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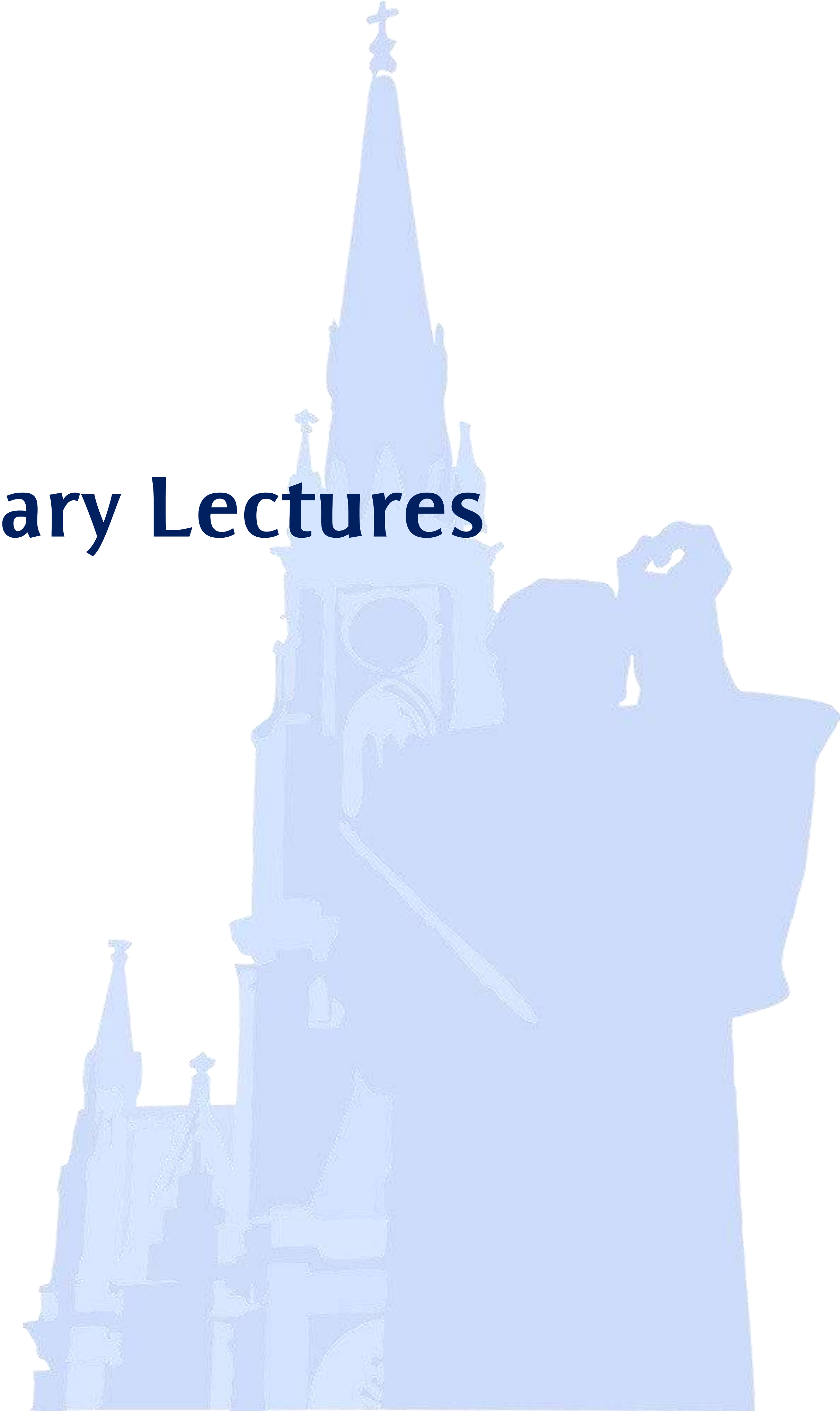

PL 01

Single atom co-catalysts in photocatalytic H_2 generation

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In 1972 Fujishima und Honda (1972) reported on the use of TiO_2 as a solar-illuminated semiconductor for the splitting of water into H_2 and O_2. Meanwhile, a large body of literature exists on photocatalytic H_2 generation using a wide variation of semiconductors, morphologies, and strategies to split water using the semiconductors suspended in an aqueous solution (with or without sacrificial agents). Many semiconductors have in common that for an efficient transfer of photogenerated charge carriers, a co-catalyst is required. For electron transfer and H_2 generation mostly Pt nanoparticles are used that are deposited onto the semiconductor surface by various techniques. Due to the precious nature of Pt, over the years, numerous efforts have been devoted to the shrinkage of the particle size and thus to enhance the utilization of the noble metal – in the most extreme case down to an insulated single atom of Pt.

In the presentation we discuss the use of Pt dispersed and anchored as single atoms (SAs) on TiO_2 surfaces and the activation to a most efficient use for photocatalytic H_2 generation. We discuss various trapping and stabilization approaches of SAs on photocatalysts that prevent agglomeration (and according to deactivation of SA Pt). Moreover, we show that only a small amount of Pt (loading density of SAs) is needed to achieve a maximum activity of a semiconductor surface.

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PL 02

The nano world of clean energy electrochemical systems – microscopy and spectroscopy of fuel cells, electrolyzers and batteries

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Governments around the world are showing a renewed, unprecedented interest in clean, renewable energy systems, such as fuel cells, electrolysers, batteries, wind and solar. An especially increased focus is on hydrogen, a zero-carbon and renewable fuel, accelerating the transition to a global hydrogen economy. World-wide, governments, companies and other organizations are announcing new developments, consortia, infrastructure programs, and financial commitments to propel renewable hydrogen production and use [1-3]. The global hydrogen market value is expected to increase from 130 billion USD in 2020 to 201 billion USD by 2025 [4]. Hydrogen offers a unique chance to decarbonize transportation, power generation, and manufacturing sectors and, thereby, address pollution and climate change challenges. Electrolysers and fuel cells, devices that produce green hydrogen and use the same to generate power, respectively, are at the hearth of this global hydrogen economy boom. Batteries are already widely accepted solutions.

However, all these electrochemical devices still face challenges with performance, cost and durability, which often originate from the nano-scale of these devices. This talk will offer an overview of the research activities in the presenter's lab, in particular, the nano-world of fuel cells, electrolysers and batteries. The talk will review advanced 2D and 3D characterization approaches in understanding the catalyst and electrode microstructures, and degradation mechanisms. Novel approaches to quantify a range of parameters from the microscopy and spectroscopy data will be presented and correlated to the performance.

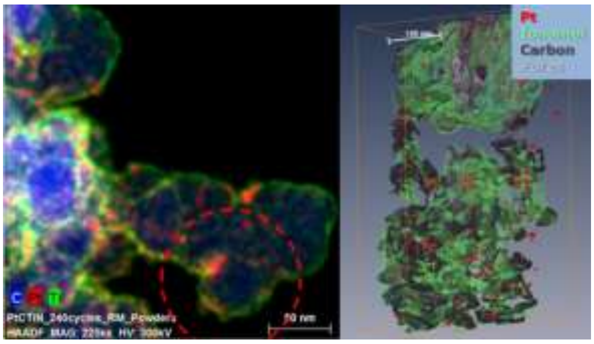

Figure 1. 2D and 3D microscopy images of fuel cell catalysts

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Beyond current frontiers of electrocatalysis

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One of the key reasons why the deployment of sustainable energy systems is at a standstill is the unusually complex phenomena of energy conversion at electrified solid/liquid interfaces. Namely, conversion of electric energy into chemical energy, and vice versa, comprises of interfacial processes whose mechanisms are still beyond comprehension. An important example is the electrolysis of water, where after decades of research it is still not clear how to significantly enhance efficiency of electricity-driven water splitting into gaseous hydrogen and oxygen. At the very core of energy conversion process are electrochemical reactions known as hydrogen evolution reaction (HER) and oxygen evolution reaction (OER), which intrinsic kinetics determines energy conversion efficiency. In order to further accelerate water electrolysis or other processes important for energy conversion devices (*e.g.* fuel cells, batteries *etc.*), central practical task is to design highly active and stable electrocatalysts.

If we ask a key question from a conceptual point of view, namely: what are the origins of electrocatalytic activity? - the answer will be, in most cases, as it was 70 years ago. Namely, the paradigm of electrocatalysis is Sabatier principle, which suggests optimal ("not too strong, not too weak") binding of intermediates as the main prerequisite for a high reaction rate. This viewpoint is usually supported by the Brønsted-Evans-Polanyi (BEP) relation, which imply that the tuning of adsorption energy of intermediates is essential for lowering of activation energy and ultimately enhancing reaction rate. However, recent systematic experimental analysis indicates that the lowering the activation energy is not necessarily beneficial for increasing the rate of electrocatalytic reaction.

Therefore, in this lecture, some fundamentally important questions about the nature of electrocatalytic activity will be raised with intention of establishing of links between material properties, interfacial structural dynamics and reaction rate. Identifying and analyzing these important links can give necessary momentum towards efficient water electrolysis as well as towards more comprehensive understanding of electrocatalysis.

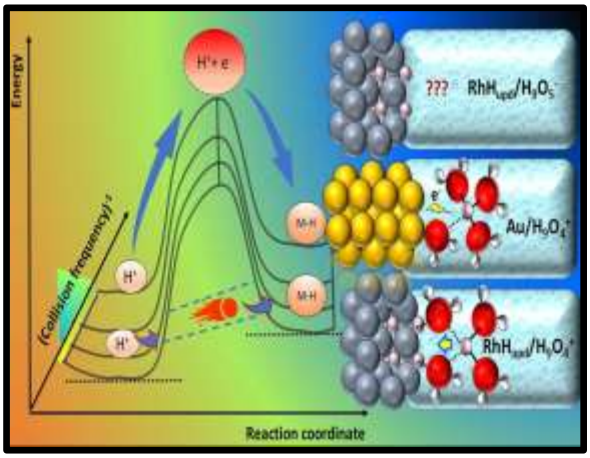

Figure 1. Illustration of how metals with specific interfacial water structure could behave as efficient electrocatalysts for hydrogen evolution reaction (HER) where high reaction rate, despite of relatively high activation energy, is possible to achieve via high values of preexponential factor by proton tunnelling. Adopted from [5] Copyright (2022) , with permission from Wiley

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PL 04

Electrochemiluminescence: new materials and devices

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Electrochemiluminescence (ECL), also called electrogenerated chemiluminescence, is a light-emitting phenomenon resulting from electrochemical reactions. It has been extensively using in immunoassays, DNA probe assays, aptasensors, enzymatic biosensors, coreactant detection, light-emitting devices, drug screening, and so on. ECL detection depends on ECL devices, luminophores, coreactants, electrocatalysts, and quenchers [1-4].
Herein, we report our recent progress on the development of some new materials, such as luminophores (*e.g.* $[Ru(bpy)_2dppz]^{2+}$), coreactants (*e.g.* 2-(dibutylamino)ethanol), electrodes (*e.g.* stainless steel electrode), and electrocatalysts (*e.g.* noble metal nanocrystal electrocatalyst with high-index facets (Fig. 1, Left), as well as devices (*e.g.* wireless ECL devices (Fig. 1, Right), single –electrode ECL device)[5-12].

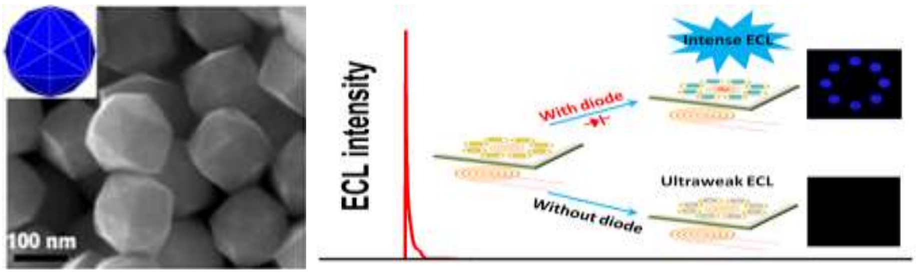

Figure 1. SEM image of convex hexoctahedral palladium@gold core-shell nanocrystals with {431} high-index facets and scheme of wireless ECL device.

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PL 05

Designing electrocatalytic materials for water reactions

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In this presentation, I will discuss the crucial parameters influencing the activity and stability of electrocatalysts in the oxygen reduction reaction (ORR), oxygen evolution reaction (OER) and CO_2 reduction reaction (CO2RR). A deep understanding of the fundamental principles governing the behaviour of these nanocomposites is essential for advancing the design of high-performance electrocatalysts [1] while minimizing dependence on critical raw materials, such as platinum group metals.

My talk will delve into insights about the structural ordering of Pt-alloy ORR nanoparticles [2], the synthesis and electrochemical characterization of various titanium oxynitride-supported Ir nanoparticles as OER electrocatalysts [3] and the dynamic restructuring of copper CO_2RR materials [4]. Furthermore, I will showcase our advanced electrochemical characterization methods, including identical location electron microscopy and online metal dissolution and gas evolution analytics. Through a variety of electrochemical measuring cells, automatization, and our feedback loop approach (Figure 1), accelerated improvements in electrocatalyst design can be achieved. Join me as we explore critical perspectives shaping the development of efficient and sustainable electrocatalysts.

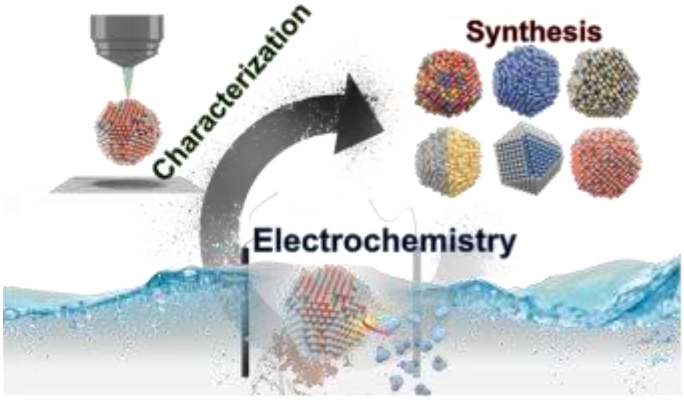

Figure 1: Schematic representation of the feedback loop in electrocatalyst design

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Keynote Lectures

KN 01

Comparison of the electrochemical sensitivity of modified sensors based on screen-printed electrodes for real-time detection of anticancer medication

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Last decade, an intensive research effort has been performed in the field of analytical electrochemistry seeking designs of electrochemical biosensors capable of providing better analytical characteristics in terms of sensitivity, selectivity, reliability, ease of fabrication and use, and low cost, especially for pharmaceutical drugs' monitoring. The incorporation of nanomaterials into composite electrode matrices presents a useful strategy for the preparation of electrochemical biosensors with improved analytical performance. These devices exhibit the characteristics of the used nanomaterials and the advantages of composite electrodes, such as low background currents, great versatility due to the possibility of incorporation of different substances into the bulk of the electrode matrix, and easy surface regeneration.

Doxorubicin hydrochloride (DOX), a potent anticancer drug, is widely used in chemotherapy due to its high effectiveness against a broad spectrum of malignancies, including breast cancer, lymphomas, leukomas, and sarcomas. Doxorubicin's anticancer and antitumor main mechanism of action is related to the inhibition of DNA replication and transcription processes through intercalation between base pairs, thereby leading to cell death[1]. Despite its remarkable efficacy, Doxorubicin's clinical use raises one major concern regarding the correlation between its dose-dependent cardiotoxicity and the long-term health quality of cancer survivors. If not properly dosed, Doxorubicin can cause serious health hazards such as organ toxicity and drug resistance. Hence, to mitigate side effects during clinical trials, evaluate toxicity, and optimize therapeutic efficacy, it is crucial to monitor and regulate Doxorubicin's concentration in patients during and after cancer treatment.

The research in our work has been primarily focused on the development of screen-printed electrode (SPE)-based sensors and their application as electrochemical platforms for drug determination and monitoring, with a specific emphasis on their suitability for surface modification. Three commercially available types of screen-printed electrodes—graphene, carbon nanotubes, and polyaniline— were utilized as the electrochemical sensing component, which were subsequently modified with polymers. The polymeric modification, achieved by coating onto electrode surfaces, offers flexibility and introduces diverse functional groups that contribute to enhancing the reactivity of the materials[2]. Polyacrylic acid, polyvinylidene fluoride, and chitosan were used for polymer modification. All developed electrodes were tested using a solution of 0.002 mol/L DOX dissolved in 0.1 M phosphate-buffered saline with a pH of 6.8. Cyclic voltammetry and differential pulse voltammetry were used as electrochemical characterization techniques, to gather data regarding the electrochemical activity of all developed electrodes. The physical characterization of the electrodes was done using Fourier-transform infrared spectroscopy (FTIR) and scanning electron microscopy (SEM). All modified electrodes demonstrate a favourable electrochemical response to DOX and exhibit higher electrical conductivity compared to commercial ones. The obtained results from the characterization indicate that polymer-modified polyaniline electrodes exhibit excellent electrochemical conductivity and demonstrate the best overall electrochemical performance.

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KN 02

Dimensional effects of the electrodeposition rate of the Co-W alloy from the citrate electrolyte

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The interest in obtaining coatings from iron-tungsten metal alloys is associated with the properties and possibilities of use of these alloys [1]. The results of the study of the dimensional effects of the deposition speed under conditions of induced coprecipitation are presented using the example of obtaining Co-W alloys from the citrate electrolyte. For this purpose, the deposition was carried out on electrodes with different surfaces, and the speed was estimated by the mass of the deposited layers based on the amount of electricity spent on their anodic dissolution. In this case, both micro-deposited electrodes and large-area electrodes were used.

Dimensional effects represent the dependence of the electrodeposition speed on the size of the electrode surface. Two types of dimensional effects were observed during the electrodeposition of Co-W coatings from the citrate electrolyte: the macroscopic and the microscopic effects. On one side, the microscopic effect is due to the influence of the size of the microelectrode on the diffusion current density [2]. On the other side, the macroscopic effect is associated with the structure of the inducing agent (cobalt citrate complex) [3].

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KN 02

Probing the correlation of interfacial chemistry and performance of electrocatalysts by surface enhanced ir absorption spectroscopy

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Electrocatalysts play a key role in the interconversion of chemical and electrical energies, and there is an increasing demand for their rational syntheses. To meet such a requirement, as a starting point, it is necessary to understand the correlation between interfacial chemistry and electrocatalytic activity and durability of a catalyst. In this talk, I will introduce our efforts in developing in situ attenuated total reflection surface enhanced IR absorption spectroscopy (ATR-SEIRAS) to investigate electrocatalytic oxidation of small organic molecules on Pd and Pt-based catalysts at molecular level, with a focus on correlating the spectral features of surface and solution species with the resulting catalytic performances. I will also showcase that spectral feature change of a probe molecule may provide a hint for a new practical electrocatalyst through electronic property tuning.

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KN 04

Material design and performance regulation of Ru-based electrocatalysts for hydrogen production

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The proposal of the carbon peak and carbon neutrality goals will inevitably accelerate energy transformation, which means a transformation from high-carbon to low-carbon, and the rapid development of hydrogen energy will inevitably take on the important mission of achieving carbon neutrality. Mastering the large-scale preparation technology of hydrogen fuel cell electrocatalysts is the key to achieving efficient conversion and storage of electrochemical energy, and it is also an urgent scientific problem to be solved. Facing the major strategic needs, we have been working on the international frontier scientific issue of hydrogen energy production and storage system and have achieved a series of innovative research results in the design and regulation of key materials for ruthenium-based electrocatalysts. We used surface modification strategy to design heterogeneous structures to change the atomic structure of the interface region, thereby accelerate the migration rate of electrons and ions, and improve the elementary process of electrochemical reactions [1-4]; Applied the doping strategy to regulate the atomic and electronic structure of the bulk catalyst, regulate the local coordination environment, defects, and adsorption energy of intermediate products, accelerate the electrocatalytic kinetic process [5]; Achieved the dual modification of catalyst by bulk doping and surface modification simultaneously, which achieving the purpose of stabilizing the structure of material and improving the performances, and applied this material to energy fields such as hydrogen production [6]. The above regulation strategies are highly universal, which provides the promising routes for designing electrocatalysts that maintain high catalytic activity under high current density and are bound to offer valuable references for building a clean, low-carbon, safe and efficient modern energy system.

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KN 05

Vine shoots-derived carbon: from Al-ion supercapacitors to Na-ion batteries

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Energy storage systems are the key element of a sustainable energy supply chain, enabling the widespread use of renewable energy sources and providing stability and efficiency in the energy sector. Their role will be increasingly important as the world moves towards more sustainable energy solutions and reduced carbon emissions [1]. In the array of different materials for energy storage, carbon materials are one of the most studied due to their versatile nature and favourable chemistry, along with simple and environmentally friendly synthesis. This talk will explore the possibilities of converting an abundant biomass waste into carbonaceous materials for the next generation of batteries and supercapacitors relying on widely available elements such as sodium and aluminium.

Vine shoots, an abundant by-product of the wine industry, was used as a precursor for obtaining two types of carbon materials. For the use in supercapacitors, a material with a large specific surface area of 1500 m^2/g was developed in a simple two-step process by carbonization/$ZnCl_2$ activation of vine shoots at lower temperature of 700 ℃. Such obtained activated carbon exhibits its typical pseudocapacitance behaviour in a non-conventional Al-ion based aqueous electrolyte. This enabled broadening the operating voltage of carbon to ≈1.8 V and reaching specific capacitance ≈216 F g^{-1} and energy density of ≈24 Wh kg^{-1} at 1 A g^{-1} in symmetric supercapacitor configuration [2]. To develop carbon material which configures in batteries, vine shoots were simply carbonized at higher temperatures yielding low specific surface area non-graphitizable carbon (hard carbon, HC), favourable for insertion of large amount of Na-ions. Optimized HC electrode showed high capacity *vs.* Na in $NaPF_6$/EC+ +DMC+2%FEC electrolyte, with ≈270 mAh g^{-1} at 37.2 mA g^{-1} and ≈253 mAh g^{-1} at 372 mA g^{-1}, low voltage and excellent cyclic stability. By pairing developed HC anode with commercial NVPF [$Na_3V_2(PO_4)_2F_3$] cathode in a HC//$NaPF_6$/EC+ +DMC+2wt%FEC//NVFP/C cell we developed a ≈4 V Na-ion battery with a reversible capacity of ≈54 mAh g^{-1} at 153.6 mA g^{-1} (per cathode mass), capacity retention of 92 % after 100 cycles and energy density of ≈216 Wh kg^{-1} at 153.6 mA g^{-1}. This lecture will address the relations between alternative ions storage performance and structural/textural properties of carbon contributing to setting possible directions towards simple design of high performance electrodes for the next generation of energy storage devices.

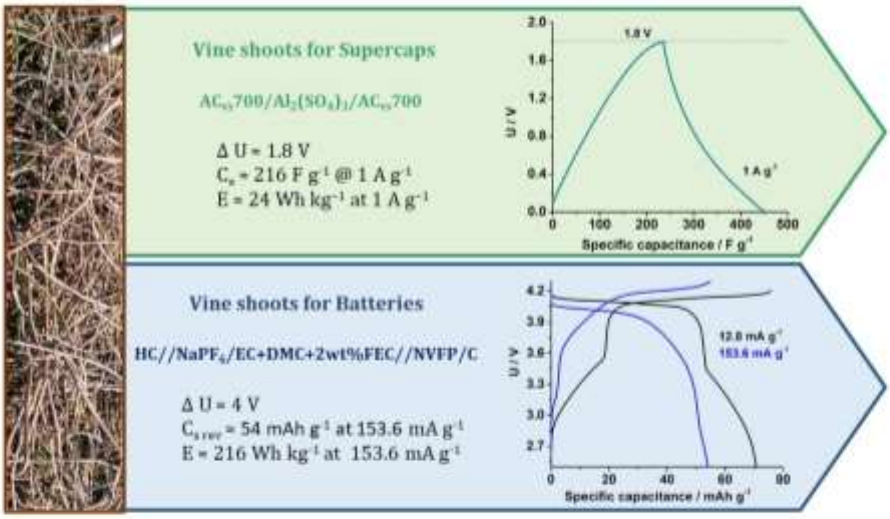

Figure 1. Next generation of energy storage systems based on vine shoots-derived carbon

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KN 06

Characterization of redox behaviour of perovskites-oxides for reversible solid oxide electrochemical cells and CO_2 valorisation

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Reversible Solid Oxide Electrochemical Cells (R-SOECs), integrating electrolysers and fuel cells into a single device, represent a promising technology for advancing the ongoing energy transition towards renewable resources and low carbon footprint energy supply chains[1]. To effectively penetrate the market, it is imperative to enhance their operational versatility and reversibility through the design of innovative, cost-effective materials and processes[2].
In recent years, there has been increasing research interest in simple perovskite (ABO_3) and double perovskite ($A_2BB'O_6$) materials as suitable components for R-SOECs. This interest stems from their relative ease of functionalization and composition modification via doping[3,4]. However, for the development of reversible devices, it is crucial to investigate the stability of these materials under various reaction atmospheres to understand how their redox properties depend on structural and surface characteristics. Exposure to different atmospheres can alter the pristine structure, thereby impacting the electrochemical and catalytic properties of perovskite oxides.
Understanding the transformations occurring during reducing and oxidizing cycles, and establishing the relationship between structural changes, redox properties, and electrochemical behaviour, is vital for identifying optimal compositions and efficient operational conditions.
In this presentation, we will outline our recent studies focusing on characterizing the redox behaviour of $PrBaMn_2O_{5+\partial}$[5] and $Sr2FeNi_{0.4}Mo_{0.6}O_{6-\delta}$[6] for the development of CO_2-reducing electrocatalysts for reversible devices. Our approach utilizes a multi-analytical strategy based on in situ temperature programmed redox cycles and XRD characterization to correlate redox behaviour with structural changes of these materials. The aim is to demonstrate the validity of this approach in assessing the suitability of the materials for the development of reversible electrodes for CO_2 valorisation.

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KN 07

Recent innovations in membrane electrode assembly fabrication for polymer electrolyte fuel cells

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Polymer electrolyte fuel cells (PEFCs) are sustainable energy converters capable of generating electrical energy directly and highly efficiently from the chemical energy bound in hydrogen through electrochemical reactions. The heart of the PEFC, which determines performance and lifetime, is the membrane electrode assembly (MEA), which consists of an ion-conducting membrane between two electrodes (anode and cathode catalyst layers), as shown in Fig. 1 in a three-layer structure (gas diffusion layers are added on both sides). The cost-effective production of long-life, high-performance MEAs by optimising electrode configuration and fabrication is key to the global commercialisation of PEFCs [1]. In addition to the materials used, the interaction between the carbon supports, the pore structure, the mass transport and the accessibility of the catalysts, the production technology also has a significant influence on the achievable power density of the cell and the mass activities of the catalyst systems used. The production techniques considered include slot die coating, ultrasonic coating, reactive spray coating, electrospinning and inkjet printing.

In addition to the industrially highly relevant slot die coating, electrospinning is being developed as an innovative method for depositing a mat of ultrafine nanofibres as an electrode. In contrast to ultrasonic spray coating, this technique is very sensitive to small changes in the composition of the catalyst ink, the dispersion of the catalyst particles, the ion-conducting binder (*e.g.* Nafion) and the solvent. The nanofibre mat has unique properties, in particular exceptional mass transport properties. Among other things, the effect of the thickness of the catalyst layer produced by ultrasonic coating on performance and resistivity is discussed. Electrochemical impedance spectroscopy shows that the mass transport resistance increases with increasing layer thickness, while the membrane resistance decreases, which can be attributed to an increased water retention resistance [2]. The durability of catalyser inks, which is crucial for the large-scale production of MEA, has been investigated. In terms of dispersion stability, the catalyst ink should be used immediately after mixing, as the catalyst particles tend to sediment quickly, in contrast to zeta potential analysis. Acetone, which impairs the pore structure of the catalyst layer, was detected as an oxidation product in the catalyst ink [3]. Catalyst ink for MEA production can be stored for up to a maximum of four weeks without any significant loss of performance for the fuel cell. Finally, an outlook on research activities to improve MEA production is presented.

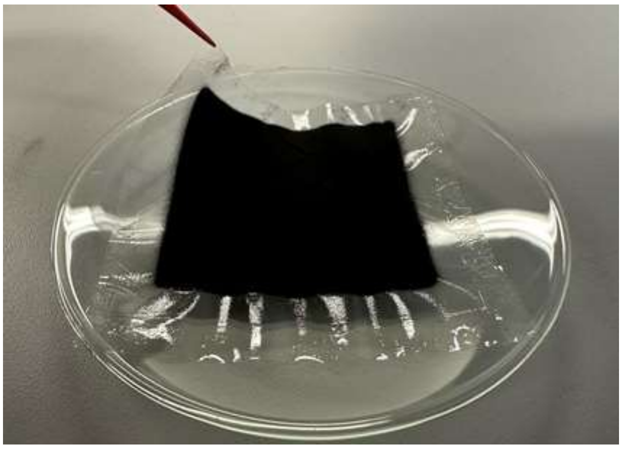

Figure 1. Catalyst coated membrane (CCM) for polymer electrolyte fuel cell (source: Kircher@TUGraz)

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KN 08

Research on new high-end, environmentally friendly and efficient leveling agent for electroplated copper

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In the field of electronic manufacturing today, high-end electroplating technology plays a crucial role as the only means to achieve nanoscale electronic interconnections. In the manufacturing of high-density interconnect printed circuit boards (HID-PCBs), defect-free copper interconnects are the key to ensuring reliable electrical connections and signal transmission integrity. The key to achieving perfect filling of blind holes in PCBs lies in the effective application of electroplating additives to precisely control the copper deposition process. Levelling agents are core additives in the electroplating of copper blind holes. Therefore, to meet the design requirements, this study is dedicated to developing a new levelling agent that is environmentally friendly, exhibits excellent performance, and is cost-effective. A comprehensive study will be conducted on the mechanism of action during the electroplating process and the performance of the copper coating after electroplating. Small nitrogen-containing heterocyclic compounds have become a hot topic in the research of new levelling agents due to their low cost, low toxicity, and stable electroplating performance. Based on 2-mercapto-5-methyl-1,3,4-thiadiazole (MMT), this study aims to design and synthesize a new environmentally friendly compound, 2-(benzylthio)-5-methyl-1,3,4-thiadiazole (BMT), as a novel levelling agent for copper electroplating in blind holes. The raw materials used for synthesis are simple, easily accessible, and the synthesis steps are relatively simple. The synthesis of the new additive was confirmed by proton nuclear magnetic resonance spectroscopy. Quantum chemical calculations, molecular dynamics simulations, and other methods were used to determine that the compound BMT exhibits strong adsorption properties on the copper surface, with an adsorption energy of -90.39 kcal/mol. Electrochemical tests (CV, LSV, GMs) were conducted to analyse the effect of the compound BMT as a levelling agent on copper deposition behaviour, and the results showed that the compound BMT has strong inhibitory ability on copper electrodeposition. Filling experiments and reliability tests were performed on blind holes with different depth-to-width ratios, and the results showed that the addition of this new levelling agent to the electroplating solution can achieve dense filling of blind holes of different sizes and good coating quality. Finally, in-situ surface-enhanced Raman spectroscopy (EC-SERS) was used to study the mechanism of action of the additive on the copper surface from a microscopic perspective. The comprehensive results indicate that the newly synthesized compound BMT exhibits excellent electroplating filling performance and is suitable as an effective levelling agent for blind hole copper plating.

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KN 09

Scalable electrochemical strategies for preparation of supported catalysts for electrochemical energy conversion

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Electrochemistry plays an important role in energy conversion and storage, particularly in characterizing active materials used in fuel cells, electrolysers, and batteries. However, electrochemical principles are crucial not only for characterization and quality control but also for the medium and large-scale production of electrocatalytic materials. Direct electrodeposition of active materials on conductive substrates is a straightforward strategy to produce electrodes for systems with liquid electrolytes, like alkaline water electrolysers. On the other hand, active materials for systems employing solid membrane electrolytes are typically prepared in powder form and deposited onto porous substrates through methods such as screen printing, dipping, or spray coating using suitable suspensions. While these approaches are convenient for laboratory-scale membrane-electrode assembly preparation, they present challenges that must be addressed when considering production scale-up.

In addition to conventional preparative chemistry variables like concentration, temperature, pH, and agitation, electrochemistry offers further process control through parameters such as current density, potential, and their variation in time, including pulse and alternating polarity profiles. The broad selection of parameters makes electrochemical routes ideal for finely tuning material properties while ensuring excellent reproducibility. Direct electrochemical deposition routes enable the deposition of active material on both rigid and soft substrates, resulting in improved adhesion essential for electrical contact and prolonged catalytic activity. All this comes with the great scalability potential, which is vital for accelerating the deployment of hydrogen technologies on a global scale.

Proton-exchange membrane (PEM) and anion-exchange membrane (AEM) electrolyser and fuel cell technologies are based on metallic catalysts supported by various carbon materials (M@C). Direct electrodeposition of M@C materials can be achieved using oxidized form of carbon material, such as graphene oxide or oxygen-functionalized carbon nanotubes, as a precursor for electrophoretic deposition of metallic nanoparticles on the corresponding reduced form (*e.g.* reduced graphene oxide or carbon nanotubes). Alternatively, oxygen-functionalized carbons can be cast onto gas diffusion layer (GDL) and galvanostatically or potentiostatically reduced with simultaneous metal deposition. In the latter approach, metal precursors may be dissolved in the deposition bath, or absorbed into the cast film, and subsequently reduced in an inert electrolyte (Figure 1). One step catalyst electrodeposition can also be carried out directly onto preformed microporous layer of the GDL. This presentation will summarize direct electrochemical routes for preparing of active electrodes for membrane-based technologies, focusing on their scalability potential to medium or large-scale production. Additionaly, a brief discussion on electrochemical methods for modification of electro-catalysts on rigid substrates, utilized in aqueous electrolyte technologies, will be included.

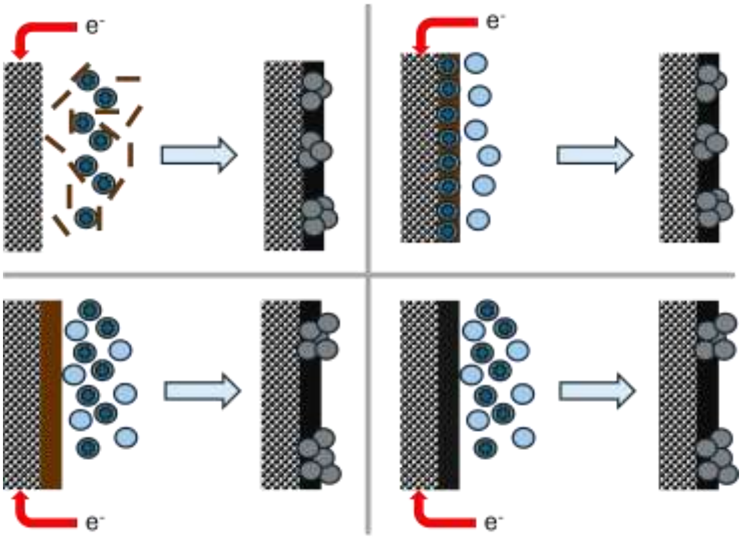

Figure 1. Routes for the direct electrodeposition of M@C particles

KN 10

Application of the electromagnetic piezoelectric acustic sensor (EMPAS) technique in electrochemistry

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The electromagnetic piezoelectric acoustic sensor technique (EMPAS)[1] can be considered a variation of the quartz crystal microbalance in which a bare quartz crystal disk as sensing element is places on top of a planar inductive coil instead of applying it as the dielectric material of a planar condenser. The resonances of the quartz disk will appear in the impedance of the planar coil. There are two advantages of the technique, namely adsorption processes on the top of the bare quartz surface can be studied and resonant frequencies up to 1 GHZ can be detected. Since resonances at different frequencies penetrate into different depth of the adsorbed layer measurements in a wide overtone range permit a deeper look into the structure of the adsorbed layer. The method is based on a high-frequency perturbation through a planar coil which is placed under the bare quartz crystal as close as possible. The high-frequency signal is stepped around the investigated resonant frequency while it is frequency modulated with an audio-frequency signal at the same time. The response signal will contain also an amplitude modulated component corresponding to the audio-frequency signal. After demodulation the change of the audio-frequency signal permits the determination of the actual value of the resonant frequency which depends on the adsorbed mass on the surface of the quartz crystal. As a development[2], in addition to the fundamental frequency of the demodulated audio-frequency signal, we measured also the 2nd, 3rd and 4th harmonics as well allowing the determination of the quality factor of the corresponding resonance.

Even though the technique was originally developed for electrodeless quartz crystal, we tested the technique in electrochemical application as well. In this case the top of the sensing quartz disk (opposite to the planar coil) is covered with a gold layer serving as electrode. We could detect resonances of a quartz crystal with 5 MHz fundamental frequency up to 1 GHZ even in this configuration.

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KN 11

3D printing in the electrochemical research: from fundamental characterization of electrodes to practical cells, sensors and catalysts

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3D printing is an outstanding manufacturing tool for prototyping customized designs at reduced time and costs, having found applications in fields such as medicine or automotive industry. The development of printable electrically conductive composite materials brought revolution to electrochemistry, with 3D printed electrodes being intensively studied from the viewpoint of charge transfer characteristics, analytical performance and stability. Bi-material 3D printing combining electrically conductive and insulating materials has enabled the manufacture of integrated electrochemical cells for sensing, synthetic and catalytic applications.

In this talk, I will summarize our recent efforts and successes in the development and manufacture of 3D printed electrochemical devices. Presented designs include cells and electrodes for mechanistic studies, electrocatalytic reactions and sensors of drugs, antibiotics, metabolites and pathogens. Additionally, a microfluidic spectroelectrochemical platform for the detection of in-situ generated reaction species (Fig. 1) and an impedimetric platform for determining (di)electric properties of liquid samples will be presented.

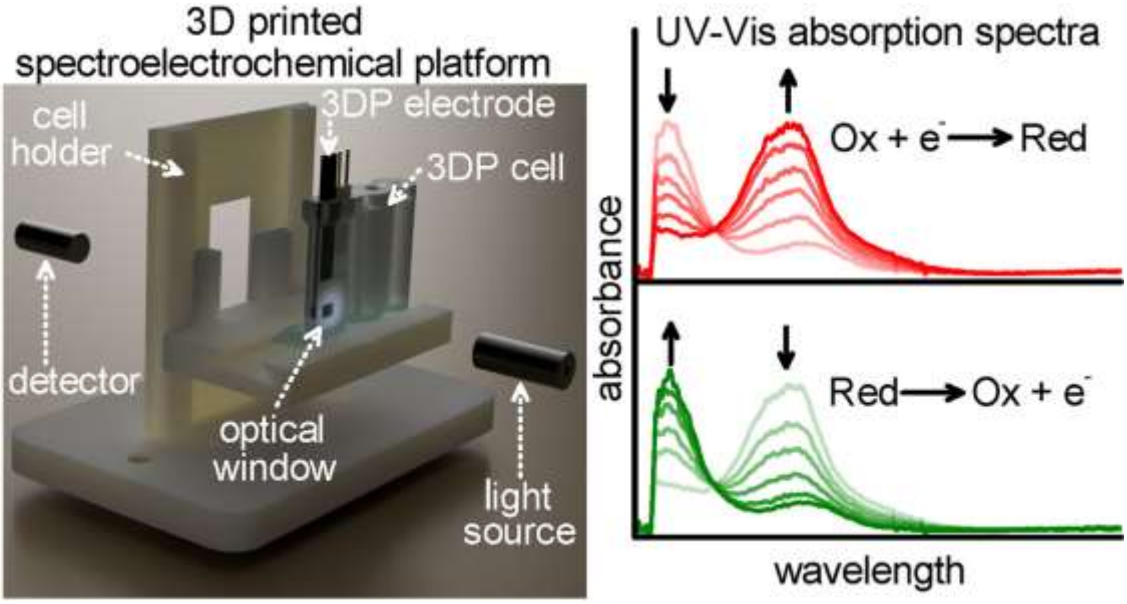

Figure 1. 3D printed spectroelectrochemical platform

KN 12

Functional coatings to enhance corrosion protection of aluminium and its alloys

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Aluminium and its alloys are important lightweight materials for various construction and transportation applications. The use is often limited due to low corrosion resistance, which can be enhanced by protecting the metal surface with additional corrosion protection. Over the last decade, research has been focused on developing several methods that will effectively protect aluminium and its alloys against corrosion and will be in line with the strict European Union's REACH regulation, such as using hexavalent chromium compounds.

In the last decade, cerium- (CeCC) or zirconium-chromium(III)) based conversion coatings (ZrCrCCs) have emerged as a substitute for (active) surface pre-treatment based on conversion coatings. Several aspects will be presented such as (i) the addition of various cerium salts *(i.e.* cerium chloride, cerium nitrate and cerium acetate) into a corrosive medium [1] and (ii) the synergistic effect with other salts such as Na_2SO_4.[2,3]

Additional corrosion (barrier) protection of Al alloys can be achieved by depositing a hybrid sol-gel coating that reflects the properties of inorganic and organic substances in one functional material.[4] Several polyacrylic/siloxanes silica coatings will be described consisting of various lengths of alkyl or perfluoroalkyl acrylate monomer and organically modified silane 3-(trimethoxysilyl)propyl methacrylate as well as an inorganic silane, tetraethyl orthosilicate.[5,6]

Combining both types of coatings (active and barrier) can also be used for developing functional coatings, Figure 1. Such coatings also have the ability to prevent the damaged area on metal surfaces.[7,8]

In the last part, the developments made in superhydrophobic corrosion protective coatings will also be presented. The definition of superhydrophobicity is based on the water contact angle of the droplet on the surface, which has to be larger than 150°, and a sliding angle smaller than 10°.[9,10] Such surface prevents the aggressive ions from reaching the surface, consequently offering an efficient mechanism for corrosion protection.[10,11] These coatings also offer additional functional abilities of the surface once exposed to the natural or industrial environments, including preventing the adsorption of pollutants and ice formation; therefore, there is a high potential for applications in different fields.

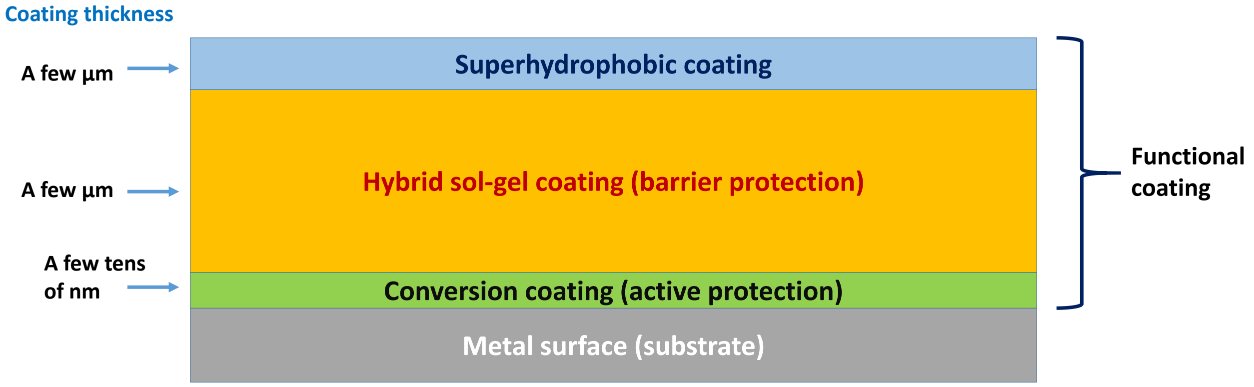

Figure 1. A schematic presentation of the example of functional coating consists of conversion, hybrid sol-gel and superhydrophobic coatings

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KN 13

Diagnostics and characterization of hydrogen technology devices

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Considering the limited natural energy reserves and environmental pollution, our current energy system is unsustainable. Thus, gradual abandonment of fossil fuel technologies is inevitable. The future definitely belongs to renewable energy sources (RES) and transition from the use of natural energy reserves to the use of natural energy flows. However, there are still many challenges, such as intermittent and variable availability, variable intensity, frequent mismatch of energy needs with production, *etc.* Promising and environmentally friendly solution in the current energy transition to the future sustainable energy system, without jeopardizing our current technological development and way of life, could be the widespread use of (green) hydrogen[1,2] as an energy carrier in the system in conjunction with RES, and the use of hydrogen technology devices. This presentation will contain an overview of hydrogen-based electrochemical energy conversion devices, which include the proton exchange or polymer electrolyte membranes (PEM), such as PEM fuel cells[3-6], PEM electrolyzers[7] and electrochemical hydrogen compressors[8]. Their current technology shortcomings and challenges, primarily considering durability, will be briefly discussed. The main focus will be given on recent achievements and advances in their state-of-health monitoring and performance diagnostics within our Laboratory for New Energy Technologies at FESB, University of Split, under the several ongoing research projects and collaborations. Additionally, attention will also be on presenting our research capabilities and potential development ideas for further collaborations. All the results obtained so far should assist in further research and development of more practical operando diagnostic and prognostic tools for a better understanding of the complex processes within hydrogen technology devices at the cell and stack level, and their more efficient way of control and management in practice.

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KN 14

Sea water electrolysis – advantages, challenges and perspectives as a cost-efficient technology for green hydrogen production

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In the last years the interest in direct seawater electrolysis as an alternative technology for green hydrogen production has increased considerably. In contrast to the advanced PEM electrolysis based on consumption of highly purified fresh-water, it uses the most abundant water resource on the Earth (almost 97 %). The sea water has high salinity, its ionic conductivity reaches 34 mS cm^{-1} at 25 °C making it an ideal electrolyte which can be easily split to hydrogen and oxygen. That is why, the sea water electrolysis is an intriguing method for sustainable energy production. However, due to the high chlorine concentration (similar to 0.5 M NaCl), a significant problem in the sea water electrolysis is the competition between the anode partial reaction of oxygen evolution known for its sluggish kinetics and the formation of Cl_2 gas (at acidic pH) or ClO (at alkaline pH). The formation of these by-products leads to severe corrosion and degradation of the anode, and in turn to lowering the system efficiency. In addition, during a long-term service the high salinity leads to precipitation of alkaline earth hydroxides and carbonates on the cathode surface which is another problem to be solved. The scientific research on the direct electrolysis of seawater deals with various aspects of this process including optimizing the electrode and catalytic materials, improving the efficiency and stability of the process, and exploring new methods to address the challenges of the high salinity.

The focus of the present study is on the synthesis of a new composite catalyst consisting of polymer matrix with appropriate conductivity and a catalytic metal incorporated in its structure. The samples under investigation are obtained by means of chemical polymerization of aniline through oxidation and introduction of both classical catalysts such as Pt and Ru and non-noble metals from the transition series (Co, Ni, Fe) aiming cost reduction of this type of electrodes.

The composition, structure, and morphology of the prepared composites are investigated using variety of spectroscopic and physicochemical methods as illustrated in Fig. 1. The reaction mechanisms and kinetics of the seawater electrolysis on conventional and newly synthesized composite electrodes are studied by means of cyclic voltammetry and chronoamperometry. The performance of the electrode materials in aqueous media with varying pH and its specific response as both anode and cathode are pre-screened following the proceeding redox reactions on the electrode surface to establish the preferable more efficient application.

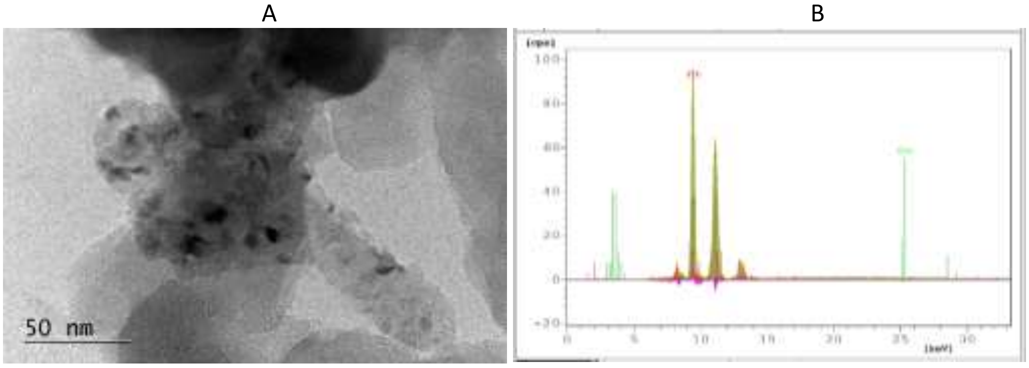

Figure 1. TEM (a) and fluorescence X-Ray (b) analysis of polymer composite with incorporated Pt

The results obtained proved the feasibility of the introduced method of synthesis. The electrochemical investigation of the obtained composite catalysts showed promising electrocatalytic activity and improved stability toward the aggressive chlorine effects. Although still in the initial stage, the research carried out gives credence for further ongoing experiments to elucidate deeper the mechanism of proceeding reactions, increase the electrode service life, and enhance the cost efficiency of sea water electrolysis.

