower limb orthoses, which could be used for walking, as well as swimming and performing various activities in the water. The customizable orthoses were designed using a prototype of AutoMedPrint (AMP) system. Three various orthoses designs were printed using FDM technology of the well-known 3D printing filaments, i.e., PET-G, PA12, and iteratively tested, checked by physiotherapist and tested by patient, to finally come up with a solution both fitting the patient and enabling him to walk and perform all the necessary activities. In the end, an usable orthosis was obtained, which will be further processed and its design fully automated.

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Keywords: AFO, 3D Printing, Individualized orthoses, Medical 3D printing, 3D scanning

Are probiotic bacteria the key to treating allergies?

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Most people love spring. But why not everyone? What's not to love: sun, warmth and long days. Unfortunately, for every third person reading this abstract, it is a period of endless runny nose, constant headache and watery eyes. Why? Because there is no cure for allergies, and the measures used by allergy sufferers are only intended to relieve or partially eliminate the symptoms. And the season begins with the flowering of the hazel at the beginning of February and ends in September, when the last grasses fade.

It is estimated that 30–40% of the entire population is affected by allergies [1]. Allergic disorders are a consequence of the dysregulation of the immune system due to insufficient exposure to microorganisms or the destruction of one's own bacterial flora [2]. Most probiotic strains belongs to *Lactobacillus* and *Bifidobacterium* species. Not only do they colonize the gastrointestinal tract in the first moments of our lives, thus preventing it from being colonized by pathogenic bacteria, but also with their presence they direct the maturation of the immune system [3]. Their lack leads to diabetes, obesity and asthma. Research shows they may offer a new solution for treating depression [4]. So why not use them in the treatment of pollen allergy? What is an effect of various strains of *Bifidobacterium* on the immune system? What molecules are responsible for the fact that one strain is considered probiotic and the other does not?

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Keywords: *Bifidobacterium*, allergy, surface antigens, probiotics, immunology

Synthetic *Cinchona* alkaloids analogues: aminoalcohols outside the chiral pool

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Cinchona alkaloids are not only known for applications as antimalarial drug, but also for their very neat catalytic properties[1, 2]. In organocatalysis they can behave in two ways: they induce high yields and more importantly - high enantioselectivity. *Cinchona* alkaloids however are very tough to synthesis in laboratory environment [3]. This is due to some functional groups (vinyl, methoxy group) within this molecule which makes total synthesis economically unprofitable. For our luck some of those functional groups are unnecessary when we consider using it only in catalysis. So there was a need to find a neat way to synthesis synthetic *Cinchona* alkaloids analogous. Those analogous should be inexpensive to synthesis and have the same or even better catalytic properties in comparison to *Cinchona* alkaloids.

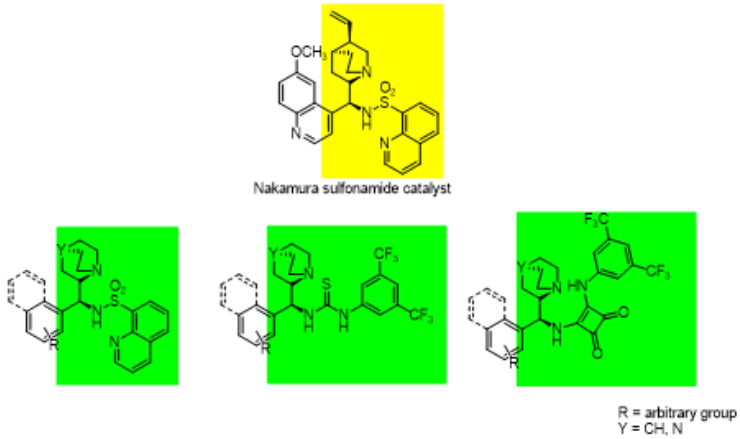

Fig. 1. Proposed principal new analogous product

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Keywords: organic chemistry, catalysis, total synthesis, DFT calculations

The role of fructose 1,6-bisphosphatase in crosstalk between astrocytes and neurons

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Abstract: The brain is the most complex human organ, and its physiology is not fully understood. It consists almost 100 billion neurons, which form a dense network of connections. Neurons constitute about 50% of all brain cells, the remaining 50% are glial cells, for example astrocytes [1]. It is known that astrocytes actively support neurons and are crucial for proper functioning of the system [2] (Fig. 1). Over the past few decades, it has been observed that maintaining homeostasis in the central nervous system would not be possible without communication between individual types of cells. One of the ways of intercellular communication is secretion of extracellular vesicles into the extracellular space (Fig. 1). Extracellular vesicles contain varied molecules, which take part in modulation of cellular molecular processes, both physiological and pathological [3]. My studies are especially focused on the role of multifunctional protein – fructose 1,6-bisphosphatase 2 (Fbp2) in astrocyte-neuronal crosstalk. Fbp2 is a regulatory enzyme of glucose and glycogen metabolism, but recent studies show that it is also engaged in memory formation, stress reactions and developmental processes (Fig. 1) [4]. Better understanding of brain physiology regulation may help identify new targets for treatment of memory disorders that result from aging or neurodegenerative diseases.

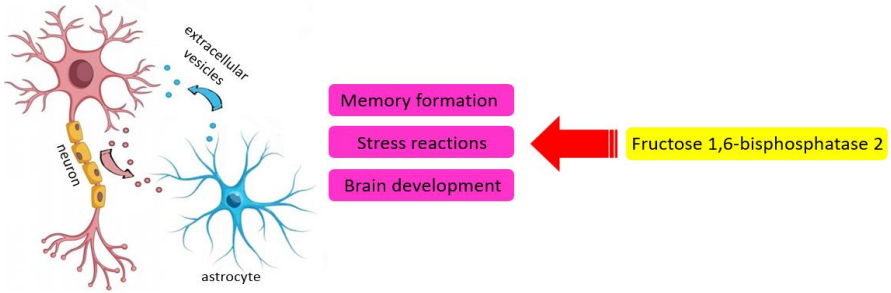

Fig. 1. Brain molecular processes are regulated by astrocyte-neuronal crosstalk and Fbp2.

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Keywords: fructose 1,6-bisphosphatase, intercellular communication, extracellular vesicles, astrocytes, neurons

Ice surface fractures detection in Synthetic Aperture Radar products

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Abstract: Synthetic Aperture Radar (SAR) products are being constantly obtained and shared free of charge by the European Space Agency (ESA). Their popularity in remote sensing is still growing despite the fact that first SAR usage is dated for 1954. SAR is based on the Doppler frequency shift phenomenon, which allows to significantly improve the spatial resolution of the image without enlarging the antenna. Additionally, because of the microwave usage, sensor can operate day and night regardless of weather conditions. All of the above resulted in wide range of SAR product applications, e.g., in ground surface monitoring [1], glacier features mapping [2–4] or faults and landslides detection [5, 6].

In my doctoral thesis, I will focus on glacier features recognition based on the SAR products. Three main glacier elements and features are currently obtained from the SAR products, namely grounding line positions, calving front positions and surface flow rate. While grounding line detection with tidal methods are well established and proven, the calving front detection method is still to be improved. I will try to implement the method used to detect in-land faults [5] to identify fractures in ice surface as an indicator of future calving events. Additionally, with successfully implemented method of cracks detection I will try to automate the mapping task with Deep Neural Network. I hope to share the final product via private webpage or at one of the services providing SAR data.

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Keywords: SAR, glaciers, remote sensing

The effect of different pro-oxidant concentrations on HEK-293 and COS-7 cell lines

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Chronic inflammation is a consequence of long-term acute inflammation in the body and may lead to the induction of many diseases, i.e. obesity, diabetes, neurodegenerative diseases. One of the reasons for this condition may be the accumulation of excessive amounts of free radicals. Under physiological conditions, this state is favourable because it accelerates many positive for human body processes, e.g., wound healing and bone fusion. Unfortunately, free radicals also have a negative role in the body that can be generated in situ and/or come from the environment external. Cell cultures are particularly useful for studying the effects of oxidative stress on cells. Cells incubated with pro-oxidant compounds constitute great models of inflammation that are triggered by persistent oxidative stress in the cell. Such models help explain the role and pathogenesis of oxidative stress in many diseases, e.g., in neurodegenerative disorders of the brain, rheumatoid arthritis.

The aim of the study is identifying the metabolic changes at different concentration of hydrogen peroxide solution for HEK-293 and COS-7 cell lines.

Research has confirmed that higher concentrations of hydrogen peroxide solution increase cell death and generate free radicals (ROS). Changes in the metabolome were observed in the NMR spectra during oxidative stress in cells. The conducted research allows to determine the extra- and intracellular metabolome of the HEK-293 and COS-7 cell lines. During oxidative stress we can observed significant changes in extracellular metabolites for both HEK-293 and COS-7 cells: glutamate, acetate, sarcosine, pyruvate, glutamine, oxypurinol, lactate, 3-hydroxybutyrate. Change is also observed in intracellular metabolite. The relative concentration of intracellular metabolite: glutamate, NADH/ NAD+, glutathione was decreased, but relative concentration of AMP and oxypurinol was increased.