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KN 15

Electrowetting for advanced electrochemical technologies

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Wetting phenomena hold a pivotal role in a vast range of physicochemical processes occurring in both nature and artificial systems. Elucidation of the chemical physics underlying these processes paves the way towards their elaborate control and inspires the development of technologically advanced devices with a diverse range of applications spanning various micro-/nano-fluidics platforms and electrotribology to electrochemical energy conversion, storage, and capacitive deionization. Several strategies have been sought to control wetting through external stimuli. The oldest such approach can be traced back to Gibbs – Lippmann theory of electrocapillarity and relies on the phenomenon of electrowetting.[1,2] Despite the experimental evidence of electrowetting on conducting substrates by Frumkin, this fascinating phenomenon has been initially overlooked due to its apparent irreversibility on solid electrodes arising by their intrinsic surface reactivity. Herein, almost a century later than these seminal works, we discuss a series of novel insights into the overall phenomenon by employing highly oriented and low dimensional carbon allotropes. A pioneering strategy is introduced to control electrowetting on graphite by effectively suppressing the underlying parasitic, electrochemically induced surface processes.[3] In this way, the electrowetting response exhibits a fully symmetric and reversible wetting/dewetting behaviour in line with the classical electrowetting theory described by the Young – Lippmann equation. To describe the thermodynamics of the electrochemical interface, a multiscale quantum mechanics–classical molecular dynamics approach is presented that establishes a conceptual framework for the investigation of wetting phenomena on a single layer graphene model surface under the application of potential bias.[4] It is shown that the charge stored at the electrochemical double layer is not the only factor that governs the interfacial energetics. Competitive effects emerging by ion adsorption and hydrogen bond number have a strong impact on the interfacial surface tension. Extending our general strategy to a reactive interface, electrowetting has been studied under the occurrence of foundational electrochemical reactions related to electrochemical energy storage and conversion systems. By exploiting the unique layered structure of graphite with its tuneable interlayer distance that sets almost ideal conditions for the accommodation of ions into its structure, we demonstrate the significant effect of anion intercalation on the electrowetting response of graphitic surfaces in contact with concentrated aqueous and non-aqueous electrolytes as well as ionic liquids.[5] Furthermore, cathodically induced intercalation is proved to drive superhydrophilicity in other materials, such as high entropy thin alloy films.[6] Both phenomena are interpreted in terms of changes in the physical properties of the substrates impelled by the intercalation reactions. Our work provides fundamental insights into wetting phenomena under the application of an external electrical field, while at the same time stimulates novel research towards utilizing electrowetting to boost the performance of devices operating based on physicochemical processes at the conductor/electrolyte interface.

Acknowledgement: A.A.P. and R.A.W.D would like to would like to thank the Leverhulme Trust (RPG-2019-250) for financial support.

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Organic electrosynthesis as an excellent tool in green chemistry; towards sustainable chemical transformation of raw biomaterials

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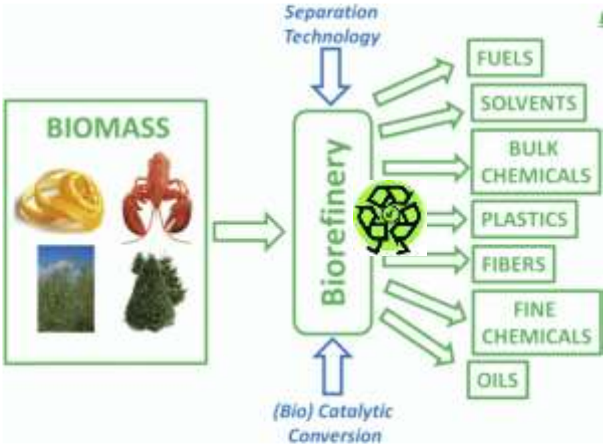
In this talk, the main aspects that make organic electrosynthesis a promising method in green organic synthesis will be discussed. Cost, advantages, and disadvantages, as well as some representative examples from literature and my research group will demonstrate that organic electrosynthesis is in a renaissance period. The organic electrosynthesis principles and benefits can also be used in the sustainable biorefineries, where environmentally friendly methodologies are required to obtain valuable chemicals from renewable biomaterials like lignin, fatty acids and glycerol.

Sustainable biorefineries concept



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KN 17

MXene as emerging materials for electrochemical energy conversion and storage

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Low-cost non-noble electrode materials are vital for taking the application of electrochemical energy conversion and storage devices to the next level. MXenes, the newest class of two-dimensional materials, are characterised by a high surface area, nanometer layer thickness, and hydrophilicity along with electrical conductivity suggesting them as good alternative for electrocatalysis and energy storage. The main focus of our work is on niobium carbide MXene (Nb-MXene) and its application for electrocatalysis and supercapacitors. Nb-MXene was obtained by chemical synthesis from its MAX phase and characterized in terms of morphology and structure. Its activity for catalysis of hydrogen and oxygen evolution reactions, as well as oxygen reduction reaction, was investigated in different electrolytic media of wide pH range. Finally, capacitance properties of Nb-MXene were also evaluated.

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Oral Presentations

ANAL O 01

Enhanced glucose detection via one-shot electrochemical enzymatic platform

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Glucose detection is crucial across industries, with excessive sugar intake linked to health issues like cardiovascular diseases and diabetes. Diabetes affects millions globally, demanding accurate monitoring for effective management. The demand for rapid, non-invasive glucose testing methods is growing, driving advancements in electrochemical sensors [1,2]. While numerous sensors have been introduced to the market, there remain considerable opportunities for further enhancements. The emergence of catalytic materials, such as two-dimensional layered materials (MXenes), Multi-walled Carbon Nanotubes (MWCNT), and bismuth ruthenate pyrochlore oxide ($Bi_2Ru_2O_7$), has opened doors to innovative sensor designs. These materials offer an array of favourable characteristics, including exceptional metallic conductivity, hydrophilicity, and biocompatibility, making them ideal candidates for next-generation electrochemical sensors. By exploiting these materials in combination with cost-effective screen-printed electrodes modified with various metals, metal oxides, polymers, carbon-based nanomaterials, and enzymes, researchers have established a robust platform for achieving highly sensitive, selective and efficient glucose detection [3]. This strategic usage of advanced materials holds tremendous promise for addressing the remaining challenges in glucose sensing, paving the way for more accurate and accessible monitoring solutions.

In this work, we will present the preparation and characterization of a novel one-shot electrochemical sensor modified with multiple layers for instant glucose detection. The sensor's design incorporates layers tailored to enhance sensitivity and selectivity, enabling immediate and accurate glucose detection. We will also discuss the sensor's advantages, shortcomings, and potential application scenarios for glucose monitoring.

Acknowledgement: This research received financial support from the fundamental research programme Analytics and Chemical Characterization of Materials and Processes (P1-0034).

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Amperometric gaseous H_2O_2 sensor based on ultra-low platinum content electrocatalyst

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Detecting gases and volatile compounds using electrochemical gas sensors presents ongoing challenges regarding sensitivity and selectivity. Many scenarios demand rapid, sensitive, and user-friendly sensors capable of detecting gaseous hydrogen peroxide (H_2O_2) at room temperature. In this study, we introduce an H_2O_2 gas sensor utilizing sodium polyacrylate aqueous gel electrolytes combined with commercially available screen-printed carbon electrodes, where the working electrode has been modified with low platinum content-MWCNT electrocatalyst. The examined electrolyte facilitates the accumulation and stabilization of the gaseous analyte, allowing for its rapid and sensitive detection of the highly active sensing material. Notably, the sensor demonstrates high sensitivity below the mg m^{-3} range, exhibiting linear responses across concentrations ranging from 10 to 70 mg m^{-3} after just 5 minutes of accumulation and 1 to 10 mg m^{-3} after 10 minutes of accumulation under ambient conditions.

The simplicity of the sensor's setup and its robust electroanalytical performance renders it highly promising for various applications in emerging fields such as clinical diagnostics [1], explosive detection [2], environmental monitoring [3], and occupational health and safety [4].

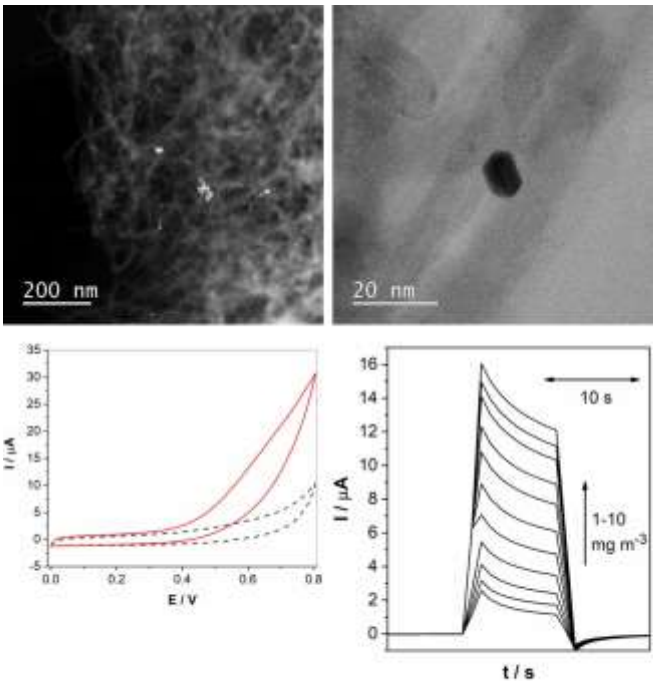

Figure 1. Above, TEM images depicting low content Pt on MWCNT. The bottom left: CV response of the gas sensor in the absence (black dashed line) and the presence of H_2O_2 (red solid line). Bottom right: chronoamperometric response of the gas sensor for different concentrations of H_2O_2, measured at 0.5 V

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ANAL O 03

Novel electrogenerated chemiluminescence peptide-based biosensing of protease

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Electrogenerated chemiluminescence (Electrochemiluminescence, ECL) occurs at/near the surface of the electrode as a result of electrochemical reactions and chemiluminescence reactions [1]. ECL methods have received considerable attentions in clinical diagnosis because of low background, high sensitivity and inexpensive instruments [2]. Recently, we have developed serial of ECL biosensing method for the detection of biomarker, such as small molecules [3], protein [4] and DNA[5]. Here, we reported a serial of novel ECL biosensing of protease biomarker in our lab. For example, we developed a highly sensitive and selective ECL biosensor for metalloproteinase 2 (MMP-2) on the basis of iridium (III) solvent complex conjugating with histidine at the end of peptide and target-induced cleavage of peptide. The ECL probe was synthesized by coordination labeling ECL reagent (iridium (III) solvent complex, $[(ptz)_2Ir(DMSO)Cl]$, pbz=3-(2-pyridyl)benzoic acid, Ir1) on recognition element (a peptide, Biotin-GPLGVRGKHH) with high ECL efficiency and good storage stability (more than 6 months). This ECL biosensing strategy was proposed to determine MMP-2 via one pot-cleavage reaction and magnetic beads separation in the linear range of 1.0~10 ng/mL with the detection limit of 0.3 ng/mL. Further, the coordination - based site-specific labeling of histidine-rich peptide strategy for MMP-2 assay by incorporation of molecular recognition and signal probe in one step and using magnetic beads on the magnetic carbon electrode amplifying the detection signal, can simplify the experimental steps and avoid the interference of other substances in the sample. Moreover, the dissociation constant Kd between Ir1 labelled peptide and MMP-2 were calculated to be 7.8 ng/mL (0.11 nM) for peptide 1 and 8.3 ng/mL (0.12 nM) for peptide 2, indicate that high affinity of two kinds of peptides for MMP-2. In addition, the ECL biosensing method can be successfully applied for the detection of MMP-2 in serum sample with a 93.0±13.2 - 108.6±10.2 % of recoveries. These ECL biosensing methods provide a promising way for the determination of biological molecules in clinical diagnosis and point-of-care test of protease.

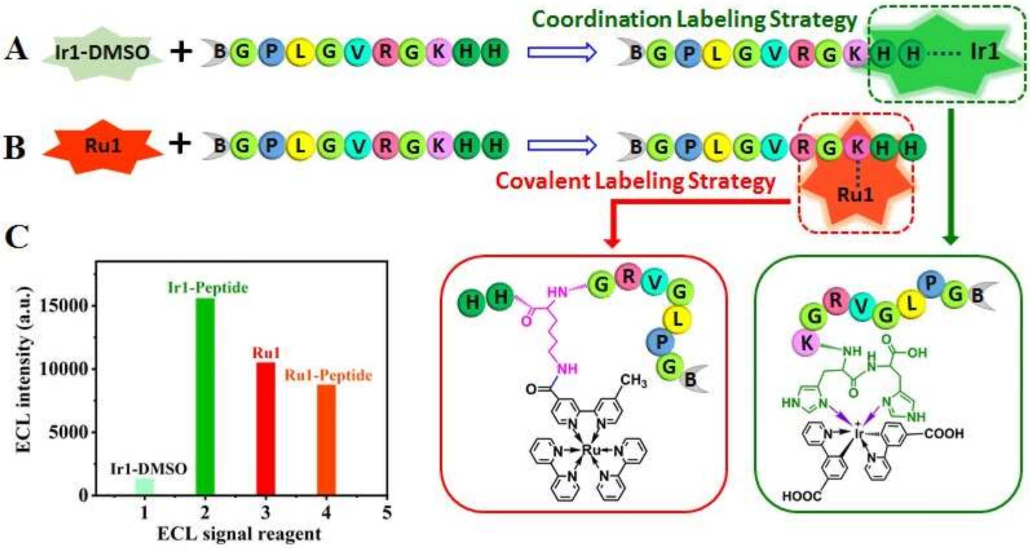

Figure 1. (A) Schematic diagram of coordination labeling strategy between Ir1-DMSO and peptide, (B) Schematic diagram of covalent labeling strategy between IRu1 and peptide and (C) ECL intensity of 14 μM Ir1-DMSO, 1 μM Ru1, Ir1-peptide and Ru1-peptide ($C_{peptide}$ = 1.0 μM) in 0.1 M PBS (pH 7.40) containing 50 mM TPA Caption

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Bisphenol detection: Screen-printed electrode comparison for rapid, cost-effective monitoring

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Endocrine-disrupting chemicals (EDCs) pose significant health hazards, impacting metabolic, reproductive, and respiratory functions. Thermal paper, commonly used in receipts and tickets, contains Bisphenol A (BPA) and Bisphenol S (BPS), a concerning EDC that can easily migrate to the skin, where it disrupts the endocrine system by mimicking the estrogen hormone, so negatively influencing human health [1,2]. Given its toxicity and widespread use, there's a pressing need for analytical methods to detect EDCs like bisphenols. Screen-printed electrodes (SPEs) offer a cost-effective solution for real-time monitoring. This study compares SPEs with carbon nanoparticles (CNPs) and carbon single-wall nanotube electrodes (SWCNTs) for BPA and BPS detection. It demonstrates their sensitivity, repeatability, and suitability for rapid, low-cost detection without hazardous waste generation. SEM was employed to examine the surface of the working electrodes of SPEs. The specificity of the SPE sensors in simultaneously detecting BPA and BPS was evaluated using differential pulse voltammetry (DPV), as depicted in Figure 1. SPE electrodes based on single-wall nanotubes demonstrated a broader linear range (0.5 to 75.0 µM) and higher sensitivity towards BPA and BPS oxidation than those with carbon nanoparticles. However, due to reduced capacitive current, CNP-based SPEs exhibited a 15-fold lower limit of detection (LOD) for BPA and a 4-fold lower LOD for BPS than SPE based on SWCNTs. These findings suggest that screen-printed electrodes based on carbon materials are promising techniques for on-site and health risk assessments in various everyday scenarios.

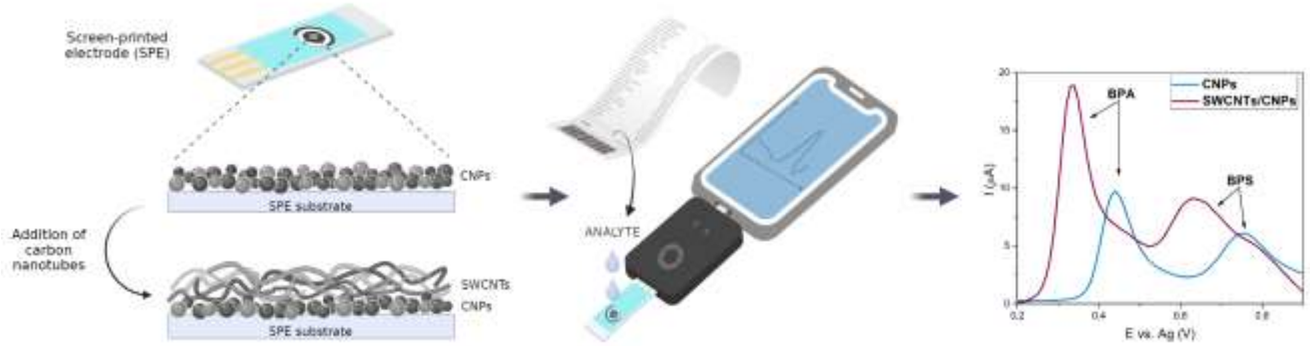

Figure 1. Comparison detection of BPA and BPS by SPE based on carbon nanoparticles and single-wall nanotubes via DPV [3]

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COR O 01

Materials characterization and corrosion behaviour of additively manufactured titanium alloys for biomedical applications

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Development of new metallic materials for biomedical applications is a long-term and complex process due to a variety of requirements the materials have to fulfil, starting from appropriate mechanical properties including strength, hardness, elastic modulus and impact toughness, high corrosion resistance in the presence of chloride ions and biomolecules and biocompatibility with human body environment. Only several classes of metallic materials align with these requirements, including titanium alloys, cobalt alloys, and stainless steel. The manufacture of these alloys has been based exclusively on the metallurgical procedures to produce wrought or cast alloys. Ti-6Al-4V does not provoke allergic reactions, is biocompatible and exhibits a good balance of strength, ductility, fatigue, fracture properties, low Young elastic modulus, low density, hardness and excellent corrosion resistance based on the formation of TiO_2 passive layer. A specific property of Ti-based materials is their osseointegration capability to form bone cells and mineralised bone matrix on the Ti surface. Contemporary productions nowadays include another possibility, namely additive manufacturing. Additive manufacturing (AM) uses data computer-aided design software or 3D object scanners to direct hardware to deposit material, layer upon layer, in precise geometric shapes. Among different AM methods available for the production of alloys, direct energy deposition (DED) was employed in this study.

Materials characterisation was conducted using scanning electron microscopy combined with energy-dispersive X-ray spectroscopy (SEM/EDS). Electrochemical measurements were carried out at 37 °C in three solutions: 0.9 % NaCl as a first approximation of physiological conditions, Hanks physiological solution imitation serum plasma, and artificial saliva. The composition of AM Ti6Al4V alloy is aligned with that of the wrought Ti6Al4V alloy, which was used as a reference. The microstructure of wrought and AM alloys differs, with the former showing α-Ti phase and intergranular β-Ti phase and the latter with a lamellar widmanstatten pattern, Figure 1a. Both wrought and AM Ti6Al4V alloys passivate in simulated physiological solutions and show no susceptibility to localised corrosion, Figure 1b. These results confirmed that the properties of additively manufactured Ti alloy are comparable with commercial wrought alloy. Further advantages offered by additive manufacturing are the possibilities of designing material composition. We aim to produce the material with inherent antibacterial properties that do not jeopardise other biomaterial properties. The newest developments will be presented.

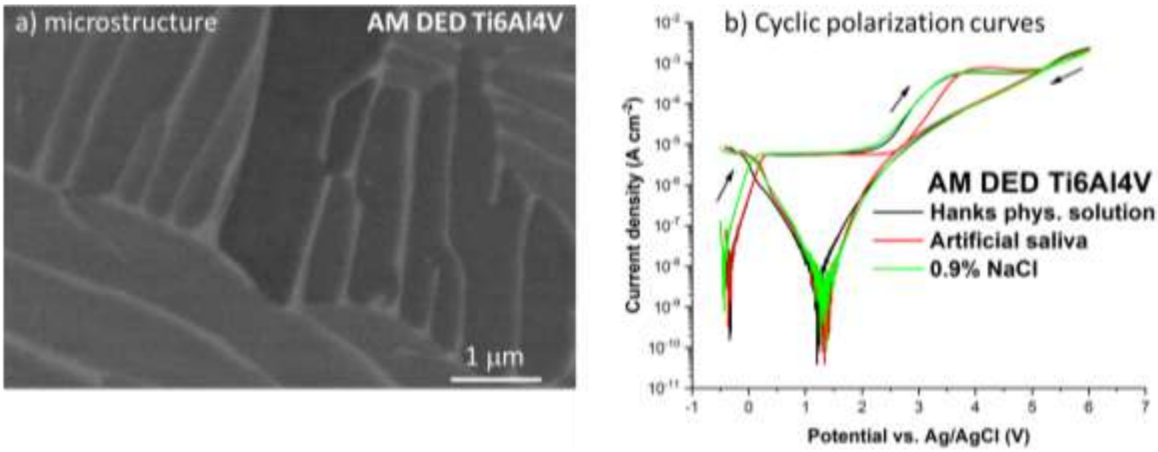

Figure 1. a) SEM backscattered image of the microstructure of additively manufactured Ti6Al4V alloy. b) Cyclic polarisation curves of additively manufactured Ti6Al4V alloys is three simulated physiological solutions.

Acknowledgement: The material was prepared at the Faculty of Mechanical Engineering of the University of Ljubljana. This study was financed by the Slovenian Research and Innovation Agency (grant BIOAD No. J7-4639).

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COR O 02

Corrosion of aluminium anodes in chloroaluminate electrolytes for secondary batteries

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Lithium battery technology faces challenges of safety, limited resources and high cost.[1] Currently, this drives tremendous efforts to replace lithium in secondary batteries by safer chemistry, based on more abundant and significantly cheaper materials. One candidate that fulfils these criteria is aluminium, which is the most abundant metal in the earth's crust and hence a cheap resource with high recycling rate. Moreover, its theoretical value of volumetric capacity of 8046 Ah/l is superior and its specific capacity of 2980 Ah/g is similar to that of lithium metal. In combination with either insertion cathodes made from graphitic carbon[2] or conversion cathodes based on *e.g.* sulphur[3] or oxygen[4], aluminium anodes could yield a highly promising battery chemistry, provided a suitable electrolyte can be found. Mainly chloroaluminate ionic liquids[5] and deep eutectic solvents (DESs)[2] have been reported as electrolytes for these types of batteries.

Similar to lithium, however, aluminium is prone to dendritic growth, which can ultimately lead to device failure.[6] The native oxide layer on the aluminium anode also poses a challenge to an efficient battery discharge/charge performance. It has been reported that soaking the aluminium anode in a suitable electrolyte has a positive effect on its electrochemical performance.[7] Accordingly, the discharge/charge characteristics of the aluminium anode were tested by galvanostatic cycling in symmetric cells with a $AlCl_3$:urea DES after various periods of soaking. The surface morphology of the aluminium anodes was then studied with scanning electron microscopy and energy dispersive X-ray spectroscopy. It turned out to be essential analysing the compositional changes of the native oxide layer during soaking in order to understand its effects on the aluminium growth morphology. This has been achieved with a combination of transmission electron microscopy and energy dispersive X-ray spectroscopy, secondary neutral mass spectrometry, as well as X-ray photoelectron spectroscopy.[8] The consistent results provide the basis for a reliable interpretation of electrochemical impedance data recorded during soaking.

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COR O 03

The role of RE in Zn and Zn-Co alloy composites

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Although rare earth (RE)-based conversion coatings have become a viable green substitute for hazardous chromium-coated ones, research in academia and industry is still ongoing to determine how they provide corrosive resistance. Numerous smart coatings incorporate nanoparticles of metal and metal oxides, offering diverse functional attributes and improved performance. In areas of the substrate that have been harmed by mechanical action or chemical interaction in a corrosion environment, these coatings may allow the substrate to heal itself [1-3]. One way to do self-healing is to incorporate inhibitor species into the coating formulation directly or encapsulate them in containers that are responsive to certain external stimuli. The corrosion protection afforded by the RE element and the small-scale phenomenon of corrosion inhibition conferred by RE doped pure Zn and Zn-Co alloy coatings are the main subjects of this work, with the aim of determining the RE contribution in corrosion protection either alone or in synergy with Co. Both Zn and Zn-Co alloy coatings are designed to modify the steel surface and offer effective corrosion protection, often as a stand-alone coating or as a as a base layer for organic top coats.

The chloride plating solutions containing Ce, Nd, or Sm were used to electrodeposit the Zn-RE and Zn-Co-RE protective composite coatings. As the primary drawback in the particle inclusion via electro-codeposition methods, particle agglomeration was minimized by adding RE to the plating solutions through synthetic RE-thioglycolate complexes and bath stability was determined as opposed to oxide containing or commercial powder containing ones. The protective qualities and self-healing capability were observed to be influenced by the type of RE, its reservoir, solubility in the composite coating, and surface morphology. The impact of these parameters was evaluated and compared using a multi-analytical approach, which involved dynamic light scattering, attenuated total reflectance, Fourier-transform infrared spectroscopy with ATR, nuclear magnetic resonance, Scanning Kelvin Probe Force Microscopy, open circuit potential measurements, and electrochemical impedance spectroscopy. It was shown that adjusting various electrodeposition parameters such as deposition current density, type of electrolyte agitation, and the source of rare earth elements can influence the RE content within the coating. The inclusion of rare earth elements in both Zn and Zn-Co coatings was demonstrated to reinforce to a different extent the barrier characteristics of composite coatings, consequently, possibly prolonging their durability in a 3 % NaCl solution. Moreover, a thorough investigation into the varying inhibition patterns displayed by bifunctional RE-complexes is clarified via theoretical computations. Predictions derived from density functional theory/molecular dynamics simulations indicate the possible development of various inhibitory compounds within the electrolyte. The corrosion inhibition mechanism hypothesized for RE-thioglycolates is based on both electrochemical and theoretical understandings, further corroborated through surface analysis techniques. Although significant, the RE loading within a coating does not singularly dictate the corrosion stability of composite coatings. The protective properties and self-healing capability were discovered also to result from an intricate interplay among the type of rare earth, its origin, solubility within the composite coating, and surface morphology.

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COR O 04

Corrosion issues of bipolar plate materials used in proton exchange membrane water electrolysers

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Renewable hydrogen obtained by water electrolysis is foreseen to have a major role in transitioning from an entirely fossil fuel-based economy to zero-emission technologies, with the goal of decarbonizing the transport and energy sector [1,2]. Amongst different technologies, proton exchange membrane (PEM) electrolysis is a promising technology for producing sustainable hydrogen, however its critical limitation is the usage of expensive electrocatalysts and construction materials, resulting in high hydrogen production costs [3]. The U.S. Department of Energy has established technical targets for PEM electrolysis, including stack-level capital costs, which should decrease from 450 to 100 $/kW by 2026, with a final target of 50 $/kW [4]. To meet these targets, low-cost alternative materials, particularly for bipolar plates (BPPs) and porous transport layers (PTLs) are urgently required. Yet, corrosion issues occurring especially at the anode side, restrict the use of more affordable alternatives to titanium. To address this issue, it is proposed to use stainless steel protected by Ti coatings. However, austenitic steels are expensive due to their high nickel content, and our research has thus focused on the high chromium ferritic stainless steels used as a support for BPPs.

In our study, we used scanning electrochemical microscopy (SECM) to investigate the localized corrosion behaviour of ferritic stainless steel AISI 446 and Ti-coated AISI 446, as candidate materials to replace titanium in BPPs construction for PEMWE. Typically, corrosion resistance is assessed using conventional electrochemical methods, which can only provide a macro-scale view of the corrosion process, as opposed to SECM, which allows for high sensitivity localization of corrosion sites. We used the SECM feedback mode with a redox mediator to evidence the passive layer formed at open-circuit potential on the surface of bare and Ti-coated AISI 446. Since BPPs experience high anodic potentials during operation, the samples were also anodically polarized to evidence the localized corrosion phenomena.

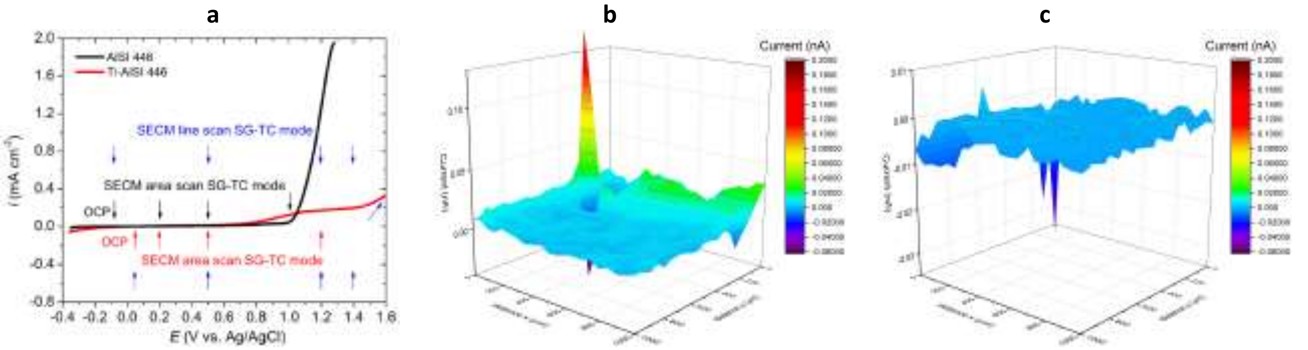

Figure 1. Potentiodynamic polarization curves at 1 mV/s scan rate (a); SECM area scans of uncoated AISI 446 at 1.0 V vs. Ag/AgCl (b) and of Ti-coated AISI 446 at 1.2 V vs. Ag/AgCl (c) in 0.1 M Na_2SO_4

The uncoated AISI 446 substrate is corrosion resistant in Na_2SO_4 solution up to an anodic potential of 1.0 V *vs.* Ag/AgCl, where the onset of localized corrosion is detected simultaneously with oxygen evolution reaction. The Ti-coated AISI 446 sample exhibits improved corrosion resistance, with no indication of iron (II) ion generation, even at anodic potentials of 1.2 V *vs.* Ag/AgCl, where only oxygen formation is observed. The results show that AISI 446 is susceptible to localized corrosion at lower anodic potentials than previously detected by conventional electrochemical methods. A thin Ti coating, deposited by magnetron sputtering, provides excellent corrosion resistance, allowing AISI 446 to be used for manufacturing BPPs.

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COR O 05

Considering the concepts of synergism and adsorption isotherms in corrosion inhibition

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The concepts of synergism and adsorption isotherms are often utilized in corrosion inhibition studies. However, the theoretical foundations underlying these concepts are not always well understood, and consequently, various pitfalls are committed sometimes.

Synergism is often quantified with the synergistic parameter. This parameter has only been applied to binary inhibitor mixtures in the literature until recently. In the corresponding equation, the mixture's inhibition efficiency is evaluated against a threshold inhibition efficiency based on the performance of pure compounds, and the threshold of Aramaki–Hackerman [1] is usually used. However, the author recently showed that the choice for the threshold value is not unique, proposed several other reasonable choices, and extended the corresponding synergistic models to multi-component mixtures [2].

In corrosion inhibition studies, the standard adsorption Gibbs energy is often estimated via the linear regression of the Langmuir isotherm in the $c/\vartheta = 1/K + c$ form (c = inhibitor concentration, ϑ = fractional surface coverage, K = adsorption equilibrium constant), where both the intercept and the slope are estimated, although the Langmuir isotherm requires the slope of 1. Hence, $c/\vartheta = 1/K + mc$ is used instead, where m is the slope. A theoretical basis for this equation was recently established [3], and a new general-purpose Type–I adsorption isotherm was proposed [4] based on considering a functional dependence of various adsorption models on the c/ϑ vs c plot. This new isotherm is flexible enough to describe various adsorption scenarios and provide relatively accurate estimates of the standard adsorption Gibbs energy, provided surface coverages are reliably determined experimentally [4,5]. Among the various adsorption models that the new isotherm can describe are those that consider lateral inter-adsorbate interactions, molecular size, surface heterogeneity, and mobile adsorption.

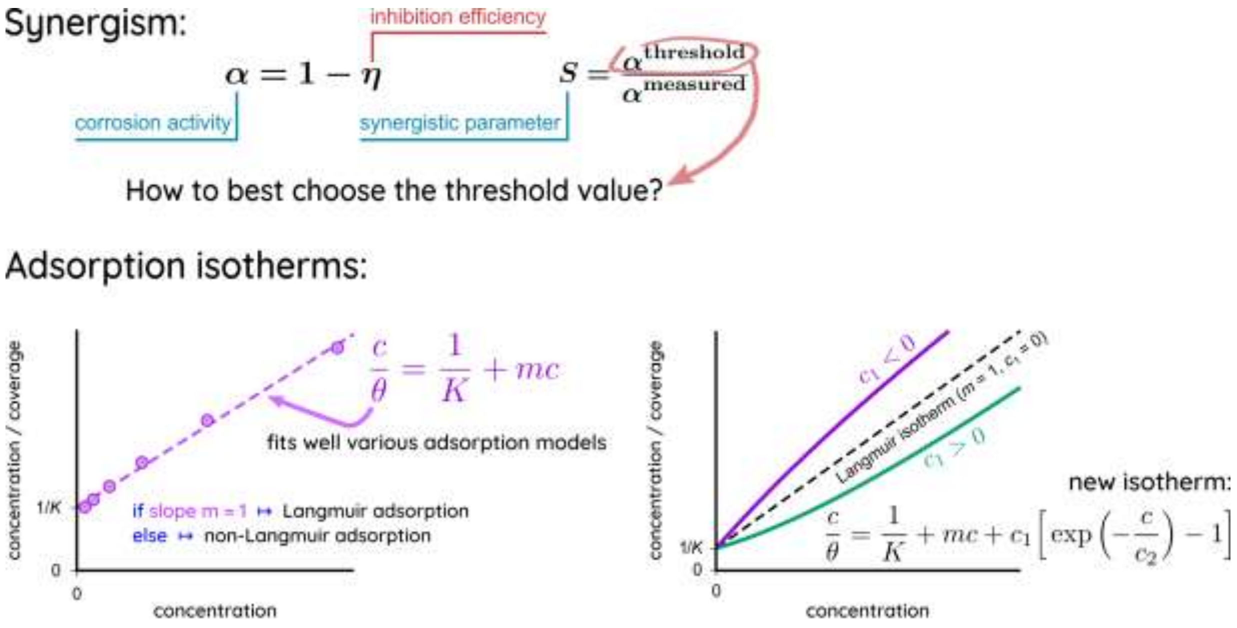

Figure 1. The equation for the synergistic parameter can be easily extended to multi-component mixtures if corrosion activity is used instead of corrosion efficiency (top). Based on the analysis of functional dependence of various adsorption models on the c/ϑ vs c plot (bottom left) a new general-purpose Type-I adsorption isotherm was proposed (bottom right).

Acknowledgement: This work has been financially supported by the Slovenian Research Agency (Grant No. P2-0393).

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Unusual adsorption of hydrogen on supported ultrathin aluminium oxide films

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It is well known that (ultra)thin oxide films can exhibit different properties with respect to their bulk counterparts and in this contribution, we report on an unusual binding site for hydrogen on the surfaces of ultrathin aluminium oxide films supported on aluminium. In particular, we find that hydrogen preferentially adsorbs on surface Al atoms instead of oxygen atoms (as one would expect based on chemical intuition). By performing systematic Density Functional Theory (DFT) calculations on a model oxide film of varying thickness (α-Al_2O_3 supported on Al(111), shown in Figure 1a) we establish that this binding mode is favoured for ultrathin films, where hydrogen adsorbs in hydride form, with the excess charge originating from Al atoms at the metal-oxide interface (Figure 1b). Finally, we propose that hydrogen bonding to surface Al ions is connected to the experimentally observed hydrogen evolution in pits formed during the pitting corrosion of aluminium.

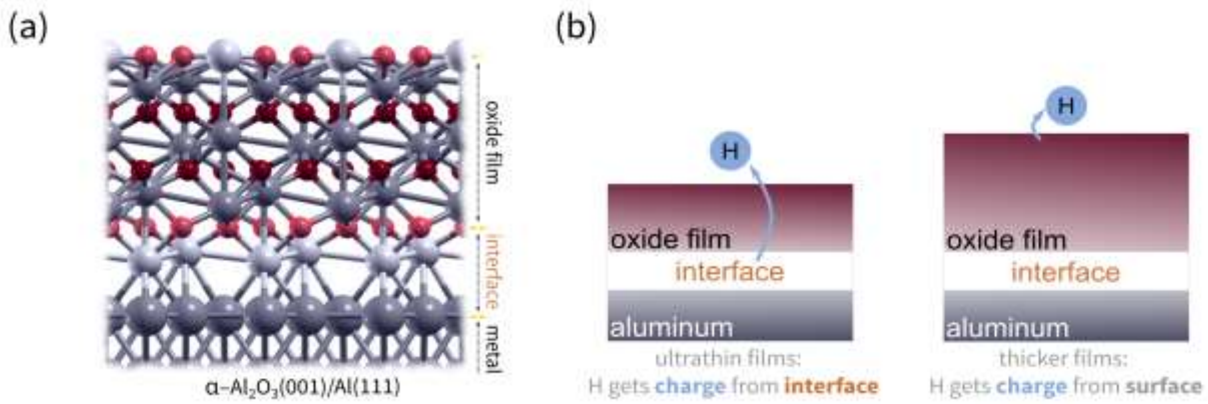

Figure 1. (a) A side-view of the model of the surface employed in DFT calculations.
(b) On ultrathin films the charge on hydrogen originates at the oxide-metal interface

ECAT O 01

Optimizing hydrogen evolution reaction on low-loaded Ru nanocatalysts supported on titanium oxynitride

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Water electrolysis (WE) is anticipated to emerge as the leading technology for decentralized, carbon-neutral hydrogen production. In the WEs, hydrogen is generated through the electrochemical hydrogen evolution reaction (HER), and the effectiveness of catalysts for HER depends largely on the adsorption energy of hydrogen intermediates and the barrier for water dissociation. Refinement of these activity descriptors offers the potential to tailor advanced electrocatalysts beyond Pt, known for its superior HER performance.[1] Modern electrocatalysts are comprised of metallic nanoparticles as the active sites, backed on support materials, expected to provide effective anchoring, high surface area, and conductivity. In certain cases, support materials can also enhance the performance of active sites via metal-support interaction (MSI).[2]

This study showcases the effective HER catalyst comprising Ru supported on a titanium oxynitride–carbon template (Ru/TiON-C) with an exceptionally low Ru loading of 6 wt.%, Figure 1. In an alkaline electrolyte, the Ru/TiON-C composite exhibited superior HER activity compared to Ru/C and Pt/C (Figures 1a and 1b), ranking among the top-performing Ru-based catalysts documented in the literature. This enhancement was attributed to the ability of TiON to induce MSI with Ru, yielding two effects: (i) TiON prompted partial growth of a distorted fcc-Ru structure known for its enhanced water dissociation properties;[3] (ii) X-ray photoelectron spectroscopy suggested a rearrangement in the electron density of Ru-sites, which can lead to an adjustment of the hydrogen adsorption/desorption energy. Furthermore, Ru/TiON-C can be upgraded to obtain highly active catalysts for acidic HER by decorating it with only 2 wt.% Pt. The obtained RuPt/TiON-C catalyst matches the practical activity of a commercial Pt/C (20 wt.%) (Figure 1c) while significantly surpassing its mass activity.

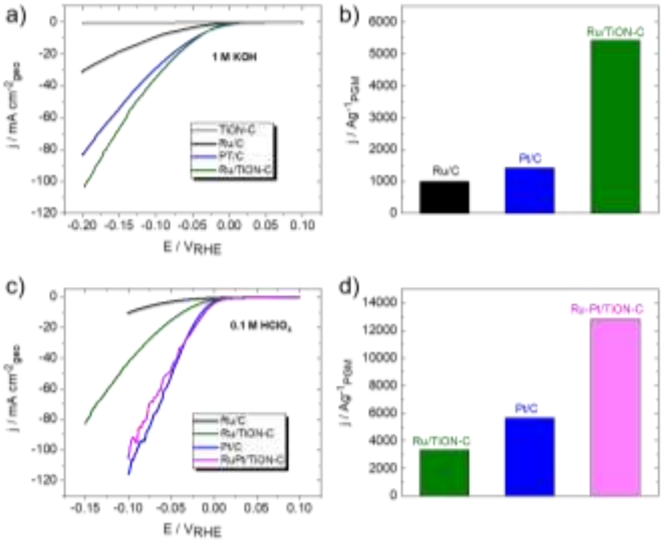

Figure 1. (a) Comparison of alkaline HER activities of Ru/C, Pt/C and Ru/TiON-C (1 M KOH, 10 mV/s) and (b) corresponding mass activities at an overpotential of 100 mV; (c) comparison of acidic HER activities of Ru/C, Ru/TiON-C, Pt/C and Pt-Ru/TiON-C catalysts (0.1 M HClO4, 10 mV/s) and (d) corresponding mass activities at an overpotential of 100 mV.

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Fine-tuning bimetallic nanostructures for enhanced hydrogen evolution reaction

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Water electrolysis, powered by electricity obtained from renewable sources, emerges as a pivotal method for green hydrogen production, a crucial energy vector. However, its widespread adoption faces challenges due to high energy consumption and resultant high costs attributed to the substantial overpotential of electrochemical reactions, specifically cathodic hydrogen evolution (HER) and anodic oxygen evolution (OER) reactions [1].

In this study, we introduce a novel electrocatalyst for HER, comprising RuIr nanoparticles supported on nitrogen-doped titanium oxide integrated into reduced graphene oxide (RuIr/TiON-C). The electrochemical activity and stability of RuIr/TiON-C are thoroughly examined in both alkaline and acidic environments and compared to RuIr/C analog as well as Ru/C, Ir/C, and Pt/C benchmarks. In alkaline electrolyte, RuIr/TiON-C outperforms all other tested materials whereas in acidic media it performs similarly to Pt/C, the current leading catalyst for HER in acid. Furthermore, RuIr/TiON-C demonstrate robust HER performance during potentiodynamic and potentiostatic degradation tests. The enhanced HER activity and stability of the investigated material can be linked to two effects: alloying of Ru and Ir and strong metal metal-support interaction (SMSI) triggered between the TiONx support and RuIr nanoparticles. The synergy of these two factors results in increased catalytic activity for the hydrogen evolution reaction.

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ECAT O 03

Guiding principles for hydrogen evolution reaction on nickel-based catalysts in aqueous electrolytes

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The development of catalytic materials for the hydrogen evolution reaction (HER) has been closely tied to the well-known concept of volcano plot, where the metal-H_{ad} bond energy is used as a single activity-descriptor. Although from a thermodynamic point of view it should make no difference whether hydrogen is produced from protons or water, there is a huge impact on the kinetics of the HER, which on most metal catalysts in alkaline media is about 2-3 orders of magnitude slower than in acid solutions, a phenomenon that cannot be explained solely by the metal-H_{ad} energetics [1]. We have persistently drawn attention to the importance of the kinetic synergy (bifunctional nature) of the HER in alkaline electrolytes, wherein both the beneficial OH_{ad}–M and H_{ad}–M energetics are necessary for achieving a highly effective catalyst. A specific example is a controlled decoration of Pt(111) surfaces by nanometer-scale $Ni(OH)_2$ clusters that manifests a factor of 8 activity increase in catalyzing the HER, compared to corresponding bare Pt(111) [2].

In recent years, many academic debates have been revived, focusing on the two aspects: *i)* the previously mentioned variation in HER kinetics between acidic and base environments, and *ii)* the impact that the spectator species have on the kinetics of electrochemical reactions. Here, we aim to highlight the contribution of 4 key factors governing the rate of HER in aqueous solutions on Ni-based catalysts. The interest in the electrochemical behavior of nickel arises from its industrial use as the cathode material in the water-alkaline electrolyzers.

Our study starts with the extended surfaces, affording insight into the fundamental kinetics of cathodic processes on the atomic/molecular level, which in the case of the Ni polycrystalline system are quite complex owing to the existence of several possible oxidation states of the metal, including numerous species such as Ni^0, $Ni(OH)_2$, NiO, NiOOH, hydride, *etc.* as well as their corresponding (pseudo)polymorphs.

We demonstrate the significance of water as a vital hydrogen-donor molecule that promotes the rate of transformation of reaction intermediates into the molecular hydrogen in alkaline electrolytes. Furthermore, a delicate balance between the availability of active sites on Ni electrode surface (the $1-\Theta_{ad}$ term) and the energetics of the activated water complex (the $\Delta G^{0\#}(H_2O)$ term) appears to be the key to maximizing the rate of the HER [3,4]. By careful design of our experiments, we were able to decouple these two factors and show their individual contribution to the rate of HER. This, in turn leads us to identifying the active sites for the HER and emphasize that the surface reactivity for the HER on Ni can be improved by simply tailoring the nature and coverage of adsorbates.

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Ni-Sn coated Ni foams – suitable cathodes for large-scale alkaline water electrolysis?

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Driven by the continuously increasing demand for electricity, diminishing carbon-based energy resources, steadily increasing ecological concerns, the focus has shifted to finding clean and renewable solutions. Electrochemical energy conversion and storage systems have taken the spotlight in shaping a greener future, with hydrogen, obtained through electrolysis, emerging as a leading energy carrier candidate. The scalability and abundance of materials used in alkaline water electrolysis, alongside the maturity of this industrial process, make it a favoured pathway for hydrogen production powered by renewables.

Electrodeposition was firstly investigated through linear sweep voltammetry and controlled potential coulometry[1] techniques, in order to obtain high-performance Ni-Sn coated Ni foam. The objective was to achieve coatings of optimal composition to enable outstanding catalytic activity towards hydrogen evolution reaction, characterized by low overpotentials that are below – 100 mV at current density of – 1 A cm^{-2}, normalized per geometric area, in 1 M KOH. Since these electrodes showed promising results, the electrodeposition was further investigated in galvanostatic setting in order to determine the most favourable conditions, as this technique is better suited for industrial-scale plating. Ni-Sn coated Ni foams, deposited at specific constant deposition current density, were additionally tested in zero-gap flow electrolysers where they have shown good stability and low value of overvoltage, which is in alignment with criteria proposed by IRENA[2].

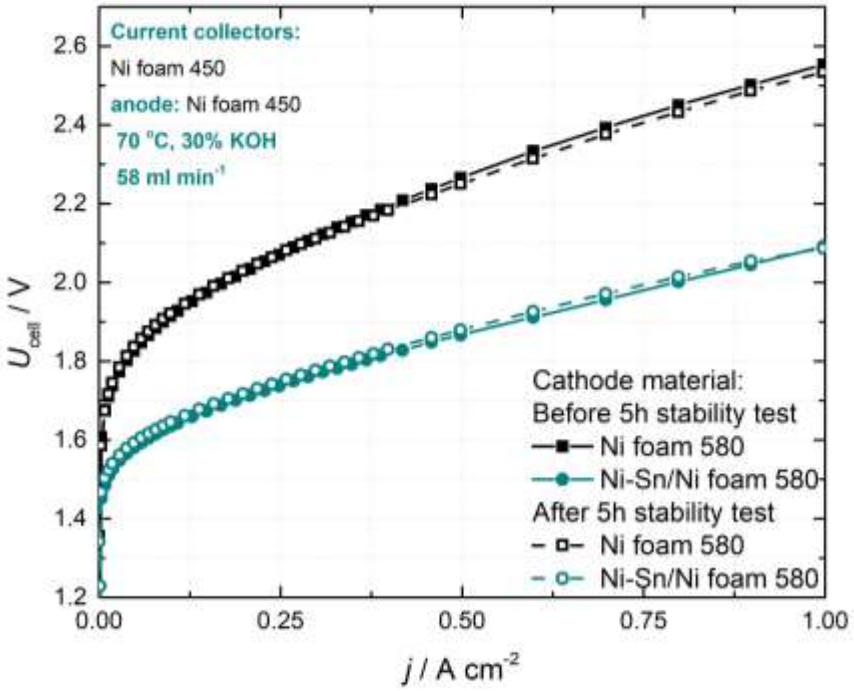

Figure 1. Cell voltage – current density dependency when two different cathodes are used – Ni-Sn coated one, and bare Ni foam

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ECAT O 05

Comparison of electrodeposited composite coatings composed of commercial and synthesized MoO_2 embedded in Ni for hydrogen evolution reaction

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It is commonly known that the need for clean source of energy with the production and manufacturing costs being at the level of current solutions is getting greater. Among other candidates hydrogen shows great potential as substitution for fossil fuels because of its high energy content and possibility to be produced with zero emissions if the right method is chosen. Water electrolysis represents an excellent candidate for that role, but to achieve high efficiency concentrated hydroxide solutions serve as electrolytes in those systems. An advantage of the alkaline media is the possibility to use non-precious metals as catalysts, such as nickel. Ni is fairly stable in alkaline media and as an abundant element it is commonly used in alkaline water electrolysis as a catalyst substrate, or electrode itself. Transition metal oxides show excellent activity for hydrogen evolution reaction (HER) and have synergetic effect with Ni [1], based on that and the previous experience of our research group [2] this work is focused on catalysts composed of composite Ni-MoO_2 electrochemically deposited on different porous Ni substrates.

Firstly, the objective was to produce coatings consisted of MoO_2 with the smallest particles commercially available embedded in Ni. Ultrasound assisted electrodeposition showed no results due to the corrosive environment of the deposition bath, as well as the erosion effect of the particles (100nm) on the ultrasonic probe. Promising results were achieved when air bubbling toward the bottom of the cell was used as a method for keeping the non-metallic MoO_2 particles suspended in the solution. Considering the cost of the catalyst in order to try to reduce the production cost (and enhance the activity for HER) the second part of the research focuses on coatings with synthesized MoO_2, which has proven before to show better results [1]. Even though the electrodes coated with Ni-MoO_2 containing MoO_2 synthesized in our lab had less electrochemically active surface area (the substrate was Ni mesh that doesn`t offer as much surface area as Ni foam used as substrate in first part of research) it showed much better activity towards HER. Overpotential on current density of -500 mA cm^{-2} was -88 mV, being 30 mV lower than on Ni foam electrode coated with composite containing commercial MoO_2 particles which can be seen od Figure 1. In the production of this type of catalyst, the method for dispersing MoO_2 through the bulk of the solution was stirring with magnetic stirrer and circulating the electrolyte during the deposition. The future goal is to continue the work on finding the optimal conditions for preparing a coating with the same characteristics on Ni foam substrate which should have even higher activity towards HER.

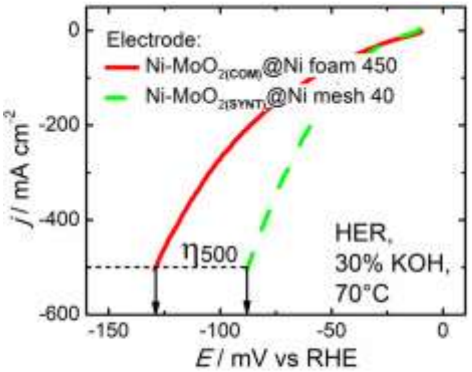

Figure 1. HER polarization curves recorded at porous electrodes coated with composite coatings based on commercial (COM) and synthesized (SYNT) MoO_2

Acknowledgement: This work was supported by the Federal Ministry of Education and Research – Germany, through the WBC2019 call – project NOVATRODES 01DS21010, and by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract No. 451-03-65/2024-03/200135)

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The forgotten mechanism in electrocatalysis: On the importance of Walden steps for the modelling of energy conversion processes

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Since the birth of the computational hydrogen electrode approach,[1] it is considered that the activity trends of electrocatalysts in a homologous series can be quantified by the construction of volcano plots.[2] This method aims to steer materials discovery by the identification of catalysts with improved reaction kinetics, though evaluated by means of thermodynamic descriptors.[3,4] While the conventional volcano approach in the oxygen evolution reaction (OER) relies on the assumption of the mononuclear mechanism, consisting of the *OH, *O, and *OOH intermediates,[1,2] in this contribution we report new mechanistic pathways comprising the idea of the Walden inversion in that bond-breaking and bond-making occurs simultaneously.[5]

In a recent communication, it was reported by our group that Walden-type mechanisms, in which the release of the product O_2 and the adsorption of the reactant H_2O occur concurrently, govern the apex of the OER activity volcano plot.[5] Applying electronic structure calculations in the density functional theory (DFT) approximation, we have gained insight into the importance of Walden steps to the mechanistic description of various OER catalysts. While IrO_2 belongs to the golden standard in acid, cobalt oxide-based materials are superb electrocatalysts in alkaline media. Pentlandites, a class of iron-nickel sulphides, are also discussed as a promising material class for the alkaline OER. Taking representative surface facets for these three materials, it is demonstrated that the neglect of Walden steps to the OER mechanism leads to erroneous conclusions in terms of activity predictions or the identification of limiting reaction steps.[6] We conclude that the mechanistic motif of Walden inversion steps has far-reaching implications beyond the oxygen electrocatalysis by referring to other electrocatalytic processes such as the electrochemical nitrogen reduction reaction.

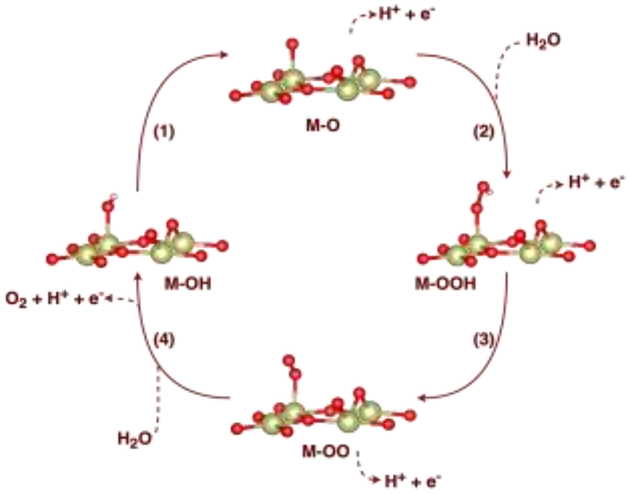

Figure 1. Example of a Walden-type OER mechanism, in which the release of the product O_2 and the adsorption of the reactant H_2O takes place concurrently in step (4).

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ECAT O 07

Mathematical model of non-equilibrium cathodic Pt dissolution

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Transformation of chemical energy, stored in hydrogen molecules, into electric energy using hydrogen fuel cells is an important building block of future green energy transition. Wider adoption of these devices is, however, still hindered by their relatively high cost and relatively high degradation rates due to harsh conditions inside the fuel cells.

An important reason for the high cost of proton exchange membrane fuel cells (PEMFCs) is utilization of expensive materials, such as Pt, which serves as a catalyst for electrochemical reactions. Despite its high resistivity to corrosion, high electric potential, temperature, and acidity in the fuel cell catalyst layer result in oxidation of Pt surface and its eventual dissolution, which severely limits the lifetime of PEMFCs. Experimental studies show that this process is further accelerated in dynamic conditions with periodically changing electric potential. When potential is increasing, Pt dissolution is suppressed by the formation of passive oxide layer, but when potential is subsequently lowered, the reduction of oxide layer results in severely increased concentration of dissolved Pt ions [1].

To improve the understanding of this process and its predictability, we propose a mathematical model of Pt surface oxidation, reduction, and dissolution. Pt oxidation at high electric potential is described as a two-step process, modelled by Butler-Volmer equations, with stable PtO oxide forming in the first step and subsequently, when the oxide surface coverage is increased, transforming into less stable α-PtO2 [2]. When the electric potential is subsequently decreased, instead of being reduced to Pt, part of α-PtO2 layer is detached from the surface, resulting in increased concentration of dissolved Pt ions in the adjacent electrolyte. The model is validated by comparing the results with experimentally measured time traces of Pt ion concentrations, determined with online ICP-MS, and with CV voltammograms, obtained during voltage cycling catalyst degradation test. Good agreement with experimental data indicates that the model meaningfully describes essential steps leading to increased Pt dissolution during the cathodic sweep of catalyst degradation. Due to its intuitive basis and computational efficiency, the model could, in future, be implemented in more complex model frameworks of fuel cell degradation, leading to development of advanced fuel cell operation strategies aimed at increasing their performance and lifetime [3].

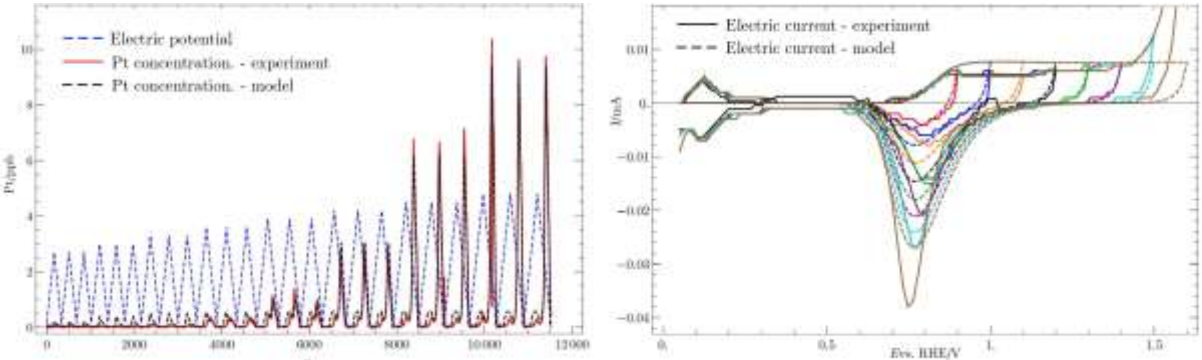

Figure 1. Comparison between experimentally measured and modeled Pt concentration and CV voltammograms

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ECAT O 08

Influence of microwave synthesis conditions on the performances of nitrogen-doped carbon-based catalysts for hydrogen peroxide electrosynthesis

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Hydrogen peroxide (H_2O_2) ranks among the top 100 most significant chemicals, finding extensive use across various chemical and medical end-user industries including paper and pulp bleaching, water treatment, food processing, electronics, and disinfection in medical and pharmaceutical sectors. The electrochemical two-electron ($2e^-$) oxygen reduction process (ORR) offers a sustainable pathway for decentralized H_2O_2 production, diverging from the energy-intensive centralized industrial anthraquinone process [1]. Metal-free nitrogen-carbon-based catalysts have emerged as promising alternatives for expensive, toxic, and scarce noble-metal or alloy catalysts like Pt, Pd, Au, Pt–Hg, and Au–Pd for $2e^-$ ORR [2].

In this study, we synthesized nitrogen-doped carbon-based catalysts (NCC) from polyaniline (PANI) using a microwave-assisted method (MW). MW heating offers a compelling alternative to conventional thermal methods, providing quicker heating, enhanced energy efficiency, and the potential for nanostructure formation with distinct morphological or structural properties [3]. The MW synthesis of NCC was performed in a microwave calorimeter equipped with a dual-mode cylindrical cavity. This setup allowed simultaneous heating of the sample and measurement of the material's dielectric properties relative to the carbonization temperature [4]. Control of heating in the PANI sample was achieved by tuning the resonant frequency near 2.45 GHz, regulating the resulting MW power delivered to the cavity. Oscillations in MW power within the 20±10 W range facilitated rapid heating and cooling cycles in the 350-500 °C temperature range, yielding uniform NCC structures ($NCC_{\text{heating-cooling}}$). Conversely, continuous MW power increase led to thermal run-away and localized superheating of the material. The ORR performance of the synthesized NCC was assessed using a rotating ring-disk electrode (RRDE) with a Pt ring and glassy carbon (GC) disk in O_2-saturated 0.1 M KOH media. $NCC_{\text{heating-cooling}}$ samples exhibited 93 % selectivity to H_2O_2, diffusion-limited current densities of 2.6 mA cm^{-2}, and H_2O_2 production current of 3.9 mA cm^{-2}, surpassing values reported for nitrogen-doped carbon-based catalysts synthesized by conventional heating documented in the literature.

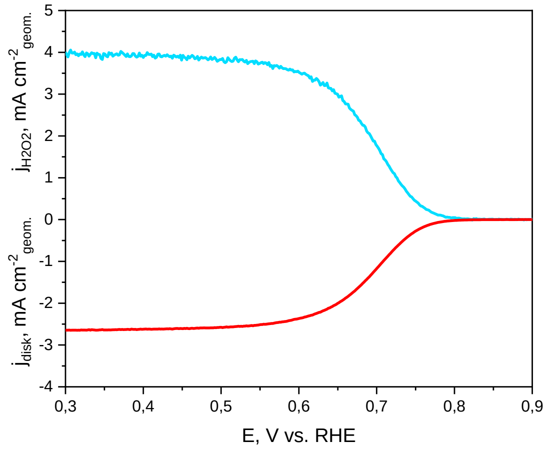

Figure 1. The RRDE polarization curves of $NCC_{\text{heating-cooling}}$ samples in O_2-saturated 0.1 M KOH, produced through rapid heating and cooling stages during MW heating.

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ECAT O 09

Galvanic deposition of subnanometric Os particles on TiO_2 nanotube arrays: Boosting the electrocatalytic hydrogen evolution performance

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Proton exchange membrane water electrolysis (PEMWE) powered by renewable energy sources is seen as the most promising technology for high-rate production of green hydrogen. The acidic environment of PEMWE systems requires the use of efficient, but expensive platinum group metal (PGM)-based catalysts for the cathodic hydrogen evolution reaction (HER), which limits the prospects for wider commercialization of this technology. One of the main research directions today is designing stable and interactive substrates and facile methods for dispersing PGMs in order to reduce their content in HER cathodes and improve their utilization in the reaction. Our previous work showed that galvanic deposition of PGM nanoparticles on self-ordered TiO_2 nanotube (TNT) arrays can produce highly active composites with low PGM loading [1,2]. In this study, we extend the galvanic displacement approach to depositing osmium particles on hydrogenated “nanograss”-covered TNT array substrates [3]. Structural characterizations show that Os particles deposited by this procedure are mainly at the sub-nanometric level and entirely cover the inner tube walls. Our systematic investigations reveal the influence of galvanic deposition conditions ($OsCl_3$ concentration/temperature/duration) on the HER overpotential and mass activity of resulting Os@TNT composites. An optimum Os@TNT composite, achieving a balance between apparent and mass activity, is prepared at 3mM/55°C/30min and contains $\sim$12 $\mu g_{Os}\ cm^{-2}$. It exhibits a low overpotential of 61 mV at a current density of 100 mA cm^{-2}, a high mass activity of 20.8 A mg_{Os}^{-1} at an overpotential of 80 mV, and a durable performance in 1 M $HClO_4$. Density functional theory (DFT) calculations suggest that the hydrogenation degree of the TiO_2 surface does not only have a large impact on the dispersion and size of deposited Os particles, but it also affects their adsorption properties. The electronic interactions between the hydrogenated TiO_2 surface and small Os clusters may weaken the strong Os–H* binding characteristic for bulk Os and thus boost the intrinsic HER activity of Os sites.

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ECAT O 10

Crystal structure of Pt-Cu nanoparticulate oxygen reduction reaction electrocatalysts

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Proton exchange membrane fuel cells are a viable alternative to fossil fuel-powered engines in the energy and mobility sector. However, the cost of the electrocatalyst for the oxygen reduction reaction (ORR) still poses an issue, as it commonly contains scarce noble metals, like platinum. Supported Pt-alloy nanoparticles are now commonly used to lower the amount of Pt but retain good ORR performance[1]. Despite numerous studies on structure-property relationships of nanoparticulate electrocatalysts, the effects of selected structural features on the catalytic activity and stability remain unexplored. Ensembles of such nanoparticles typically vary in size, shape, composition, crystal structure, and defects, all of which can impact their performance. Therefore, advanced characterization methods are needed to obtain both bulk and local information about the catalyst structure to properly correlate it to its properties. In this presentation, I will focus on studying the crystal structure of carbon-supported platinum-copper nanoparticulate electrocatalysts, used for the ORR, specifically on anti-phase boundaries inside the catalytic nanoparticles[2]. Those planar defects, contributing to chemical disorder, were previously described for a bulk alloy, but not for a nanoscale catalyst. X-ray powder diffraction patterns were used in conjunction with simulations and Rietveld analyses to reliably determine the defect placement. Electron diffraction and atomically resolved scanning transmission electron microscopy (STEM) were used to confirm the defect presence locally, and ORR performance was evaluated for several platinum-copper analogs with and without anti-phase boundaries. Furthermore, I will discuss what STEM and its advanced modalities, such as 4D-STEM, can offer in the context of nanoparticulate electrocatalysts using a platinum-copper system as an example, especially to show how identical location microscopy brings added value to stability studies. This work represents a step towards a deeper understanding of electrocatalysts' structure-property relationships by providing insight into the crystal structure of alloyed nanoparticles.

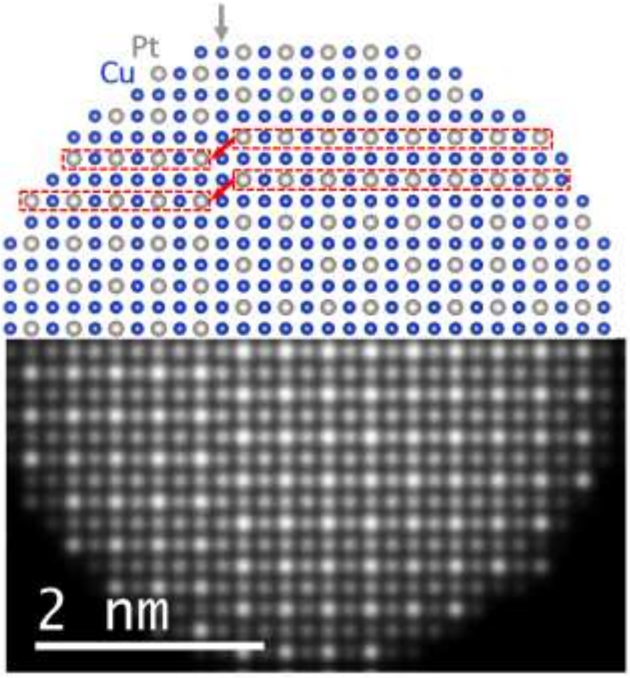

Figure 1. A Pt-Cu nanoparticle with an anti-phase boundary, depicted with a simulated STEM image, and the model, used for the simulation

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Nickel electrodes in energy conversion reactions: The determination of the electrochemically active surface area and its influence on the activity of structured Ni electrodes produced by additive manufacturing

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Ni electrodes are widely implemented in electrocatalysis, most notably in alkaline electrolysis. Additively manufactured (AM) nickel electrodes offer a great potential as an efficient solution for the fabrication of structured high surface area electrodes with complex geometries. This would be particularly important for reactions involving a gas phase, but also in generally furthering the understanding of mass transport effects at complex interfaces. The accurate determination of the electrochemical active surface area (ECSA) is a key step in the evaluation of the intrinsic electrocatalytic activity of such complex electrodes. In this work[1], we fabricated six Ni electrodes with different macroscopic geometries using laser powder bed fusion of metals (PBF-LB/M). X-ray photon spectroscopy (XPS) and a non-contact optical profilometer (NCOP) were used to investigate the composition and surface morphology of the electrodes. The ECSA was determined by different approaches: linear and non-linear allometric fitting of the double layer capacitance from voltammetric experiments; the integration of the $Ni^{2+/3+}$ transition; assessing double layer capacitance determined from electrochemical impedance spectroscopy (EIS) at open circuit potential (OCP) and the adsorption capacitance for the oxygen evolution reaction (OER) intermediates. Comparing these methods, large deviations in the resulting ECSAs were found, motivating a comprehensive discussion. In addition, four different reactions were investigated: the ferri-ferrocyanide redox system, hydrogen evolution, ethanol electrooxidation, oxygen evolution and nitrogen reduction reaction. Based on the results, it will be shown that increasing the surface area of the electrode has different effects depending on the type of reaction and the applied electrode architecture. The obtained results demonstrate the potential of AM to tailor electrode performance by altering electrode geometry and underline the importance of the ECSA determination for the comparison of the electrocatalytic activity in different electrodes.

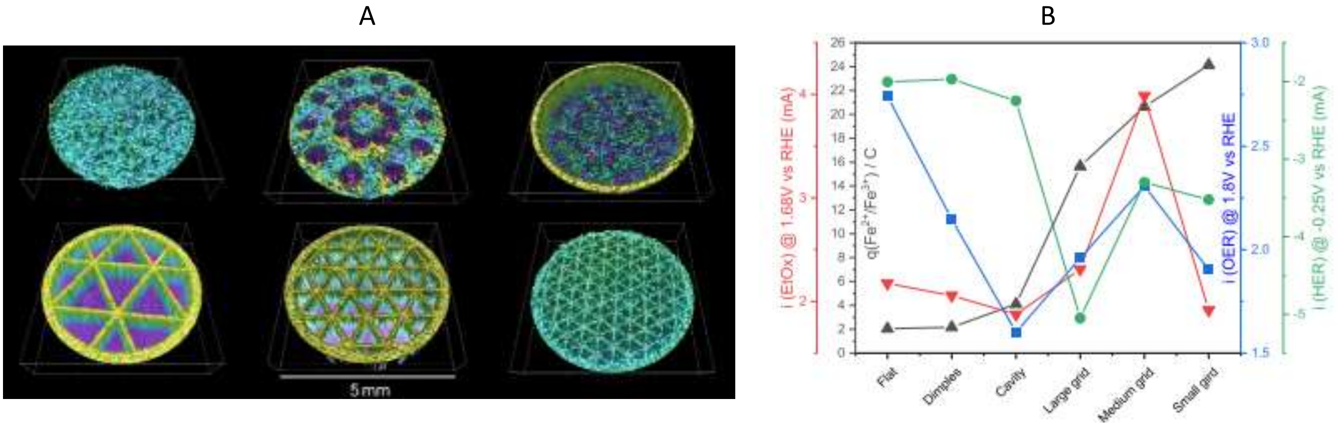

Figure 1. (A) Images taken by NCOP (B) Activities of the manufactured electrodes towards the $Fe^{2+/3+}$ redox, oxygen evolution, hydrogen evolution, and ethanol oxidation reactions

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Interaction of cathodically evolved hydrogen with electroless Ni-P electrode

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Transition metal phosphides have received considerable attention as electrocatalysts [1]. Among them, nickel phosphides have been widely explored for electrocatalytic HER [2,3]. The improved electrocatalytic properties of Ni–P alloy coatings are explained by the influence of different factors. One of them is the ability of amorphous Ni-P electrode to adsorb and absorb significant amounts of hydrogen, which changes the electron structure of the basic metal [4].

Our previous works are devoted on the electrocatalytic properties of electroless Ni-P coatings on a steel substrate in terms of hydrogen reaction in alkaline or acidic media in a wide range of phosphorus content of the coatings [5,6]. The present research is focused on evaluation of the interaction of cathodically released hydrogen with the electroless Ni-P alloy coating. It is well known that the phosphorus compounds play the role of promoters for the penetration of hydrogen during the cathodic polarization of steel, nickel, *etc.* [7]. The electroless deposition of Ni-P itself is accompanied by the evolution of hydrogen, part of which is incorporated into the coating. By electrochemical methods, Devanathan-Stachurski permeation cell, differential thermal analysis, X-ray diffraction and X-ray microanalysis, data are obtained on the process of interaction of hydrogen with Ni-P coating when used as an electrode for HER in alkaline or acidic media - diffusion of hydrogen in the alloy coating, phase transformation, composition and morphology of the alloy coating before and after electrochemical treatment.

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EDP O 01

Electrodeposition and characterization of homogeneous and graded composition Co–Fe–Ni–Zn multi-principal element alloy films

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One of the most dynamically developing fields of materials science focuses on studying equiatomic or near-equiatomic materials with three or more elements. In these materials, neither of the components can be classified as either solvent or solute. This material family is frequently called as multi-principal element alloys (MPEAs) or compositionally complex alloys (CCAs). These material classes also include high-entropy alloys (HEAs) in which the number of principal elements is five or higher with near-even atomic concentrations.

MPEAs can be manufactured with a wide range of traditional metallurgical techniques (such as mechanical alloying, arc-melting, quenching, physical vapour deposition, laser ablation, *etc.*), but the number of electrochemical processing attempts is very limited. MPEA electrodeposition works apply various approaches: (i) dilute solution of the precursor materials in a non-aqueous solvent; (ii) classical electrodeposition from aqueous baths; and (iii) electroreduction of metal oxide pellets. Due to the small number of paper published so far, only a few selected compositions were studied.

In this study, a Co–Fe–Ni–Zn MPEA was processed by pulse electroplating for the first time [1]. The reason of choosing pulsed electrodeposition as preparation technique~~s~~ was multifold, such as to achieve an even in-depth composition, to obtain nanocrystalline layers and to curtail the surface roughening commonly observed in electroplating. The bath used was based on metal chloride precursor compounds and traditional additives. Electrodeposition was performed at 55 °C for obtaining a relatively homogeneous material on a tantalum substrate (deposits prepared at ambient temperature were prone to both a phase separation and a development of local morphological diversities).

In a custom-made symmetrical electrochemical cell, a compositionally very homogeneous deposit could be obtained with a nominal component ratio of 32 at.% Co, 27 at.% Fe, 21 at.% Ni and 20 at.% Zn. The optimization of the bath composition was a time-consuming procedure due to the large variation in the relative deposition preference of the alloy components (mostly because of the anomalous nature of the codeposition process).

The film has a main fcc phase with the lattice constant of about 0.3620 nm. The average grain size was as small as ~12 nm. The size distribution was wide spanning from 5 to 27 nm. The microstructure also contains a bcc minority phase and ~2 nm thick amorphous boundaries separating polycrystalline columns. This amorphous phase is enriched in Ni and depleted of Fe. XRD suggests that the bcc minority phase has a smaller crystallite size compared to the main fcc structure.

The average hardness and elastic modulus determined by nanoindentation were 9.2 and 197 GPa, respectively. This hardness is much higher than the values reported formerly on fcc MPEAs processed by other methods (3.6 to 6.9 GPa) which can be explained by the very small grain size and the existence of the bcc and amorphous minority phases.

An asymmetric electrodeposition cell configuration was developed for preparing alloys of gradient composition (sample library approach, [2]). It was found that the element with the smallest precursor compound concentration, Zn, was gradually replaced with the next element in the preference row, Co. Therefore, the Zn concentration range of 14-44 at.% could be scanned. Since this study could be performed with a different type of substrate (brass), the texture of the main fcc phase changed to 211, and the amorphous regions were also missing, hence leading to somewhat smaller hardness values than the homogenous sample plated onto Ta foil. The lattice constant scaled with the Zn concentration of the deposit, and the hardness optimum was found at 36 at.% Zn.

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EDP O 02

Is electrodeposition indeed versatile? – A case of Al-Mg alloy deposition from organometallics

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Electrodeposition is often lauded as versatile in obtaining the desired composition, morphology and phases in the deposits. However, can all these features be achieved together to any desirable extent through electrodeposition? To address this question the dependencies among composition, morphology and phases need to be analysed meticulously; and the reasons for these dependencies must be understood. Electrodeposition is, primarily, driven by either applied potential or current. These parameters govern the concentrations of depositing ions in a multi-component system *(i.e.* two or more metals) from the electrolyte near the cathode. Eventually, how these ions settle on the cathode depends on various coupled kinetically and thermodynamically imposed effects. For instance, the rate of ion deposition, temperature, cathode *etc.* decide the phases (equilibrium or otherwise) and morphologies (*via* surface diffusion of ions). This offers an extremely complex scenario and renders it extremely difficult to answer the above mentioned, fundamentally, and industrially, important question.

Addressing the question is attempted through electrodeposition of Al-Mg alloys – an industrially important system. Al-Mg alloys were galvanostatically electrodeposited from $Na[AlEt_4]+2Na[Et_3Al–H–AlEt_3]+2.5AlEt_3+6toluene$ at permissible ranges of current densities (60-150 mA cm^{-2}) and temperatures (60, 90 °C) using Mg anode on rotating Cu cathode in an inert atmosphere using a PAR 263 workstation [1]. Beyond these permissible ranges, either no deposit was obtained, or the electrolyte evaporated. Within the permissible ranges, Surprisingly, higher current densities and temperatures encourage less noble-Mg deposition, falsely suggesting 'Regular' electrodeposition behaviour by Al-Mg system according to Brenner's categorisation. However, the plot between Mg/Al ratios in deposits vs those in electrolytes is always above the composition reference line *(i.e.* line of Mg/Al in deposit = Mg/Al in electrolyte, Figure 1(a)) [2,3]. This classifies this system as 'Anomalous' (Brenner's categorisation). This is because of the difficulty in extracting Al^{+3} from $[Et_3Al–H–AlEt_3]^-$ for its deposition. An almost unique relation can be seen between the obtained morphologies and composition ranges. Crystallographically consistent faceted/feather-like morphology always possesses 1-7 at.% Mg [4]; Smooth globules contain up to ~20 at.% Mg [5]; and rough globules always form over smooth ones and possess ~65-80 at.% Mg (Figure 1(b)) [5]. These relations are mostly due to the surface energy effects experienced by these morphologies. Moreover, irrespective of the morphology, the compositions below ~20 at.% Mg always yield metastable supersaturated Al-rich fcc solid solutions. Those within ~65-80 at.% Mg form metastable supersaturated Mg-rich hcp solid solutions. Compositions between 20-65 at.% Mg are always prohibited due to spatially drastic switchover from fcc to hcp phases – confirmed by extensive microstructural characterisation and supported by thermodynamic common tangent construction in ΔG-composition curves [6]. The results clearly indicate that only certain compositions, morphologies and phases are possible in the Al-Mg system. Hence, electrodeposition of Al-Mg is not versatile unlike, possibly, those of the well-established systems *e.g.* Ni-Co or Ni-Cu. Most probably this is because Al-Mg is not a thermodynamically isomorphous system the latter. Being non-isomorphous, accommodation of any concentration of Mg in Al or vice versa in the deposits is not possible, resulting in only certain composition ranges, morphologies and phases.

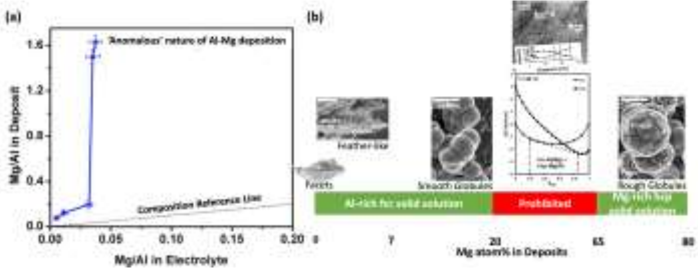

Figure 1. (a) Al-Mg composition line; (b) Feasible Mg compositions in deposits corresponding morphologies and phases.

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Understanding the nature and scheme of Al-Mg electrodeposition using chloride-based molten salt electrolyte system

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Aluminium-magnesium (Al-Mg) alloys were electrodeposited on commercial copper strip using $AlCl_3$, NaCl, KCl, and $MgCl_2$, employing Al or Platinum (Pt) as the counter electrode (C.E.) and Al as the reference electrode. Potentiostatic technique was employed for all the depositions at overpotentials (η) of -1.05 to -1.30 V at 180 °C in an Ar-filled glove box maintaining oxygen and moisture levels at <0.1 ppm and using CHI660E potentiostat. The deposits, upon employing Al as C.E., were categorised into two groups based on the obtained steady-state current density values. Moreover, the salt sedimented on Al C.E. in Group 2 showed the signs of $AlCl_4^-$ from FTIR; whereas, that in Group 1 was only $AlCl_3$. In both these groups, the deposit morphology coarsened with the increase in overpotential. The Mg (less noble) content in the deposits of Group 1 (η: -1.05 to -1.10 V) was negligible (~0.10-0.08 atom %), while that in Group 2 increased from 0.26 at.% (η = -1.15 V) to 4.02 at.% (η = -1.30 V) with overpotential. This agreed with one of the conditions for 'regular' deposition: the content of less noble metal increased with overpotential. For examining the other conditions of regular deposition spent electrolyte composition was also analysed. In both the groups employing Al C.E., the Al (more noble) content in the spent electrolyte was more than that initially added, suggesting anodic Al dissolution (confirmed with anodic weight loss). Al/Mg atomic ratio in deposit was plotted versus that in spent electrolyte. From this plot, a slight decrease in the Al/Mg ratio in the spent electrolyte paralleled with a drastic decrease in this ratio in the deposit. Further, the Al/Mg composition line was completely above the composition reference line *(i.e.* line of Al/Mg in deposit = Al/Mg in electrolyte) as seen in Figure 1. These trends along with the above-mentioned η-Mg (at.%) relation confirmed the 'regular' nature of Al-Mg alloy electrodeposition using chloride-based molten salt electrolyte. This nature was further ascertained by analysing deposits and spent electrolytes upon using Pt C.E., to mitigate the anodic Al dissolution. Interestingly, this nature is different from 'anomalous' and 'equilibrium' natures of Al-Mg deposition from organometallics and Grignard reagents, respectively [1-3]. This shows that electrolytic system (electrolytes and electrodes) plays an important role in deciding the deposition nature. The results were used to design schemes for Al-Mg electrodeposition using the chloride-based molten salt electrolyte system with Al as C.E. for both groups.

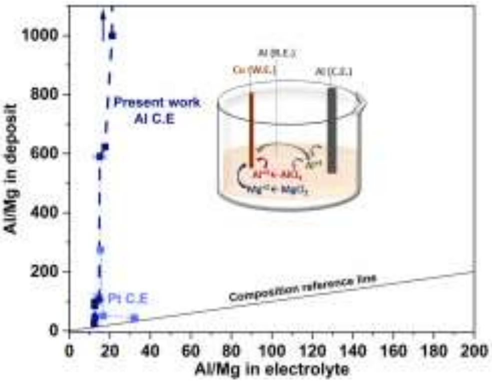

Figure 1. Composition plot of Al-Mg electrodeposition using chloride-based molten salt electrolyte system

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High capacitance composite materials obtained by carbonization of MOF-5/polyaniline composites

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Developing high-performance capacitive materials is of utmost importance for the rapidly growing field of electrochemical supercapacitors, which can offer complementary performance to batteries where short, high-power outputs are needed [1]. This study introduces a novel approach for synthesizing electroconducting composites, namely C-(MOF-5/PANI) composites, by carbonizing MOF-5/PANI composites [2], Figure 1. These composites, namely C-MOF/ES and C-MOF/EB, were derived from precursor composites with different forms of polyaniline (PANI) and varying ratios of MOF-5 to PANI. A comprehensive characterization of these composites was conducted using a suite of analytical techniques, including scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDX), thermogravimetric analysis (TGA), X-ray powder diffraction (XRPD), atomic absorption spectroscopy (AAS), Fourier-transform infrared spectroscopy (FTIR), Raman spectroscopy, as well as measurements of electrical conductivity, nitrogen physisorption, and cyclic voltammetry. The results revealed that the composites exhibited excellent electrical conductivity (ranging from 0.08 to 0.24 S cm^{-1}), attributed to the formation of conducting graphitic structures during the carbonization process. Notably, despite having lower specific surface areas compared to precursors, the C-MOF/ES composites demonstrated remarkably higher specific capacitance (ranging from 146.3 to 238.2 F g^{-1}) compared to the C-MOF/EB composites (ranging from 91.2 to 136.2 F g^{-1}). This behaviour was ascribed to the higher content of covalently incorporated nitrogen in the C-MOF/ES samples, which facilitated enhanced wettability and pseudocapacitance. Furthermore, the composition and properties of these composites were found to be tunable based on the precursor composition, allowing for the production of composites with tailored properties suitable for various energy storage and conversion applications. Specifically, PANI component served as a source of nitrogen heteroatoms, with its emeraldine salt (ES) form enabling the production of the zinc sulphide (ZnS) phase. On the other hand, the MOF-5 component acted as a source of zinc ions and a template for the formation of zinc oxide (ZnO) and ZnS phases, contributing to the overall specific surface area of the final composite. Further increase of specific capacitance (to ~340 F g^{-1}) was achieved by acid etching treatment of C-(MOF-5/PANI) composite. In summary, this study presents a versatile synthetic approach for fabricating binary N,O-doped carbon/ZnO and ternary N,O-doped carbon/ZnO/ZnS composites with excellent electrical conductivity, specific surface area, and specific capacitance, thereby offering promising prospects for applications in supercapacitors and other energy storage and conversion devices.

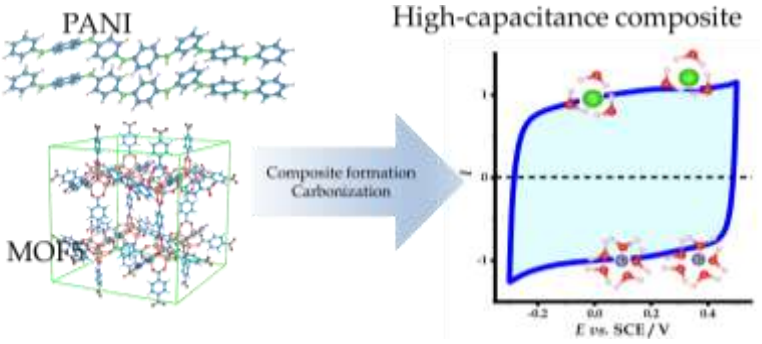

Figure 1. Composite formation between PANI and MOF5, followed by carbonization, leads to high capacitance binary and ternary carbon-based composites

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Electrochemical hydrogen pump/compressor – gas diffusion electrodes, membrane electrode assemblies, cell performance and back diffusion effects

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The electrochemical hydrogen pump/compressor (EHP/EHC) offers numerous advantages over mechanical compressors, such as superior energy efficiency, stationary mechanical components, and the ability to operate at high pressures without pre-treatment of the supplied reactant. However, a key challenge lies in the membrane electrode assembly (MEA), which determines the electrochemical conversion rates and differential pressure between gas diffusion electrodes, affecting overall energy efficiency. This work presents a newly developed laboratory prototype of the electrochemical hydrogen pump/compressor (EHP/C), operating with the proton-conductive membrane Nafion 117 at a differential pressure of up to 10 bar and commercially available gas diffusion electrodes with 0.38 mg/cm^2 Pt-based catalyst loading and an average thickness of 250 µm.
The initial laboratory tests demonstrate that the design of the developed device and the architecture of the electrodes ensure high efficiency of both hydrogen oxidation reaction (HOR) and hydrogen evolution reaction (HER), with a cell energy efficiency of 85%. Additionally, the device exhibits the capability to operate with an identical rate of gas compression at different input hydrogen pressures. The differential pressure of the cell was set at 10 bar, while the current density varied from 0.6 to 1.6 A cm^{-2} at temperatures ranging from 20 to 60 °C, respectively. Back diffusion pressure was also characterized under different operating conditions. The hydrogen gas crossover reached values of 3.85 mA cm^{-2} at 80 °C and an absolute humidity of 11.7 g kg^{-1}.

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EIF O 01

Galvanostatic current sweep for end-of-line catalyst layer characterization

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Hydrogen fuel cells convert chemical energy contained in hydrogen fuel directly into electric power, without emitting any pollutants, and on demand. This makes fuel cells a competitive technology for both stationary and mobile applications. Polymer electrolyte membrane fuel cells (PEMFC) are fitting for use in vehicles because they operate at relatively low temperatures and can rapidly vary their power output. However, high cost of PEMFC remains a barrier to widescale deployment of fuel cell vehicles.

The main challenge for cost reduction is associated with the ability to manufacture fuel cell stacks in large numbers at a rapid rate. The main bottleneck in the existing manufacturing process occurs at the end of the manufacturing line where diagnostic techniques, borrowed from R&D, are used to determine if the product meets market-ready quality standards. These techniques are time-consuming for end-of-line (EOL) testing in mass production and any improvements translate into significant cost reductions and increase in throughput.

Conventional diagnostic techniques can be applied to manufactured fuel cells only after they have gone through long break-in treatments. In this research, we aim to develop EOL test methods that can be applied to manufactured cells at the end of the manufacturing line, thereby eliminating the time spent on break-in of undetected faulty cells and reducing the complexity of the EOL test stations.

Cyclic voltammetry (CV) is a widely used in-situ technique for characterization of the electrode catalyst layer. CV is a potentiodynamic method that gives insight into the quality of the catalyst layer by measuring the electrochemically active surface area (ECSA). Being a potentiodynamic method, CV cannot be applied to full stacks consisting of many serially connected cells. For this reason, an alternative galvanostatic technique was used in this research to test both pre break in and post break in single cells to determine if this technique is a good fit for use in EOL testing. To quantify hydrogen gas crossover rate, used in ECSA calculations, a hydrogen/nitrogen concentration cell test is used as an alternative to commonly used potentiodynamic linear sweep voltammetry (LSV). Both-pre-break in and post-break-in experiments included CV analysis, used as a benchmark for ECSA, hydrogen crossover, and double layer capacitance estimates.

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ENM O 01

Design and optimization of low-power DC-DC converter for efficient fuel cell applications

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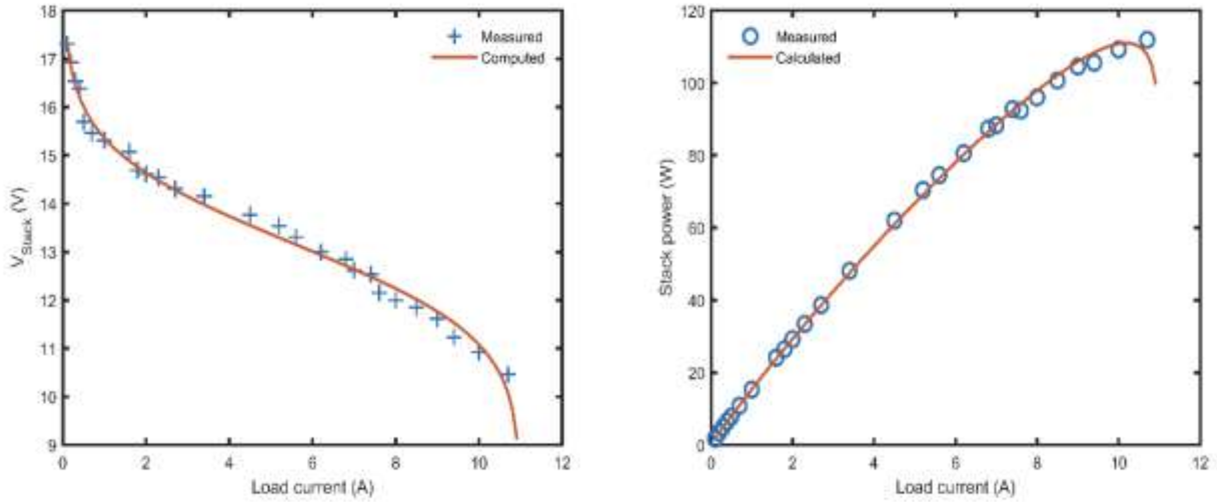
The abstract presents the design and optimization of a low-power DC-DC converter tailored for efficient fuel cell applications [1]. The study focuses on developing a converter system that minimizes power losses and maximizes energy efficiency within the context of fuel cell technology [2-6]. Through a comprehensive analysis of converter topologies, control strategies, and optimization techniques, the research aims to address the specific power requirements and operational characteristics of fuel cells [7-8]. The proposed converter design seeks to enhance the overall performance and reliability of fuel cell systems by achieving optimal power conversion efficiency while minimizing energy wastage, thereby contributing to the advancement of sustainable energy technologies.



(a) V-I curve (b) P-I curve

Fig. 1. Polarization curves of 100W Horizon PEMFCs' stacks as in our previous data in [1]

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ENM O 02

Experiments and calculation on new N,N-bis-tetrahydroacridines

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New bis tetrahydroacridines were synthesized by Pfitzinger condensation of 5,5'-(ethane-1,2-diyl) diindoline-2,3-dione with several cyclanones [1]. They were characterized by NMR, MS, FT-IR. Their optical and electrochemical properties were investigated by use of UV–Vis and voltammetric (cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry) measurements [2]. The computational study was carried out with the software Spartan14 from Wavefunction, Inc. Irvine CA, USA for the lowest energy conformers of each structure, in vacuum conditions, at ground state using DFT models. B3LYP levels of theory [3] with basis set 6-311G (d, p) [4] was chosen for properties computations.

Their study recommended this class of π-conjugated heteroaromatic compounds for potential applications in different branches of medicinal chemistry, dye industry and metal chemosensing.

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ENM O 03

Electrochemical investigation of symmetric aminoquinones

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Quinones have a wide range of valuable properties and potential applications in medicinal chemistry, materials science, optoelectronic devices, and batteries.[1] Molecular redesign using different functional groups, like amines, can optimize their properties and prevent unwanted side reactions. However, particularly the synthesis of aminoquinones can be challenging at times, and there is a need for simple and efficient routes to access these compounds without metal catalysts or halogenated starting materials.[2] Here, we demonstrate the synthesis and electrochemical characterization of a series of aminoquinones derived from renewable sources, namely vanillin or 2-methoxyhydroquinone.[3] We employ a series of primary and secondary amines, varying in their electronic situation as well as steric demand. Depending on the type of starting material, either the desired aminoquinone or the related Schiff-base adduct was obtained. The aminoquinones were further explored for their stability at different pH values. At extreme pH values, the deeply colored aminoquinones decompose, accompanied by decolorization of the solutions within a few minutes (pH 14) or hours (pH 1). At intermediate pH values (3-8) the aminoquinones are stable upon storage in solution, where they feature a quasi-reversible redox chemistry and fast, diffusion limited kinetics.[4]

Figure 1. Redox reaction of symmetric aminoquinones

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ENM O 04

Electrochemical and optical experiments and DFT calculations for an allyl-thiophene substituted azulene

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Ethene-2,1-diyltetrathiophene azulene (L2064) was obtained and used to prepare modified electrodes, based on our results on the electrochemical behaviour of other azulene-based push-pull organic systems [1]. L2064 belongs to azulene compounds, with potential nonlinear optical responses, and staining properties [2,3]. Its electrochemical and optical properties were evaluated, in connection with the heavy metal (HM) ions complexation. The main structural characteristics and the molecular descriptors of the investigated ligand have been predicted by means of computational tools using B3LYP method [4] with 6-31(d, p) basis set [5]. Estimation of relevant global reactivity parameters according to Koopmans' theorem [6] was also carried out starting from calculated energies levels of frontier molecular orbitals, as in our previous works [7].

Novel chemically modified electrodes (CMEs) were prepared by electrooxidation of L2064. To evaluate their electrochemical behaviour, CMEs based on L2064 were characterized by ferrocene redox probe. They were also tested for the analysis of synthetic samples of HMs (Cd, Pb, Cu, Hg) ions. The influence of preparation conditions (ligand concentration, solvent, electric charge and potential) on the properties of these CMEs was examined. This study is relevant for further design and development of advanced materials based on this azulene derivative for the HMs analysis in polluted water samples. Electrochemical experiments and DFT computer-aided calculations recommended L2064 as a new suitable ligand for electrode surface modification in view of HMs ions analysis.

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ENV O 01

Conducting polymers for ion extraction from aqueous solutions

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Pure water is a globally significant commodity. It is widely known that the presence of some ionic contaminants in water and wastewater causes serious environmental and health problems. In contrast to *e.g.* neutral organic contaminants, which can undergo biodegradation, many ionic pollutants remain in the environment, and their speciation and bioavailability might change over time. They can enter the food chain and accumulate in living organisms. To this end, specific instances in which water purification is important include environmental remediation, industrial processes and, critically, water for human consumption.

Conducting polymers are attractive materials for use in a variety of applications that require materials which are both electrically conducting and mechanically compliant, *i.e.* in energy conversion/storage, sensing applications and supplement the quest for powerful yet small/thin and flexible devices. Most of the above devices work in an electrochemical environment and can be considered to be "modified electrodes". One of the most notable features of the conducting polymers is the potential-dependent variation of their charging state. It can, in principle, be applied to remove ionic species including organic ones (such as metabolites of medicines, neurotransmitters, antibiotics *etc.*) that are potentially harmful to the environment and human health from aqueous solutions (including wastewater, drinking and groundwater) via stripping, and release those by changing the charging state of the polymer layer. In principle, conductive polymer-coated electrodes may be used as "intelligent" stationary phases of separation columns. Similarly, it is possible to regulate the dosage of different medicines even in vivo.

The electrochemically controlled ion extraction by electrochemically active films (modified electrodes) for water purification has already been considered sporadically in the literature [1,2], but not in a systematic way, and the scenarios described are rather restricted. As a consequence, the available experimental results are contradictory and do not give sufficient or definite evidence regarding the reliability, validity and feasibility of the methods used.

The following questions arise regarding the applicability of the proposed methods: 1) What is the effectiveness of electrochemically active polymer films and polymer composites *(i.e.* modified electrodes) in the electrochemical detection and removal of ionic species? 2) Which are the most effective materials (conducting polymers, substrates, *etc.*) and procedures for the electrochemically controlled ion extraction? 3) Since the stability of polymer films is one of the most serious problems in applications, it is extremely important to find out how to stabilize the applied films.

The main objective of the work presented in this study is to answer the above questions based on systematic (laboratory scale) experimental and theoretical studies. We discuss our results obtained with different polymers, more precisely with PEDOT (Poly(3,4-ethylenedioxythiophene)) and three polymer blends (or macromolecular salts): PEDOT:PSS (PSS: polystyrene sulfonate) [3], PEDOT:SDS (SDS: Sodium Dodecyl Sulfate) [4], and PEDOT:DS (DS: dextran sulfate) [5]. One of the biggest problems during the experiments is the stability of the films. It could be shown that conducting polymer films reinforced with non-conducting polymers are more resistant to degradation that may occur during the process [6,7]. That is, the reinforcement is "mechanical" in nature (thus referred to as "mechanical reinforcement", as well) because the reinforcing polymer "fixes" the conducting polymer layers that tend to delaminate from the substrate. In addition, it protects the conducting polymer layer as a non-enclosed cover layer but does not completely close it from the environment, allowing the conducting polymer to contact the medium surrounding it.