Keywords: oxidative stress, metabolomic, cell culture, metabolom, hydrogen peroxide solution

Hybrid DES-CTS Multiple Mobile Robot Systems

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Abstract: Development of multiple mobile robot systems is progressing rapidly, creating a need for fast and formally correct automated synthesis of their motion control. My work focuses on a hybrid layered model of MMRS with transportation tasks, in which the supervisor controller operates using a discrete event system. Events are generated by the continuous movement of autonomous mobile robots in a space that is discretized during system synthesis (so-called *space-as-a-resource*). Each robot requests the allocation of further resources needed to finish its task and emits resource release events. The discrete supervisor checks if the requested resources can be allocated without creating collision or first-order deadlocks with other robots. My research methods involve the use of special methods for discretising space and pathways, such as second degree Bezier splines, continuous-time control of AMR (e.g. with artificial potential fields) and different safety checks on the supervisor level for restricted family of tasks with additional constraints (e.g., one or more robots in the resource). Example results of successful system synthesis can be find in the [1] and [2].

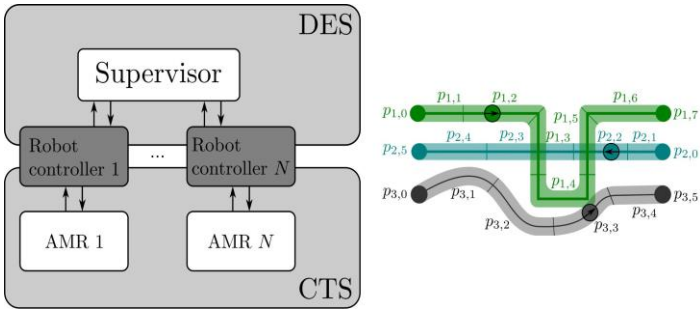

Fig. 1. Layers of control in the hybrid MMRS (left) and example 3 transportation tasks (right)

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Keywords: mobile robots, discrete event system, continuous-time control, system synthesis

Design of miniprotein inhibitors of cancer-causing protein–protein interaction

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Cancer is a type of civilization disease and is one of the most common causes of death worldwide. There are lots of various types of cancers that differ from each other substantially. One can name a common cause of cancerogenic changes in tissues – the uncontrolled growth of cells that form tumours or neoplastic infiltrations. Such cells divide in the organism in an uncontrolled way, moreover the newly formed cells do not differentiate in the appropriate manner for a certain type of tissue [1]. Loss of control under the cell division is caused by mutations of genes encoding proteins that are involved in the cell cycle. These mutations lead to lack of response or inappropriate response of the organism for the signals sent to mobilize the immune system to fight with the cancerogenic process inside the cells.

Increased knowledge about the PD-1/PD-L1 interaction and its influence on the tumour cell microenvironment[3] have broadened the possibility of scientific considerations about anti-cancer drug design. The interaction between the ligand and the receptor leads to blockage of the apoptotic response of the immune system [2, 3]. My aim is to synthesize an inhibitor or group of inhibitors of the interaction between PD-L1 and PD-1, targeted towards the latter one. Rational drug design [4] is a scientific methodology in use for that purpose. In order to implement a miniprotein of certain sequence as a partner that would interact with the target protein, computational remodelling of the structure is applied. The spatial arrangement of amino acid residues and the physicochemical characteristics of those which are exposed towards cavities in the surface of the target protein are key points in optimization of a model to obtain a potentially effective inhibitor. All the synthesized products are obtained with use of solid-phase peptide synthesis approach and then their purity, manner of folding and affinity towards PD-1 protein are examined.

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Keywords: miniproteins, inhibitors, anti-cancer drugs, rational drug design, solid-phase peptide synthesis

Graphene-based composites for the electrochemical detection of neurotransmitters

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Nowadays, there is growing interest in health-state monitoring which involves an urgent need on improving the detection of target analytes with high accuracy [1]. Dopamine (DA) is one of the most crucial neurotransmitters as it plays a key role in functioning nervous system [1]. So far, determination of DA is being performed using complex and expensive HPLC or spectroscopy which, at the same time, display low sensitivity of measurements. In this context, electrochemical techniques appear to be an attractive alternative as they allow facile, quick, and low-cost measurements for detecting analytes of interest. Electrochemical detection is a powerful analytical method that can detect electric currents generated from red-ox reactions in the analyzed compounds [2]. Nevertheless, bare electrodes show negligible electrochemical response originated from analytes under evaluation. To overcome this drawback, graphene related materials and their composites are being proposed. Application of graphene-based composites in electrochemical detection results in synergistic effect between the composite counterparts and improved sensor working parameters such as limit of detection (LOD), linear range (LR), sensitivity and long-term stability (after 30 days). Some examples of prepared glassy carbon electrode (GCE) modifiers for DA sensing and the resulting sensor working parameters are summarized in Table 1.