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ENV O 02

Preparation and characterization of ceramic materials for cathodes of intermediate temperature solid oxide fuel cells

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Solid oxide fuel cells (SOFCs) are energy conversion devices that produce electricity with high efficiency and negligible pollution. Other advantages such as multi-fuel capability, a modular construction design and environmental compatibility make them to be considered as one of the most promising future power generation devices. YSZ (yttria stabilized zirconia with 8 mol.% of Y_2O_3) represents the state of the art electrolyte for high temperature (800–1000 °C) SOFCs. This material possesses an adequate level of oxygen-ion conductivity combined with excellent mechanical properties and stability in both oxidizing and reducing atmospheres. However, many problems related to the correct use of the other components (anode, cathode, and interconnector) of the SOFC are to be present during service at the above operating conditions which also leads to many disadvantages in the selection of interconnects and sealing materials. Therefore, a lower operating temperature becomes necessary to reduce manufacturing costs and to increase their durability. For that purpose, new materials are required demand for materials that can efficiently operate a lower temperature, *i.e.* electrolytes with higher conductivity such as Gd-doped Ceria (GDC) (1) or $La(Sr)Ga(Mg)O_3$ (LSGM) (2) and also is crucial the development of more effective cathode materials with increased electrocatalytic. This is the main purpose of this work.

The cathode materials should be characterized by increased oxide ion transport in addition to high electronic conductivity. $La_{1-x}Sr_xFeO_3$ (LSF) has demonstrated higher electrical and ionic conductivity than the conventional $La_{1-x}Sr_xMnO_3$ (LSM). In this same way, $La_{1-x}Sr_xCoO_3$ (LSC) can be considered as a promising cathode for intermediate temperature SOFCs with high values of conductivity. However, the good electrocatalytic performance of this Cobalt-based-cathode is somehow limited by a thermal expansion coefficient (TEC) mismatch with other components of the SOFC and also low stability. TECs of both the electrolyte and electrode layers should be well matched to ensure long-term operational stability of the SOFCs. Considering all the above aspects, alternative materials could be ferrite/cobaltite cathodes as $La_{0.6}Sr_{0.4}Fe_{1-y}Co_yO_{3-x}$ (LSFC). The electronic conductivity of these samples in air is characterized by the higher values at increasing Co contents and besides, the presence of Fe helps to minimize mechanical stresses as it can reduce the TEC mismatch.

However, substitution of Co as a major B-site cation in the perovskite air electrode is highly desirable due to potential disruptions in the cobalt supply chain as early as 2030, as well as its related high price and risks to health. Moreover, its presence (Co) in electrochemical cells is associated with high thermal expansion coefficient as mentioned before. Other phases, as Ruddlesden-Popper phases, must be considered as air electrodes (or cathodes). Doped $Sr_3Fe_2O_7$ (SF) (n=2 R-P phase) with Ni (Sr_3FeNiO_7) increased the conductivity by a 3x factor. The substitution in A position of the structure with Pr or La, $(Pr/La)_{0.2}Sr_{2.8}FeNiO_7$, allow to stabilize the phase and have better mechanical performance. Also, the conductivity has reached over 200 S cm^{-1} and over 100 S cm^{-1} at all times (100-1000°C).

The solid state reaction of the corresponded oxides is an easy synthesis process to obtain ceramic powders of different materials. However, the homogeneity of the final synthesized powder is poor. The compositional complexity of the materials above mentioned due to the number of cations involved require a synthesis method that ensures optimal chemical homogeneity to determine its final properties. Here we show a low cost and simple alternative, with excellent results, based on the chelation of complex cations leading to the formation of an intermediate resin, which, on charring and calcining, leads to a sinterable powder. In this work we present two alternatives, one is substituting citric acid with EDTA and ethylene glycol with glycerol for producing $(Pr/La)_{0.2}Sr_{2.8}FeNiO_7$. And other based on the auto-combustion of an ethylene glycol-metal nitrate polymerized gel precursor that can be efficiently used to easily produce a range of $La_{0.6}Sr_{0.4}Fe_{1-y}Co_yO_{3-x}$ (LSFC) at moderate temperatures. This method generates less carbon residues than other similar techniques of synthesis as that based on the Pechini method. The results here presented are important not only for the synthetic route itself but also because they establish practical cathode operational parameters on sintered samples for the selection of the most suitable composition, considering the TECs of the electrolyte utilized and the operating temperature of the cell.

Acknowledgement: The financing support by PID2021-123308OB-I00 project, funded by MCIN/AEI in Spain and the ERDF by the EU.

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ENV O 03

Comparative study of pure iron and white cast iron for ferrate ion production using dual dynamic voltammetry

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Ferrate ions can be produced electrochemically with the transpassive dissolution of iron-containing anodes. Two of the most widely investigated materials are Pure Iron (PI), and White Caste Iron (WCI). It is assumed that the alloyers in the iron can change the structure of the oxo-hydroxide passive layer, enhancing or inhibiting the transpassive dissolution of the anode. The iron carbide in the WCI seems to disintegrate the passive layer, making it porous, and less resistant to the attack of hydroxide ion, making the passivation less complete, and ultimately the transpassive dissolution a more favorable reaction.

During the transpassive dissolution, the parasitic oxygen evolution process is inevitable. The oxygen evolution decreases the current efficiency of ferrate production and makes the characterisation of the ferrate ion formation process difficult. Usually, the electrochemical ferrate production is characterized by the accumulated ferrate ion concentration, and quantities derived from it (effective current density, current efficiency)[1]. Ferrate ions are highly unstable, and their decomposition rate depends on many circumstances (including cell design) that are difficult to control, making most characterization of electrochemical ferrate synthesis inadequate, leading to uncertain and sometimes misleading results.

Dual Dynamic Voltammetry (DDV) is a novel method that can be used for Rotating Ring Disk Electrodes (RRDE)[2]. DDV makes the simultaneous, independent polarization of the two electrodes (ring and disk) possible. Since ferrate ion can be properly characterized with its reduction at Platinum electrode, an RRDE setup was used in a generator-collector arrangement for the investigation of ferrate ion production. During the measurements the transpassive dissolution of the iron-containing (Pure Iron or White Cast Iron) disk yielded ferrate, which could be reduced at the Platinum ring. Using a very slow polarization rate at the disk and a fast polarization rate at the ring, the amount of ferrate ion produced could be determined for each potential with relatively high resolution.

Using this arrangement the ferrate ion formation reaction could be independently investigated at the different anode materials, and the results could be compared accordingly. The effective current (current responsible for ferrate ion production) was much higher, and the onset potential of ferrate ion production much lower in the case of White Cast Iron. However, the effective current did not differ that much in the case of the two anode materials, caused by the different rates of the oxygen evolution process.

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ENV O 04

On site electrochemical production of water disinfection agents by Hlorogen® electrolyzers: Design, materials and reaction products

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Clean drinkable water, globally available, is one of the major challenges of the modern society, recognized by the United Nations as one of the Sustainable Development goals [1]. Contaminated water, containing pathogenic bacteria or viruses is a constant threat to public health, as waterborne diseases can easily grow into pandemics due to the prevalence and survival of these microorganisms [2]. Water disinfection is thus a crucial step in water treatment. Although there are many water disinfection strategies using physical (UV irradiation, membrane filtration) or chemical methods (chlorination, monochloramination, chlorine-dioxide, ozonation) and other emerging technologies, chlorination is the most widely used procedure for over a century [2,3]. However, not all chlorine sources are the same, as the traditional chlorination is based on the use of gaseous chlorine or sodium-hypochlorite. Even though their addition to water will result in formation of active chlorine (mixture of $HClO$ and ClO^-), their use is regarded unsuitable as they are toxic and corrosive, so their storage and transportation is utterly unsafe.

Another way of producing active chlorine is by electrolysis of sodium chloride solution [4]. This way, the use of hazardous chemicals is avoided, while the water disinfection is achieved by an affordable and efficient technology, producing the active chlorine in a form of a 1 % solution. Sigma doo Crvenka has developed HLOROGEN® electrolyzers for this use, and by electrolysis of 3 % NaCl, 1 % active chlorine is produced and dosed directly into the drinking water system, as this equipment is installed on-site in a water processing plant. The optimization of the process, regarding the complicated electrochemical reactions occurring at the anode, has been a major challenge over the past two decades. In this regard, different electrode materials have been investigated, as well as the electroylzer design, with adjustment of the reaction products customized according to the local water composition. Today, over 110 HLOROGEN® plants have been installed in Serbia, providing drinking water for 1.500.000 citizens, including the city of Novi Sad, also expanding to neighbouring countries. As an extension of HLOROGEN® technology, OksiHLOROGEN® devices were developed, with ClO_2 as additional disinfecting component, produced simultaneously in the electrolytic process, to address more demanding water supplies.

During the COVID-19 pandemic, the company has expanded its portfolio to production of AqualorH disinfectants by HLOROGEN® technology [5], for the use in hand disinfection, and other disinfection domains such as healthcare, household, veterinary, agriculture, HoReCa, *etc.*

This research delves into the innovations of the electrolyzer design, used electrodes materials, as well as the electrode manufacturing procedures used by Sigma doo Crvenka in HLOROGEN® technology.

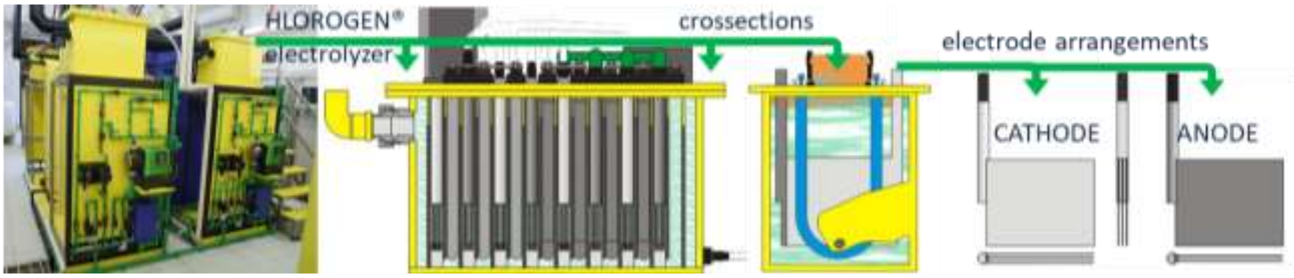

Figure 1. HLOROGEN® electrolyzers: a) complete plant – Novi Sad water supply, b) crossections – side views with electrode compartments and cooling system, c) electrode arrangement with 3 cathodes and 2 anodes per electrode compartment

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Electrochemical precipitation potential for recovering phosphorus

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Phosphorus is irreplaceable in nature. Predictions indicate a yearly increase of 1.5 % in phosphorus demand [1]. The effluent from anaerobic digesters contains nutrients such as concentrated phosphorus and ammonia nitrogen, facilitating convenient nutrient recycling [2]. Previous research has indicated that extracting struvite from such wastewater is favourable, as it presents a reusable resource - struvite, a slow-release fertilizer [3]. In this study, a synthetic sample reflecting the anaerobic digestion supernatant of a wastewater treatment plant was created to represent actual content of nitrogen (737 mg/l) and phosphorus (121 mg/l). Subsequently, electrochemically induced struvite precipitation was conducted utilizing magnesium electrodes. This method introduces a new way of sourcing magnesium, decreasing dependence on chemical additives for struvite formation. Four experiments were conducted at pH levels of 7.5, 8, 9, and 10, investigating the impact of pH on nitrogen and phosphorus release. The experiments were carried out in a borosilicate beaker with a total volume of 600 ml and an effective volume of 500 ml (Figure 1). A current of 25A/m^2 was applied, and each experiment lasted for 4 hours. The results obtained reveal complete removal of phosphorus (P) across all tested pH levels. However, nitrogen (N) content decreases progressively with higher pH values; for instance, at pH 10, 55 % less nitrogen was detected compared to the initial level (Figure 2). Similar observations were published in Kim *et al.* [4]. Analysis of magnesium (Mg) in the water post-treatment indicated excessive extraction, with concentrations of approximately 500 mg/l detected after all treatments. Given these findings, the next phase of this research will involve investigating the impact of time and current strength to identify the optimal conditions for extracting nitrogen and phosphorus in the form of struvite. Additionally, to confirm the composition of the resulting precipitate, X-ray diffraction (XRD), scanning electron microscopy with energy-dispersive X-ray spectroscopy (SEM-EDS), and Fourier-transform infrared spectroscopy (FTIR) analyses will be conducted.

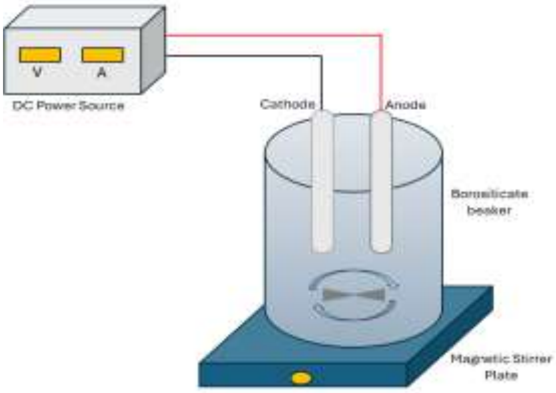

Figure 1. Schematic of the batch reactor

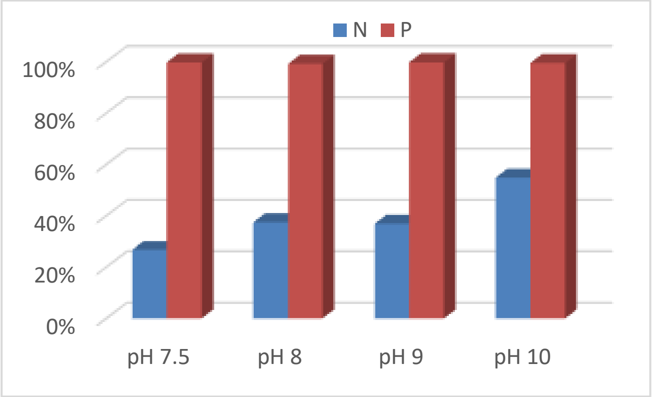

Figure 2. Efficient removal of N and P after treatment

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ENV O 06

Recycling of plastic waste into valuable products

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Recently, many kinds of plastics are widely consumed in the world, which are mainly composed of carbon and hydrogen. However, “white pollution” is becoming more and more serious due to the accumulation of waste plastics on earth. It is a great challenge to reuse these wastes due to the strong stability of plastic in nature. Because the traditional way does not fully take use of the polymer and induces environmental concerns, it is highly urgent to develop an environmentally friendly way to recycle plastics waste to high-value-added products. Carbonization plastic waste is one choice due to the wide applications of carbon materials, we have developed a series of methods to produce carbon materials from plastic wastes. More importantly, the obtained carbon nanomaterials were used in lithium-ion batteries and supercapacitors.[1] In another way, converting plastic waste into MOFs and using the resulting MOFs as OER catalyst is also presented. The results prove it is a cost-effective way for the recycling of plastic waste into high value-added products. These results pave a potential way to upcycle plastic wastes into valuable products.

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Time-variance in electrochemical impedance spectroscopy: The simple case study of dilution

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Classical analysis of electrochemical impedance spectroscopy (EIS) measurements requires them to be performed on a linear,
time-invariant system. Many electrochemical systems are time-variant (battery under charge/discharge, corroding sample).[1] The effect of time-variance on these systems is not easy to study because there is no reference to which the time-variant results could be compared to.
A simple dilution experiment[2,3] was performed to illustrate the time-variance on EIS measurements performed at a rotating disk electrode (RDE), in an electrolyte containing the classical $K_3Fe(CN)_6/K_4Fe(CN)_6$ redox couple.
Using simulations based on analytical expressions of the Faradaic impedance, experimental parameters are defined. Fitting EIS data using equivalent circuit models (ECM) allows us to qualify the errors made when trying to fit time-variant data with time-invariant impedance expressions.
Repeated impedance measurements and reconstruction of instantaneous impedance graphs via interpolation[4,5] allows to reduce the effect of time-variance and improve the fitting quality.
Finally, another approach is presented, which consists in fitting the time-variant data by an analytical time-dependent expression of the Faradaic impedance where the concentration evolution and its effect are accounted for.[6]

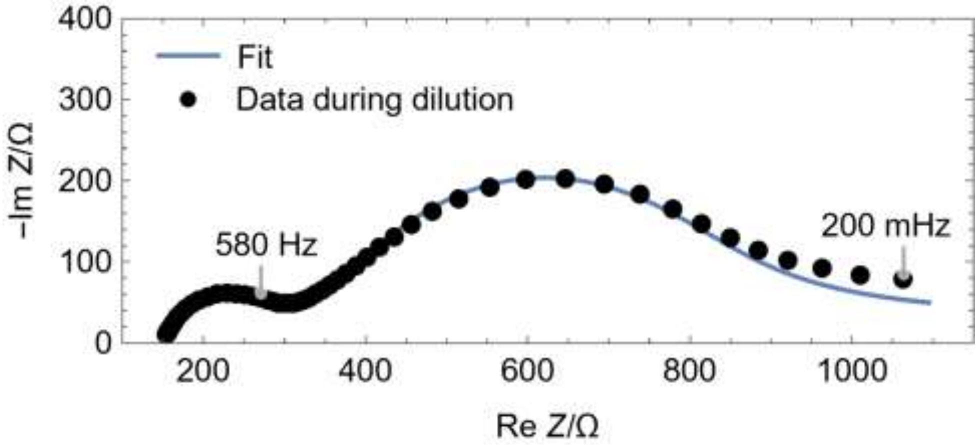

Figure 18. Nyquist diagram of the impedance measured during dilution at an RDE and fitting curve using the time-dependent analytical expression of the Faradaic impedance.

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GEN O 02

Highly stable Pt single atoms on TiO_2 for efficient photocatalytic H_2 production

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Semiconductors have been widely used as photocatalysts and/or photoelectrodes for solar-driven water splitting. In the context of solar-driven H_2 production, effective utilization of many semiconductors typically requires co-catalyst functionalization. While noble metal nanoparticles have traditionally served as co-catalysts, a more promising approach involves the use of noble metal single atoms (SAs). This strategy has the potential to achieve maximum atom utilization efficiency and exceptional catalytic performance due to the spatial atomic isolation, distinct electronic structures, and unsaturated coordination centers.[1-3] However, achieving the stabilization of isolated atoms on semiconductors for practical applications remains a considerable challenge, mainly due to the insufficient trapping sites available on unmodified semiconductor surfaces.

Recently, we developed a fluorine stabilization strategy for the synthesis of Pt SAs on fluoride-modified TiO_2, a method applicable to TiO_2 with different morphologies.[4] The modulation of fluorine speciation on TiO_2 has emerged as a critical factor for achieving uniform and stable dispersion of Pt SAs, resulting in high efficiency of Pt SA co-catalyzed photocatalytic H_2 production. Remarkably, maximum photocatalytic activity is achieved with fluorine-stabilized Pt SAs on TiO_2 catalysts even at low Pt SA loading levels, surpassing the performance of Pt nanoparticles on TiO_2 despite equivalent or higher loading levels. Pt SAs on TiO_2 exhibit superior photocatalytic activity and photocurrent compared to conventional Pt nanoparticles on TiO_2. Furthermore, Pt SAs on TiO_2 exhibit exceptional photocatalytic stability during prolonged photocatalytic reactions. This study provides an effective approach to exploit the interaction of stable fluorine in TiO_2 to design stable and active single atom catalysts on semiconductors for applications in photocatalysis and photoelectrocatalysis.

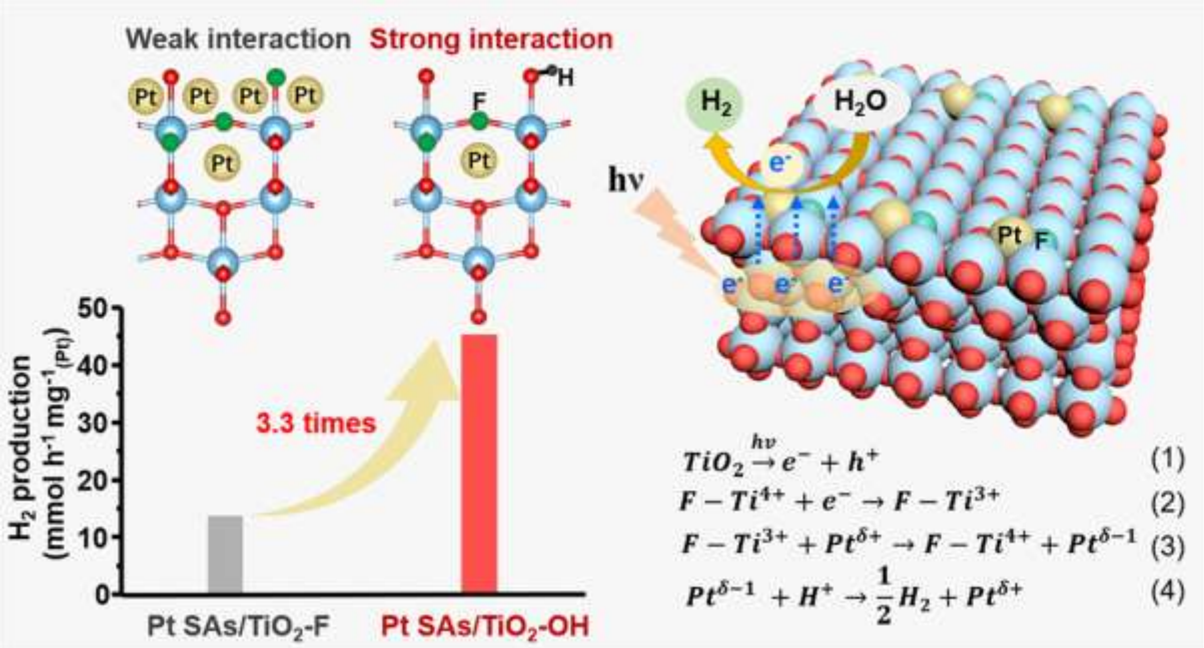

Figure 1. Schematic illustration of the fluorine-aided stabilization of Pt SAs and corresponding photocatalytic H_2 production performance and photocatalytic mechanism.

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Reactive deposition *vs.* strong electrostatic adsorption: A key to highly active single atom co-catalysts in photocatalytic H_2 generation

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Single atoms (SAs) have become a highly investigated topic in heterogeneous catalysis. In photocatalysis, they have reached a very high significance as co-catalysts, namely in photocatalytic production of H_2 from aqueous electrolytes. A key issue in terms of exploiting SAs is the deposition approach used to establish the SA state and its stabilization.

The most classic approach to achieve maximum dispersion of noble metals on oxide supports is so-called strong electrostatic adsorption (SEA) – it is a backbone of classic catalyst preparation. In catalytic literature it is widely perceived that this SEA approach in general is superior to other approaches due to the strong noble-metal attachment and the high loading that can be achieved while maintaining a high metal dispersion. The concept has accordingly been widely used to attach SA Pt on various oxides, including TiO_2.

In the presentation we show that a reactive attachment based on hexachloroplatinic(IV) acid leads directly to SA configuration with a significant higher specific H_2 evolution activity than achieved with strong electrostatic adsorption – and this is at a significantly lower Pt loading without any post deposition treatment. Due to the significance of the work for the SA-field, we anticipate a particularly wide interest in the materials science and solar energy communities.

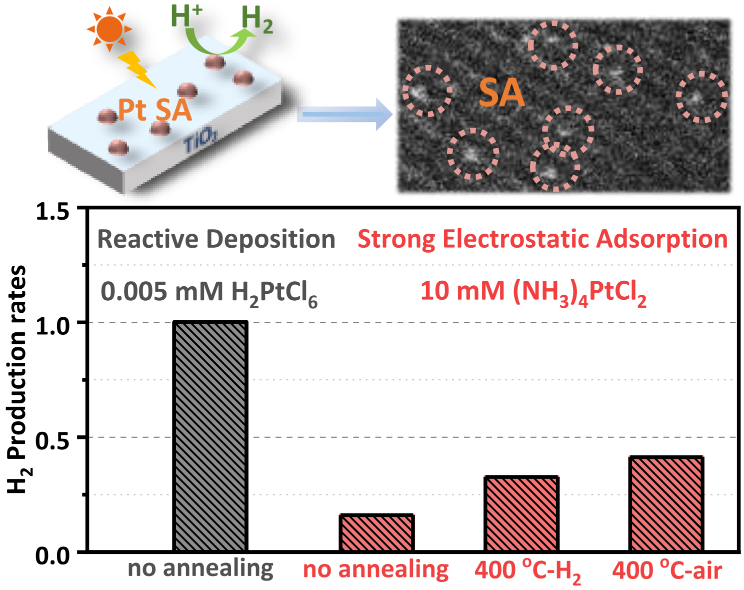

Figure 1. Schematic of the H_2 evolution reaction on Pt single atoms. HAADF-STEM image of Pt-SA-decorated TiO_2 anatase layer. Mass specific photocatalytic H_2 evolution rate for Pt-SA-decorated TiO_2 anatase layers treated under different deposition approaches and post annealing conditions

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GEN O 04 & GEN P 04

ElectroKitty: A Python based electrochemical simulator

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To this day almost all electrochemical experiments made to elucidate the underlying mechanism are done on the RDE. However almost all of the reports of the surface mechanism are done qualitatively. The major reason for this is that simulating electrochemical experiments is hard and requires a good understanding in how to solve the set of differential equations, used in describing the observed system. To make the electrochemist's job easier, in quantifying the observed system, I developed an electrochemical simulating tool in Python. We chose Python as it is currently the most popular programming language and is easy to use. Python's another major advantage is that it has a rich repository of various other libraries for data analysis, thus combining ElectroKitty with a data treating package is almost seamless.[1] ElectroKitty is based on an implicit finite difference approximation, making it both stable and efficient in computing an electrochemical signal.[2] The simulator is capable of calculating a current response for virtually any potential input with a predefined mechanism. To demonstrate the workflow and functionality of the simulator, we show a comparison of simulated and experimental data for two well-known systems. First, we show that the simulator can accurately simulate both the CV and alternating-current CV (FTacCV)[3] response of the ferro-ferri cyanide couple. Second, we show that using the PINTS[4] library for parameter inference, we can accurately fit the data for HER on Pt in alkaline. It is the authors hope that such a tool will further help electrochemists in understanding the underlying mechanisms of their systems.

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Characterization and dealloying of micelle-nucleated Ag_xAu_y nanoparticles by scanning electrochemical cell microscopy

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Bimetallic nanoparticles (NPs) are highly interesting electrocatalyst materials due to synergistic effects generated by their additional active sites [1], and the ability for tuning their activity by (electro-)chemical dealloying-treatments [2]. Synthesis routes using 0D confinement in micelles give enhanced control over composition and morphology of these bimetallic NPs [3]. However, an unavoidable distribution of catalytic performances and dealloying properties remains among NPs. This calls for electrochemical tools that offer activity measurements at the single-entity level. Scanning electrochemical cell microscopy (SECCM) is such a tool, probing electrocatalytic current locally in a nanodroplet cell, and collecting many data points on one sample that can be post-characterized by *e.g.,* scanning electron microscopy (SEM). This allows a direct correlation between NP activity and morphology/composition. The great potential of SECCM to probe single entities has already been demonstrated in correlative multi-microscopy studies [4] and the technique is being continuously developed further.

In this work, precursor-loaded reverse block co-polymer micelles are electrodeposited on a conductive substrate forming Ag_xAu_y alloy NPs. Electrochemical dealloying of these bimetallic NPs is then used to tune their electrocatalytic activity for the hydrogen evolution reaction. This is done locally with SECCM using a big probe to create areas of NPs in different states of dealloying on a single sample. In a second SECCM experiment, the NPs in the different areas are then characterized as to their specific activity and Ag:Au ratio, followed by co-located SEM. This data is linked with identical-location STEM (scanning transmission electron microscopy) and EDX (energy-dispersive x-ray spectroscopy) at a high number of particles at different dealloying states. Thus, statistical distributions of morphology and composition can be correlated with the statistical distribution of specific activity of dealloyed bimetallic nanocatalysts, paving the way towards a knowledge-based design of electrocatalysts.

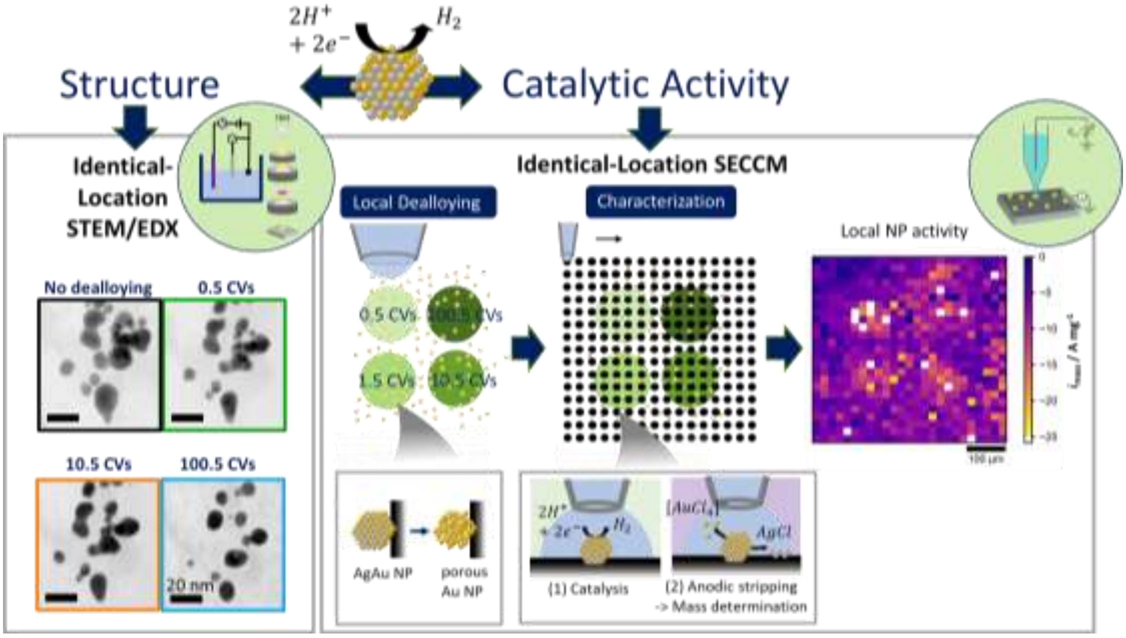

Figure 1. Schematic measurement concept for dealloying of Ag_xAu_y NPs by successive cycling in acid. Left: Identical-location STEM images of NPs at four different dealloying states (numbers of cycles). Right: Local dealloying with big SECCM tip, followed by catalytic activity measurements on many locations with a small tip for statistical analysis

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ORG O 01

Optimisation of electrochemical synthesis of 2-iodosylbenzoic acid

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Oxidising agents with heavy metal atom (*e.g.* Cr^{VI+} such as Collins reagent or pyridinium chlorochromate) were historically used for oxidising primary and secondary alcohols to correspond carbonyl compounds [1]. Moving beyond Cr-based oxidants, hypervalent iodine compounds present a promising avenue for safer and environmentally friendly oxidations. Amongst the well-known λ^3-iodanes belongs 2-iodosylbenzoic acid (2-IsBA) which proved to be valuable asset for oxidative reactions, *e.g.* oxyarylation [2] or oxyalkenylation [3]. When it comes to production of iodanes, toxic, and potentially dangerous substances (Selectfluor®, Oxone®, $KBrO_3$) are handled, therefore, the price and environmental footprint in form of waste is significant [4]. Alternatively, it is possible to produce iodanes utilizing electrochemical synthesis. Such alternative method of 2-IsBA synthesis (Figure 1), which is highly efficient, scalable and environmentally friendly will be presented within this contribution.[5]

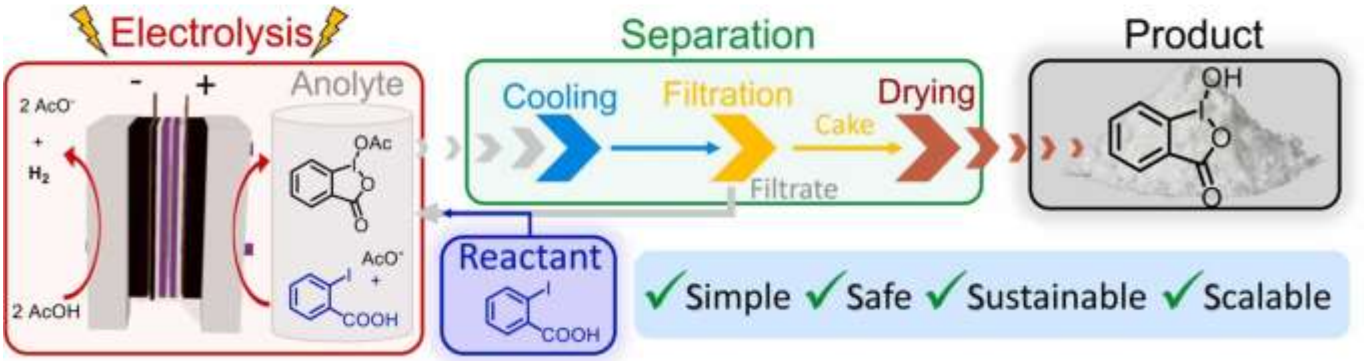

Figure 1. Scheme of electrochemical synthesis and followed up separation of solid 2-iodosylbenzoic acid [5].

Electrolysis was performed at constant potential of 1.9 V vs $Hg|Hg_2SO_4|K_2SO_{4(sat.)}$ in flow electrolyser divided by cation-exchange membrane. Electrochemical oxidation of 2-iodobenzoic acid at concentration of about $0.1\ mol\ dm^{-3}$ takes place on a boron doped diamond anode in an anhydrous AcONa-AcOH solution. Electrolysis conditions such as electrode potential, time, and substrate and electrolyte concentration were examined in order to optimise the production of 2-IsBA. The optimised parameters provide excellent electrolysis yield (93%) and current efficiency (94%). The separation process exploits low solubility of 2-IsBA in AcOH resulting in 2-IsBA precipitation during the electrolysis and upon cooling the anolyte solution. The precipitate was then filtered/decanted and air-dried resulting in white solid 2-IsBA. The product was analysed utilizing iodometric titration and nuclear magnetic resonance. The analyses confirmed that the white solid product is 2-IsBA with purity of 97 wt.%. It should be pointed out that product separation was performed without any washing steps and did not require any organic solvents.

Additionally, the reusability of most involved compounds through partial recycling of both anolyte and catholyte, along with efficient product separation was confirmed. This significantly reduces waste generation compared to traditional methods, leading to lower 2-IsBA production costs and a minimized environmental footprint.

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ORG O 02

Self-powered troponin biosensors: Integration of OFET technology, and low-power CMOS-based interfacing circuits

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Recently, sensors in general, and biosensors in specific, are reconsidered adopting new technological trends, including but not limited to; IoT, IoT^2, and wearable electronics. Low power consumption, flexible substrate computability, and nontoxic material utility in such an operating environment meet the sensor's design requirements [1]. As a flexible transistor (FET), the field effect transistor showed significant adaptability in detecting various bioreactors. Literature attempts demonstrated the utilization of FET in the detection of the regulatory protein cardiovascular troponin I (cTnI), which is a crucial biomarker for the identification of myocardial infarction. Moreover, FETs also recorded interesting observations with other bioreactors, as listed in [1].

Although inorganic FETs demonstrated potential capabilities to detect various bioreactors, it still faces some problems related to biocompatibility, cost, and sensor sensitivity. Consequently, the organic field effect transistors (OFETs) tackled the biosensing application with low-cost, reliable, robust, and highly sensitive biosensors. Interestingly, the SARS-CoV-2 detection was successfully recorded using OFET [1]. Antigens and antibodies associated with the SARS-CoV-2 were observed as a variation in the drain current of the OFET biosensors based on a soft and stretchable semiconducting polymer [1].

OFETs, play a critical role in up to date biosensing technology. However, the numerical and analytical models provided in the literature are minimal, focusing on the I-V characteristic of the transistor. The utilization of machine learning (ML) models in optimizing or predicting the OFET as a device or sensor was discussed in [2]. As stated earlier in this section, immobilization is the primary essential process in interacting between the biological reactor and the semiconductor-interfacing surface. Immobilization can be treated as a biological and chemical reaction process. Alternatively, the literature needs to include modelling the electronic point of view for immobilization.

The motivation behind developing self-powered Troponin biosensors integrated with OFET technology and low-power CMOS-based interfacing circuits stem from the need for efficient and portable diagnostic tools for cardiac diseases. Troponin is a crucial biomarker for the detection and diagnosis of cardiac conditions, such as myocardial infarction. Traditional laboratory-based assays for Troponin detection often require complex instrumentation and external power sources, limiting their accessibility and usability in resource-constrained settings or remote areas. By integrating OFET technology and low-power CMOS-based interfacing circuits, a self-powered biosensor can be realized, offering a portable, cost-effective, and efficient solution for Troponin detection. This innovation has the potential to revolutionize point-of-care diagnostics, enabling early detection and monitoring of cardiac diseases, ultimately improving patient outcomes, and reducing healthcare costs.

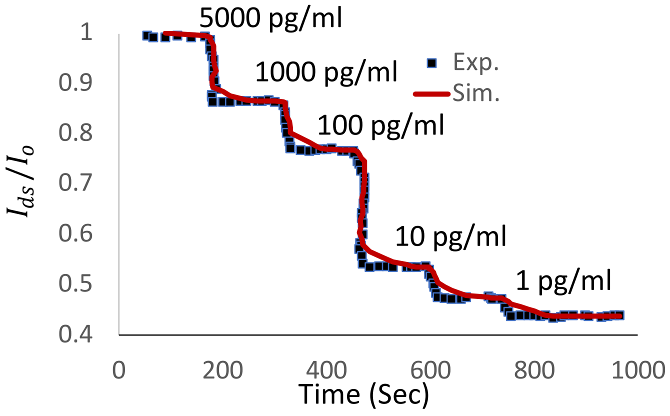

Figure 1: Current ratio-time variation under staircase accumulative signal for the troponin concentration, numerical results against experimental data

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GSP O 01

From Novice to Pro: Five facts about your everyday research partner, your PGSTAT

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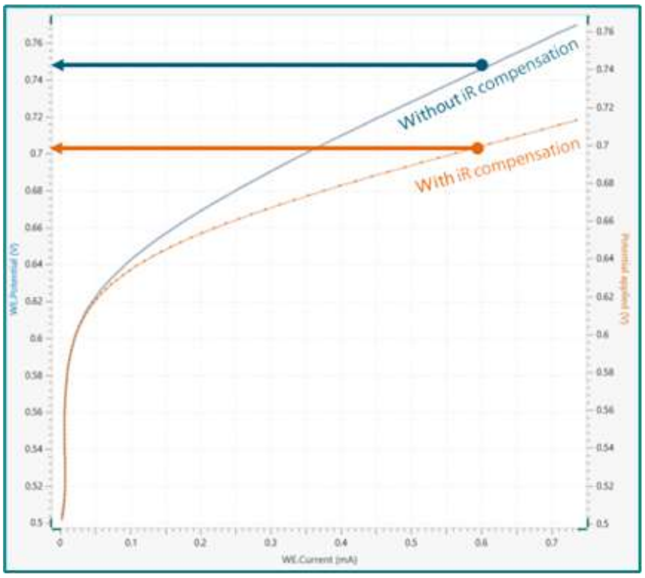
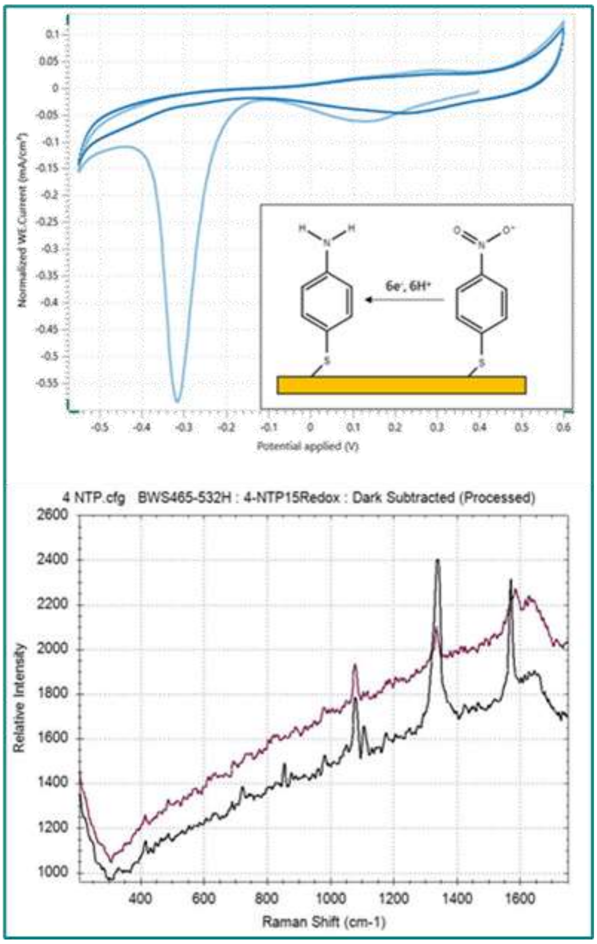
Metrohm – Autolab, Utrecht, Netherlands

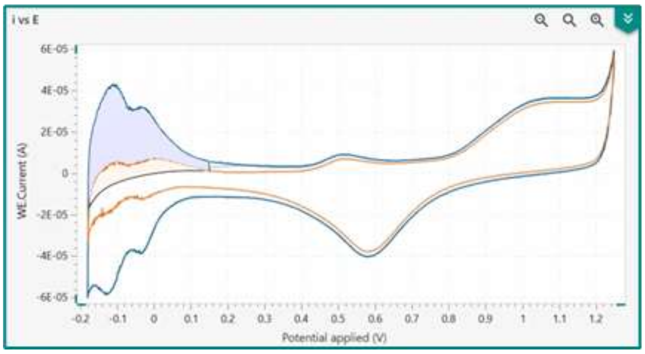
With electrochemical research gaining popularity and applications becoming more and more diverse, it is imperative for the researchers not only to use the state-of-the-art instrumentation and software but also to exploit the research tools they have for achieving the most accurate and unique results in the shortest time.

In this presentation, five facts related to your experimental setup which could have an immediate influence on your experimental results are presented:

1. Know your PGSTAT.
2. Use the right technique.
3. Use specific features when needed: iR-compensation.
4. Routine vs Exploratory workflow?
5. Enhance discovery with hyphenation.







Poster Presentations

ANAL P 01

Biochar-modified carbon paste electrode as an advanced material for electrochemical investigation of pesticide mancozeb

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Biochar (BC) is a carbonaceous material produced from naturally abundant raw materials (biomasses – mostly from the agricultural tailing and forestry ecosystem wastes or municipal wastes) *via* a pyrolysis process. With the growth of green chemistry concepts, the preparation and application of BC have attracted strong interest owing to the combination of fascinating physicochemical properties including large surface area, high porosity, surface charge, sustainability and low-cost which are beneficial in various fields, such as the remediation of polluted environments, soil amendments, wastewater treatment, and electrochemical sensors [1-3]. From the various electrode materials available nowadays, the classical carbon paste electrode (CPE) has widespread popularity as a working electrode due to its unique properties such as wide potential range, long-time stability, good conductivity, renewable surface, ease of preparation and modification, whereby the modifying agents can be added directly to the paste, either to the material in its final state or during its preparation [4]. In this work, CPE was bulk modified with biochar obtained from the hardwood source (BC-CPE) with the aim to develop a reliable alternative method for the determination of broad-spectrum fungicide mancozeb (MCZ). Cyclic voltammetric experiments showed that the oxidation of MCZ is irreversible and an adsorption control process at the BC-CPE surface. In the next step, a simple, sensitive and selective electroanalytical method for the determination of MCZ using differential pulse adsorptive stripping voltammetry (DP-AdSV) was proposed. Optimization of various experimental parameters was carried out including the pH of the supporting electrolyte, the amount of the modifier and the preconcentration step. At pH 7.0 of Britton-Robinson buffer, with accumulation potential of -0.2 V and accumulation time of 30 s, a linear relationship between MCZ concentration and peak current intensity was established between 0.025 and 2.78 μg mL^{-1}, the relative standard deviation did not exceed 3%, while achieved detection limit in the model solution was 7.5 ng mL^{-1}. The BC-CPE showed adequate selectivity for MCZ in the presence of various interfering compounds. The obtained results indicate that BC-CPE with an optimized DP-AdSV method could be applied for the trace-level electroanalytical determination of MCZ in real samples.

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ANAL P 02

Transition metal-embedded MWCNT carbon paste sensors: Innovative platforms for pharmaceutical analysis

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Electroanalysis, finds widespread application in determining electroactive species, notably pharmaceuticals, due to its versatile and potent analytical performances. Electroanalytical methods offer several advantages, including simple operation, high sensitivity, low cost, and rapid response. The pivotal aspect of electroanalytical methodologies is the working electrode, where the analyte's redox reaction occurs. Thus, the careful selection of electrode material is a crucial step in ensuring the efficacy and accuracy of the sensing process. Moreover, enhancing the performance of electroanalytical methods often involves employing modifiers.

One prevalent approach in modern electroanalysis involves utilizing a carbon paste electrode as the sensing element. This method relies on carbon material, specifically graphite powder mixed with a suitable binder (pasting liquid). The preparation of the paste is straightforward, and these sensors offer the advantage of easy modification by incorporating the modifier during the mixture preparation. This practice is extensively employed in detecting organic analytes in electroanalysis.

To enhance sensor performance, scientists employ hybrid materials, which combine different types of substances. One notable example is the combination of carbon nanotubes (CNTs) with metal (nano)particles. CNTs exhibit remarkable tensile strength, excellent electrical conductivity, large surface area, and high chemical stability. Depending on their structure, CNTs exist as single-walled carbon nanotubes (SWCNTs) or multi-walled carbon nanotubes (MWCNTs). Incorporating CNTs as modifiers improves electron transfer rates, thereby enhancing the sensitivity and selectivity of the modified sensor. Various nanoparticles, particularly those of transition metals, possess a high surface-to-volume ratio and high surface energy, rendering their surface atoms highly active and demonstrating catalytic activity (1).

Several hybrid materials have been synthesized and employed as carbon paste sensors for detecting compounds such as ibuprofen and estradiol. For ibuprofen determination, a modifier composed of MWCNTs-supported Ni electrocatalyst was applied, resulting in the construction of Ni-MWCNTs-CPE. Under optimized conditions, this sensor exhibited a linear range of 25-500 μmol/L and a LOD value of 0.13 μmol/L (2). Similarly, for estradiol determination, functionalized MWCNTs with immobilized Fe electrocatalysts (Fe/f-MWCNTs) were utilized to create Fe/f-MWCNTs-CPE. This sensor demonstrated the capability to detect estradiol in a concentration range of 0.25 to 20 μmol/L, with a detection limit of 0.02 μmol/L. The prepared sensor proved directly applicable for estradiol determination in water, urine samples, and pharmaceutical formulations of estradiol. These studies underscore the enhanced performance of modified carbon paste-based sensors using hybrid material-based modifiers that combine the benefits of carbon nanotubes with transition metals such as Ni and Fe.

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ANAL P 03

Exploring biochar potential for electrochemical sensing of pesticide maneb

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The great potential of biochar as a low-cost material obtained from renewable resources for the development of electrochemical sensors is recognized for the analysis of various electroactive organic compounds [1-3]. In this study, an electrochemical sensor based on biochar derived from a hardwood source as an environmentally sustainable material is used as a modifier of carbon paste electrode (CPE) to improve the voltammetric determination of pesticide maneb (MAN). Maneb belongs to the group of dithiocarbamate fungicides that could be used for the treatment of fruits and vegetables. The increase of dithiocarbamates metabolite concentrations in the environment may disrupt protein synthesis and metabolism. Therefore, a rapid, simple, and sensitive analytical approach for the analysis of MAN is needed [4]. Biochar (BC) material was prepared from hardwood at two temperatures, 400 °C (BC400) and 700 °C (BC700), and characterized by scanning electron microscopy, and specific surface area analysis. Obtained results showed a porous structure of BC with relatively high surface areas, *i.e.* 176 $m^2 g^{-1}$ at 400°C and 284 $m^2 g^{-1}$ at 700 °C. As it is expected, BC produced at high temperatures has a higher surface area and better conductivity [5]. Due to the good catalytic properties of BC as a material, an enhanced sensitivity of electrochemical sensors based on BC could be achieved [6]. Accordingly, observed oxidation peak intensities have shown the differences between an unmodified CPE, CPE modified with a BC400 (BC400-CPE), and CPE modified with a BC700 (BC700-CPE) for the analysis of MAN whereby BC700-CPE provides the most favourable analytical response of target analyte. Cyclic voltammetric investigations revealed that the electrode reaction is irreversible and controlled by the adsorption of MAN at the surface of the working electrode, which led to an optimization of the differential pulse adsorptive stripping voltammetric (DP-AdSV) method for quantifying MAN in a model solution. Under the optimized experimental parameters (10.0 % BC700 in CPE, Britton-Robinson buffer pH 7.0, E_{acc} = -0.2 V, t_{acc} = 90 s), the oxidation peak of MAN (at 0.55 V) showed a linear response in a concentration range from 0.049 to 1.84 μg mL^{-1} with evaluated limit of detection of 0.015 μg mL^{-1} and relative standard deviation of 3.23 %. The obtained results open the possibility of exploring BC700-CPE potential for MAN determination in environmental samples.

Acknowledgement: This research was supported by the Science Fund of the Republic of Serbia, #10810, Sustainable solutions in environmental chemistry: exploring biochar potential–EnviroChar.

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ANAL P 04

Enhanced voltammetric detection of hydrogen peroxide using a glassy carbon electrode modified with reduced graphene oxide and TiO_2

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Hydrogen peroxide (H_2O_2) is important in various fields such as environmental monitoring, clinical diagnostics, and industrial processes due to its omnipresence. Additionally, hydrogen peroxide is a by-product in reactions catalysed by numerous oxidase enzymes, making it a valuable reporter molecule for the electrochemical detection of non-electroactive compounds (1). This detection is made possible through electrodes modified with substrate-specific oxidative enzymes, leveraging intermediary role of H_2O_2 in these enzymatic reactions. The accurate and sensitive analysis of H_2O_2 is imperative in understanding its dynamics and impacts in these diverse domains. Conventional methods for hydrogen peroxide determination, such as titration and spectrophotometry, have provided valuable insights into its concentration levels. Nonetheless, these methods often suffer from limitations such as low sensitivity, interference from other substances, and the requirement for complex sample preparation procedures. However, electroanalytical techniques have emerged as promising alternatives for the sensitive and selective detection of hydrogen peroxide. Electroanalytical methods offer distinct advantages for H_2O_2 analysis, enabling rapid, selective, and cost-effective detection with high sensitivity and low detection limits. Usually, determination of hydrogen peroxide relies on its electrochemical oxidation or reduction at suitable electrode materials. Typically, in electrochemical processes hydrogen peroxide yields oxygen gas and protons, accompanied by the transfer of electrons, which can be detected as a current response. The choice of electrode material plays a crucial role in determining the sensitivity and selectivity of the electroanalytical method.

In this study, the modification of a glassy carbon electrode (GCE) with reduced graphene oxide (rGO) and titanium dioxide (TiO_2) is reported for improved electrochemical detection of hydrogen peroxide. The modification was done to enhance electrochemical properties and sensitivity of bare GC towards H_2O_2. The detailed preparation procedure and characterization of this modified GCE-rGO-TiO_2 electrode will be presented. By modification, the GC electrochemical properties can be enhanced, primarily affording improved sensitivity and selectivity towards H_2O_2. The synthesis and characterization of the modifiers will be discussed, elucidating the integration of rGO and TiO_2 to the electrode surface. Through comprehensive characterization, including cyclic voltammetry and chrono-amperometry, the electrochemical behaviour and sensing capabilities of the modified electrode will be presented. Additionally, the analytical performance of the sensor will be assessed, demonstrating its applicability for real sample analysis. The proposed electrochemical sensor exhibits promising characteristics for H_2O_2 detection, offering improved performance in terms of sensitivity, selectivity, and stability.

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The effect of surface metallographic preparation on corrosion behaviour of Ti-6Al-4V alloy in the simulated physiological solution of artificial saliva

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Titanium alloys are found in various sectors, such as aviation, biomedicine, and marine industry.[1] The formation of protective passive layers on the surface of titanium alloys occurs spontaneously, contributing also to their remarkable corrosion resistance. For biomedical use, the preference for Ti-6Al-4V is due to its suitable mechanical properties.[1] The microstructure of Ti-6Al-4V comprises both alpha (α) and beta (β) phases, with aluminium (Al) stabilizing the α-phase and vanadium (V) stabilizing the β-phase. Apart from elemental composition variations, surface properties affect its corrosion resistance.[2] Overall, mechanical preparation has an important impact on optimizing surface characteristics, ensuring enhanced performance across diverse fields. According to the literature, different surface preparations and treatments, including mechanical, physical, chemical, or biochemical methods, can significantly impact the properties of the passive layer.[2,3] Usually, mechanical preparation (grinding and polishing) of Ti-6Al-4V surfaces involves a series of steps to tailor surface properties for specific applications to modify surface texture and morphology.[4]

This work was focused on commercial Ti-6Al-4V distributed by Goodfellow. The main aim was to study the influence of mechanical surface preparation (after grinding using SiC emery papers (grids 320, 1200, 2400, and 4000), diamond (DP-L) polishing, and silica (OP-S) polishing) on its surface. The surface roughness was measured using a contact profilometer. The surface appearance and microstructure characterization were performed using scanning electron microscopy (SEM) coupled with energy-dispersive X-ray spectrometry (EDS). Electrochemical behaviour after 1.5 hours of immersion to physiological solutions (simulating the components and pH of the natural saliva fluid) at 37 °C was assessed using cyclic potentiodynamic measurements in a three-electrode corrosion cell.

The results revealed that surface preparation significantly impacts roughness, surface microstructure, and corrosion behaviour, especially at potentials above 3 V *vs.* Ag/AgCl, Figure 1.

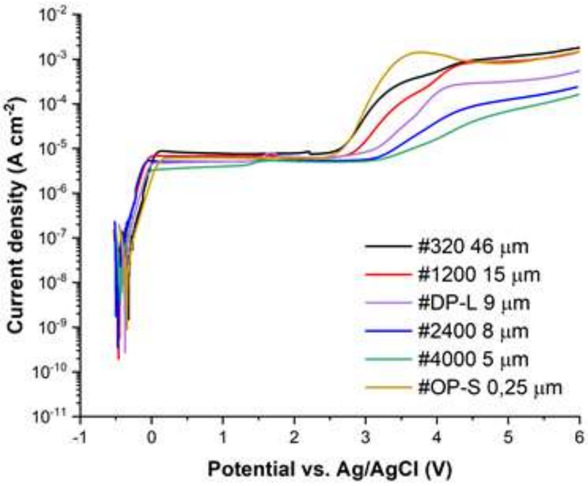

Figure 1. Potentiodynamic polarisation curves of Ti-6Al-4V samples subjected to various metallographic preparations. Curves were measured after 1.5 hours of immersion in artificial saliva solution (simulating the components and pH of the natural saliva fluid) at 37 °C.

Acknowledgement: This research is supported by the Slovenian Research and Innovation Agency (grant No. J7-4639 for the project "Antibacterial alloys. Development by additive 3D manufacturing, characterization, and clinical applications",

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Collagen coating for bioactivation of the titanium implant surface

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Implant materials are used to replace damaged or irreversibly lost parts of the body, providing support, restoring functionality, and contributing to the improvement of patients' quality of life. With the global aging population and due to different traumas, injuries, and degenerative diseases among various demographic groups, there is an increasing demand for implant materials, among which metallic implant materials, especially titanium and its alloys, are most commonly used [1,2]. As titanium implant materials, despite exhibiting good biocompatible properties (including corrosion resistance), belong to the group of bioinert materials, various procedures for surface modification or coating with bioactive substances are employed for their surface bioactivation [1,2].

Collagen is the most abundant protein in the human body and is found in the skin, bones, muscles, tendons, and ligaments. It provides strength and structure to tissues, helping to maintain their shape and integrity. Collagen is made up of amino acids, primarily glycine, proline, and hydroxyproline, which are essential for its structure and function. There are several types of collagens, each with specific roles in the body. Overall, collagen plays a crucial role in supporting skin elasticity, joint health, and overall tissue integrity [3,4]. Enhancement of the implant's integration into surrounding bone through coatings using bioactive organic molecules has been approached in various ways [1,2,5,6]. Among the biomacromolecules used, collagen has been widely explored as a ubiquitous component of the extracellular matrix with a positive effect on cell adhesion, proliferation, and migration [1,2,7].

The aim of this study was the surface modification of the titanium material by collagen coating to improve the osteconductivity of the underlying implant material. The uncoated and collagen-coated Ti substrates were immersed in the Fusayama artificial saliva solution as simulated body fluid for three months to test collagen coating's bioactivity on the basis of monitoring the spontaneous calcium phosphate deposit formation. The corrosion behaviour of the unmodified and the collagen-coated titanium was tested *in situ* employing electrochemical impedance spectroscopy (EIS) during prolonged immersion artificial saliva solution under *in vitro* conditions. The morphology, microstructure and chemical composition of the substrates were characterized by scanning electron microscopy (SEM), energy dispersive X-ray spectroscopy (EDS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR) prior and after artificial saliva solution immersion. Additionally, quantum chemical calculations at the density functional theory level (DFT) enabled a determination of a formation mechanism of the collagen coating onto the titanium surface and investigation of interactions occurring during spontaneous calcium phosphate deposit formation.

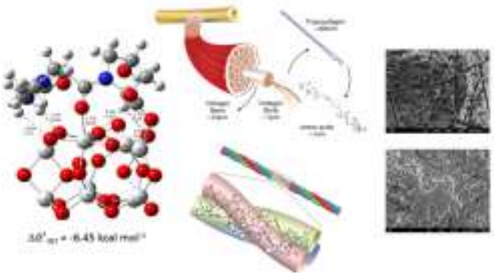

Figure 1. $(TiO_2)_{10}$–collagen binding mechanism as predicted by DFT calculation, collagen chemical structure, SEM images of collagen-modified Ti implant surface prior and after prolonged immersion in the artificial saliva solution.

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Electrochemical deposition of functional bioactive calcium phosphate coatings on the TiAlNb implant alloy

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Increased life expectancy and rising expectations regarding quality of life have underscored the growing significance of implant materials, with metals emerging as the predominant choice [1,2]. Titanium and its alloys, particularly prominent in dentistry and orthopaedics, owe dominance to their favourable physical, chemical, and mechanical properties. TiAlNb alloy represents good alternative to TiAlV alloy since it contains non-harmful Nb instead of cytotoxic V. Although exhibiting good biocompatibility and good corrosion resistance based on spontaneous formation of TiO_2 oxide layer on its surface [2,3], the titanium alloy is classified as bioinert material [1,4].

Hence, the calcium phosphate-based (CaP) materials are employed as coating agents on titanium-based implants due to their good osteoconductive properties based on resemblance to the human bone [5]. CaP coatings promote bone apposition and osseointegration ensuring the structural integrity and continuity of implant material with the surrounding bone [3,4]. Among various techniques that can be employed for CaP coatings production, electrochemical deposition garnered significant attention due to its distinct advantages over conventional methods [3,4,6,7]. By adjusting process parameters, such as temperature and voltage, one can precisely control the thickness, composition, and microstructure of the deposited coating. However, synthesizing CaPs with controllable crystal shape and structural characteristics remains a major challenge due to significant variations in chemical composition, crystallization kinetics, phase stability, and dissolution behaviour among different CaPs.

In this work, the CaP coatings were electrochemically deposited on the TiAlNb alloy. The corrosion behaviour of the unmodified and the CaP-coated titanium alloy was examined *in situ* in simulated physiological solution, Hanks' solution, under *in vitro* conditions of real implant applications, using electrochemical impedance spectroscopy (EIS). The electrochemical behaviour and corrosion parameters were also investigated by linear polarization measurements (the LPR method and the Tafel extrapolation method). The morphology, microstructure and chemical composition of the electrodeposited CaP coating were characterized by scanning electron microscopy, energy dispersive X-ray spectroscopy (EDS) and attenuated total reflection Fourier-transform infrared spectroscopy (ATR-FTIR). The focus of this work was to optimize the electrodeposition conditions to form the compact functional CaP coating that improves corrosion resistance of the underlying titanium alloy while contributing to enhanced biocompatibility and bioactivity. *In situ* investigations carried out under *in vitro* conditions provide useful information and further insight towards the understanding of the electrodeposition mechanism and implant surface functionalization.

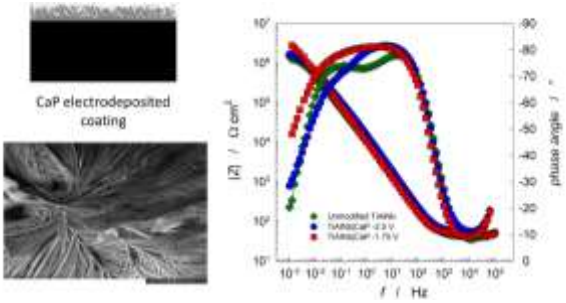

Figure 1. The SEM image of electrodeposited CaP coating presented with Bode plots of the unmodified and the CaP-coated TiAlNb alloy recorded in Hank's solution at open circuit potential.

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COR P 04

Impact of biofilm formation on the electrochemical behaviour of marine grade steel

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Corrosion of metals and alloys in demanding environments such as seawater represents complex chemical, electrochemical, and biological interactions that require a comprehensive understanding. Since more than 70% of the corrosion in marine environments is associated with microorganisms, costing billions annually [1], this work focused on examining the impact of *Pseudomonas aeruginosa* biofilm formation on the electrochemical behaviour of 304 stainless steel (SS) in the simulated marine environment. Electrochemical behaviour was studied directly after incubation of 304 SS in the sterile artificial seawater (ASW) and ASW inoculated with PA (biotic ASW), using electrochemical impedance spectroscopy (EIS), and potentiodynamic polarization (PP) measurements. The characterization of the film formed on 304 SS surfaces after incubation in sterile and biotic ASW was performed by scanning electron microscopy (SEM), non-contact optical profilometry, Fourier transform infrared (FTIR) spectroscopy, and inductively coupled plasma-optical emission spectrometry (ICP-OES). During the incubation of coupons in sterile ASW, charge transfer resistance (R_1) and film resistance (R_2) increased with the increasing incubation time, indicating the properties of the surface layer against a corrosive marine environment enhanced over time. On the contrary, in the presence of bacteria, R_1 and R_2 decreased compared to sterile ASW for the same exposure time. The negative impact of PA on the film formation of 304 SS in ASW was also evident from PP curves obtained for coupons incubated in biotic ASW, where both anodic and cathodic current densities were shifted toward higher values compared to sterile ASW. As revealed by surface analysis, the latter was due to the formation of PA biofilms on the 304 SS surfaces that accelerated local dissolution of the material and increased pitting corrosion with the pit depth reaching up to 3.75 µm. The synergistic effect of biofilm and chlorides led to the formation of a porous α-FeOOH and γ-FeOOH surface layer. The limiting factor for the repair and growth of the surface film was also restricted concentration of available oxygen. A decrease in the concentration of O_2 and pH of biotic ASW due to metabolic activity of bacteria, resulted in the transition of the primary cathodic reaction from the reduction of oxygen to the reduction of protons, as suggested by an increase in alkalinity of biotic ASW after 30 days of incubation. The loss of Cr (3.72 ± 0.25 µg L^{-1} cm^{-2}) and Fe (10.21 ± 0.63 µg L^{-1} cm^{-2}), as confirmed by ICP-OES, made it more difficult to repair the surface film.

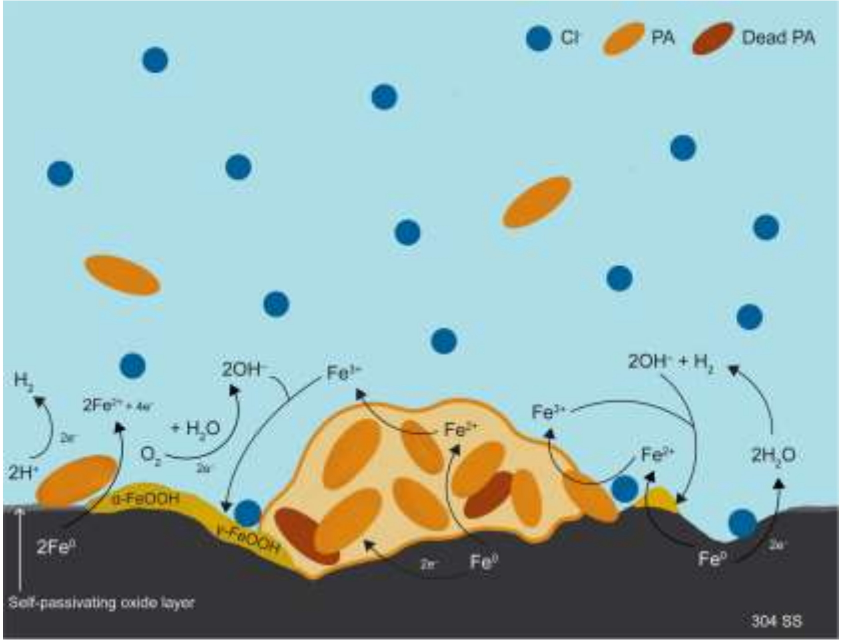

Figure 1. Illustration of corrosion mechanism of 304 SS in artificial seawater inoculated with Pseudomonas aeruginosa (PA)

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Expired N-acetyl cysteine-containing drug as green corrosion inhibitor for bronze exposed to 3.5 wt.% NaCl and simulated acidic rain environments

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The present paper aims at exploring the performance of an expired commercially available drug named "Fluimucil solution for inhalation" as green corrosion inhibitor for bronze in two corrosive environments simulating the basic seawater (3.5% *wt.* NaCl) and an acidic rain (0.2 g L^{-1} $NaHCO_3$ + 0.2 g L^{-1} Na_2SO_4 + 0.2 g L^{-1} $NaNO_3$, pH 3.4) encountered in a highly polluted industrial atmosphere. The active ingredient from "Fluimucil solution for inhalation" is N-acetyl cysteine (NAC) which is a safe and inexpensive medication approved by the Food and Drug Administration.

The electrochemical investigations performed by Tafel polarization and EIS measurements consistently revealed that the inhibiting behaviour of the expired drug on bronze depends on its concentration in both investigated electrolytes. NAC-containing drug acts mainly as a cathodic-type inhibitor, and its maximum inhibition efficiency is higher in the acidic rain simulating solution as compared to 3.5 *wt.*% NaCl media.

The surface analysis showed that the addition of the expired drug in the two corrosive electrolytes resulted in the formation of a thin adsorbed inhibitor film on the metallic surface, which effectively protects the bronze against corrosion.

The adsorption of NAC on bronze surface obeys Langmuir isotherm in both corrosive media.

The environmentally friendly properties of the expired NAC-containing drug make it favourable to be used in practice, replacing some toxic corrosion inhibitors, in accordance with the ecological policies for the use of chemicals.

Corrosion behaviour of nickel and nickel alloy coatings on stainless steel in highly alkaline environments: effects of chloride and bromide

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Alkaline water electrolysis is a mature technology for production of renewable hydrogen. However, projected demands for clean hydrogen will be hard to achieve without consideration of direct seawater electrolysis, because its abundance and availability. Because of its maturity, alkaline water electrolysis represents a convenient basis for the improvements and adjustments for direct seawater electrolysis, which include design of active and corrosion-resistant materials, with improved selectivity. If this is to be achieved, it is important to identify the seawater components that significantly contribute to the corrosion, quantify their contribution, and understand mechanism of their detrimental behaviour, which leads to the loss of activity and selectivity. This study explores the corrosion behaviour and stability of nickel-based coatings for the hydrogen evolution reaction in alkaline media. Nickel strike and nickel-molybdenum coatings on stainless-steel mesh were obtained by constant current electrodeposition at different deposition times. Electrochemical characterization was conducted using linear and cyclic voltammetry, Tafel analysis, and electrochemical impedance spectroscopy. Tests were performed in 1 M KOH solution, 1 M KOH solution with chloride ions (0.5 M), and 1 M KOH solution chloride (0.5 M) and bromide (5 mM) ions. Corrosion behaviour is significantly altered by both anions and is generally decreased in the order KOH -> KOH+Cl^- -> KOH+Cl^- +Br^- for all samples, which is important to notice not only because of the loss of electrocatalytic activity, but also because of the detrimental effects on the steel support.

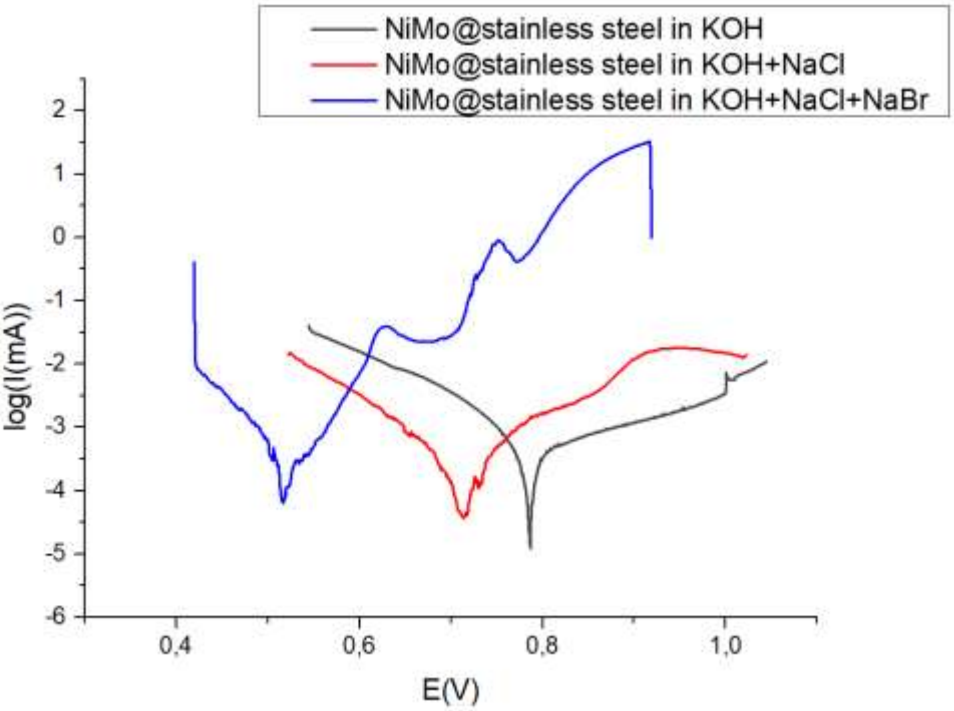

Figure 1. Tafel plots of NiMo alloy on stainless steel in various electrolytes

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ECAT P 01

Electrocatalytic oxidation of *L*-lactate by *Saccharomyces cerevisiae* flavocytochrome *b*$_2$ on redox mediator-modified glassy carbon electrodes

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L-lactate detection plays a significant role in healthcare and food industries. For that purpose, amperometric biosensors based on lactate oxidizing enzymes are often used. Among them, lactate electrodes based on flavocytochrome *b*$_2$ (*L*-lactate: cytochrome *c* oxidoreductase, fcb$_2$) have attracted some interest. This enzyme consists of four 58 kD subumits which contain protoheme IX and flavinmononucleotide (FMN). Since direct electron exchange between conventional electrodes and fcb$_2$ is largely impossible, electrodes with surface redox mediators are used for this purpose.

In this work we investigated the electrocatalytic reactions of *Saccharomyces cerevisiae* fcb$_2$ on glassy carbon (GC) electrodes, modified either by their electrochemical pretreatment or by the products of electrochemical reduction of dinitrobenzenes. After electrochemical pretreatment of GC electrode in the range of 1.8 to -0.8 V (*vs.* Ag/Agcl) [1], its cyclic voltammogram shows reversible redox peaks centered at 0.08 V (*vs.* Ag/AgCl, pH 7.0). The electron transfer rate constant (k_s) of the electrogenerated quinone/hydroquinone redox pair, determined by the method of Laviron, is equal to 0.7 s^{-1}. The pH dependence of the redox peaks corresponds to the $2e^-$, $2H^+$ transfer at pH 5.5-9.0. In the presence of 30-100 μM fcb2 entrapped on the electrode surface, *L*-lactate oxidation started at 0.05 V. The linear part of the response was observed up to 0.4 mM *L*-lactate, and the maximum catalytic current obtained at 0.2 V was 4.5 μA/cm^2. Glassy carbon electrodes can also be modified with the products of reduction and reoxidation of nitroaromatic compounds ($ArNO_2$), most likely polymers containing azoxy (Ar-N=N(-O)-Ar) groups [2]. We modified the electrodes by the potential scanning (10 cycles, -0.8 - 0.6 V) in the presence of 1.0 mM *p*- or *o*-dinitrobenzene. This resulted in the formation of stable surface electroactive compounds with redox peaks centered at 0.06 V (*p*-dinitrobenzene) and 0.1 V (*o*-dinitrobenzene) with k_s values of 0.62 and 0.72 s^{-1}, respectively. Like in the case of electrochemically pretreated GC, the pH dependence of the redox peaks was characterized by the slope of -0.06 V/pH unit. In the presence of entrapped fcb2, in both cases *L*-lactate oxidation started at 0.1 V, the linear part of the response reached 0.3-0.4 mM *L*-lactate, and the maximal catalytic current at 0.2 V was 12 to 18 μA/cm^2.

Although these electrodes were good in terms of their catalytic currents and linear part of the response, they were not sufficiently stable. Their activity dropped by 50 % after 24 h storage at pH 7.0 and 4 °C. In comparison, previously studied electrodes based on fcb2 from *Hansenula anomala* and carbon black [3], and fcb2 from *Ogataea polymorpha* and gold nanoclusters [4] were at least one order more stable. The reason for the rapid inactivation may be the reactions of Cys200,216,233 with surface quinones and other electrophiles. These cysteines are at 0.7 to1 nm distance from the FMN isoalloxazine ring [5] and are not conserved in fcb2 from *H. anomala*.

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ECAT P 02

Local coordination effects on stability and reactivity of single-atom catalysts supported on graphene: Insights and implications

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Single-atom catalysts (SACs) are rapidly advancing across various application domains, particularly in electrocatalysis of diverse reactions, often occurring under challenging pH and electrode potential conditions [1]. Therefore, there is a critical need for a comprehensive atomic-level comprehension of the active sites under realistic electrochemical environments, recognizing that the state of SACs' active centres may be modified by the adsorption of spectator species. In this study, Density Functional Theory (DFT) is utilized to perform a thermodynamic analysis of SACs comprising metal atoms (Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, or Au) incorporated into N_4 moieties within graphene [2]. Various surface electrochemical processes on such SACs are examined, their Pourbaix diagrams are generated, and their activity, selectivity, and stability under operational conditions are deliberated. The DFT outcomes showcased in this research validate that the characteristics of metal sites in M@N_4-graphene SACs (M = Mn, Fe, Co, Ni, Cu, Ru, Rh, Pd, Ag, Ir, Pt, or Au) evolve depending on the operational electrode potential and pH. Concerning the impact of electrode potential, the investigated SACs demonstrate heightened thermodynamic stability of metal centres against dissolution compared to bulk metal phases. Stability rises along the periods of transition elements and decreases for coinage metals (Cu, Ag, Au). Regarding the influence of pH, while some metal centres (Mn, Co, Ni) are prone to dissolution in acidic media, others (Ru, Rh, Ir, Pd, Pt) are anticipated to remain stable across all pH levels. The localization of the primary catalytic activity of SACs is contingent upon the electronic configuration of the utilized metal via preferential adsorption of electrolyte species. Metals with an electron configuration of $d^{n\leq 8}$ are identified as the reactivity centres in M@N_4-graphene, serving as the preferred sites for all investigated adsorbates. The affinity of M@N_4-graphene SACs towards H_{ads} and their oxophilicity diminishes along the period as H_{ads} formation initiates at more negative potentials, while the potentials for OH_{ads} and O_{ads} deposition shift to higher potentials. Depending on the electrode potential, the examined metals can exist either bare or covered by H_{ads}, O_{ads}, or OH_{ads}. These afore mentioned spectator species can obstruct metal sites and prompt alterations in the SACs' electronic structure. The potential occurrence of such changes must be acknowledged when dealing with SACs, both in theoretical modelling and in interpreting the outcomes of their ex-situ characterization. Moreover, we conducted systematic replacements of nitrogen atoms with oxygen or sulphur atoms to achieve M@O_xN_y-graphene and M@S_xN_y-graphene SACs (x + y = 4) [3]. Our findings reveal that the local coordination significantly influences the electronic structure and reactivity towards hydrogen and oxygen species. However, stability is notably more impacted. By employing the concept of Pourbaix diagrams, we demonstrate that substituting nitrogen atoms in metal coordinating centres with O or S destabilizes the SACs against dissolution, while the metal centres become readily covered by O and OH, serving as additional ligands at high anodic potentials and elevated pH values. Therefore, it is imperative not only to consider local coordination concerning the SACs' activity but also to account for its effects on the speciation of SAC active centres under diverse potentials and pH conditions.

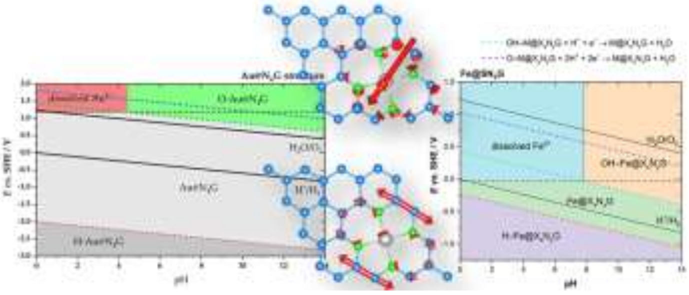

Figure 1. Pourbaix diagram for chosen M@X_4G systems.

Acknowledgement: A.S.D and I.A.P acknowledge the support provided by the Serbian Ministry Science, Technological Development, and Innovation (451-03-65/2024-03/200146). The computations and data handling were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at the NSC center of Linköping University, partially funded by the Swedish Research Council through grant agreements no. 2022-06725 and no. 2018-05973.

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Evaluation of 3D porous electrodes in a zero-gap cell for alkaline water electrolysis

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In modern AWE systems, a zero-gap cell architecture is used where electrodes are directly pressed on the membrane to reduce the ohmic losses related to the electrolyte. This technology requires perforated plates or novel porous 3D electrodes. Additionally, at high H_2-production rates, the enormous gas evolution leads to losses which are related to the blocking effect of adherent gas bubbles and/or the increased electrolyte resistance [1]. In this regard, optimized porous structure is required which enables enhanced removal of gas bubbles and a direct flow to the backside of the electrodes resulting in high cell efficiency.

In this contribution, powder metallurgy route in combination with a space holder method [2,3] were used to produce novel porous 3D electrodes so called porous metal foil and porous sintered metal papers. Additionally, powder metallurgic modified porous metal foams were investigated. This approach allows to adjust the porosity, the thickness as well as the pore size of the catalytic material. Consequently, the accessible surface area of the electrode can be enhanced and the flow of gas bubbles through the porous structure can be optimized. The implementation of the porous electrodes in a zero-gap single cell were investigated with respect to the cell resistance, cell voltage and the pressure distribution on the separator. Here, the porous electrodes were used as anode, whereas electrodeposited Ni-Sn electrodes [4] or Raney-Ni electrodes [5] were utilized as cathode. Single cell measurements indicates that the efficiency at high current densities (up to 1 A cm^{-2}) is mainly related to the efficient gas bubble removal. Cell voltage of 1.83 V at 1 A cm^{-2} was determined if an anode with an optimized pore structure is utilized.

Additionally, a single lab-electrolyzer was equipped with reference electrodes to get access to the half-cell potential with the objective to evaluate the cathode and anode in-operando [6].

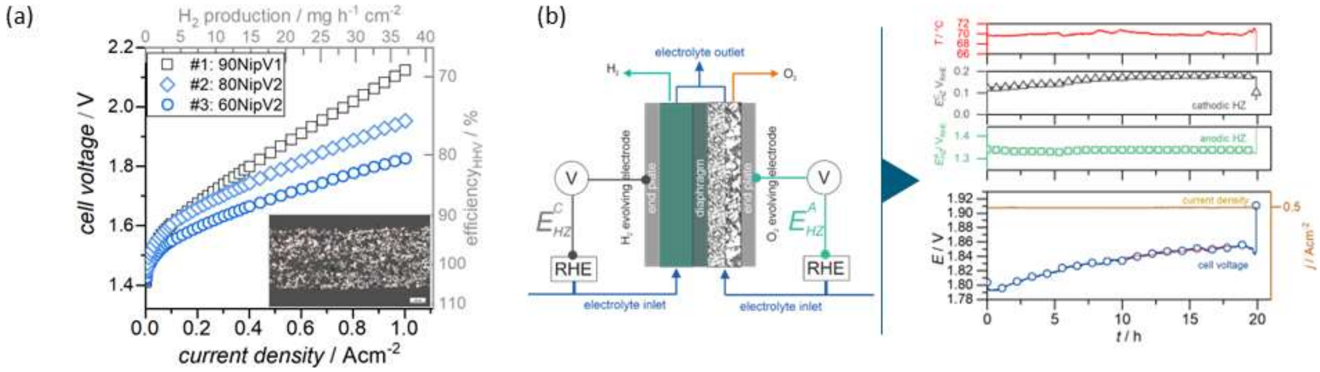

Figure 1. (a) Cell performance of different porous electrodes and (b) Single cell equipped with reference electrodes to evaluate in-operando the cathode and anode performance.

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6. P. Naumann research intership thesis 2023

Controlled synthesis of high-index faceted Pt nanocatalysts directly on carbon paper for methanol electrooxidation

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Platinum (Pt) nanocatalysts as the best catalysts for direct methanol fuel cell (DMFC) still face a huge challenge such as high cost, low utilization rate, activity and stability to be improved. Adjusting the surface structure of Pt nanoparticles (NPs) to achieve high-index facets with more active sites is an effective method to resolve the problems. Furthermore, the controlled synthesis of high-index faceted Pt (HIF-Pt) nanocatalysts directly on carbon paper, which is an important component of membrane electrode, can greatly promote the practical application of HIF-Pt nanocatalysts in DMFC. Herein, the HIF-Pt nanocatalysts supported on carbon paper (HIF-Pt/CP) were realized by developing an electrochemically controlled synthesis method. The fishbone-like and concave cube shaped Pt NPs surrounded by some high-index facets such as (200), (220), and (311), were achieved by adjusting the frequency and treatment time of applied potential. Hence, these HIF-Pt/CPs exhibit excellent activity and stability towards methanol electrooxidation during both cyclic voltammetry characterization and potentiostatic test. Especially, the specific activities and mass activities of HIF-Pt/CP-1Hz reached 3.78 and 1.53 A·mg^{-1}, which were 6.5 and 2.78 times higher than those of commercial Pt/C, respectively. It is worth mentioning that the direct growth of HIF-Pt NPs on carbon paper effectively reduces the contact resistance of the catalyst layer which shows great potential in the practical application in DMFC.

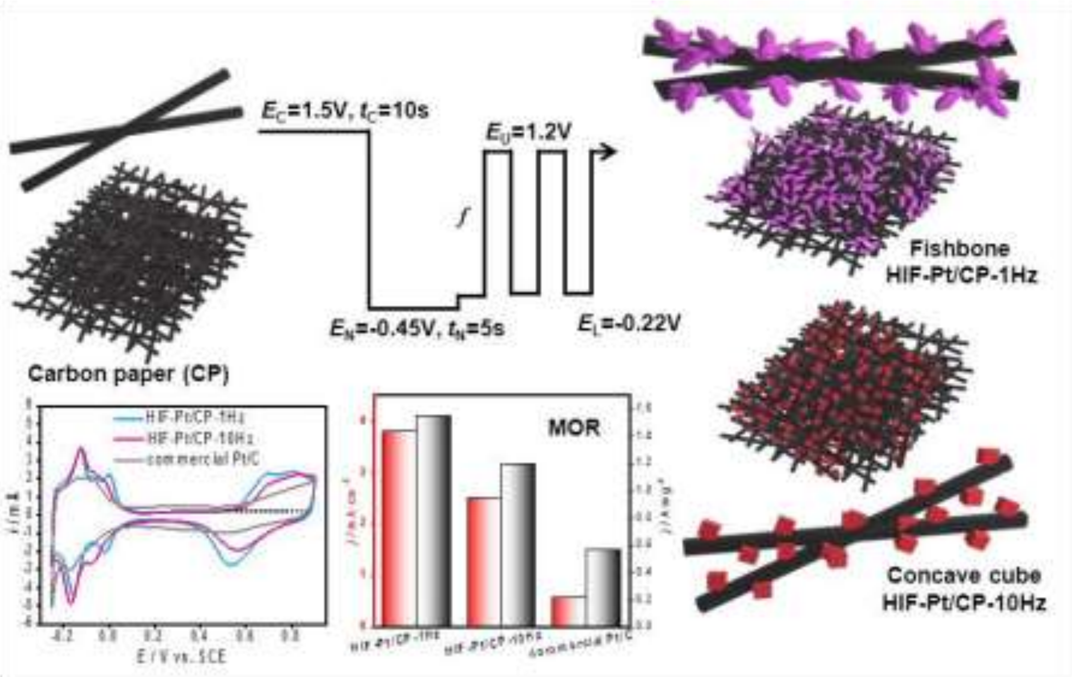

Figure 1. Carbon Paper supported High-index Faceted Pt Nanocatalysts and their catalytic performance

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Seizing gaseous Fe^{2+} to O_2-accessible densify NC sites for proton exchange membrane fuel cells

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It is well known that the commercial applications of proton exchange membrane fuel cells (PEMFCs) rely heavily on efficient and low-cost catalysts to drive the cathodic oxygen reduction reaction (ORR). Platinum (Pt), the noble metal, has the highest kinetic activity in cathodic ORR. Nevertheless, the extensive use of Pt in fuel cells will add significant cost to PEMFCs, which is an obstacle to its large-scale and sustainable deployment. Much attention has been therefore paid to the development of Pt group metals free (PGM-free) ORR catalysts. The US Department of Energy (DOE) has set a 2025 ORR target for PGM-free PEMFCs cathode as a current density of 0.044 A cm^{-2} under 1.0 bar H_2–O_2 at 0.9 $V_{iR\text{-}free}$, comparable to the ORR activity of PGM-based catalysts.[1] The utilization of Fe is a crucial parameter for evaluating Fe-N-C catalysts in proton exchange membrane fuel cells (PEMFCs), yet it exhibits a decreasing tendency as the density of Fe-N_4 sites increases. Herein, gaseous Fe^{2+} was seized into NC support with surface-rich pyridinic-N to form surfaced Fe–N_{2+2} with higher density and intrinsic activity on carbon substrate. The surfaced Fe–N_{2+2} has improved both the site density and Fe utilization, which provided a large number of O_2-accessible active sites at the three-phase interface (TPB) of the fuel cells. Moreover, dense Fe–N_{2+2} exposed to the outermost layer of the catalyst layer could shorten the transport pathways of protons and O_2, reducing mass transfer resistance. These structural advantages make Fe_g-NC/Phen the best ORR catalysts evidenced by a high current density of 0.046 A cm^{-2}@0.9$V_{iR\text{-}free}$ and a high peak power density (P_{max}) of 1.53 W cm^{-2} in a H_2–O_2 PEMFCs, which outperformed almost all the reported M–N–C catalysts.

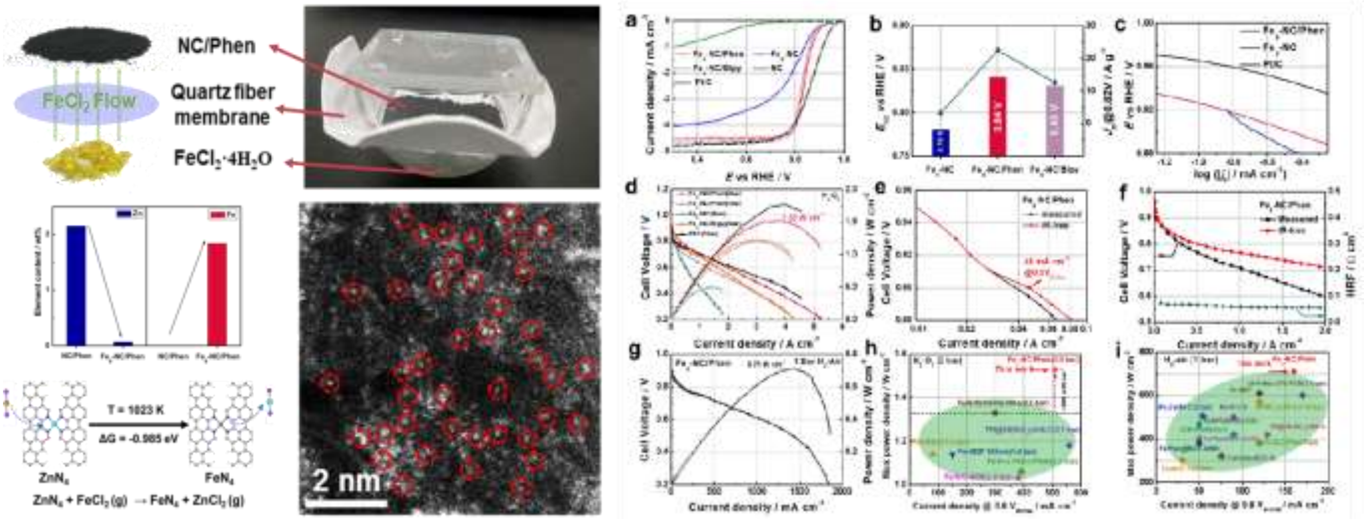

Figure 1. LEFT: Schematic diagram illustrating the bottom-up "confined steaming" strategy, and; AC HAADF-STEM images of Fe_g-NC/Phen; RIGHT: ORR and PEMFC performance measurements. (a) ORR polarization curves; (b) $E_{1/2}$ and J_m at 0.82 V; (c) Tafel plots curves of Fe_g-NC/Phen, Fe_g-NC and Pt/C; (d) H_2-O_2 PEMFC polarization and power density curves. Cathode, 3.5 mg_{cat} cm^{-2} for Fe-N-C; anode, 0.4 mg_{Pt} cm^2; Nafion 211 membrane; 4.41 cm^2 electrode; 80 °C, 100% relative humidity (RH); 400 mL O_2 min^{-1} and 300 mL H_2 min^{-1}. (e) Tafel plots of Fe_g-NC/Phen; (f) Polarization curves of Fe_gNC/Phen with and without iR-free. The atrovirens dotted curve represents the high-frequency resistance (HRF). (g) H_2-air PEMFC polarization and power density curves. The max powder density and the area metric current density at 0.8 $V_{iR\text{-}free}$ between Fe_g-NC/Phen and the literature reported Fe-based catalysts in (h) H_2-O_2 fuel cell and (i) H_2-air fuel cell

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ECAT P 06

Methanol oxidation reaction on electrodeposited Pd and SbPd electrocatalysts in alkali metal hydroxide solutions

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Electrochemistry in alkaline solution is substantial for the examination on electrooxidation of liquid fuels [1]. Recently, alkaline direct alcohol fuel cells (ADAFCs) have shown the interest of researchers due to their advantages in performance and cost of materials, as an important characteristics for the commercialization of fuel cells. Within this context, Pd-based catalysts are attracting a great deal of attention as catalysts for the methanol oxidation reaction (MOR) in alkaline solution. Some metals may have a promoting effect on electrooxidation of alcohols and among them is antimony [2]. We report the galvanostatic preparation of Pd and bimetallic Sb–Pd catalyst from a surfactant free electrolyte. The bimetallic catalyst was obtained in two-step electrochemical deposition route with electrodeposition of Sb (the first step) followed by Pd electrodeposition (the second step). Aim of the work is to examine the role of Sb in the bimetallic Sb–Pd catalyst as well the impact of the selected alkali metal cations on the electrocatalytic activity of Pd and Sb–Pd electrocatalysts in MOR. In order to understand the correlation between the morphology and electrocatalytic activity of Pd and Sb–Pd catalysts, they were analysed by scanning electron microscopy (SEM) technique.

The electrocatalytic activity of Pd and Sb–Pd catalysts for MOR was evaluated by CV technique in 1 M NaOH and 1 M LiOH as displayed in Fig. 1. The shift in the initial oxidation potential along with two-fold increase in peak current density observed on Sb–Pd catalyst demonstrates that bimetallic electrode have higher catalytic activity than Pd catalyst. It is clear that the MOR activity is affected by the presence of Sb most probably due to the hasctronic modification of Pd induced by Sb.

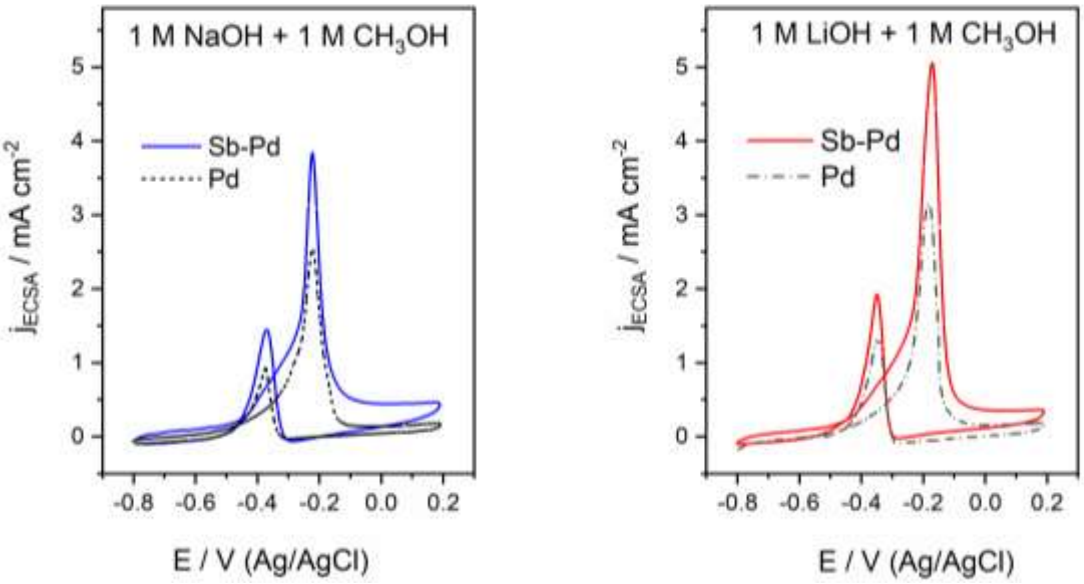

Figure 1. CVs for the electrochemical oxidation of 1 M CH_3OH at Pd and Sb–Pd in 1 M NaOH and 1 M LiOH at v = 0.05 Vs^{-1}.

Inspection of the results presented in Fig. 1 reveals the importance of the selection of alkali metal hydroxide for MOR. Electrochemical oxidation of methanol starts at rather negative potentials in LiOH solution in regard to NaOH indicating the active role of OH_{ad} and impact of the nature of alkali metal cations. It was stressed that the choice of alkali metal cations govern the electrocatalytic activity and can be considered as one of the tuning parameters in electrocatalysis. Taking into account the role of Sb in bimetallic catalyst it was observed that Sb adjusts the extent and persistence of OH_{ad} surface coverage combining at the same time the contribution of the cation in solution. It can be concluded that Sb–Pd electrocatalyst possess excellent electrochemical characteristics and has a potential in methanol fuel cell application.

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Role of copper and gold in improvement of the electrochemical oxygen reduction on palladium nanoparticles in alkaline solution

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Carbon supported nanocatalysts Pd/C, Pd-Cu/C and Pd-Cu-Au/C were synthesized using a borohydride reduction method and characterized by energy-dispersive X-ray spectroscopy, X-ray diffraction, and transmission electron microscopy. Crystallite size of ≤3 nm and low Cu and Au contents were found for Pd-Cu and Pd-Cu-Au catalyst; 8.2 at.% Cu and 4.4 at.% Au for Pd-Cu-Au/C and 17 at.% Cu for Pd-Cu/C catalyst with alloy structure [1].Thin layers of synthesized catalysts, supported on a glassy carbon rotating disk electrode, were examined for the electrochemical oxygen reduction reaction (ORR) in an O_2 saturated 0.1 M NaOH solution and compared with a commercial Pt/C. The electrochemically active surface area (EASA) was determined from CO_{ads} stripping voltammetry in deaerated 0.1 M NaOH solution [1], both initially and after a short stability test consisting of 500 potential cycles in N_2 and O_2 saturated solution (Fig. 1a). In addition, thin layers of Pd-Cu/C and Pd-Cu-Au/C catalysts were subjected to a short acid treatment, which resulted in the removal of surface Cu atoms and the production of Pd@Pd-Cu/C and Pd-Au@Pd-Cu-Au/C skin catalysts. Examination of the ORR kinetics showed first-order kinetics with respect to O_2, with nearly four electrons transferred per O_2 molecule on all catalysts. Bimetallic and trimetallic catalysts were more active for ORR than monometallic Pd/C and Pt/C catalyst with the highest specific activity (SA) achieved on skin-type catalysts (Fig. 1b). This indicates that the Cu atoms just beneath the surface of the nanoparticles are crucial for the high activity. The skin-type catalysts also exhibited higher activity after the stability test (Fig. 1b and 1c). The catalyst with the highest SA and mass activity (MA) after the stability test was skin-type Pd-Au@Pd-Cu-Au catalyst. Therefore, it was concluded that Pd-Au skin contribute to the stability during the ORR, as it was reported for Pt-Au skin catalyst [2].