Table 1. Graphene-based composite materials for electrochemical DA detection

Active electrode material	LOD, nM	LR, μM	Sensitivity, $\mu A\ \mu M^{-1}$	Long-term stability, %
RGO	998	5 – 70	2.29	60
AuNPs/RGO	700	1 – 100	1.78	68
PANI/TRGO-700	430	0.8 – 20	6.71	80
PANI/Fe_2O_3-SnO_2/RGO	76	0.1 – 20	1.10	95

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Keywords: graphene based-materials, composites, electrochemical detection, dopamine

Carbon nanostructures with encapsulated metal nanoparticles as bifunctional electrocatalysts for OER and ORR

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Zinc-air batteries are a promising solution to the energy storage problem. Their low cost, high safety, environmental friendliness, and high energy density make them a promising alternative to lithium-ion batteries. In addition, with the use of a solid electrolyte and a flexible air electrode for their construction, flexible batteries can be obtained which can be used, for example, in foldable displays. The main limitation of zinc-air batteries is the low rate of reactions occurring at the air electrode - i.e., oxygen reduction reaction (ORR) and oxygen evolution reaction (OER). Therefore, bifunctional electrocatalysts are being developed to increase the rate of both reactions and improve their efficiency [1, 2].

Among the electrode materials under investigation, those based on carbon materials are of particular interest. One example are carbon nanotubes, that are characterized with high electrical conductivity and a developed specific surface area, and thus possess a large number of active catalytic centers. However, recent studies have shown that such good electrocatalytic activity of carbon nanotubes may also be due a result of the presence of residual metal nanoparticles encapsulated in their structure after synthesis. Metal nanoparticles significantly affect the charge distribution in the carbon material in which they are encapsulated, thereby increasing electrocatalytic activity [3].

The aim of the project is to synthesize electrodes with bifunctional electrocatalytic activity toward OER and ORR for use as air electrodes in zinc-air batteries. These electrodes were successfully obtained by direct synthesis of carbon nanotubes with encapsulated transition-metal nanoparticles on carbon cloth.

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Keywords: Zn-air batteries, carbon nanotubes, electrocatalysis, carbon cloth

Microbial fuel cells towards biosurfactants production and petroleum compounds degradation

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Microbial fuel cell is a kind of bioelectrochemical device that converts chemical energy into electricity using microorganisms as a catalyst. As a fuel for the bacteria different carbon sources can be used. During my PhD studies I focus on using petroleum compounds such as hydrocarbons, which are really common pollutants in the environment.

One of the way of biodegradation this contaminants is associated with production of biosurfactants, which increasing the bioavailability of substrate through emulsification and by facilitating association of hydrophobic compounds with bacterial cells through reduction of cell surface hydrophobicity of bacterial cell.

Pathways of synthesis of biosurfactants in electricity generation conditions are still unknown. Discovering metabolism associated with bioelectrochemical synthesis will improve the efficiency of contaminants biotransformation.

Keywords: microbial fuel cell, MFC, biosurfactants, microorganisms, biotransformation

Arsenic contamination of the Baltic Sea

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The Baltic Sea is a semi-closed reservoir of water, connected to the North Sea only through the Danish Straits. On the shores of the Baltic Sea there are countries with significantly developed industries, and its limited connection to the North Sea severely limits the possibility of water exchange, resulting in high pollution levels in the Baltic Sea [1, 2]. Chemical weapons dumped in the Baltic Sea, over time, and under the influence of chemical and physical factors, corrode, and the chemical compounds contained in the weapons get into the Baltic Sea waters and circulate in the sea waters for a very long time [1, 2]. There is no precise information on how long and how much toxic chemicals were dumped, but it is assumed that this precedent may have lasted until the 1980s [1]. The presence of arsenic in the environment is mainly anthropogenic and can result from application of pesticides, combustion of coal, mining and smelting processes, ship sewage discharges, marine and drilling industries. However, chemical weapons offshore storage sites provide about 70% of the arsenic content in the environment. Such a sorbent should possess high sorption capacity, shows not only strong affinity to and selectivity for arsenic but also remarkable resistance against biofouling. Additional breakthrough needed to result in a commercially feasible technology is fast sorption rate required for maximization of the yield of the sorbent field per volume of seawater [3]. The production of water filters using 3D printed technology could meet these demand. Recently, specific clay filters with good adsorption capacity and effective separation have been designed and fabricated. It is possible to modify the 3D structures printed from PLA by acid hydrolysis and subsequent attachment of iron(III) hydroxide to the surface. Such a material was identified as an effective sorbent with high affinity for As(III) and As(V) oxyanions.