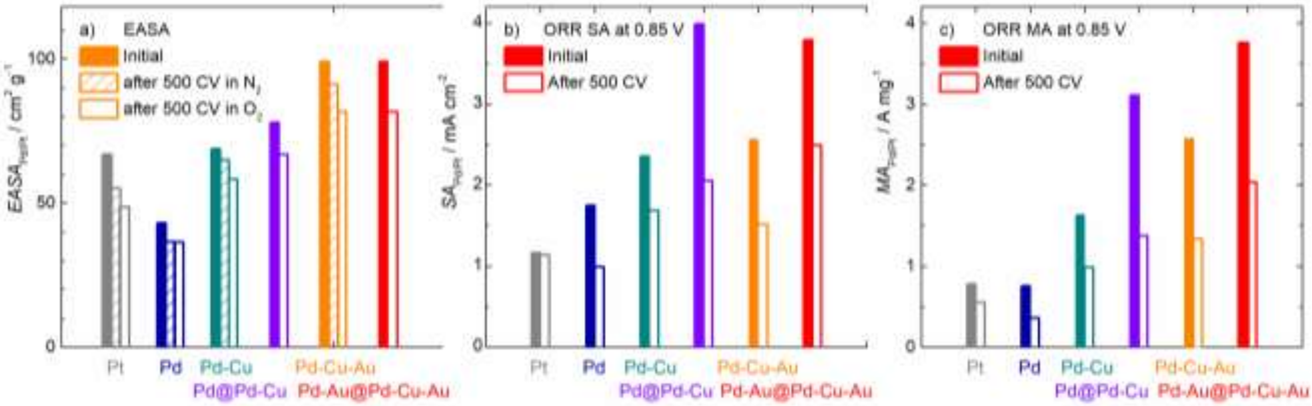

Figure 1. a) EASAs of investigated catalysts, their b) specific activity and c) mass activity for the ORR at the potential of 0.85 V. Specific and mass activity were calculated per area/mass of Pd or Pt

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ECAT P 08

Comparison of lanthanum strontium manganite and lanthanum strontium cobaltite perovskite oxide catalytic properties for application as bifunctional gas-diffusion electrodes for secondary Zn-air batteries

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Recently the perovskite-based oxides are intensively studied because of their high efficiency for both the oxygen reduction reaction (ORR) during discharge and the oxygen evolution reaction (OER) during charge of secondary metal-air batteries with alkaline media. Most papers reported about their reduction activities, as the ORR is the kinetically slower process than OER and it is governing the practical application of these materials. In this paper we investigate both oxygen reactions ORR and OER of $La_{0.80}Sr_{0.20}MnO_{3-\delta}$ (LSM) and $La_{0.60}Sr_{0.40}CoO_{3-\delta}$ (LSC) perovskite oxides, which are widely applied as cathode materials for fuel cell and electrolysis devices, but for energy storage, more especially for metal-air batteries its electrocatalytic properties is still subject of interest for many researchers. The presented here GDE electrodes are produced by classical technology, using Teflonized (60 wt.% Teflon) carbon blacks (Vulcan XC-72) as gas-diffusion layer (GDL) and perovskite powders, mixed with poly tetra flour ethylene (PTFE) emulsion, and catalytic layer (CL) hot pressed onto the GDL together with a nickel mesh (as a current collector). Half-cell testing was carried out in 6 M KOH in three-electrode cell with nickel mech counter electrode and Reversible Hydrogen Electrode (RHE) as reference electrode. To eliminate the carbon corrosion during charge the loading of carbon blacks was decreased and compered with electrodes containing perovskite alone, *i.e.* monolithic design. A comparison of electrocatalytic activities of LSM and LSC perovskite with and without carbon support was done as many electrochemical techniques including impedance spectroscopy were applied. The results show that the contribution of carbon is more pronounced at ORR where the increase of the carbon content leads to suggestion for series $2e^{-}+2e^{-}$ pathways mechanism of the oxygen reduction. Additionally, the need of activation time is registered. The perovskite electrodes that did not contain carbon possess an increased mechanical stability and potential for the electrode recovery after 200 charge/discharge cycles. Better stability, catalytic activity and electronic conductivity was registered for LSM electrode which works at conditions 1.7 to 1.8 V *(vs.* RHE) during OER, while LSC is limited by Co^{3+} reduction at these potential values.

ECAT P 09

Influence of various types of additives on molybdenum disulfide electrocatalytic activity for hydrogen evolution

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Molybdenum disulfide (MoS_2), as a typical transition metal dichalcogenide, has shown promising catalytic activity for hydrogen evolution reaction (HER) due to its layered structure with a large number of active sites. MoS_2 structure consists of several layers connected with weak Van der Waals attraction between them, while strong covalent bonds are within the layer. Due to this structure, MoS_2 exhibits distinct surface sites and significantly faster electron and hole mobility along the basal plane than perpendicularly between the layers [1]. Different nanostructured forms showed a variety of catalytically active sites such as plane edges, defects in the structure (vacancies, dislocations, dopant atoms), or unsaturated bonds. The layered structure of MoS_2 is easily modified to obtain a large number of active sites for HER. The main drawbacks are a lack in conductivity and a basal plane that is catalytically inert. Consequently, the performance of the material is largely limited by its conductivity and concentration of available active sites. Therefore, different strategies are employed in order to increase charge transport and create more active sites in the material. Mechanochemical modification of the material can cause a decrease in the size of the particles, *i.e.* increase in specific surface area, creation of structural changes (formation of defects and displacement of atoms, splitting of layers), amorphization, *etc.* The changes that the mechanochemical modification will cause in the material depend on the different milling parameters, among which is the milling time. The additional incorporation of conductive additives can be further beneficial for the catalytic activity of MoS_2. MoS_2 composites with different conductive materials can be easily prepared using mechanochemical milling. This method is shown to be very suitable for the preparation of composites - apart from homogenization, it also leads to morphological changes and the creation of defects, which is favourable for HER [2].

In this work, to improve the electrical conductivity of electrocatalysts, composites of MoS_2 with graphene oxide or bismuth selenide are prepared. Graphene oxide is a carbon nanomaterial that has high specific surface area, adjustable surface chemistry and electronic properties [3], which makes it suitable for the synthesis of composites with MoS_2. Bismuth selenide is a topological insulator, a material that is an insulator in the bulk but possesses metallic surface states [4] and therefore are expected to be good conducting channel for electron transport. Therefore, combining such materials with the catalytic active but poorly conductive MoS_2 could result in enhanced electron transfer and improved HER activity of the material.

The molybdenum disulfide and bismuth selenide were obtained by hydrothermal synthesis, while graphene oxide was prepared by the modified Hummers' method. Thus, prepared constituents are combined in different mass ratios and milled using a high-energy ball mill (SPEX Mixer/Mill 5100). The obtained composites were studied as catalysts for hydrogen evolution reaction in an acidic solution. SEM images of prepared composites showed that constituents are homogeneously mixed and cannot be distinguished separately. XRD analysis showed that bismuth selenide remained unchanged after the milling of composites, while graphene oxide undergoes some amorphization. These changes lead to different catalytic behavior of composites, depending on the type of additives. Therefore, composites with bismuth selenide exhibit significantly better catalytic activity for HER than composites with graphene oxide under the same conditions.

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ECAT P 10

MXene-supported platinum catalyst for effective methanol electrooxidation

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In recent years, direct methanol fuel cells (DMFC) as renewable energy sources are increasingly considered one of the most environmentally friendly and promising alternatives for meeting growing energy needs. Although some DMFC technologies are already commercially available there are still several challenges that need to be improved for successful commercialization of DMFC. The biggest challenges are how to overcome the high cost of Pt-based catalysts used in fuel cell reactions, the high catalyst loading required for methanol anodic oxidation reaction, poisoning of Pt catalysts with CO interemdiers during methanol electro-oxidation, methanol crossover issues, and most significantly long-term catalyst durability. One of the main reasons for agglomeration and detachment of platinum nanoparticles from the catalyst support is degradation of the support due to poor oxidation stability, *i.e.* non-resistance to electrochemical degradation in extremely difficult conditions in the working environment of fuel cells. Recent studies have shown that MXenes can be stable and promising support for Pt nanoparticles with improved reaction kinetics for methanol electro-oxidation reaction. MXenes, a rapidly developing family of two-dimensional layered materials, has shown great potential for use in energy conversion and storage technologies due to its high specific surface area, good resistance to electrochemical corrosion, strong interaction with metal support and also enhanced electrical conductivity. For this reason, MXenes may find use as a catalyst support material for anode processes in fuel cells. This is mainly contributed by the composition of MXenes since they have various functional groups and metal nitride or metal carbonitride materials. The chemical formula of MXenes is $M_{n+1}X_nT_n$, where M represents transition metals, X represents C/N and T represents chemical functional groups such as –OH, -O, and –F groups on the MXene surface.

In this research, platinum nanoparticles deposited on MXenes were synthesized by the microwave-assisted polyol method. The electrochemical behaviour of the synthesized catalyst was investigated by cyclic voltammetry, the electro-oxidation of adsorbed CO, and hronoamperometric method. The physicochemical properties of prepared catalysts were characterized by X-ray diffraction (XRD) and X-ray photoelectron spectroscopy (XPS). The high catalytic activity of the Pt/MX catalyst was achieved thanks to the well-balanced conditions of the microwave synthesis, as well as the choice of MXene as the catalyst support.

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ECAT P 11

Carbonized ZIF-67 as catalyst for oxygen reduction reaction

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Metal-organic frameworks (MOFs) have garnered considerable scientific attention due to their tuneable characteristics which include surface area, pore structure, and chemical functionalities. Among these, zeolitic imidazolate frameworks (ZIFs) are particularly interesting for their chemical and thermal stability, making them a focal point of extensive research in various fields including catalysis, gas adsorption, electronic devices, and sensors [1]. Within the domain of catalysis, the oxygen reduction reaction (ORR) holds particular significance as a key process [2].

In this study, a novel hydrothermal method employing aqueous solutions at ambient temperature was employed to efficiently synthesize ZIF-67, thereby eliminating the need for harmful organic solvents, and reducing costs. ORR catalysts were fabricated by carbonizing ZIF-67 under an inert atmosphere at different temperatures sand ramping times. An essential parameter in the production of ZIF-derived MOFs is the annealing temperature, which appears to govern both the structure of the resultant product and its electrocatalytic performance [3]. It is widely agreed that activity notably decreases at elevated temperatures thus the carbonization was carried out at 800 and 900 °C with different ramp holding time. While cobalt is presumed to act as the catalytic centre, its exact nature remains unclear. Research suggests that combining cobalt with other metals enhances ORR activity compared to using cobalt alone, while others propose that cobalt loading and the atoms surrounding the cobalt ion determine ORR reactivity. In this study, we investigated the influence of carbonization temperature and found that holding the temperature at 800 °C for three hours results in the catalyst with the most positive onset potential for ORR. Additionally, the highest currents were observed in the explored potential range for material treated in this fashion, confirming its excellent properties. The apparent number of exchanged electrons was evaluated using the Koutecky-Levich equation, with the number of exchanged electrons being above three in studied potential range, and close to four at most negative potentials scanned.

Present results suggest that carbonization step can enhance the catalytic behaviour of the material, paving the way for further improvements in energy conversion applications. The fine-tuning of the ZIF-67 temperature transformations addresses challenges associated with increasing energy demands and underscores the potential of ZIF-67-derived materials in electrochemical applications.

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Catalytic performance of Pt-decorated nitrogen-doped Mn_2O_3-NiO for oxygen reduction and evolution

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The oxygen reduction reaction (ORR) and oxygen evolution reaction (OER) represent pivotal electrochemical processes with wide-ranging implications in energy conversion and storage technologies. However, both reactions are inherently sluggish, necessitating efficient catalysts to accelerate kinetics and enhance overall performance. Transition metal-based catalysts, including platinum, palladium, and non-noble metals such as iron, cobalt, manganese, and nickel, have gained significant attention for their catalytic activity and durability. Furthermore, using nanostructured catalysts, heteroatom-doped carbon materials, and metal oxides has broadened the spectrum of catalyst options, improving efficiency and cost-effectiveness.

In this work, we synthesized nitrogen-doped Mn_2O_3-NiO with a binary metal oxide (BMO) to N ratio of 2:1 by mixing BMO and melamine, followed by annealing in an inert environment. Subsequently, the synthesized material was decorated with Pt nanoparticles using the microwave-assisted polyol method, as described in the authors' previous work [1].

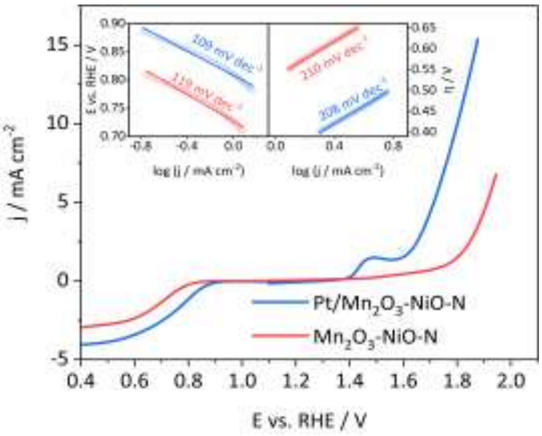

Figure 1. Polarisation curves for two tested materials in ORR and OER potential regions with the corresponding Tafel plots in the inset.

The catalytic activity of synthesized catalysts toward oxygen reduction and oxygen evolution was investigated in 0.1 M KOH; obtained polarization curves are depicted in Figure 1. Pt-decorated material showed notably better performance in comparison with non-decorated N-doped BMO in the ORR potential region, with 3.4 e^- exchanged in the elementary step of the reaction, a higher value of diffusion-limited current density reached at 1800 rpm, and a lower value of Tafel slope of 109 mV dec^{-1}. This was expected, given that Pt is well known as one of the best ORR catalysts. However, Pt-decorated catalyst also showed better performance in the OER potential region with lower onset potential, overpotential to reach benchmark current density of 10 mA cm^{-2} of just under 0.6 V, and lower value of Tafel slope of 208 mV dec^{-1}. Moreover, a relatively low value of ΔE ($\approx$ 1 V) as a measure of bifunctional performance was calculated for this material. The acquired value of ΔE is comparable with the value of 0.95 V calculated for the commercial Pt/C tested under the same experimental conditions [2]. Nevertheless, it is important to highlight that commercial Pt/C contains 40 wt.% Pt, whereas the material synthesized herein comprises only 20 wt.% Pt, rendering it significantly more cost-effective to produce.

Considering the preliminary findings, subsequent experiments will prioritize enhancing performance by making slight adjustments to the synthesis procedure and evaluating the synthesized materials' long-term stability.

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ECAT P 13

The design of advanced thin-film catalysts for electrooxidation of formic acid

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Successful development of catalysts for electrochemical formic acid oxidation (FAO) requires finding an optimal balance between catalytic performance (activity/stability/selectivity) and the catalyst cost. While platinum is one of the most active catalyst materials for FAO, it suffers from performance loss at low overpotentials due to poisoning with CO, which is one of the intermediates formed in the so-called indirect path of FAO.

In this work, we explored the synergistic effects of the supporting material and annealing temperature on the performance of Pt thin films over Cr support for FAO in acidic media. In an attempt to reduce the proneness of Pt to poisoning species *i.e.* CO and improve the catalytic performance of Pt/Cr at low potentials in the formic oxidation reaction, the as-prepared catalyst was modified using controlled thermal treatment. The influence of thermal treatment on the surface morphology was monitored using atomic force microscopy (AFM). The catalyst was electrochemically characterized with cyclic voltammetry and oxidation of CO monolayer, while the performance of the catalyst was tested in formic acid oxidation reaction.

Based on the obtained results it was concluded that the improved activity on the annealed Pt/Cr system is a consequence of surface reconstruction of Pt film with predominant (111) orientation. Compared to other facets, the (111) facet selectively favors the oxidation of HCOOH via the direct path, avoiding the formation of CO_{ad} at low potentials. Moreover, the Pt (111) facets offer improved stability of the catalyst compared to the as-prepared polycrystalline film. Finally, the Cr substrate also experiences improved stability after annealing, presumably due to the formation of a protective oxide layer. Thus, with the successful choice of the supporting material and annealing temperature, we were able to create a thin film catalyst with improved activity, selectivity, and stability, challenging conventional trade-offs in electrocatalysis.

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ECAT P 14

NiSe-doped carbons as cathodes for primary Zn-air batteries

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Zinc-air batteries represent promising devices for sustainable energy solutions, yet their widespread applications are limited due to the need for efficient, non-noble metal catalysts for oxygen reduction reaction (ORR). In this study, we address this challenge by synthesizing a series of NiSe-doped porous carbon materials through a straightforward, one-step carbonization process involving an ionic liquid containing Ni and Se. Characterization via XRF and FTIR confirmed the successful doping of NiSe into the carbon matrix. Subsequent electrochemical testing in both alkaline (0.1 M KOH) and neutral (0.1 M PBS) electrolytes revealed the superior ORR activity of the synthesized carbon materials. Our findings demonstrate high electrocatalytic performances and $4e^-$-ORR pathway in both electrolytes, underscoring the potential of NiSe-doped porous carbons as cathode materials for primary Zn-air batteries, thus advancing the quest for efficient and sustainable energy storage solutions.

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EDP P 01

Morphology and structure of electrolytically produced zinc dendrites from the alkaline electrolyte

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The alkaline electrolytes of zinc are widely used in a Zn-air secondary batteries which represent promising candidate for energy storage with many advantages relative to the other types, such as Li-air, Al-air, and Mg-air batteries [1]. These advantages are related with an abundance of Zn, low toxicity, and low cost, as well as by the fact that Zn possess a relatively high specific energy density [1]. One of the largest problems in a development of Zn-air batteries is dendritic growth caused by the uneven deposition of zinc in the charging process [2]. The solving of this problem implies the good knowledge of all phenomena related with Zn deposition, and regarding it, this study aims to establish a correlation between morphology and structure of electrolytically produced Zn irregular forms, especially Zn dendrites. Zinc was electrodeposited potentiostatically from the concentrated electrolyte (0.35 M ZnO in 6.0 M KOH) at overpotentials belonging to the end of the plateau of the limiting diffusion current density (η = 160 mV), and to the zone of the fast growth of the current density after the end of the plateau of the limiting diffusion current density (η = 220 and 280 mV). Morphology and structure of Zn particles were characterized by scanning electron microscope (SEM) and X-ray diffraction (XRD), respectively.

Morphology of Zn electrodeposits changed with the increase of overpotential of the electrodeposition from regular hexagonal and other regular crystal forms (Figure 1a) to the mixture of 2D (two dimensional) and 3D (three dimensional) dendrites (Figure 1b and 1c). The increase of overpotential of the electrodeposition led to an appearing and then intensification of hydrogen evolution reaction as a parallel reaction during Zn electrodeposition at the high overpotentials.

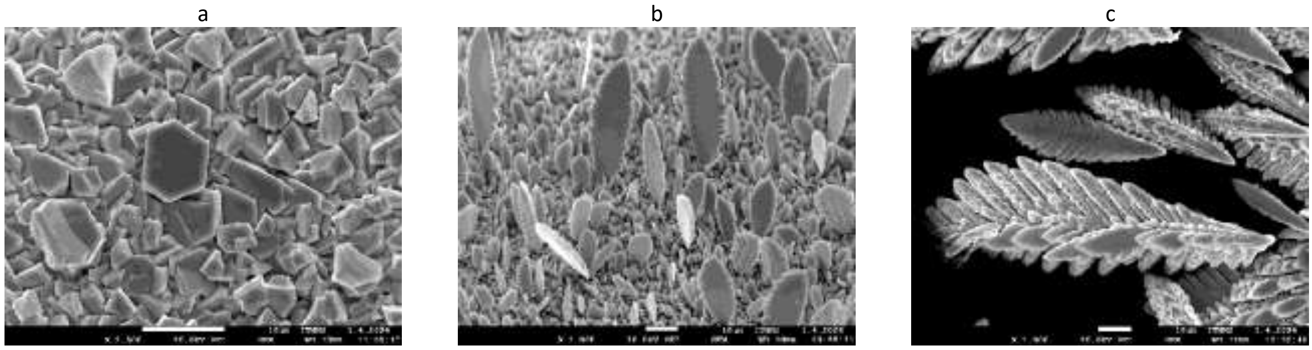

Figure 1. Morphology of Zn disperse forms electrodeposited at overpotentials of: a) 160 mV, b) 220 mV, and c) 280 mV. The amount of electricity: 3.0 mAh cm^{-2}.

In spite of various shapes, Zn particles electrodeposited at all three overpotentials exhibited the strong (002) preferred orientation. The explanation for this predominant preferred orientation can be found in an analogy with a electrolytic growth of lead dendrites from the concentrated electrolyte [3]. Although these two metals belong to different types of crystal lattice (Pb - face-cantered cubic type, and Zn - hexagonal close packed type), the common characteristic of dendritic growth is the preferred orientation in a crystal plane with the lowest surface energy. Namely, during growth of dendrites, this plane survives, while other crystal planes with the higher surface energy values disappear, causing the predominant orientation of Zn disperse forms in (002) crystal plane. In this way, interior of the Zn dendrites is constructed from (002) crystal plane, while tips and edges of Zn dendrites and other types of particles are from other crystal planes.

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EDP P 02

Electrochemical deposition of ruthenium oxide from deep eutectic solvent

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Transition metal oxides (TMOs) have gathered increasing attention in material science due to their good electrical, mechanical, optical properties and great chemical and thermal stability. Among them, ruthenium oxide (RuO_2), with its excellent catalytic performances has been the subject of numerous studies. It serves as a crucial material for electrodes in (electro)catalysis, energy storage systems, and semiconductor devices. RuO_2-based catalysts have shown good potential in many important reactions such as the low-temperature dehydrogenation of small molecules (NH_3, HCl, methanol), and have been utilized in industrial electrolysis for chlorine-alkali production [1,2]. There are numerous techniques to synthesize RuO_2 [1]. In response to the challenges associated with RuO_2 synthesis, and to customize the particle size and shape of RuO_2, an electrochemical deposition from a new class of non-aqueous electrolytes, namely the deep eutectic solvents (DESs), can be a good alternative. So far, there have been recorded some attempts to electrochemically deposit ruthenium/ruthenium oxides from DES [3,4].
This study focuses on the electrochemical deposition of ruthenium oxide onto palladium working electrode from choline chloride (ChCl): urea (1:2 ratio) DES at 80 °C with 0.01M Ru(III) ions concentration. $RuCl_3$ was added as a source of Ru ions in the working electrolyte. To determine the potential range available for Ru electrodeposition in DES, cyclic voltammetry (CV) on Pd working electrode in the electrolyte containing ChCl and urea was recorded. The potential window of electrochemical stability was between -1.2 and +0.3V *vs.* Pt. The electrochemical behaviour of Ru(III) in choline chloride-urea has been investigated at palladium using cyclic voltammetry (CV) and square wave voltammetry (SWV). The CV results showed only cathodic peaks without corresponding anodic counterparts, and SWV was used for further investigation in order to gain a better understanding of the Ru(III) electroreduction process. The electrochemical impedance spectroscopy (EIS) results indicate diffusion-controlled RuO_2 deposition. Relatively small deposition overpotential (-1.0 V) applied in the electrodeposition experiments, resulted in ruthenium oxide being electrodeposited. The morphology of the obtained deposits was characterized using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). X-ray diffraction (XRD) analysis of the produced particles provided conformation that the RuO_2 was formed onto a palladium working substrate.

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Development of electrodes for metal hydride-air batteries

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The rechargeable metal hydride (MH)-air battery features a cell configuration analogous to that of the Ni-MH battery, wherein the heavy nickel electrode is replaced with the lightweight air electrode, representing a primary advantage of these batteries. In general, the air battery is expected to have no limitations on potential discharge capacity, given that the positive active mass is oxygen sourced from the air. This implies that the rechargeable MH-air battery theoretically has an unlimited capacity of the gas diffusion electrode (GDE). The energy density of this battery depends on the specific capacity of the MH electrode, which varies depending on the type of alloy used, such as AB_5, AB, A_2B, AB_2, and others. A major problem facing the commercialization of an MH-air battery is the development of a charge-discharge stable GDE. Over the past 30 years, enormous efforts have been made to overcome this problem, mainly focusing on the development of bifunctional GDEs through their integration into rechargeable zinc-air batteries. On the other hand, MH electrodes have been widely studied and found practical applications. The development of a laboratory MH electrode and its adaptation in an MH-air battery is also a challenge facing researchers in the field. In this study, mechanically, chemically, and electrochemically stable GDEs with a composite structure (CGDE) of clinoptilolite + Teflonized carbon black in the gas diffusion layer were developed. More than 1000 cycles with a current density of ±10 mA cm^{-2} in continuous operation mode in half cell configuration were achieved. The as-developed GDEs meet the condition for predominantly Knudsen diffusion (average size of mesopores 7-15 nm). The optimization of the composition and structure of the MH electrode (with an alloy composition of $LaNi_{4.5}Co_{0.4}Al_{0.1}$) by introducing additional carbon black and spinel oxides of transition metals aims to improve its main characteristics: a discharge capacity increase of over 30 % and a charge/discharge endurance more than three times that of the basic MH electrode.

The design and construction of electrochemical cells allowing the systematic study of a large part of the main electrochemical characteristics of an MH-air battery resulted in satisfactory values for charge and discharge voltage, smooth loss of capacity, and a lifetime of about 1000 hours in continuous operation (with no pause between charge and discharge).

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EES P 02

Evaluation of nanostructured ZnO materials on the structure and performance of Pb/$PbSO_4$ electrode

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Batteries in micro-hybrid electric vehicles operate in partial state of charge and experience short charge and discharge pulses with high currents during regenerative braking (High-Rate Partial-State-of-Charge, HRPSoC duty). Research efforts in the past few years have demonstrated the benefits of carbon materials as additives to the negative plates of lead-acid batteries (LABs) providing higher levels of charge acceptance and delaying lead sulphate accumulation on the surface of the negative plates. At the same time, however, other properties such as high rate discharge and accelerated hydrogen evolution reaction (HER) leading to increased water loss may be negatively affected by carbon addition. Several different approaches are proposed in the literature to suppress the hydrogen evolution reaction on lead and lead-carbon electrodes. One example is addition of different metal oxides, organic substances, and metal ions with high HER overvoltage to the negative active mass (NAM) formulation or to the electrolyte. The influence of seventeen residual elements in lead on hydrogen- and/or oxygen-gassing rates of LABs has been investigated [1]. Only Bi, Cd, Sn and Zn are considered as "beneficial elements" for lead-acid batteries. Addition of ZnO and ZnSO4 to NAM is proposed in order to improve the HRPSoC performance and to control the HER [2].

The goal of the present study is to evaluate the effect of crystal morphology of ZnO powder samples with different crystallite size as additives to NAM aimed to improve the HRPSoC cycling performance of LABs and suppress the HER. The studied ZnO samples are synthesized by ultrasound assisted precipitation (UAP) and by a sucrose-assisted solution combustion method (SASC). The latter method was applied to prepare ZnO samples doped with Al or Mg ions. The thus synthesized materials are evaluated by means of powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) techniques. The XRD analysis confirms that materials obtained by the different methods have similar average crystallite size of about 30 to 40 nm. The TEM images demonstrate that the samples obtained by the UAP method have spindle-like morphology, while those obtained by the SASC method comprise almost spherical particles [3].

Small-sized laboratory lead-acid cells with one negative and two positive plates per cell are assembled and set to capacity, cycle life and hydrogen evolution tests. The nominal capacity of cells is 115 mAh. The tested ZnO samples are added during negative paste mixing in concentration of 0.05 % versus the leady oxide. All negative paste formulations contain also 0.5 % PBX51 carbon black (1400 m^2/g) (Cabot Corp. product). The thus prepared paste is applied to small-sized PbCaSn grids and these are subjected to standard curing and formation processes. For comparison, reference cells without ZnO additives are tested as well.

The impact of the studied ZnO additives on the discharge capacity of the negative plates is estimated at C/20 discharge current rate. The preliminary results show that ZnO additives to NAM do not have negative impact on cell discharge capacity. The effect of addition of ZnO in the negative plate on the cycle life of lead-acid cells is evaluated under simulated high-rate partial state-of-charge (HRPSoC) cycling conditions. The negative plate potential is measured during the cycling test. The control cell (without carbon additive) completes only 600 micro-cycles. Addition of ZnO (SASC) to NAM leads to considerable improvement in cycle life, more than 3800 micro-cycles. In contrast, the reference cell with 0.5% PBX51 but no ZnO in NAM completes about 3000 micro-cycles, against about 2900 for the cell containing also ZnO (UAP) additive and about 3500 micro-cycles completed by the cells with ZnO (SASC), doped with Al^+ or Mg^+, in NAM. In general, addition of ZnO (SASC), comprising spherical particles of 50-60 nm average size, to NAM produce 15-25 % improvement in cell cycle life in the HRPSoC duty.

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EES P 03

Investigating the influence of cell orientation, type of zinc electrode and electrolyte immobilization on the electrochemical performance of Ni-Zn battery cells

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The growing need for durable, environmentally friendly, and low-cost energy storage systems, characterized by high specific power, combined with the essential search for safe alternatives to Li-ion batteries, serves as the main factor for an ever-increasing number of research efforts devoted to rechargeable Ni-Zn power sources. Despite their safer nature and competitive power density and price, the rechargeable alkaline Ni-Zn battery system has not yet penetrated deeply into the market due to its tendency to gradually decrease in capacity over multiple charge and discharge cycles and its relatively limited cycle life The performance-limiting issues include passivation of the surface of the zinc electrode during discharge, electrode shape changes over repeated cycling, and formation of zinc dendrites during charge. These undesirable processes are primarily attributed to the gradual dissolution of zinc in the electrolyte, which mainly consists of an aqueous solution of potassium hydroxide. Therefore, the main challenge is to find suitable solutions for improving zinc electrode design, electrolyte composition and the development of innovative materials in order to achieve high resistance of zinc against dissolution, leading to an increase lifespan of the Ni-Zn batteries.

For successful operation of a nickel-zinc battery, it is necessary to know a number of important technological parameters - the composition and amount of the active mass of the electrodes, the volume and composition of the electrolyte, the types of separators, the geometric position of the element under test, *etc.* In this regard, the effect of the orientation of the nickel-zinc battery element on the initial capacity for two types of zinc anodes - pasted and electrochemically deposited over copper foam current collector was experimentally investigated. Additionally, the dependence of discharge/charge capacity during cycling of different types of Ni-Zn symmetric cells has been studied. The cells were assembled with an electrode package containing a commercially available sintered Ni cathode and Zn anode, prepared either by pasting zinc powder with AGAR binder or by zinc electroplating. The electrolyte utilized was potassium hydroxide, which was either immobilized within the pores of the active material or incorporated into a gel formulated from PVA with suitable additives. Phase composition and morphology analysis of the active mass before and after cycling by X-ray Diffraction (XRD) and Scanning Electron Microscopy (SEM) were analysed.

The results obtained show that the cell assembled with the electroplated Zn anode, combined with the gel electrolyte possesses a slightly longer cycling life (up to 470 cycles) compared to that prepared by pasting, although the latter demonstrated a more stable capacity versus time.

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Insertion of Li^+, Na^+ and Mg^{2+}-ion into VO_2(B) from aqueous nitrate solutions

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The metastable VO_2(B) is known for its ability to reversibly intercalate different ions. The nanostructured VO_2(B) was suggested as cathode material for Na^+-ion and Mg^{2+} -ion batteries with organic electrolytes[1,2]. The composite VO_2(B)-reduced graphene oxide was tested in organic electrolytes as a cathode for Li^+-ion and Na^+-ion batteries[3]. In our previous research VO_2(B) was tested as an anode in aqueous Li^+-ion battery VO_2(B)/$LiNO_3$(sat.)/$LiCr_{0.15}Mn_{1.85}O_4$.[4] The electrochemical performance of VO_2(B) for battery applications may be highly dependent on morphology and preferential growth of crystals. Herein, the insertion of Li^+, Na^+ and Mg^{2+} into solvothermally prepared VO_2(B) from aqueous nitrate solutions is presented in comparative electrochemical study, using cycling voltammetry (CV) and galvanostatic (GS) cycling.

CV conducted at 10-50 $mV \cdot s^{-1}$ showed fast and stable insertion/deinsertion of Li^+, Na^+ and Mg^{2+}-ions into/from VO_2(B).[5] The insertion of each of three ions from nitrate solutions ($LiNO_3$, $NaNO_3$ and $Mg(NO_3)_2$), at scan rate 10 $mV \cdot s^{-1}$, appeared as a strong cathodic peak at negative potentials (-0.677 V - Li^+, -1.040 V - Na^+ and -0.795 V - Mg^{2+}) *vs.* SCE. The deinsertion of Li^+-ions occurred also in the form of single peak, at -0.502 V, while the extraction of both Na^+-ions and Mg^{2+}-ions appeared as a multi-step, most likely as a two-step process, Figure 1. In the case of Na^+-ion the first anodic peak of relatively low intensity, appears at -0.860 V while the remaining two, much stronger and overlapped peaks, are significantly shifted in the positive direction at 0.0 V and +0.240 V *vs.* SCE. The extraction of Mg^{2+}-ions is accompanied by a strong peak at -0.583 V and lower intensity overlapped peaks at 0.030 and 0.160 V. The interrelationship of all redox peaks, obtained for $NaNO_3$ and $Mg(NO_3)_2$ aqueous solutions, was further investigated by shifting upper scan limit to lower potentials which exclude anodic peaks at positive potentials and then by returning this scan limit to starting value. In this way it was found that main deinsertion peaks of Na^+-ion are strong overlapped peaks at positive potentials, while all deinsertion peaks of Mg^{2+}-ion should be taken as important. Galvanostatic (GS) experiments with VO_2(B) electrode in aqueous nitrate solutions were performed at current rates 200, 500, 1000 $mA \cdot g^{-1}$, also in three electrode cell (Pt – counter and SCE reference electrode). The most stable discharge/charge process, with smallest capacity fade, was obtained for all three ions at highest current rate 1000 $mA \cdot g^{-1}$. At the end of GS cycling at current rate 1000 $mA \cdot g^{-1}$ the insertion/extraction capacities of VO_2(B) were 99.1/96.2 $mAh \cdot g^{-1}$ for Li^+, 92.3/77.8 $mAh \cdot g^{-1}$ for Na^+ and 136.0/118.8 $mAh \cdot g^{-1}$ for Mg^{2+}. The best GS performance of VO_2(B), with the highest Coulombic efficiency (97 % at 1000 $mA \cdot g^{-1}$), was obtained for Li^+-ion. Voltage profiles in charge indicate a two-step extraction of Mg^{2+} ions, while the extraction of Na^+ ions manifest itself more as a one-step than a two-step process.

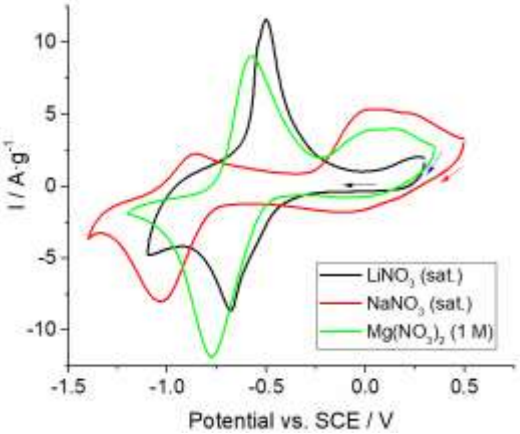

Figure 1. Cyclic voltammograms of VO_2(B) at 10 $mV \cdot s^{-1}$ in different nitrate solutions

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EES P 05

Hybrid supercapacitors with nickel manganite as a cathode and sodium alginate-derived carbon as an anode material

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Electric energy storage (EES) devices are mainly batteries and supercapacitors. Each have their own set of characteristics. While batteries store energy via diffuse-controlled, Faradaic redox processes, supercapacitors store energy by rapidly forming electrostatic double-layer. Batteries exhibit high energy density, while supercapacitors exhibit high power density [1]. Supercapacitors can have hundreds of thousands life cycles while lithium ion batteries, for example, have around 1000 of them. Hybrid supercapacitors are relatively novel devices that tend to combine advantages of both batteries and supercapacitors while overcoming their disadvantages. Hybrid supercapacitors employ both types of electric energy storage mechanisms, Faradaic redox and capacitive processes [2]. One electrode, typically composed of metal oxides, hydroxides, or phosphates, stores energy through redox reactions, while the other electrode, typically constructed from carbonaceous materials, stores energy through capacitive processes.

Nickel manganite, $NiMn_2O_4$, is a versatile transition metal oxide, with interesting electrical and magnetic properties. Its inverse cubic spinel structure indicates that it contains a variety of nickel and manganese ions at different sites in different oxidation states. This unique arrangement enables high electrical conductivity [3]. $NiMn_2O_4$ has been in the focus of electric energy storage research along with other transition metal oxides in order to downsize the production of cobalt- and lithium-derived oxides in devices that are already commercially used.

Sodium alginate is a polysaccharide naturally found in brown algae. It can be used to synthesize carbonaceous materials [4].

The work presented contains details on synthesis, characterization and EES properties of nano-sized nickel manganite synthesized via electrospinning and glycine-nitrate sol-gel combustion processes followed by calcination at 400 and 800 °C to obtain pure spinel oxide. Amorphous carbon was also synthesized via pyrolitic carbonization of lyofilized sodium-alginate hydrogel. Nickel manganite and amorphous carbon were tested in 6 M KOH, 2 M LiOH, 1 M Na_2SO_4 and 1 M H_2SO_4 in a three-electrode cell via cyclic voltammetry and galvanostatic chronopotentiometry. $NiMn_2O_4$ showed the highest activity in alkaline electrolytes, while amorphous carbon showed capacitive-type energy storage performance in both alkaline and acidic electrolytes. Standard two-electrode sandwich cell was formed with $NiMn_2O_4$ as a cathode and amorphous carbon as an anode material. The cell performance was evaluated via cyclic voltammetry and galvanostatic chronopotentiometry followed by stability tests. Considerable capacitance values of the formed hybrid supercapacitor devices were obtained.

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EES P 06

Exploring the impact of temperature variation on the specific surface area evolution of hydrothermally synthesized MnO_2 for supercapacitors application

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Manganese dioxide is well known technologically attractive and extensively researched material, offering variety of applications due to its polymorphic variations. The physicochemical and surface characteristics of MnO_2, important for its electrochemical behaviour, are tightly related to its crystalline structure, particles size and morphology. Consequently, this material in different polymorphs attracts substantial attention as an electrode material among different energy storage systems, including alkaline batteries, Li-ion batteries, and supercapacitors.

This work represents the possibility of modifying the phase structure and morphology of hydrothermally prepared MnO_2 by variation of the synthesis temperature. Our main objective is to clarify the impact of the synthesis conditions on the specific surface area of the final material, thereby assessing its potential suitability as an electrode material in hybrid supercapacitors.

The hydrothermal synthesis of the MnO_2 nanostructures was performed using initial aqua solutions of $KMnO_4$ and $MnSO_4{\cdot}H_2O$, subjected to varying temperatures (100, 120, 140, 160, 180 °C).

Phase composition analysis was conducted via X-ray diffraction (XRD), while scanning electron microscopy (SEM), transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were employed for morphology and structural characterization. Specific surface area was determined using the Brunauer-Emmett-Teller (BET) method, with total pore volume calculated following Gurwitsch's rule. The pore size distribution was estimated using the Barrett-Joyner-Halenda method.

The XRD patterns prove the formation of α-MnO_2 crystallographic phase together with co-formed intercalating compound $K_{0.27}MnO_2{\cdot}0.54H_2O$ at elevated temperature.

The results obtained demonstrate the highest specific surface area (156.7 m^2/g) of the sample thermally annealed at 160 °C among the series under investigation. This observation motivates further exploration of the electrochemical properties of this mixed phase to elucidate its potential as an electrode material in solid-state supercapacitors.

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Zn-ion battery improved by reduced graphene oxide/MXene 2D materials

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Rechargeable batteries are one of the most important issues at present, especially given their application in portable electronic devices and electrical vehicles. Li-ion battery has made a significant influence to our society due to high available energy density. However, it does not meet the needs of modern society. One of the disadvantages of this battery is usage of organic electrolyte and its flammability, high cost, toxicity, and the need to provide perfectly dry environment during the manufacturing process. Additionally, conductivity of the organic electrolyte used in Li-ion battery is two orders of magnitude lower compared to aqueous media, which decreases performance rates. All aforementioned properties encourage development of safe, less expensive and green battery devices, such as aqueous Zn-ion battery (ZIB). ZIB shows high potential for commercialization, however, to achieve its practical application an additional investigation of fundamental knowledge on Zn dendrite formation, Zn^{2+} intercalation and reaction mechanisms, electrolyte performance and optimization related to cathodes materials needs to be done [1]. The aim of this work was to study Zn deposition process on various supports such as reduced graphene oxide (rGO) or MXene. It is expected that these materials will influence Zn deposition process and prevent dendrite growth. Furthermore, high surface area of rGO or MXene, along with their flexibility and freestanding properties will contribute to the development of new improved Zn anode materials. The investigation of anode materials was carried out in three/two electrode system by using chronopotentiometry, chronoamperometry, cyclic voltammetry and electrochemical impedance spectroscopy methods. Morphological characteristics of the layer were monitored by scanning electron microscopy and optical microscope.

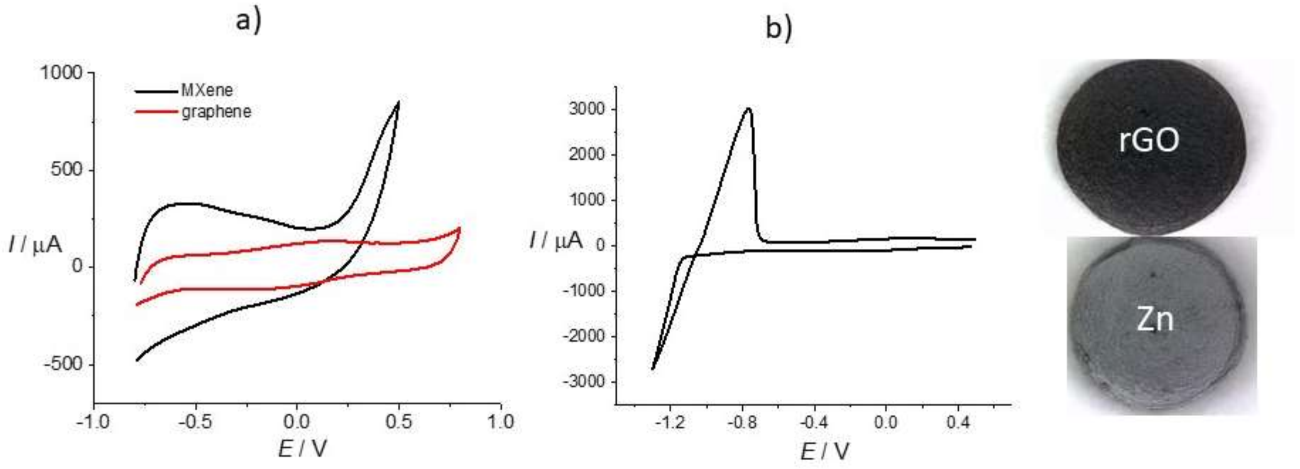

Figure 1. Cyclic voltammetry response of a) rGO and MXene, b) Zn deposition at rGO electrode

Acknowledgement: This research has been supported by NATO Science for Peace Multi-Year Project ˝High Energy Calcium - Oxygen Batteries˝, NATO SPS G5910.

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Electrochemistry of calcium electrode in organic solvents

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Multivalent battery technologies based on alkali-earth metals anodes have arisen as a promising alternative for replacing lithium-ion batteries, alleviating some inherent problems connected with resources, value chains and also performance. Metallic magnesium and calcium anodes possess high energy densities, much higher than the graphite used in current lithium-ion batteries and are comparable to lithium metal anodes. Additionally, these metals are not as prone to dendrite formation as lithium metal, reducing the risks of fires or explosions. However, the inhibiting layers, which form on these metals in organic solvents, are very stable and do not allow fast migration and/or diffusion of calcium cations through them, quite unlike the SEI layers enabling the operation of lithium-ion batteries. To develop calcium batteries with reversible redox reactions it is therefore necessary to carefully optimize the electrolyte and tailor the surface layers formed on the metal anode.

In this work we have tested a series of different electrolyte solvents (ethylene carbonate, propylene carbonate, dimethylformamide, acetonitrile, THF, DME *etc.*) with either $Ca(BF_4)_2$ or $Ca(TFSI)_2$ salts to understand the mechanisms and kinetics of calcium plating/stripping. We used Ca metal disc electrodes or inert Pt electrodes in three-electrode cells with Pt-pseudo reference electrodes, and activated carbon as counter-electrodes. A range of different electrochemical methods were used: cyclic voltammetry, electrochemical impedance spectroscopy, EQCM, potential step methods, *etc*. Detailed characterization of the composition and the structure of the obtained surface layers was done by FTIR spectroscopy and X-ray diffraction.

We correlate the influence of the solvents and salts with the electrochemical behaviour of the calcium metal anode, which advances the field of calcium metal layers and opens ways to improved stability and efficacy in calcium battery-based energy storage solutions.

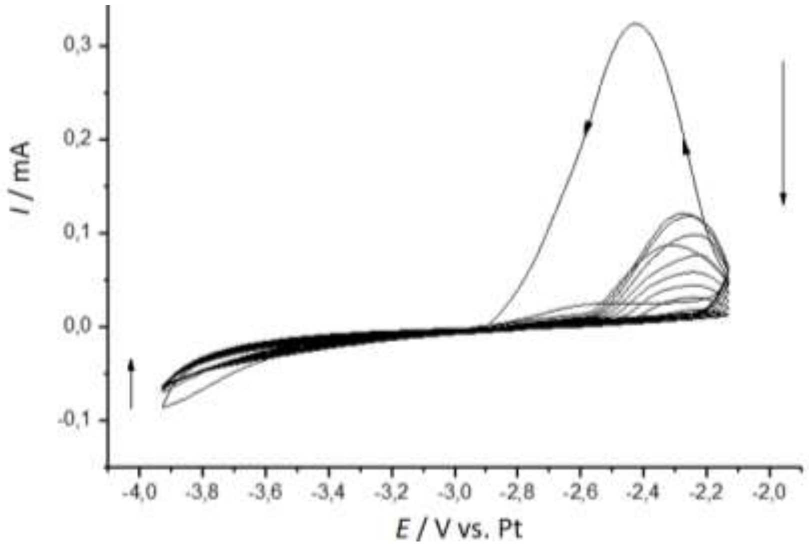

Figure 1. Plating and stripping of calcium electrode in $Ca(BF_4)_2$ / ethylene carbonate. Scane rate 10 mV /s

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EES P 09

Influence of phosphate containing additive in the formation electrolyte on the structure and cycling performance of lead battery positive active mass

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Lead batteries are one of the most popular energy sources that have applications in micro and mild electric hybrid vehicles, stationary energy storage systems and smart utility grid units. Their low cost and high reliability generally make lead batteries an appealing choice. The lead battery capacity decline over time as the battery is repeatedly charged and discharged. This effect is especially noticed at partial state-of-charge (PSoC) cycling conditions. In many cases, this is due to the processes taking place on the positive electrode of the battery. The major factors contributing to the decline in capacity of the positive plates during operation are progressive decrease of the electrical contact between the PbO_2 particles of the positive active mass (PAM) and the grid, and formation of a layer of $PbSO_4$ crystals on the electrode surface that isolates a fraction of the active mass thus reducing its utilization. During charge of a lead battery, the positive grid is oxidized, and a boundary layer forms between the grid and the active mass.

The focus of our investigation is to study the effects of phosphate containing substance as formation electrolyte additive on the structure of PAM at 17.5 % depth-of-discharge (DoD) employing PSoC protocol for automotive applications. The electrolyte additive selected for this study is similar to the one of the substances recently reported by our team [1, 2]. The investigated amounts of phosphate substance added to cell electrolyte (0.1, 0.3, 0.6 and 1.2 wt.%) were dissolved in 1.25 g/cm^3 H_2SO_4 solutions. Flooded type laboratory test cells with 2 positive plates and 3 negative plates with rated capacity of 4.0 Ah at 20 h rate of discharge and 50 % utilization of PAM were used to evaluate the influence of the selected electrolyte additive. Blank cell without the additive in the electrolyte was also tested. After formation the cells are subjected to the following electrical tests: C_{20} capacities and 17.5 % DoD test. The phase composition, morphology and microstructure, specific surface, and pore structure of freshly formed and cycled PAM samples was determined by X-ray diffraction, scanning electron microscopy, BET method and Hg porosimetry.

On grounds of the obtained results of the present study, it can be concluded that in the presence of studied additive in the formation electrolyte the specific surface area of PAM enlarged. The cycle life of the cell doped with 0.3 wt.% phosphate containing substance is 2100 cycles, which is a remarkable ~2× improvement *vs.* the blank cell. After cycling test with 17.5 % DoD XRD data confirm that addition of phosphate containing substance in the electrolyte suppresses formation of β-PbO_2 structure with high degree of crystallinity whereas preserves higher content of the α-PbO_2 phase. After cycling for the PAM of Blank sample the volume of pores with radii below 0.2 µm considerably decrease. In contrast, for the PAM of sample formed and cycled in the presence of 0.3 % A, the volume of pores with radii below 0.2 µm increases.

These results demonstrate that selected substance is promising additive for lead batteries that operate under partial-state-of-charge conditions.

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EES P 10

Performance and corrosion of aluminium-air battery in mixed electrolyte system

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Aluminium-air battery is a type of metal-air battery that utilizes aluminium as the anode, air as the cathode, and an electrolyte solution to facilitate the electrochemical reactions. It is regarded as one of promising battery for future because it offers several advantages including high theoretical energy densities, as well as environmental friendliness, abundancy, and relatively inexpensiveness of aluminium metal [1,2]. Major challenges of aluminium-air battery, however, are limited rechargeability and corrosion of the aluminium anode upon its utilization. This research studies performance and corrosion of aluminium anode in aluminium-air battery with copper as a cathode and mixed electrolyte solution with different ratio of sodium hydroxide (NaOH) and sodium chloride NaCl). To elucidate the influence of air, the battery was operated with and without aeration at the cathode side. All the experiments were conducted under temperature of 30 °C. Performance of the constructed battery is tested using the battery-testing system (Landt, CT3002A Model), while corrosion of the aluminium anode is evaluated by measuring the weight loss of the anode upon its use. The Surface Morphology of aluminium anode before and after the use is characterized using scanning electron microscope (JEOL, JSM-6010LA Model). Monitoring the change of anode mass as well as analysis of the aluminium anode surface (Figure 1) indicates that although aluminium-air battery with NaOH electrolyte gave the highest power output due to the strong-base property of NaOH using NaOH-NaCl mixed electrolyte could significantly lead to much lower corrosion rate of aluminium anode in comparison with the battery that used only NaOH as its electrolyte. The aluminium-air battery using mixed electrolyte with NaOH:NaCl ratio of 1:19 was further tested for its performance under constant discharge current of 0.75, 1.5 and 3 mA. As shown in Table 1, discharge current clearly affected the battery performance and corrosion rate of the anode. The lowest anode corrosion of 0.64 mg·cm^{-2}·h^{-1} and highest energy density of 193.15 Wh·kg^{-1} was achieved under the discharge current of 0.75 mA.

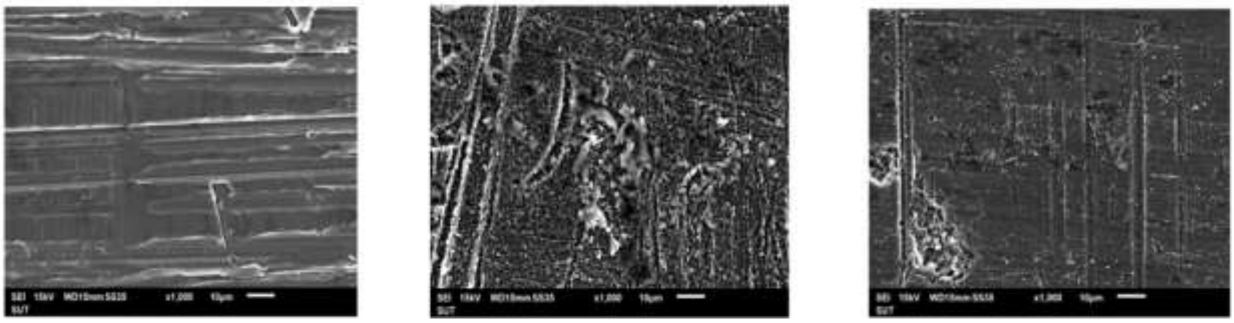
(a) (b) (c)

Figure 1. SEM image of aluminium (Al) electrode surface (a) new (unused) Al electrode (b) Al electrode of Al-air battery with mixed electrolyte with NaOH:NaCl ratio of 1:1 and (c) Al electrode of Al-air battery with mixed electrolyte with NaOH:NaCl ratio of 1:19

Table 1. Corrosion rate and performance of Al-air with mixed electrolyte with NaOH:NaCl ratio of 1:19 under different discharge current

Discharge current, mA	Corrosion rate, g·cm^{-2}·h^{-1}	Working time, h	Discharge capacity, mAh	Energy density, Wh·kg^{-1}
0.75	0.64	5.50	4.13	193.15
1.5	0.83	6.00	9.00	104.03
3	1.28	3.23	9.69	23.85

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Environmentally friendly electrode materials for solid-state supercapacitors: Green synthesis of MnO_2 nanoparticles from plant extracts

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Recent advances in the field of nanotechnology and nanoscience are focused on the development of new materials with diverse structures and shapes using a green synthesis approach that is as environmentally friendly as possible. Plant extracts, rich in natural biological compounds, have emerged as valuable resources for synthesizing nanomaterials due to their reducing and capping properties. These nanomaterials find applications across various fields such as catalysis, batteries, sensors, microelectronics, and optoelectronics, including energy storage systems. In this study, MnO_2 nanoparticles were synthesized using plant extracts of *Calendula officinalis* or *Tilia cordata*. The obtained materials were subjected to comprehensive physicochemical characterization by UV-Vis spectrophotometry, transmission electron microscopy (TEM), X-ray diffraction (XRD) and Brunauer-Emmett-Teller (BET) analysis. The successful synthesis of MnO_2 nanoparticles was confirmed. In particular, MnO_2 synthesized with extracts *of Calendula officinalis* (CO-MNO_2) showed a specific surface area four times higher (80 $m^2\ g^{-1}$) than that obtained for MnO_2 synthesized with *Tilia cordata* (TC-MnO_2, 19 $m^2\ g^{-1}$). There was a significant difference in their average pore diameter (13 *vs.* 9 nm), which can be explained by the lower percentage of antioxidant activity for CO-MnO_2 compared to TC-MnO_2, suggesting a slower formation of MnO_2 with higher BET surface area.

The electrochemical properties of MnO_2-NPs as a positive electrode material in a hybrid solid-state supercapacitor were evaluated using CV curves, galvanostatic discharge/charge and long-term tests. A carbon xerogel was employed as the negative electrode material, while a commercial membrane, Aquivion®E87-05S membrane pre-activated in 1 M Na_2SO_4, served as the electrolyte. For comparison, parallel experiments were conducted in a symmetric cell.

The obtained results showed that MnO_2 synthesized from Calendula officinalis extract exhibited the highest discharge capacitance, superior cycling stability, high current efficiency and energy density of 37 $Whkg^{-1}$ at 384 Wkg^{-1} in the voltage range of 0 to 1.6 V.

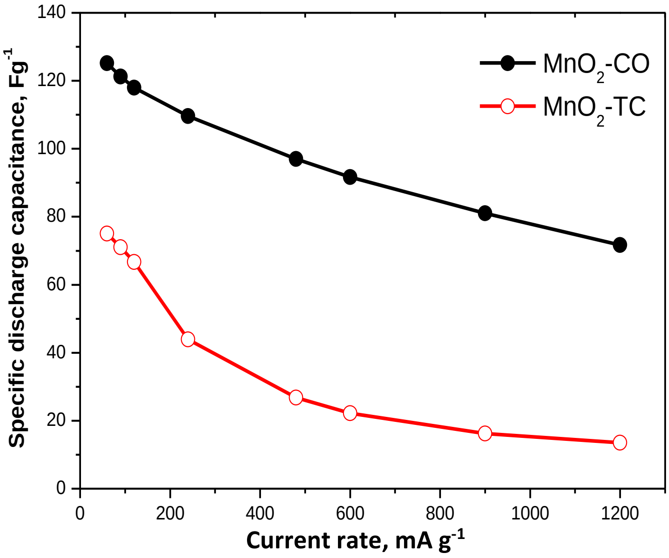

Figure 1. Specific discharge capacitance as a function of the current rate of solid-state supercapacitors with "green" MnO_2

The obtained results can be attributed to the differences in the structure and morphology of the synthesized samples. Furthermore, they underscore the potential of MnO_2 derived from Calendula officinalis extract as a promising eco-friendly electrode material for solid-state supercapacitors.

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Are fractals useful for supercapacitor applications? – A case of Fe_2O_3 negative electrodes

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Materials for supercapacitor applications need high specific surface area to encourage surface charge storage. Hence, several types of morphologies *e.g.* nanoflowers, nanorods, nanofibers *etc.* have been engineered for these applications by various research groups. Most of these materials show promising charge storage performance.

Recently, a different class of morphologies *viz.* 'Fractals' – spatially self-repeating structures – have been explored for supercapacitors. Hota *et al*. reported that fractals of RuO_2 exhibit the highest areal capacitance of ~11 mF cm^{-2} at 0.1 mA cm^{-2}. We recently demonstrated that fractal-like structures of Fe_2O_3 show a remarkable performance of ~2700 F g^{-1} at 1 A g^{-1}. Inevitably, fractals always have the surface area effects coupled with them. Hence, a morphology with large fractal dimension can possess high specific surface area.

Consequently, some questions are: (i) Are fractals indeed useful for supercapacitor ap-plications? (ii) Can fractality be exploited? (iii) How to decouple surface area effects from fractality? (iv) What are the exclusive effects of the fractal on charge storage mechanism?

These questions are addressed here by studying Fe_2O_3 – a constituent of the commonly available iron oxide – as a negative electrode material. Fe_2O_3 was hydrothermally synthesized in fern, flake and microsphere morphologies with similar specific surface areas (Figure 1a). This was purposefully done to keep the surface area effects the same across these morphologies. The negative electrodes are fabricated by supporting them on nickel foam (NF). The fractal dimensions of these morphologies were estimated geometrically and from electrochemical impedance spectroscopy (FD_{EIS}). The estimated FD_{EIS} for Ferns, Flakes and Microspheres are ~2.50, ~2.36 and ~2.19, respectively. The Fern@NF electrode exhibits the highest specific capacitance (C_{sp}) of ~2708 at 1 A g^{-1}, respectively with a ~94 % capacitance retention after 2000 charge/discharge cycles. Interestingly, the non-Faradaic capacitive surface charge storage from cyclic voltammetry increases with FD_{EIS} from microspheres to ferns. Often, this surface charge storage contribution is modelled using constant phase element (Z_{CPE}) in equivalent electrical circuit (Figure 1b). Our study shows that Z_{CPE} scales inversely with FD_{EIS}. Thus Ferns, with the highest FD_{EIS} exhibit the lowest Z_{CPE}, leading to the highest C_{sp} (Figure 1c).

Hence, fractal-like structures are useful for supercapacitor applications by promoting capacitive surface charge storage through low Z_{CPE}. Fractality of the morphology can be exploited in supercapacitor applications as it is a natural feature in some morphologies of materials which grow freely in nature – *e.g.* iron oxide.

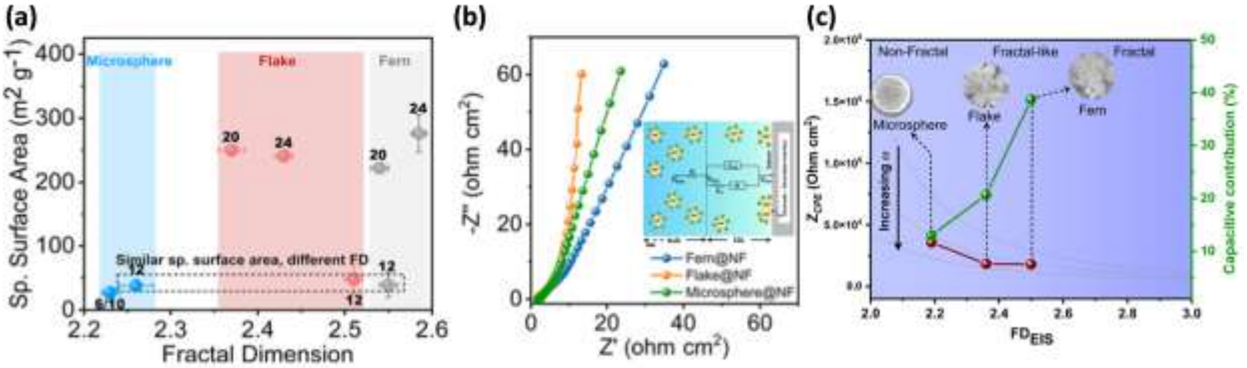

Figure 1. (a) Morphologies with similar specific surface area but different fractal dimensions (the numbers show synthesis duration in hours); (b) Obtained Nyquist plots are modelled using the equivalent circuit shown in the inset; (c) Lower Z_{CPE} leads to higher capacitive contribution in morphologies with larger fractal dimension (FD_{EIS}).

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EIF P 01

Discretization of the basic electrochemical properties of oxygen-evolving IrO_2-Ta_2O_5 electrodes as a tool to evaluate the electrode uniformity and operational behaviour

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Analysis of basic electrochemical properties of oxygen-evolving IrO_2-Ta_2O_5-coated titanium electrodes is presented as a tool to evaluate the coating uniformity and corresponding electrode electrolytic stability. Coating was prepared using conventional thermal decomposition. Three random positions at the electrode surface were subjected to the potentiodynamic polarization, cyclic voltammetry, electrochemical impedance spectroscopy and accelerated stability test in 10 % H_2SO_4 solution.

Ti anode was prepared before applying the coating. After cleaning in acetone and deionized water, the anode was immersed in a boiling 10 % oxalic acid solution to obtain a uniform and rough surface. The anode was then cleaned in ethanol and dried at room temperature. Precursor, which is used for the preparation of the coating, $H_2IrCl_6 \times 6H_2O$ and $TaCl_5$, in a certain molar ratio, were dissolved in alcohol mixture and applied in layers, using the drop casting method, on the Ti porous anode.

Evaluated electrocatalytic and electric parameters and their changes upon coating destabilization during oxygen evolution at different current densities were correlated to coating morphology and presented as the coating uniformity indicators. It was found that coating activity relates to morphology-caused distribution of electric parameters, whereas the activity loss is the consequence of IrO_2 exhausting from the coating surface layers. Interior of destabilized coating was found still reach in IrO_2. Presented analysis appears useful for managing the coating composition and structure with respect to required operational conditions.

Acknowledgments: This research has been financially supported by the Ministry of Science, Technological Development and Innovation of Republic of Serbia (Contract No: 451-03-66/2024-03/200026) and the Science Fund of the Republic of Serbia under grant no 6666.

EIF P 02

Electrochemical dissolution of gold using ionic liquids

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In this presentation we will address the environmental impacts of traditional gold mining and refining methods, highlighting the use of hazardous chemicals and the resultant pollution, together with the significant energy consumption and carbon emissions associated with gold production from ore, contrasting it with the relatively lower environmental impact of gold recycling [1]. Various alternative recycling methods [2], including electrochemical processes and the use of ionic liquids, are explored as means to reduce chemical usage and environmental harm. Ionic liquids, with their unique properties [3], are investigated as promising media for the electrochemical dissolution of gold, offering insights into the formation of gold complexes and their effectiveness in the recycling process. The study employs in situ Raman spectroelectrochemistry and ab initio calculations to elucidate the mechanisms underlying gold dissolution in ionic liquids, aiming to optimize environmentally friendly recycling methods while minimizing ecological footprint.

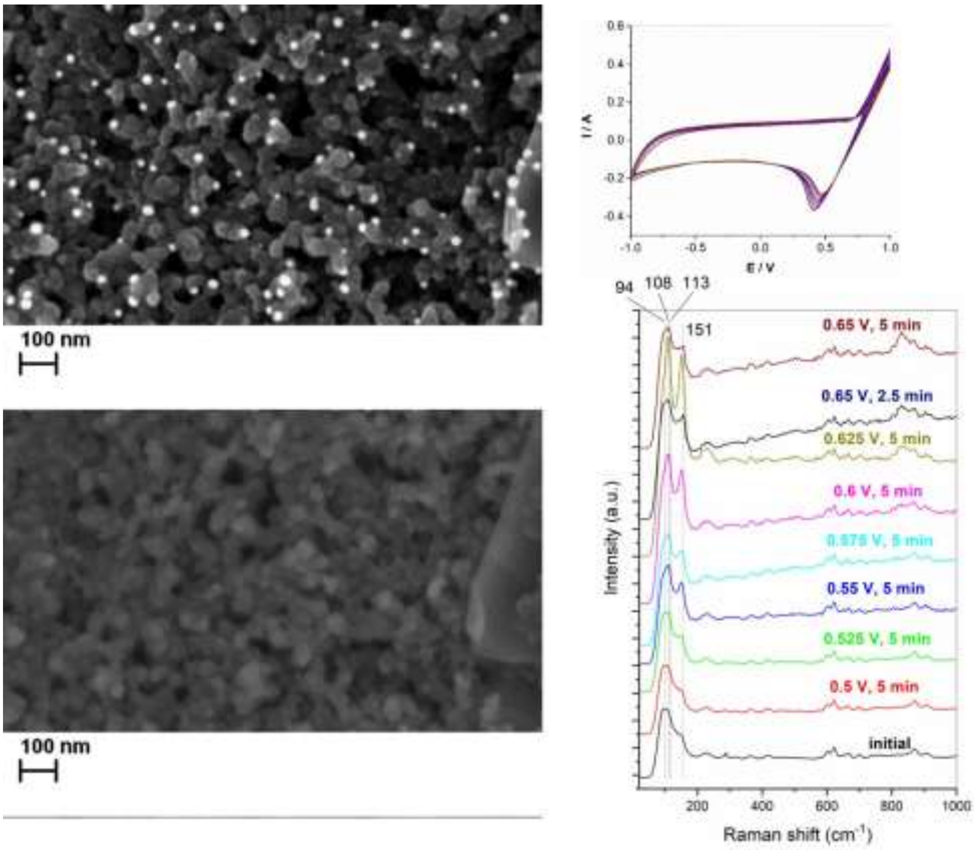

Figure 1. Top and bottom left: before and after SEM image of AuNP dissolution in 1-methyl-3-propylimidazolium iodide using 10 CV cycles depicted in top right image. Bottom right: in-situ Raman spectroelectrochemistry using amperometry at different potentials.

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Extended characteristic polynomial estimating the electrochemical behaviour of azulene thiophen–vinyl–pyridines

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A series of 6 azulene thiophen–vinyl–pyridine ligands for which two electrochemical properties (oxidation (E_a) and reduction (E_c) potentials) were collected in a recent study (see Table 3 in [1]) was subjected to (i) raw molecular modelling with Merck molecular force field (MMFF, see [2]), followed by (ii) computational analysis using families of molecular descriptors. Two descriptor families were considered in this analysis, Fragmental Matrix Property Indices (FMPI, as seen in [3] and [4]) and Extended Characteristic Polynomial (EChP, as seen in [5] and [6]). The results show that EChP is able to well distinguish between ligands as well as to provide a high estimation capability (R^2> 0.9990 for E_a; R^2> 0.9998 for E_c). As it is known, MMFF method is a very good first level of approximation for molecular geometry. Thus, further investigation is required in order to validate these preliminary results. The results with FMPI are not spectacular - they are inferior to those with EChP, and this suggests that the nature of the property - the reduction and oxidation potentials - is localized. A functional group or a position in the structure is more suitable to express an electrochemical property. Figures 1 and 2 give estimates of the association between the chemical structure and the electrochemical potentials by means of the individuals "RDCN0940" and "LEGN0705" members of the family of extended characteristic polynomials.

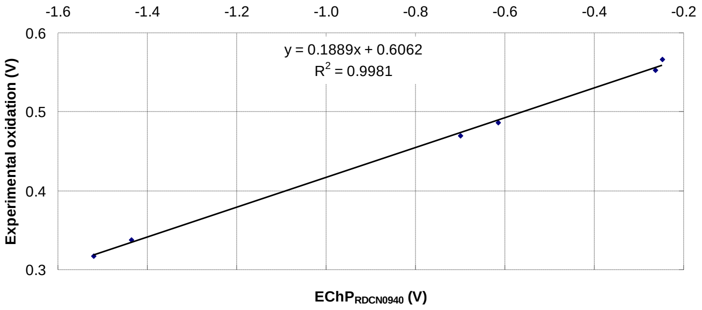

Figure 1. Oxidation as linear function of RDCN0940 extended characteristic polynomial

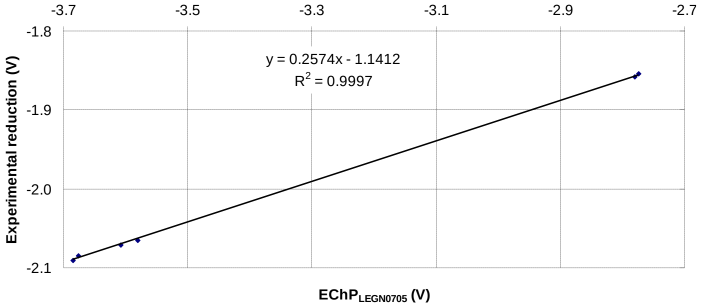

Figure 2. Reduction as linear function of LEGN0705 extended characteristic polynomial

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ENM P 02

Electrochemical and biological studies on bis tetrahydrocridine derivatives

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In order to modulate their biological activity, new species of bis tetrahydroacridines were synthesized and characterized by chemical analysis, ESI-MS, IR, UV-Vis-NIR, EPR spectroscopy.

In this research electrochemical, antimicrobial activity, quantum computed investigations (DFT) and molecular docking studies were conducted in order to highlight the correlation between electrochemical parameters (redox potentials) and the predicted quantum reactivity parameters derived from energetical levels of frontier molecular orbitals; also, correlations between antimicrobial analyses results and the biomolecular interactions of the complexes with some enzymes responsible for the survival of these microbes were obtained using molecular docking.

The electrochemical study was performed by cyclic voltammetry, differential pulse voltammetry and rotating disk electrode voltammetry in acetonitrile/ dimethylformamide in presence of tetrabutylammonium perchlorate for different concentrations of each target, at different scan rates and electrode rotation rates. Combination of electrochemical analysis and DFT simulations allowed investigating systematically the effect of different substitution on the tetrahydroacridine skeleton, which affects the electrochemical behaviour.

Previous works confirmed the possibility to assess electrochemical properties with good accuracy by quantum mechanical calculations using hybrid density functionals [1,2]. B3LYP/DFT/6-311 (d,p) method [3] was used to predict quantum chemical reactivity parameters for tetrahydroacridines derivatives and to correlate the calculated energies of HOMO and LUMO orbitals with the oxidation and the reduction potentials, respectively.

The antimicrobial activity tested of the newly synthesized derivatives (i) allowed qualitative and quantitative evaluation of the influence of these derivatives on microbial growth and (ii) and highlighted the influence of 1,2-di(quinolinyl)ethane derivatives on microbial adhesion to inert substrate. The in vitro screening of the antimicrobial activity was performed against Gram positive *(S. aureus*, *E. faecalis*), Gram negative (*E. coli*, *P. aeruginosa*), and one fungal strain (*C. albicans*). The derivatives showed high CMI values compared to the tested bacterial strains, while the qualitative tests showed reduced antimicrobial activity. Zones of inhibition of growth were observed for some derivatives. All compounds have the ability to inhibit the biofilm adhesion on inert substratum, and they may be the basis for the development of new anti-biofilm agents.

The molecular docking study was conducted to predict the probable binding site and mode of binding of the tested compounds with *S. Aureus* DNA gyrase, retrieved from the Protein Data Bank (PDB ID: 2XCT) [4]. The docking simulations have been performed using CLC Drug Discovery Workbench Software using the docking protocol established in our previous studies [5], and Molegro Virtual Docker Software with the docking protocol referred in [6]. Molecular docking allowed us to establish an accurate prediction of the optimized conformation of tested ligands and their target receptor protein to achieve a stable complex. The analysis of the data obtained by *in silico* simulation shows that all compounds reveal docking scores higher than those of the natural ligand (ciprofloxacin), thus suggesting a good affinity to the chosen target.

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ENM P 03

An alternative view on the electrochromism of Ni-deficient nickel oxide

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The escalating global energy demand and its environmental ramifications necessitate swift advancements in renewable energy solutions. A comprehensive understanding of the mechanisms governing sustainable energy systems is imperative for further advancement. A key concern is the substantial energy usage in residential and commercial buildings for heating and cooling purposes. Addressing this challenge, innovative applications are emerging, focusing on electrochromic (EC) materials [1]. These materials can reversibly switch between transparent (bleached) and coloured states upon the application of a DC voltage. EC materials encompass metal oxides, conductive polymers, and inorganic non-oxides blended with ionic and electronic conductors. Nickel oxide (NiO) is one of the best-known EC materials. While the exact mechanism of EC in NiO is discussed for a long time, it is generally considered that in hydrated nickel oxide, particularly focusing on color changes in Li^+-containing electrolytes. One of the proposed mechanism involves transition between transparent $Li^+_{2x}Ni^{2+}_{(1-x)}O^{2-}$ and colored $Li^+_{(2x-y)}Ni^{2+}_{(1-x-y)}Ni^{3+}_yO^{2-}$, following the reaction $Li^+_{2x}Ni^{2+}_{(1-x)}O^{2-} \leftrightarrow Li^+_{(2x-y)}Ni^{2+}_{(1-x-y)}Ni^{3+}_yO^{2-} + yLi^+ + ye^-$ [2]. In the present work, through DFT+*U* calculations, we investigated the electrochromism of Ni-deficient NiO and found a new mechanism distinct from the conventional view associating optical spectra changes solely with variations in Ni^{2+}/Ni^{3+} oxidation states [3]. First, considering bulk NiO, our results reveal the formation of a hole bipolaron in Ni-deficient NiO, with Li insertion filling one hole state, leaving one-hole polaron in the system. Consequently, electronic structure alterations directly impact optical spectra, resulting in reduced absorption coefficients in Li-intercalated NiO compared to initial Ni-deficient NiO (Figure 1, a). Interestingly, we observed minimal changes in Ni oxidation states during Li insertion, indicating a general process where hole bipolaron states are filled by adding a single electron, largely independent of specific positive counter ions. Our findings, supported by results with Li^+, Na^+, and K^+ ion insertion in Ni-deficient NiO(001) surface, suggest a broader applicability of this mechanism, potentially explaining NiO electrochromism observed across various electrolytes beyond Li-containing ones, as well as doped NiO-based materials where the distortion of the NiO lattice by dopants could lead to more efficient stabilization of polaronic structures.

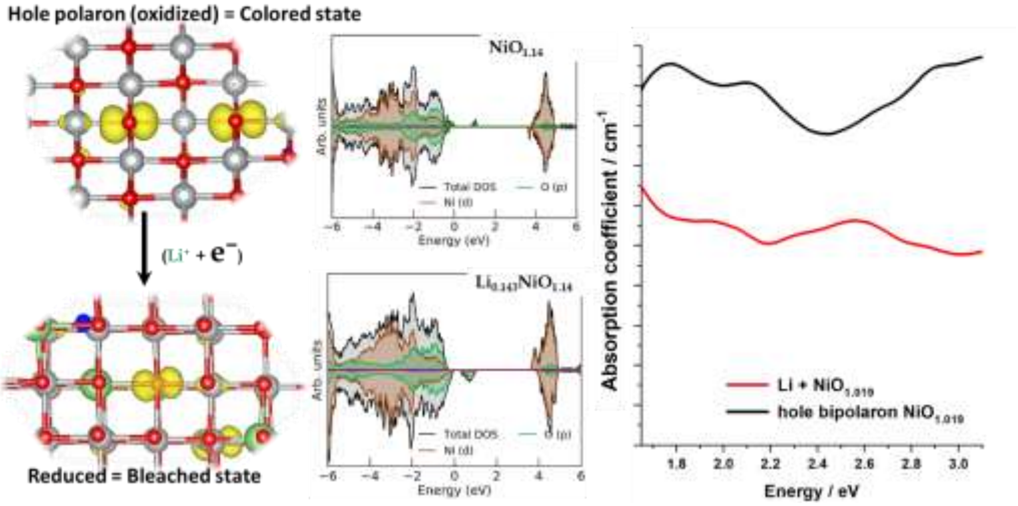

Figure 1. Electronic structure and optical spectra changes upon (Li^++e^-) insertion in Ni-deficient NiO bulk

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ENM P 04 & SSRSE 09

Exploring mechanochemistry for fluoride-free MXene synthesis

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Transition metal carbides and nitrides, known as MXenes, have emerged as one of the fastest-growing groups of 2D materials with great potential for application in supercapacitors, micro-supercapacitors, batteries, fuel and solar cells, composite materials, photocatalysis, biosensors, photodetectors, *etc.* They are represented by the chemical formula $M_{n+1}X_nT_x$ (n=2-4), where M represents transition metals like Sc Ti, Zr, Hf, V, Nb, Ta, Cr and Mo, X is carbon and/or nitrogen, and T stands for surface termination groups (-OH, -F, -O or -Cl) [1]. To date, most MXenes have been prepared through a wet chemical etching method that requires: (1) preparation of precursors, known as MAX phases (chemical formula $M_{n+1}AX_n$, where A is an element from groups 13 or 14 of the periodic table, *e.g.*, Al, Si, or Ga, (2) selective etching of the A layer from the MAX phase followed by delamination into multilayer MXene and (3) intercalation and delamination process to obtained monolayer MXene [2]. The etching process conventionally involves fluoride solutions such as HF or LiF/HCl due to their high efficacy and selectivity. However, fluoride-based solutions are highly hazardous and, their use is associated with considerable safety and handling concerns that are a major barrier to scaling up MXene production. Besides, -F terminal functional groups inevitably exist in these MXenes, detrimental to supercapacitor and battery performances. It is therefore desirable to develop simple, safe, reliable as well as sustainable synthetic routes for MXene preparation and practical application.

In this work, we explore mechanochemistry (MC) to prepare fluorine-free MXenes. This is a viable approach to promote reactions of solids quickly and quantitatively that can be easily scaled-up to manufacturing levels [3]. $Ti_3C_2T_x$ was prepared by mechanochemical ball-milling of Ti_3AlC_2 MAX phase with zinc chloride ($ZnCl_2$) at room temperature. Additionally, 20 µL of solvents (HCl or NaOH) were introduced to the MC reactions through liquid-assisted grinding (LAG). The obtained material was then treated in tetramethylammonium hydroxide (TMAOH) to complete the delamination process. The prepared MXene have been studied by cyclic voltammetry (CV), powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet-visible (UV/Vis) spectrophotometry, Raman (RAMAN) spectroscopy and low-energy ion scattering (LEIS) spectrometry.

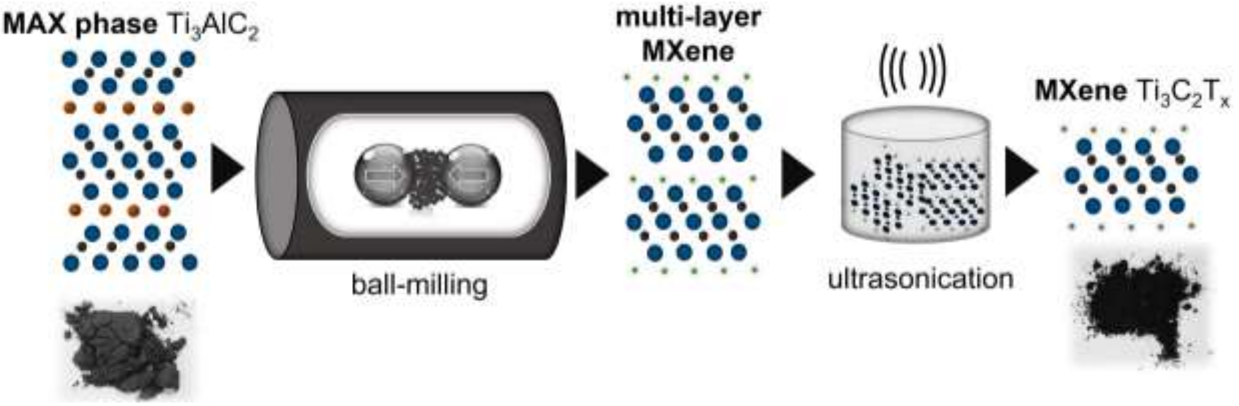

Figure 1. Schematic illustration of the synthesis procedure to obtain MXene using ball-milling and ultrasonication treatments [4].

Acknowledgement: This research has been supported by Institutional project ("MehanoMX"), co-funded by the Faculty of Mining, Geology and Petroleum Engineering (2023-2024).

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ENV P 01

Electrochemical detection of diclofenac on ZnO-modified glassy carbon electrodes

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Diclofenac (DCF) is widely used anti-inflammatory drug, which due to its stability and poor degradation in water represents chemical contaminant that can cause negative effects on the environment. Considering the use of DCF in pharmacology and its negative impact on the environment, the development of sensitive, selective, cheap, and fast, analytical devices is recently in focus of environmental scientists and engineers. It has been shown that electrochemical sensors (ECS) have advantages over traditional analytical methods for detection and monitoring of chemical pollutants in water. Crucial performances of ECS: selectivity, sensitivity, response time and portability, can be improved by modification of bare electrodes. Until now different materials have been used for electrodes modification, among them are noble metals, metal oxides, polymers and variety of carbonaceous materials [1].

We synthesized and characterized zinc oxide particles to modify the glassy carbon electrodes and to test them as sensors for electrochemical detection of DCF. Zinc oxide particles were synthesized by a glycine-nitrate combustion process using 1 M aqueous solution of zinc-nitrate hexahydrate and glycine in the molar ratio 6:5. Precursor mixture was heated on a magnetic stirrer, at first up to 80 °C in order to release excess water, then heating was continued to 170 °C, with dwell time of 2 hours, until slow flameless combustion occurred. In addition, to prepare highly crystalline particles, the obtained amorphous powder was calcined in air atmosphere, at 400 and 500 °C for 4 hours; prepared samples were denoted as ZnO-400 and ZnO-500, due to the calcination temperature. To determine phase composition and purity the prepared samples were characterized by XRD, Raman and FTIR spectroscopy, while field emission scanning electron microscopy (FESEM) was applied to determine particles morphology and size distribution.

Linear sweep voltammetry (LSV) was applied for electrochemical quantification of DCF using a three-electrode system that included a glassy carbon electrode as the working electrode, a saturated calomel electrode (SCE) as the reference electrode, and Pt foil as the counter electrode. The ink was prepared by mixing 10 mg of prepared particles, ZnO-400 and ZnO-500, and 1.5 mg carbon black with 40 µL of 5 % Nafion solution, 225 µL ethanol, and 225 µL water. LSV is performed in 25 mL of phosphate buffer (0.1 M, pH 7.0) with the addition of diclofenac infusion solution (75 mg DCF / 3 mL, Galenika a.d.) in a portion of 1 µL to completely 12 µL. All measurements were done in a potential window of 0.2–1 V *vs.* SCE at a scan rate of 20 mV·s^{-1}.

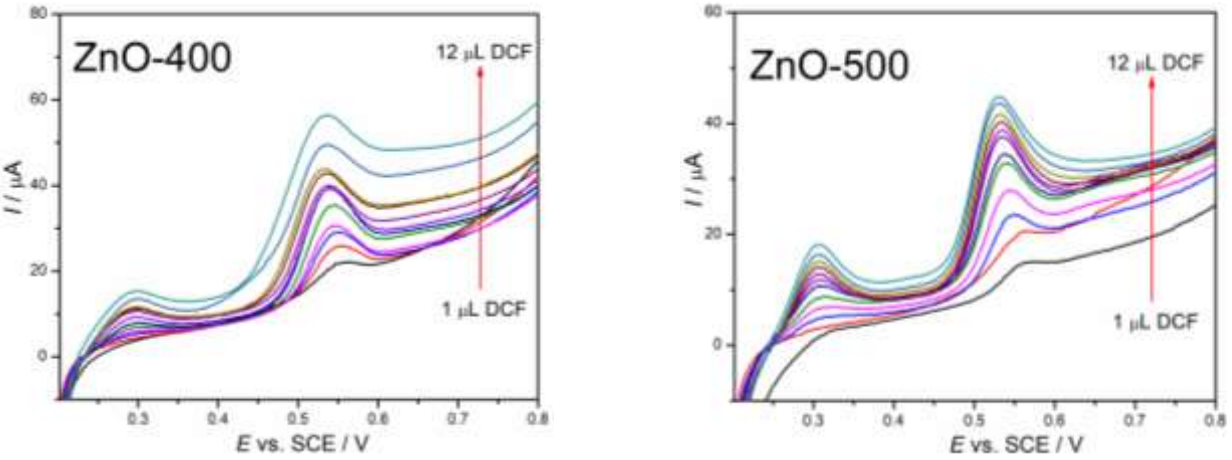

Figure 1. LSVs of ZnO-400 and ZnO-500 for different concentrations of DCF in 0.1 M Phosphate buffer (pH = 7.0)

Acknowledgement: This research was funded by the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (contract nos. 451-03-66/2024-03/200175 and 451-03-65/2024-03/200146). The authors KA, ISS and SM acknowledge the financial support from the Science Fund of the Republic of Serbia, The Program PRISMA, WaPoDe - 7377.

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ENV P 02

Conifers as green renewable inhibitors for steel acid cleaning

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While traditional corrosion inhibitors are quite effective at protecting metal, they also pollute the environment. Since conifers are renewable plants, there has been a lot of interest in using plant extracts as green corrosion inhibitors [1,2]. They fit industry standards and make excellent raw materials for corrosion inhibitors. However, because of the high dosage and unclear composition of these corrosion inhibitors, they have not been successfully used in industry. In this work black pine (Pinus nigra, PN) and Pančić spruce essential oils were synthesized from fresh needles, which were further tested as a mixture of green organic substances that inhibit steel corrosion. In addition, the active substances of black pine essential oil (α-pinene, β-pinene, and caryophyllene) were tested under the same conditions and their effect on the corrosion rate was compared with the effect of black pine essential oil. The influence of phytochemicals (bornyl-acetate, borneol, and camphene) on the effectiveness of the essential oil of Pančić's spruce, as well as on the adsorption on steel, was evaluated by theoretical and surface methods. Through experiments and theoretical calculation, the corrosion inhibition effect of these inhibitors on steel was studied in 1 M HCl solution at 25 °C. The optimal inhibitor concentration as well as the time of immersion were assessed by Electrochemical impedance spectroscopy.

It has been demonstrated that all inhibitors become more effective over time. At the same concentration of 80 ppm, the most prevalent component of the PN essential oil, α-pinene, demonstrated a poorer corrosion prevention efficacy than β-caryophyllene, that reached 96% inhibition efficiency. Both PN and Pančić essential oil were mixed types of inhibitors with prevalent influence on the inhibition of the cathodic reaction, as shown by polarization measurements. SEM and XPS analysis confirmed the presence of borneol and bornyl-acetate, along with non-soluble oxides that formed a protective film on metal surface. Binding mechanism of the Pančić essential oil inhibitor molecules was resolved with the analysis of the projected density of states [3]. The theoretical calculations [4] indicated that some of the phytochemicals in Pančić essential oil bond to the steel by chemisorption (bornyl-acetate and borneol) while others by physisorption (camphene). This has also been confirmed by values of adsorption free energy determined from Langmuir Isotherm.

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ENV P 03

Enhancing solar cell performance: Electrochemical reduction of titanium dioxide for energy alignment tuning

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Metal oxides have emerged as pivotal components in advancing energy conversion and storage technologies, spanning from Li-ion batteries, electrocatalysts/photocatalysts for water splitting and CO_2 reduction, environmentally friendly dye-sensitized solar cells (DSSCs) to the latest developments in perovskite solar cells [1]. Titanium dioxide, in particular, holds a prominent position, serving as a photoanode in DSSCs and as an electron transport layer (ETL) in perovskite solar cells [2]. The high efficiency of converting solar energy to electricity depends on the spontaneous flow of charge in these systems [3]. Consequently, optimizing the energy alignment in these complex systems is crucial for achieving optimal performance [4]. One promising method for tuning the Fermi level of titanium dioxide is electrochemical reduction/oxidation [5]. The objective of this study is to investigate the most suitable electrolyte and optimal parameters for adjusting the energy levels of commercial titanium dioxide paste to best fit the energy requirements of the DSSC, which utilizes N719 dye as the sensitizer, I^-/I_3^- electrolyte, and platinum counter electrode. The electrochemical reduction of titanium dioxide will induce a shift in its Fermi level, leading to n-doping of the semiconductor. This shift is anticipated to increase the open circuit voltage of the solar cell, consequently enhancing its efficiency (Fig. 1) [6]. We will validate the reduction process through cyclic voltammetry and Mott-Schottky analysis [7]. The efficiency of this Fermi level tuning approach will be assessed by comparing the efficiency and other pertinent parameters of fabricated solar cells. By systematically investigating the impact of Fermi level adjustment on device performance, we aim to contribute to the advancement of efficient and sustainable solar energy technologies.

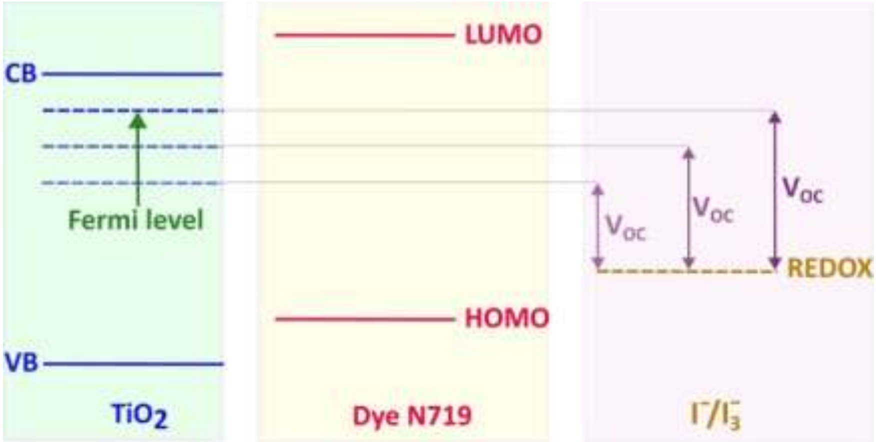

Figure 1. Schematic representation of energy level alignment in DSSC and the increase of open circuit voltage after reduction of TiO_2

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Tin sulfide film as a potential photocatalyst for the degradation of methyl orange

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Tin sulfide films have a great potential for application in a wide range of fields, such as opto-electronic materials [1], lithium-ion batteries [2], electrical switching [3], sensors [4], photocatalysis [5] and more. Azo-dyes are frequently used dye in the textile industry and methyl orange is well-known azo dye that is easily detectable making it a suitable representative for tracking water pollution [6]. Utilizing photocatalysis for MO degradation represents an advanced method to eliminate this dye from water-based environments. In that purpose, tin sulfide film was synthesized on fluorine doped tin oxide (FTO) covered glass substrates by silar method [7] and it has been characterized by scanning electron microscopy and X-ray diffraction. The optical characterization was performed in order to calculate the energy bandgap. The photocatalytic degradation activity was tested on MO under visible light at different pH levels. The film showed similar activity at neutral pH and in acidic solution. However, it showed no activity in alkaline solution. This observation aligns with methyl orange's nature as an anionic dye. In acidic conditions the surface of material is positively charged and interactions with dye molecules are attractive, whereas in alkaline conditions repulsion occurs. This research has a potential application in the photodegradation of azo dyes in both industrial waste water and natural water sources.

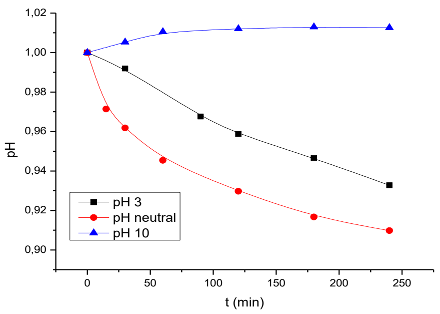

Figure 1. Photocatalytic degradation of methylene blue on tin sulfide at different pH levels)

Acknowledgement: This work was supported by the Ministry of Education, Science and Technological Development of the Republic of Serbia (Contract No. 451-03-66/2024-03/200053 and 451-03-66/2024-03/200017).

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ENV P 05

Electrochemical characterisation of $BiVO_4$ for perfluorinated compounds degradation

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In the last two decades, perfluorinated organic compounds have attracted significant attention and caused concern due to their impact on the environment and human health. Of particular concern is the fact that these compounds are extremely stable and prone to bioaccumulation. During their production, distribution and disposal, large amounts of perfluorinated alkyl compounds (PFAS) were released into the environment. Their presence has been recorded in the oceans and surface and underground waters, where concentrations ranging from pg/L to µg/L have been determined. There are several ways to remove PFAS from water media such as physical, electrochemical or sonochemical methods and photochemical processes. The most preferred methods are those that break the C-F bond, which degrades PFAS into less toxic compounds. One such method is the photocatalytic process [1].

In this work, the electrochemical characterisation of the photocatalyst $BiVO_4$ modified with Fe_2O_3 and Ag was carried out with the aim of their application in the degradation of perfluorooctanoic acid (PFOA). The methods used to characterise the photocatalyst are linear polarization, electrochemical impedance spectroscopy, chronoamperometry and monitoring of the open circuit potential over time. The test was performed in 0.5 mol dm^{-3} Na_2SO_4 solution and Na_2SO_4/PFOA solution. In addition, solar photocatalytic degradation of PFOA was conducted by using investigated photocatalytic material while degradation of products was monitored by liquid chromatography-mass spectrometry (LC-MS/MS) method.

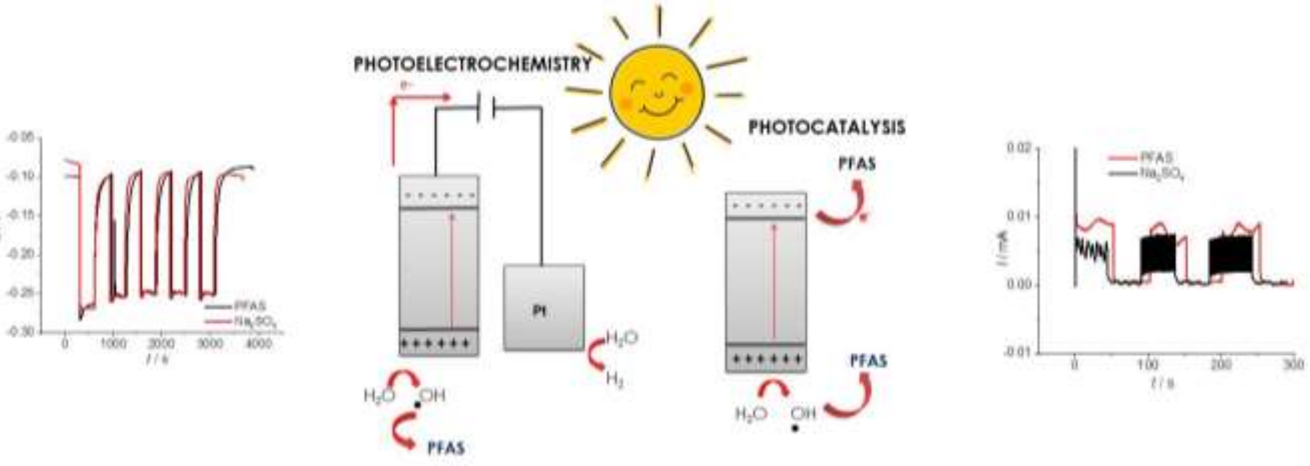

Figure 1. Schematic illustration of the photocatalytic and photoelectrochemical degradation of PFAS

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ENV P 06

Detection of carbendazim fungicide in water using a carbon paste electrode modified with pyrophyllite

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This work aims to design a pyrophyllite-modified carbon paste electrode for potential use in the detection of pesticides in aqueous solutions. Pyrophyllite is a phyllosilicate which consists of is an $AlO_4(OH)_2$ octahedron sheet between two SiO_4 tetrahedral layers (2:1 structure) (1). Mechanochemical activation introduces structural disorder, causing amorphization and reducing particle size and an increase in the chemical reactivity of material [2]. After milling, the structural and morphological characterization of natural pyrophyllite clay and mechanically modified pyrophyllite was done. It is observed that with increasing milling time, particle size decrease and specific area increase. However, for ore pyrophyllite from a deposit in Parsovići, Bosnia and Herzegovina, up to 20 minutes of milling, the specific surface area increases and the particle size decreases. After that, the agglomeration process becomes more pronounced. It has been shown that the best structural and morphological characteristics are those when pyrophyllite is milled for 15 minutes for construction of the electrode. The electrochemical characteristics of this electrode were investigated by cyclic voltammetry in 1 mM $K_4Fe(CN)_6$ in 0.1 M KCl and 0.5 M H_2SO_4 and differential pulse "striping" voltammetry in Britton-Robinson buffer at pH 4 , 6 and 8. The best results were obtained at pH 4. It was shown that the maximum at +0.96 V *vs.* Ag/AgCl electrode originates from carbendazim oxidation at pH 4 in Britton-Robinson buffer. Good stability and sensitivity were shown by the electrode containing 50 % carbon paste and 50 % pyrophyllite mechanically modified for 15 minutes in a ball mill. The developed method is linear in the range from 1 ppm to 10 ppm with $r = 0.999$ and a detection limit of 0.3 ppm.