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Keywords: sorption, surface modification, ICP-OES, heavy metal removal

Heterometallic 3d-4f alkoxide precursors for the synthesis of binary oxide nanomaterials

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In this study, a new method for the synthesis of heterometallic 3d–4f alkoxides by the direct reaction of metallic lanthanides (La, Pr, Nd, Gd) with MCl2 (M = Mn, Ni, Co) in 2-methoxyethanol was developed. The method was applied to the synthesis of the heterometallic oxo-alkoxide clusters $[Ln_4Mn_2(\mu_6\text{-}O)(\mu_3\text{-}OR)_8(HOR)_4Cl_6]$ (Ln = La (**1**), Nd (**2**), Gd (**3**)); $[Pr_4M_2(\mu_6\text{-}O)(\mu_3\text{-}OR)_8(HOR)_xCl_6]$ (M = Co (**4**), Ni (**5**); x = 2, 4); and $[Ln_4Mn_2(\mu_3\text{-}OH)_2(\mu_3\text{-}OR)_4(\mu\text{-}OR)_4(\mu\text{-}Cl)_2(HOR)_4Cl_6]$ (Ln = La (**11**) and Pr (**12**)). Mechanistic investigation led to the isolation of the homo- and heterometallic intermediates $[Pr(\mu\text{-}OR)(\mu\text{-}Cl)(HOR)Cl]_n$ (**6**), $[Co_4(\mu_3\text{-}OR)_4(HOR)_4Cl_4]$ (**7**), $[Ni_4(\mu_3\text{-}OR)_4(HOEt)_4Cl_4]$ (**8**), $[Mn_4(\mu_3\text{-}OR)_4(HOR)_2(HOEt)_2Cl_4]$ (**9**), and $[Nd(HOR)_4Cl][CoCl_4]$ (**10**). In the presence of an external M(II) source at 1100 °C, 1–4 and 12 were selectively converted into binary metal oxide nanomaterials with trigonal or orthorhombic perovskite structures, i.e., $LaMnO_3$, $GdMnO_3$, $NdMnO_3$, $PrMnO_3$, and $PrCoO_3$. Compound **5** decomposed into a mixture of homo- and heterometallic oxides. The method presented provides a valuable platform for the preparation of advanced heterometallic oxide materials with promising magnetic, luminescence, and/or catalytic applications.

We gratefully acknowledge financial support by the Polish National Science Center, grant number 2018/29/B/ST5/00341.

Keywords: heterometallic complexes, alkoxides, aryloxides, rare-earth elements

Contemporary trends in shaping school greenery and school gardens

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School gardens have been accompanying educational processes for centuries, supporting the multi-directional development of students. Over the years, their function has changed from recreational to preventive and today they have primarily an educational function [1].

Properly designed space for outdoor education, supports the emotional development of the child, paying attention to ecological sensitivity and social ties. Thanks to the orientation of didactics towards direct learning, didactic processes are much easier, and their effects are more quickly assimilated and consolidated. Integrating environmental education into didactic processes builds good habits from an early age, thus rooting a sense of caring for the environment and nature. In addition to the obvious benefits of learning in a green environment, children experience vegetative processes and have the opportunity to learn how to manage water, resources and waste. The design of educational buildings, including school gardens at concept level, is one of the answers to changing climate conditions and the need to implement solutions and practices to prevent the worsening of environmental problems.

The importance of school gardens should be analysed as an interdisciplinary issue, combining the achievements of many fields, including didactics, pedagogy, psychology, philosophy, botany, architecture or landscape architecture. In the age of changing standards (didactic, urban and ecological), the subject of school green areas is extremely topical and poses many challenges for designers, researchers, teachers and students, raising the question of trends in shaping the architecture of school gardens in the coming years.

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Keywords: school garden, school farm, school architecture, environmental education, adventure education

Index of Authors

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