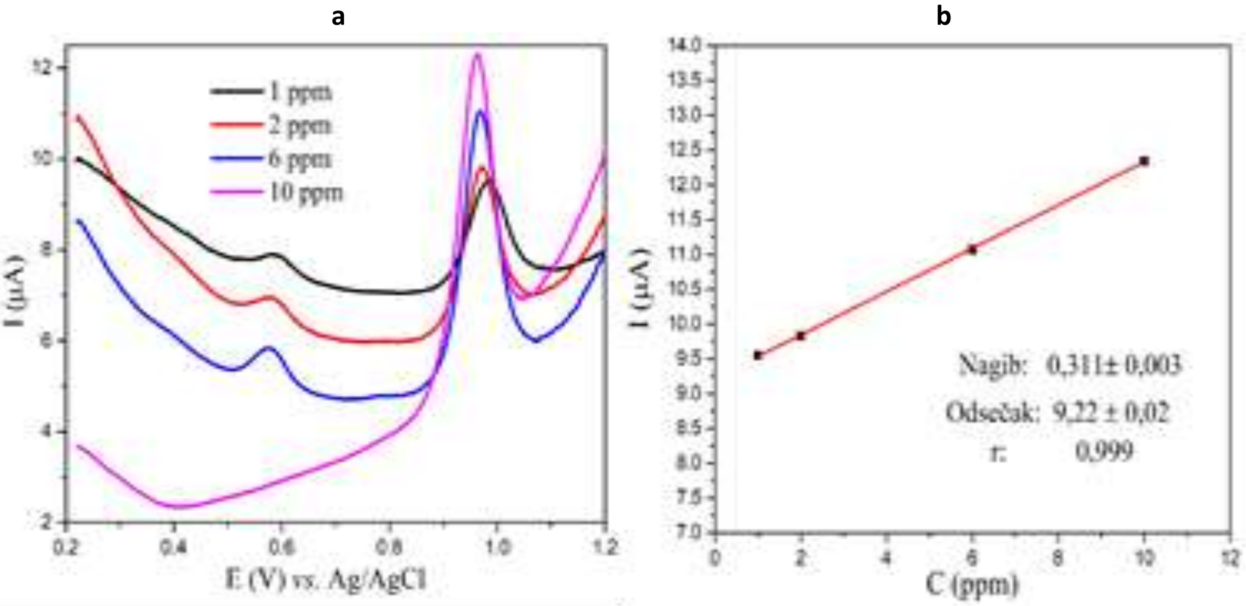

Figure 1. a) Differential pulse voltammogram for determination of carbendazim in Britton-Robinson buffer at pH 4; b) Dependence of current on concentration of carbendazime for a pyrophyllite-modified carbon paste electrode with paraffin oil as a binding fluid for the detection of carbendazime in Britton-Robinson buffer at pH 4 in the concentration range from 1 ppm to 10 ppm

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ENV P 07

Off-gases emission during the rare earth electrolysis from magnet recycling derived oxides

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In the progressive energy transition process, rare earth elements (REE) became key components in crucial products that play a central role in the development of renewable energy and low-carbon technologies. With China currently producing more than 90 % of the world's REE output, many of the world's economies are facing REE supply risk [1]. To address this problem, many countries need to look for alternative resources of rare earths, *e.g.* recycling of these elements from REE-containing end-of-life products. A new route for recovery of REE from NdFeB magnet scrap, using a combination of pyrometallurgical treatment of spent NdFeB magnets, and a subsequent molten salt electrolysis process, has been investigated in the authors' laboratory [2]. The magnet recycling derived oxides (MRDO), were produced from spent NdFeB magnets by oxidation in air and subsequent carbothermal reduction under an 80 mbar Ar gas atmosphere. High-temperature molten salt electrolysis was introduced as an option that enables the separation of rare earth elements from fluoride-based molten salts using produced MRDO [3]. One of the challenges in this electrochemical approach for REE electrowinning is effective control of the anode effects to make the electrolytic production of rare earths more environmentally friendly [3,4]. Minimizing the perfluorocarbon compounds emission (PFC), in rare earth electrolysis, should be the primary goal, owing to their high global warming potential [4,5].

In the present work, we investigated the off-gases emissions during the REE electrolysis from NdFeB magnet scrap using in-situ FTIR-spectrometry, in order to understand the formation pathways of CO, CO_2, and perfluorocarbon gases (CF_4 and C_2F_6) made at the anode. The electrolytic extraction of rare earths from fluoride-based molten salts with different contents of MRDO present was performed using molybdenum (Mo) as a cathode, tungsten (W) as a reference electrode, and a glassy carbon (GC) electrode as an anode. It was found that depending on the content of the starting material, the dissolution of MRDO in their corresponding fluoride molten salts most probably induces the formation of different oxyfluoride complexes and their subsequent reactions on the GC anode. The anode reactions in the fluoride-based melts are, most likely, results of either oxide or fluoride formation by exchange with the fluoride or oxide complexes present in the electrolyte. The produced oxygen subsequently reacts with carbon to generate CO and CO_2. With F^- present, PFC compounds such as CF_4 and C_2F_6 can also be formed from a GC anode. The anode gas products are composed mainly of CO and CO_2. The average CO_2 concentration was approximately 450 ppm, while CO concentration was around 40 ppm. CF_4 emissions in off-gas products were detected periodically, except for some spikes, and even then, the concentration was below 4 ppm. C_2F_6 was not detected. The results indicate that the electrodeposition of REE within the applied potential range occurs at the expense of their corresponding oxides, provided by MRDO. To develop a more efficient RE recovery process, we opted for a low deposition overpotential to suppress the emission of greenhouse gases and further enhance the control of their emission in rare earth electrolysis.

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ENV P 07

Electrochemical characterization of WO_3 and $WO_3/BiVO_4$ photoelectrodes and their application in the photoelectrochemical degradation of amoxicillin

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The widespread use of antibiotics, pesticides, and other organic pharmaceuticals leads to their accumulation in aquatic environments, including surface and wastewaters. Stringent environmental regulations require new water treatment approaches for various industries and municipal systems. Amoxicillin, a commonly used antibiotic, is considered an emerging contaminant [1] due to its uncertain impact on human health and the environment. Existing wastewater treatment methods often fail to efficiently remove amoxicillin, leading to its persistence in drinking water and natural water bodies. Photoelectrochemical processes offer a promising solution for decomposing organic contaminants in aquatic systems.

Both semiconductor materials examined in this work, WO_3 and $BiVO_4$, exhibit valuable properties for photoelectrochemical applications, including strong chemical stability and long lifespan, low toxicity, cost-effectiveness, and efficient charge carrier separation. Due to the bandgap in the range of 2.6–2.8 eV, WO_3 very efficiently absorbs photons within the UV range. However, its absorption in the visible light region (wavelengths above 400 nm) is limited. $BiVO_4$, on the other hand, has a bandgap of ~2.4 eV and absorbs solar radiation in the visible light region of the spectrum, specifically wavelengths ranging from approximately 400 to 600 nm. Combining these two materials results in a broader range of absorption across the visible light spectrum. According to literature findings, a $WO_3/BiVO_4$ heterojunction enables improved charge transfer and reduced charge recombination compared to the individual materials, thereby enhancing the efficiency of photoelectrochemical processes.

In this study, WO_3 was electrodeposited onto an FTO (fluorine-doped tin oxide) glass substrate from an acidic aqueous solution, following an electrochemical procedure adapted from Yourey and Bartlett [2]. The photo-electrochemical activity of the fabricated electrode was assessed under irradiation from a LED lamp (COB, 50 W, 4400 lm, 6000K). Various electrochemical techniques, including linear sweep voltammetry (LSV), electrochemical impedance spectroscopy (EIS), open circuit potential measurement (OCP), Mott-Schottky analysis, and chronoamperometry (CA), were employed to characterize the electrodes. The electrodes exhibiting the most promising responses were then coated with a $BiVO_4$ layer using a drop-casting approach, characterized using the aforementioned electrochemical methods, and further evaluated for the photoelectrochemical degradation of amoxicillin. In addition to the electrochemical measurements, UV-Vis spectroscopy and X-Ray diffraction analysis were also conducted.

Acknowledgement: This work has been fully supported by Croatian Science Foundation under the project NaSCEnT (IP-2018-01-1982).

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ENV P 09

Electrochemical detection of benzisothiazolinone on screen-printed electrodes

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Benzisothiazolinone (BIT) is a member of isothiazolinone derivatives, which are used as powerful antimicrobial and antifungal agents in a wide variety of everyday products, including detergents, cleaning products, water-based paints, varnishes, food packaging and more. The widespread use of BIT and other isothiazolinone-based biocides seriously threatens the integrity of waste and natural waters. BIT is released into aquatic ecosystems directly from consumer products, such as cosmetics and cleaning products or indirectly through wastewater treatment plants. It is harmful to aquatic life, including fish, algae, and other organisms. Additionally, contact with BIT-containing products may lead to skin sensitisation and contact dermatitis. Other harmful properties, such as cytotoxicity have also been observed. Due to these concerns, the use of BIT in cosmetics has already been restricted in the EU; however, it is still widespread in other consumer products. BIT is persistent in the environment, with a half-life of more than 30 days, and can be transported through soil and water pathways. For this reason, fast, reliable, in-situ detection of BIT is of utmost importance, with electrochemical sensors being good candidates for this purpose. [1,2]

According to a literature review, no electrochemical sensors for BIT have yet been developed, although electrochemistry of some other isothiazolinone-based compounds has been studied. We report on direct BIT detection in aqueous media on screen-printed electrodes (SPE) using cyclic voltammetry (CV) and square wave adsorptive stripping voltammetry (SWV). Different types of SPE with carbon and gold-based working electrodes were used. The various SPEs proved to have a good electrochemical response to BIT in wide concentration ranges and low limits of detection. The SPE-C with a carbon nanoparticle-based working electrode proved to be the most suitable for the direct analysis of BIT, with an LOD of 40 nmol/L. The sensor's performance was tested in environmental samples in the presence of several possible interferences, and good recovery values were obtained.

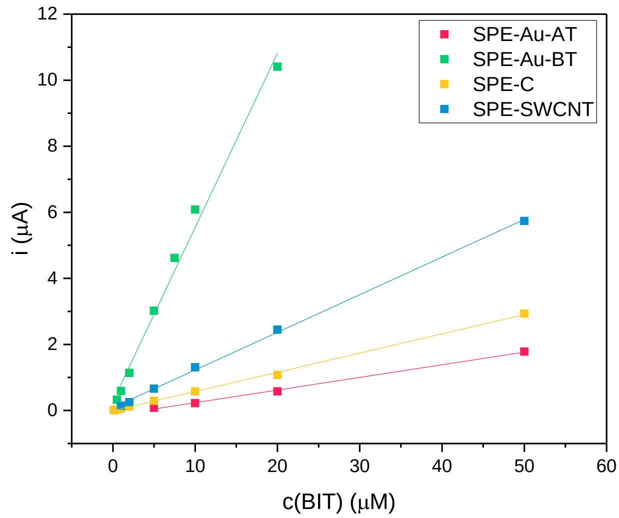

Figure 1. Current response to BIT on carbon-based (SPE-C and SPE-SWCNT) and gold-based (SPE-Au-AT and SPE-Au-BT) SPEs.

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GEN P 01

HLOROGEN - In-situ electrochemical process for active chlorine production: Specificity and optimization

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Active chlorine, obtained by the process of non-membrane electrolysis from a dilute aqueous sodium chloride solution, has found wide application in the areas of water disinfection, disinfection in medicine and veterinary medicine, as well as for general use [1-3]. The quality and efficiency of the products obtained in this way depend on many parameters, which makes the process of optimizing the quality of the final product difficult, and often impossible.

SIGMA doo has conducted a series of experiments, focusing on monitoring the influence of the following input parameters on the quality and efficiency of electrochemically obtained active chlorine: Concentration of the dilute aqueous salt solution entering the electrolyser; pH of the dilute salt solution entering the electrolyser; Nature of the anode used for the electrolysis process, from different manufacturers.

Part of the analysis was carried out in the internal laboratory of Sigma Crvenka doo, while the remaining data were acquired in cooperation with faculties, institutes and laboratories in the Republic of Serbia and the European Union. The capacity of the equipment used for the tests is 2.5 l/h of the solution, with a maximum concentration of 10 g/l of active chlorine.

The obtained experimental data, together with a 30-year data set collected from more than 200 locations where HLOROGEN technology equipment is installed in Serbia and abroad [4], resulted in the development of a mathematical model for the non-membrane electrolysis process. Under certain initial assumptions, the stationary material balance of the non-membrane electrolysis process showed that the yield of active chlorine can be represented by the following dependence:

$$C_{\mathrm{Cl}_2} = f\,(F_\mathrm{v}, x, y, z, \mathrm{U}, \chi(C_{\mathrm{Cl}_2}), \xi)$$

where:

C_{Cl_2} - Yield of active chlorine
F_v - Volume flow of the solution through the electrolyser
x, y, z - Electrode geometry
U - Electrolysis voltage
$\chi(C_{\mathrm{Cl}_2})$ - Electroconductivity of the electrolytic solution as a function of active chlorine concentration
ξ - Degree of electricity utilization

The complex dependence of these parameters and a large number of experimental data make it difficult to optimize the non-membrane electrolysis process. Therefore, a fully connected PINN neural network (physics-informed neural network) with supervised learning was applied in this work [5,6]. The work does not focus on optimizing the hyperparameters of the network itself, but on the interpretation of the application of the neural network to a specific example.

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GEN P 02

Innovative electrochemical detection of genetically modified organisms amplified via LAMP method for agricultural applications

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The increasing diversity and complexity of genetically modified organisms (GMOs) create obstacles in their detection, impacting food traceability, safety, and monitoring. Current research indicates that GM crop technology may pose risks to human health and the environment. This study focuses on developing a LAMP-based GMO detection device implementing electrochemical methods.

Electrochemical DNA sensor was used to detect LAMP products that are complementary to single-stranded DNA probes using methylene blue as a redox indicator through the hybridization process. The probes were attached to the gold electrodes functionalized by gold nanoparticles, and 2D nanomaterials (such as MoS_2 or MXenes). The electrochemical methods, such as alternating current voltammetry, square wave voltammetry, and differential pulse voltammetry were employed in testing the electrochemical detection response.

The experiments show that electrochemical detection methods and setup parameters, as well as the choice of nanomaterial for electrode modification, significantly influence the GMO detection signal. Conformational changes in DNA probes upon binding to the target DNA result in a decrease in signal intensity. This phenomenon is explained by the increased resistance to electron transfer to the electrode materials by methylene blue molecules located at the top of the DNA probes. These results are promising for the development of a device that will enable a specific, sensitive, fast, cost-effective, and precise in-field detection system for the routine detection of GMOs.

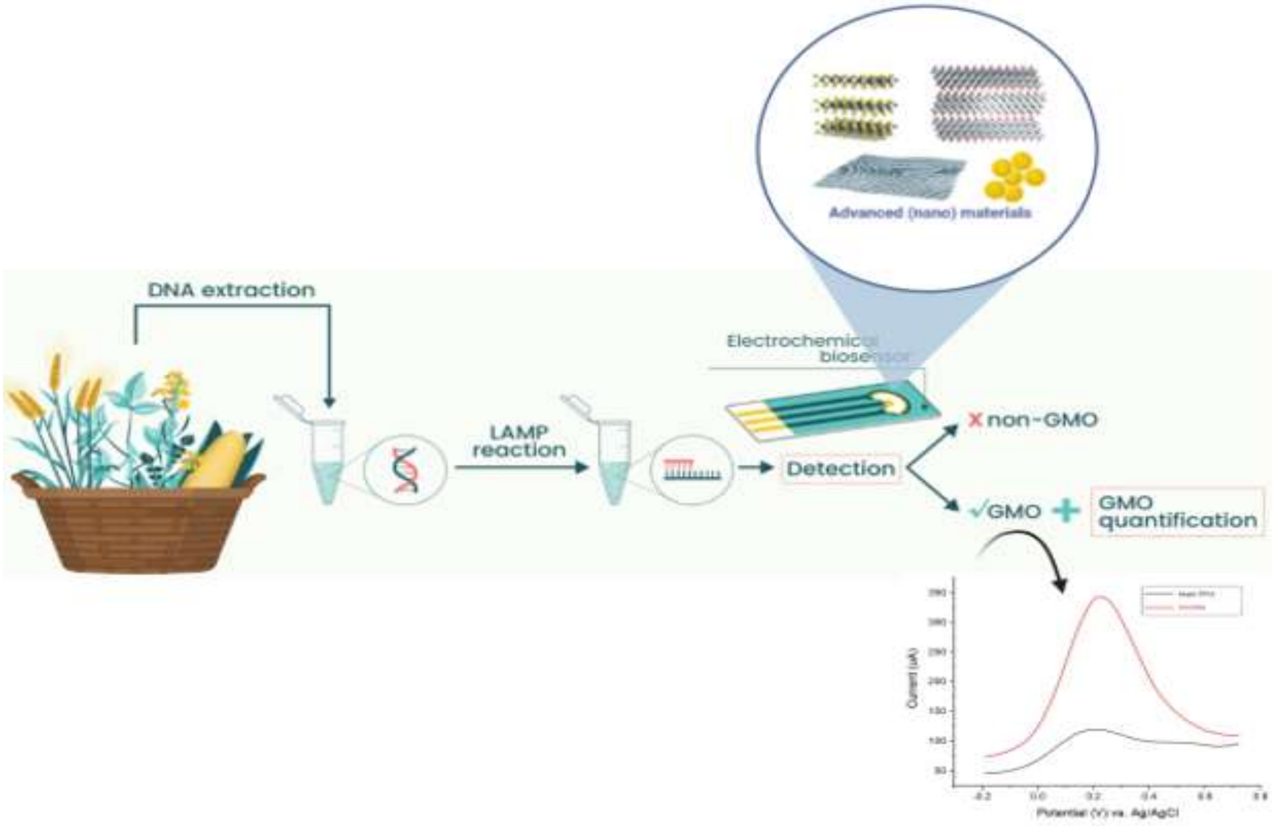

Figure 2. Electrochemical detection of LAMP products

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Advancing agricultural NPK detection with electrochemical sensors utilizing 2D nanomaterials

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NPK electrochemical soil sensors serve as vital instruments for sustainable agriculture, empowering farmers to refine nutrient management techniques, enhance crop output, and safeguard the environment for upcoming generations. These sensors are crafted to predominantly gauge nitrogen (N), phosphorus (P), and potassium (K) levels in the soil. These nutrients are fundamental for plant growth and vitality, and tracking their concentrations aids in optimizing fertilizer usage, boosting crop productivity, and reducing environmental repercussions, thus effectively bolstering precision agriculture methods.

Innovative 2D nanomaterials have the potential to enhance the electrochemical capabilities of sensors, allowing them to detect even minute levels of nutrients with exceptional precision. The operational principle of these sensors relies on electrochemical reactions taking place at the surface of 2D nanomaterials upon interaction with target ions in the soil solution, facilitated by an ion-selective membrane. Variations in the presence and concentration of these ions induce changes in the electrical properties of the nanomaterial, which are then quantified and correlated with nutrient levels. Through the utilization of specially engineered composite nanomaterials comprising transition metal dichalcogenides, Mxenes, graphene-based materials, conjugated conducting polymers, and ion-selective membranes, it becomes feasible to measure soil ion content either as discrete batches or accurately and consistently through continuous monitoring. These materials possess notable characteristics such as high surface area-to-volume ratios, excellent electrical conductivity, and responsiveness to alterations in the chemical milieu, rendering them well-suited for sensing applications. Laboratory experiments demonstrate that various combinations of nanomaterials in composites at the sensor working electrode significantly enhance the selectivity of the ion-selective membrane in filtering soil ions, as well as the reproducibility and longevity of the sensor, compared to electrodes solely coated with the ion-selective membrane. Numerous nitrate ionophores and ion-selective membrane cocktails are evaluated and compared for their efficacy in achieving ionic selectivity.

Electronic circuitry governs the operation of the electrochemical sensors, designed to provide input and retrieve data from the sensing elements, as well as facilitate sensor conditioning, calibration, data storage, and wireless communication. Various electrochemical methods, such as Open Circuit Potentiometry, Chronopotentiometry, and Chronoamperometry, are utilized for sensor control and data collection by manipulating electronics. These methods have been subjected to testing and comparison concerning the response time and durability of the sensor.

In summary, the integration of electrochemical sensors with 2D nanomaterials marks a significant leap forward in precision agriculture. It equips farmers with the necessary tools to effectively manage soil nutrient levels and enhance crop productivity. This advancement contributes to the traceability and quality assurance of food production processes.

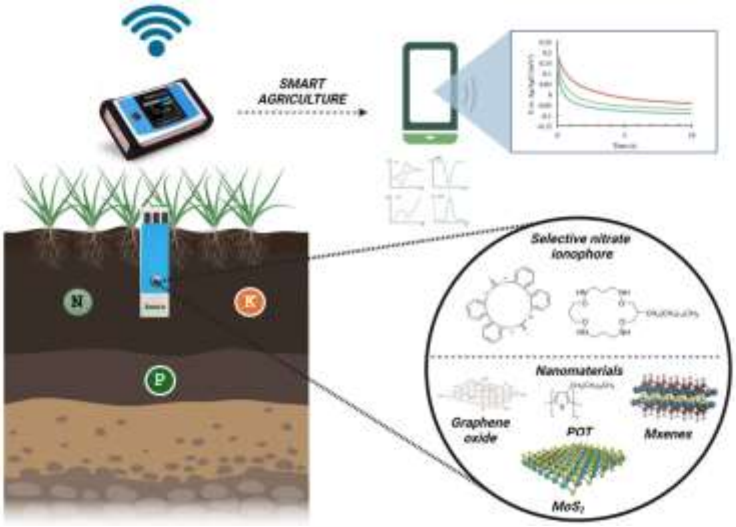

Figure 1. NPK detection by ion-selective membranes and 2D nanomaterial composites

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Enhanced hydrogen production from cracking of liquid toluene by applying liquid plasma and perovskite catalysts

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In this study, a process for producing hydrogen from liquid hydrocarbons by applying plasma is proposed. Toluene was decomposed by discharging a pulse-type plasma into liquid toluene directly. The changes in the rate of hydrogen production and reaction characteristics owing to injecting a perovskite catalyst were also investigated. A high hydrogen production rate of approximately 130 NL/h·g was obtained from the liquid–phase plasma reaction of toluene using the $BiFeO_3$ catalyst. The investigation into the reaction characteristics based on the plasma generation conditions indicated that the reaction was mainly affected by the plasma voltage. When titanium dioxide and perovskite ($SrTiO_3$, $BiFeO_3$) photocatalysts were applied to this reaction, the reaction activities also varied depending on the light-absorption capacity of the catalysts. The highest hydrogen evolution rate was obtained using the $BiFeO_3$ catalyst, which absorbs visible light as well as UV light, compared with the TiO_2 photocatalyst, which absorbs only UV light. Because the plasma emission from toluene is predominantly in the visible region, the reaction activity was also determined to be the highest for the $BiFeO_3$ catalyst. The $BiFeO_3$ absorbs visible light up to about 550 nm, and it has a small bandgap energy of about 2.15 eV. This led to high photocatalytic degradation activity in visible light generated by plasma discharge in toluene. The carbon obtained had a particle size of less than 20 nm and purity of approximately 99 %.

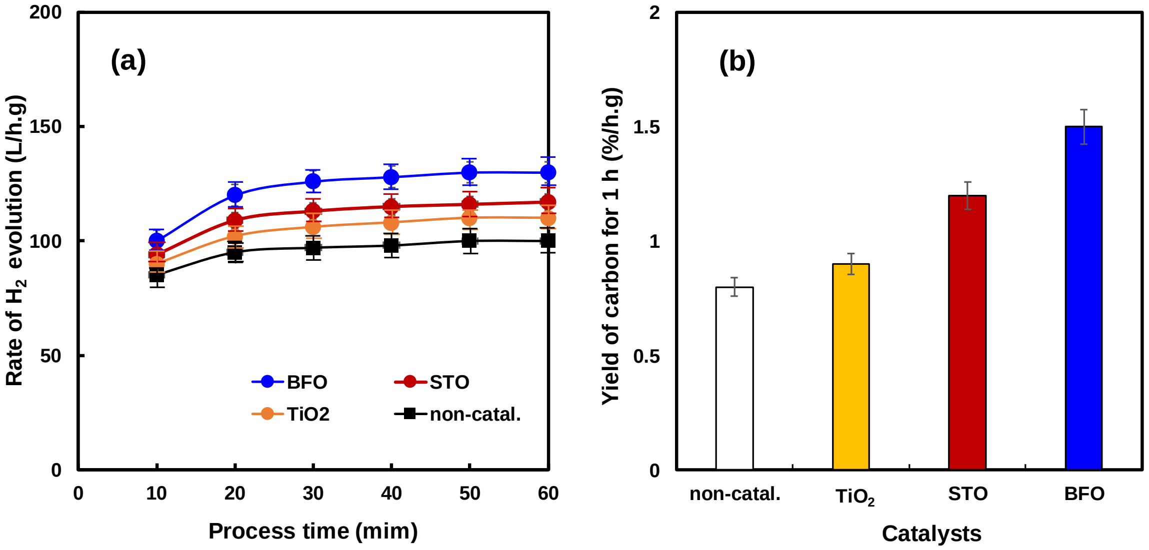

Figure 1. (a) Rate of hydrogen evolution on various catalysts and (b) yield of carbon generated from the toluene cracking on various catalysts.

Acknowledgement: This research was supported by the National Research Foundation of Korea (2021M3I3A1084797).

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Voltammetric determination of binding constant of newly synthesized potential COX-2, 5-LOX dual inhibitors with human serum albumin

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Many research papers showed strong inflammatory correlation with some cancer types [1]. Transferring of dual COX-2 and 5-LOX inhibitors into the oncology field has been intensively studied in last 15 years so the aim of this work was to examine the redox behaviour, as well as interaction with human serum albumin (HSA), of newly synthesized dual COX-2 and 5-LOX inhibitors: 1-(4-aminophenyl)-3-(4-fluorophenyl)prop-2-en-1-one (4FNH2), 1-(4-aminophenyl)-3-(3-fluorophenyl)prop-2-en-1-one (3FNH2) and (1-(4-aminophenyl)-3-(2-fluorophenyl)prop-2-en-1-one (2FNH2).
Voltammetric techniques, cyclic voltammetry (CV), square wave voltammetry (SWV) and differential pulse voltammetry (DPV) with GCE were used. When analysing the CVs, all compounds were found to have an oxidation peak (I_a) around + 0.75 V and a reduction peak (I_c) at potentials around −1.0 V. No significant influence of the substituents on the electrochemical behaviour of the compounds was observed. For all three compounds, a preliminary study of the interaction with HSA was performed at a concentration of each compound of 5×10^{-5} M and different HSA concentrations (5×10^{-8} M - 10^{-5} M) using DPV. The decrease in current intensity was similar for all three compounds after interaction with HSA, while the most intense change in the position of the oxidation peak after interaction was observed for compound 4FNH2 (ΔE_p = 122 mV). The results of relative decrease in peak current and shifting of peak potential upon the interaction with HSA for all compounds are shown in Table 1.

Table 1 Normalized peak currents and DPV peak potentials shift after the interaction of compounds with HSA

Compound	Normalized peak current, %	ΔE_p / mV
4FNH2	46.42	122
3FNH2	45.97	85
2FNH2	48.56	58

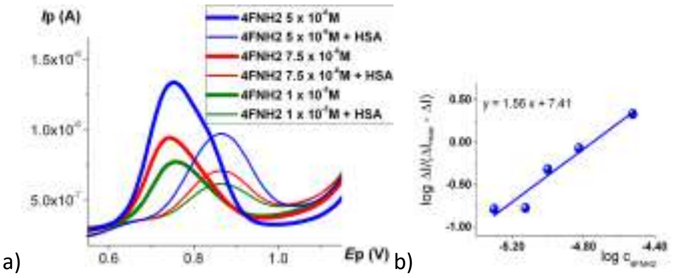

Figure 1. a) DPV voltammograms of different concentration of 4FNH2 before and after interaction with HSA b) Dependence of log (ΔI /(ΔI_{max} - ΔI)) vs. log c_{4FNH2} used for 4FNH2–*HSA binding constant determination(c_{HSA} = 2×10^{-6} M)*

Since compound 4FNH2 showed the most intense interaction with HSA, the detailed investigation of its electrochemical behaviour is presented. The peak current of 4FNH2 increased linearly with the square root of ν($I_{p,Ia}$ / µA = 5.36×10^{-6} $\nu^{1/2}$ / $V^{1/2}$ $s^{-1/2}$ - 2.04×10^{-7}); r = 0.993) indicating that the oxidation process was diffusion controlled. This is confirmed by the log $I_{p,Ia}$ *vs.* log ν linear dependence [2], with slope values of 0.67, which was close to theoretical value of 0.5 for diffusion-limited process. In addition to diffusion of electroactive material, some adsorption also took place, as indicated by the small intercept in the $I_{p,Ia} = f(\nu^{1/2})$ regression equation and small variance of the slope of log $I_{p,Ia} = f$(log ν) plot from theoretical value of 0.5.
The DPV was used to thoroughly investigate the interaction 4FNH2 with HSA and to determine the binding constant (Fig. 1). The concentration of 4FNH2 was increased (5×10^{-6} - 5×10^{-5} M) while the HSA concentration was kept constant (2×10^{-6} M). The differential peak current intensity was measured before and after the interaction of 4FNH2 with HSA and by using log (ΔI/(ΔI_{max} - ΔI)) *vs.* log c_{4FNH2} dependence [3], the binding constant, K was calculated, K = 5.62×10^{4} M^{-1}.

Acknowledgement: This research was supported by the Science Fund of the Republic of Serbia, 7739840, Utilization of interplay between inflammation and cancer in the development of compounds with anticancer activity—INFCANPLAY.

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Transferring the photoredox catalytic conditions to organic electrosynthesis; electrogeneration of oxygen centered radicals from *N*-alkoxyphthalimides employing rapid alternating polarity

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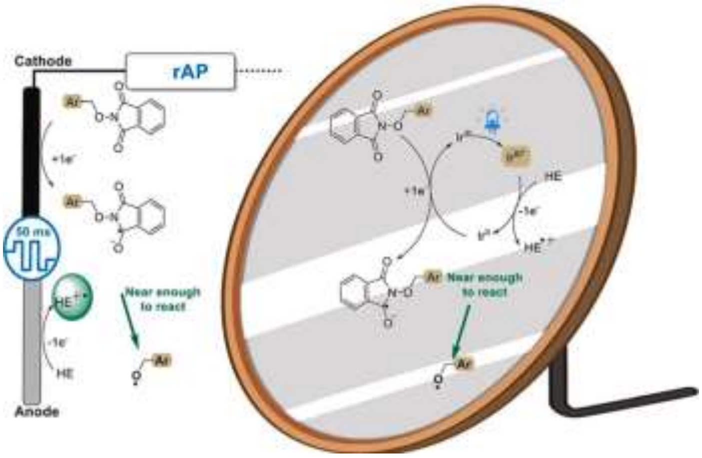
The first electrogeneration of *O*-centered radicals from *N*-alkoxyphthalimides *via* rapid alternating polarity (RAP) electrolysis, using previous experimental conditions of photoredox catalysis (PRC) is reported. The electrochemical methodology emulates satisfactorily the redox cycle behavior accepted to explain the PRC technique. Notably, the contribution of oxidized Hantzsch ester produced during the anodic reaction is emphasized, which behaves as an efficient proton donor to facilitate *N–O* cleavage and to extinguish the radical sequence efficiently. The reaction is conducted in a practical way using an undivided cell fitted with glassy carbon electrodes, allowing the same reactions to occur on both electrodes during the overall transformation reaching a 77 % yield of the corresponding alcohol. This yield is higher than the electrochemical protocol using direct current electrolysis, confirming that the use of RAP electrolysis favors the proximity where the reactive intermediates are produced, facilitating their reaction to promote the desired reaction pathway.



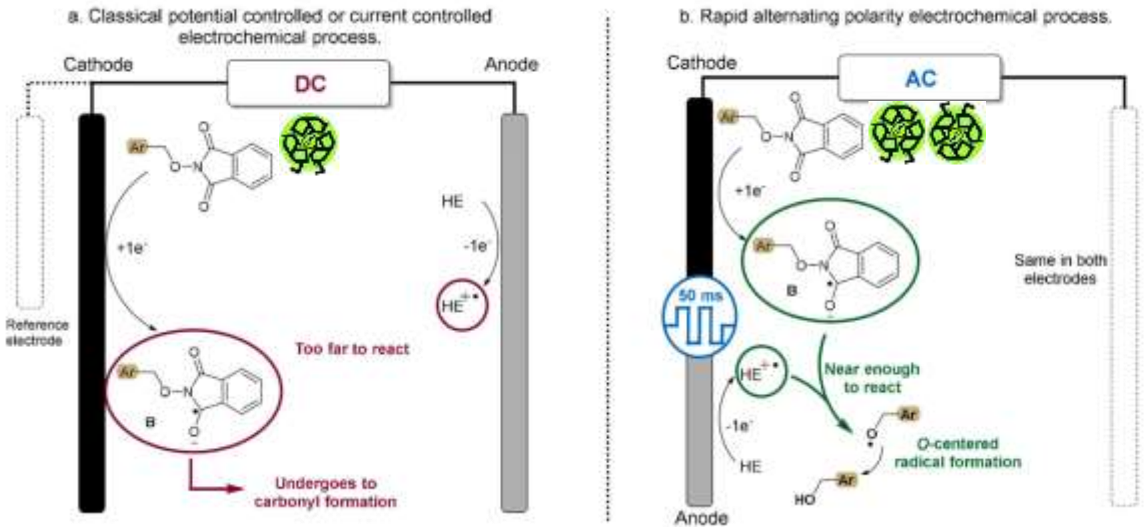


Figure 1. Comparison between a) Classical potential controlled or current controlled electrochemical process, and b) Rapid alternating potential (rAP) electrochemical process.

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ORG P 03

The interaction of newly synthesized potential COX-2, 5-LOX dual inhibitors with human serum albumin in the presence of Tween 80

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Due to the very important relationship between inflammation and cancer, there is an increasing need for synthesizing new compounds with potential for activity in both processes. Therefore, new dual inhibitors of the COX-2 and 5-LOX enzymes, which inhibit the inflammation mediators, may also play a potential role in cancer therapy [1] and could be promising agents. In the development of new compounds, parameters characterizing the formation of complexes with human serum albumin (HSA) are particularly important, and electrochemical methods have been shown to be important because of their versatility, high sensitivity, and simplicity.

Differential pulse voltammetry (DPV) with GCE was used to investigate newly synthesized compounds, potential dual COX-2 and 5-LOX inhibitors (3-(4-fluoro-2-methylphenyl)-1-(2-hydroxy-4-methylphenyl)prop-2-en-1-one - H12, 3-(2--chlorophenyl)-1-(5-fluoro-2-hydroxyphenyl)prop-2-en-1-one - H13, 1-(5-fluoro-2-hydroxyphenyl)-3-(2-(trifluoromethyl)phenyl)prop-2-en-1-one - H14, and 1-(4-aminophenyl)-3-(4-fluoro-2-methylphenyl)prop-2-en-1-one - H20)[2].

It was found that it was not possible to obtain a repeatable electrochemical signal (peak potential and peak current) when testing these compounds, probably due to the limited solubility of these compounds in the aqueous medium. A literature search revealed that possibly the application of Tween 80 could influence the enhanced dispersion and thus enable a reproducible signal [3]. For a detailed investigation compound H20 was used as it showed the highest intensity of the oxidation peak current at a concentration of 5×10^{-5} M.

The influence of different concentrations of Tween 80 (10^{-7} - 3×10^{-5} M) on the reproducibility of the signal of the compound H20 (5×10^{-5} M) in PBS pH 7.3 was investigated using DPV. Satisfactory reproducibility was achieved at a Tween 80 concentration of 2×10^{-5} M (Figure 1).

After achieving a stable H20 signal, the interaction between H20 and HSA was examined. In order to determine the binding constant, the measurements were performed at a H20 concentration of 5×10^{-6} to 6×10^{-5} M, while the HSA concentration was constant at 2×10^{-6} M. The differential peak current intensity was measured before and after the interaction of H20 with HSA and by using the log (ΔI / (ΔI_{max} - ΔI)) *vs.* log c_{H20} dependence [4] the binding constant, K was calculated, $K = 5.5\times10^4$ M^{-1}.

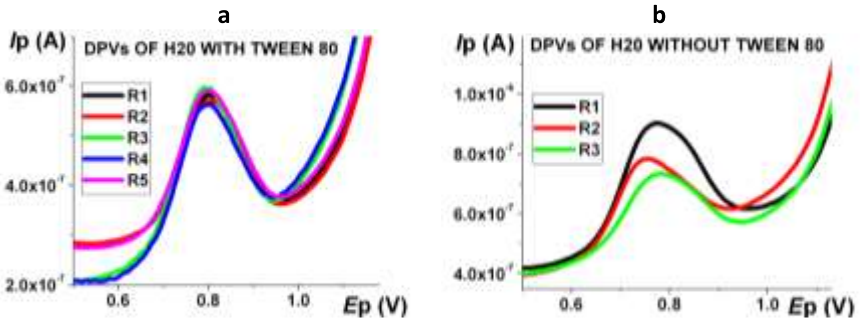

Figure 1. DPVs of a) H20, c = 5×10^{-5} M in PBS with Tween 80 (2×10^{-5} M); b) H20, c = 5×10^{-5} M in PBS without Tween 80

A simple, accurate, inexpensive, and sensitive voltametric method was developed for the investigation of redox behaviour and interaction with human serum albumin in the presence of Tween 80 of the newly synthesized compound H20 which has low solubility in aqueous solutions.

Acknowledgement: This research was supported by the Science Fund of the Republic of Serbia, 7739840, Utilization of interplay between inflammation and cancer in the development of compounds with anticancer activity—INFCANPLAY.

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ORG P 04

Electrochemical investigation of antioxidative properties of ivermectin in biological medium

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Oxidative stress is defined by an imbalance between an increased level of reactive oxygen species (ROS) and a low activity of antioxidant mechanisms, which can lead to damage to the cell structure and potentially destroy tissues (1). Antioxidant activity is usually analysed using spectrophotometric methods, which have their own drawbacks. Therefore, an electrochemical approach could be useful as an independent and comparative method to measure antioxidant activity. Electrochemical methods in drug analysis are widely used due to their low cost, high speed and ease of performance. Ivermectin (IVM) is a well-known anthelmintic but also a potential antitumor and antiviral drug (2) and is still being investigated today. The aim of this study was to investigate the redox activity of IVM in a human serum pool of healthy individuals not only using spectrophotometry, but also using a new electrochemical approach to confirm the results of the oxidative stress testing (Figure 1) and to suggest which part of the structure is responsible for the effect. The antioxidant activity of IVM was tested *in vitro* in a human serum pool and compared with a known antioxidant (Trolox) and pro-oxidant (tert-butyl hydroperoxide, TBH). Known spectrophotometric methods (PAB, TOS, TAS and SHG) were used to calculate the pro-oxidant, antioxidant and oxy-scores of IVM after 2 and 24 hours of incubation at 37 °C. Most of the studies using an electrochemical approach to measure antioxidant activity are designed to determine polyphenolic compounds, but our study took a different approach – estimating the antioxidant properties of IVM using differential pulse voltammetric (DPV) measurements in human serum samples after the incubation for different times. The recorded voltammetric peak parameters were compared with DPV results obtained with Trolox and TBH under the similar conditions. Electrochemical confirmation of the spectrophotometric analysis was performed in a small electrochemical cell (total volume of 1.5 mL) using a three-electrode system: glassy carbon electrode (GCE) as the working electrode, an Ag/AgCl as the reference electrode (3M KCl) and a Pt wire as the auxiliary electrode. Voltammograms were recorded after 0, 2 and 24 h incubation at 37 °C. The redox behaviour of IVM showed a noticable antioxidant potential, similar to that of Trolox during short-term incubation, while a longer stay in the presence of TBH resulted in a loss of antioxidant activity. Electrochemical results suggest that IVM has similar antioxidant properties to Trolox after incubation in human serum samples, which is consistent with the spectrophotometric results (3). Since the antioxidant potential of IVM was confirmed by voltammetric methodology, which is proposed for the first time, the presented results show the possibility of the use of electrochemical methods in addition to the accepted methods in the analysis of the antioxidant properties of drugs.

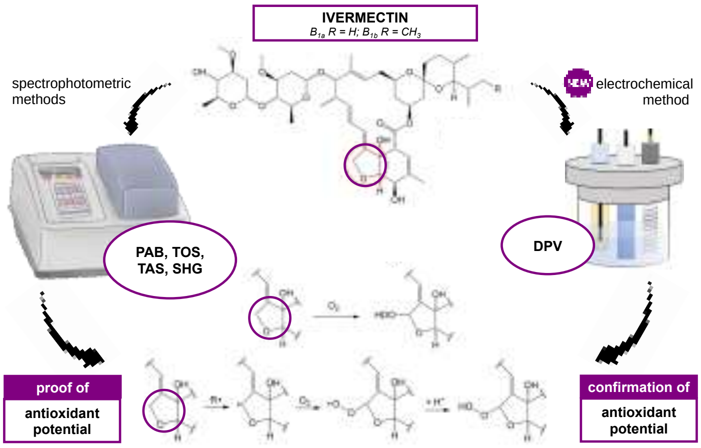

Figure 1. Graphical abstract of the study

Acknowledgement: This research was funded by the Ministry of Science, Technological Development and Innovation, Republic of Serbia through Grant Agreement with University of Belgrade-Faculty of Pharmacy No: 451-03-47/2023-01/200161. The authors would like to express their gratitude to Union-Medic d.o.o. Novi Sad for the financial support.

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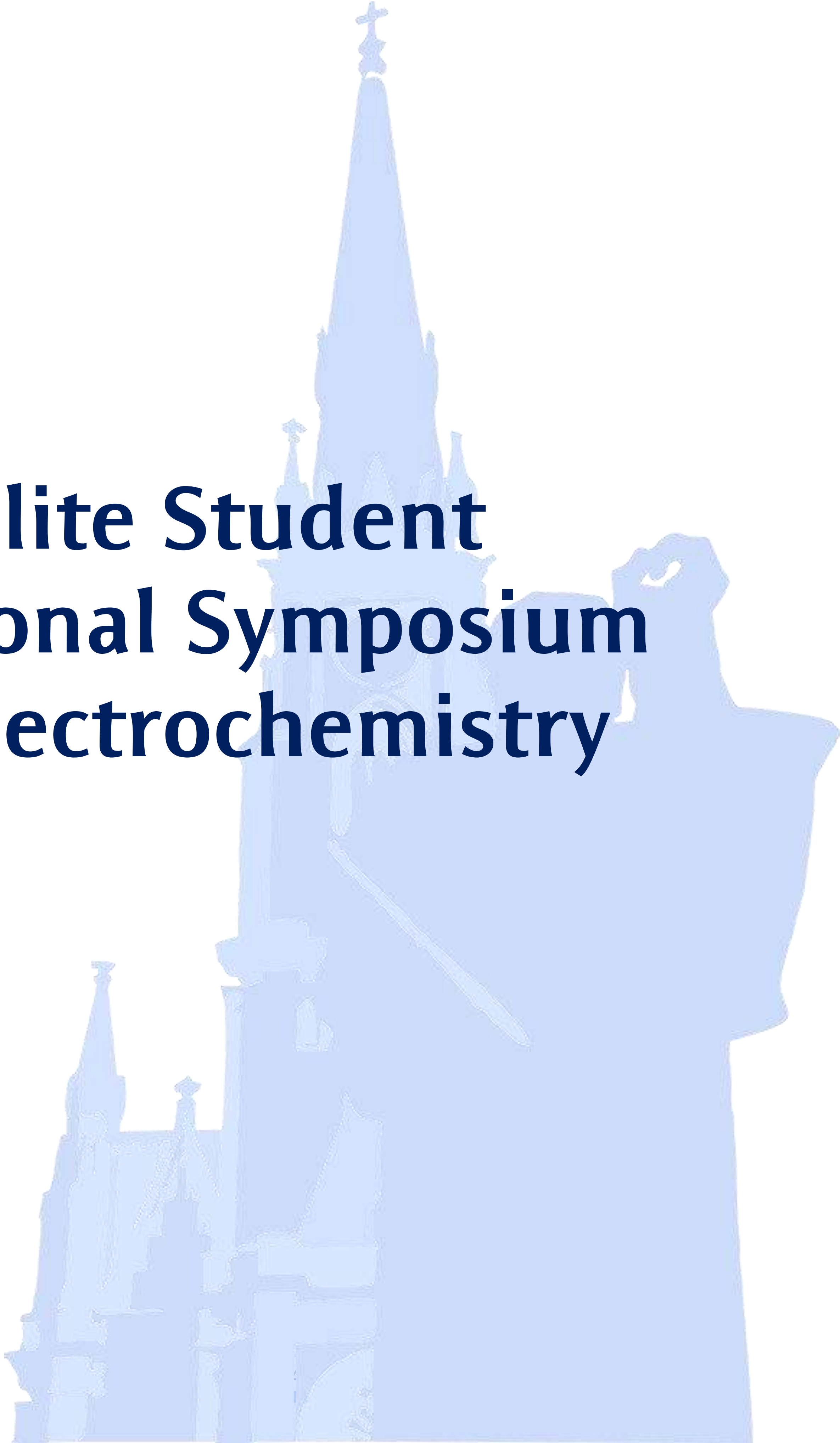

Satellite Student Regional Symposium on Electrochemistry

Electrochemical synthesis and characterization of conducting polymers

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The traditional understanding of polymers as excellent insulators was altered in the seventies of the last century when scientists succeeded in synthesizing polyacetylene with conductivity close to that of metals. This fact indicated a new property of polymeric materials and launched an entirely new multidisciplinary scientific field. Although sometimes the term "conductive polymers" encompasses a large group of compounds classified according to the nature of charge carriers, the term is most commonly used in the literature for polymeric materials from the group of so-called synthetic metals that possess electronic conductivity as a result of the specific molecular structure. In addition to the requirement of the molecular structure, which involves a conjugated system of double bonds, doping is necessary for the conductivity of conductive polymers. The term doping, although borrowed from the terminology of classical inorganic semiconductors, involves a significantly different process. Doping of conductive polymers involves oxidation (rarely reduction), during which, in order to maintain the electroneutrality of the polymeric chain, a stoichiometric amount of ions has to be introduced. Doping is also achievable by the involvement of acids such is the case of one of the most studied conducting polymers named polyaniline. By introducing such a large quantity of ions, the starting structure of the polymer is altered, and the properties of the resulting conductive material depend largely on the properties of the dopant. The presence of dopants is a key factor in electrochemical applications of conducting polymers since these ions can be almost reversibly doped/dedoped during the oxidation/reduction process. Although at the beginning of the development of this field, conductive polymers were synthesized by chemical methods, gaining insight into the mechanism of chemical synthesis which is oxidative radical polymerization, made it clear that these materials could also be obtained by electrochemical methods. Electrochemical synthesis has advantages, as the polymer is obtained by oxidation on the electrodes (anodes), avoiding the use of an oxidizing agent and enabling greater product purity. On the other hand, the conductive polymer is, in most cases, obtained in the form of a coating on the electrode, facilitating its further characterization by electrochemical techniques. The interest in the field of conductive polymer synthesis and applications especially in electrochemical technologies, remains strong, the topic of this lecture is dedicated to the basic principles of electrochemical synthesis and characterization with a special focus on the most popular conductive polymers, polyaniline and polypyrrole.

SSRSE 01

Scalable synthesis of CoAu/rGO nanocomposite for sensing of As^{3+} ions in acidic media

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One of the most toxic heavy metals present in water is arsenic (As), which is why it is necessary to regularly monitor its content in drinking water[1]. In this work, a CoAu/rGO nanocomposite was synthesized by a scalable method and investigated for the detection of As ions in acidic media using anodic strip voltammetry. First, the operational parameters (deposition potential, E_d = -0.3 V and deposition time, t_d = 60 s) were optimized in 1 mM $NaAsO_2$in 1 M HCl, after which the limit of detection (LOD)was determined in a wide range of concentrationsfrom30 to 1000 µM. In the mentioned range, shown in Figure 1, two areas of linearity were obtained (for low and high concentrations). LowLOD of $As^{3+}$of 3.06 µM was determined for the low-concentration region (30 to 90 µM).

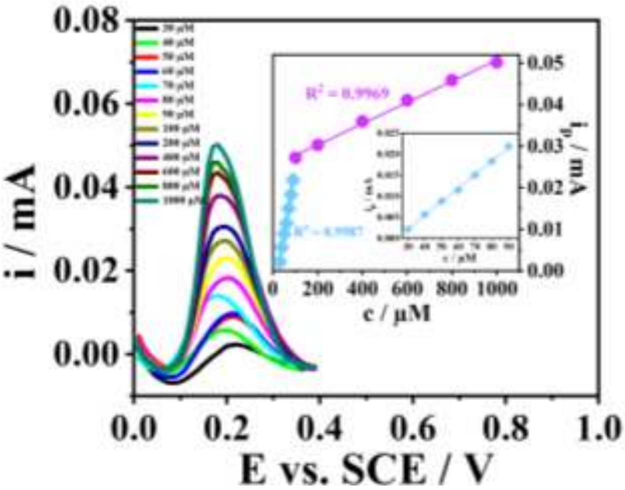

Figure 1. Voltammograms of CoAu/rGO electrode in 1 M HCl with increasing concentrations of As^{3+} with the corresponding standard addition plots in inset.

Acknowledgement: The authors would like to thank the Ministry of Science, Technological Development and Innovation of the Republic of Serbia (Contract number: 451-03-65/2024-03/200146; 451-03-66/2024-03/200146; 451-03-66/2024-03/200051 and 451-03-47/2024-01/200168), Fundaçãopara a Ciência e a Tecnologia (FCT, Portugal) (contract no. IST-ID/156-2018, B.Š.)and the Turkish Academy of Sciences (TUBA) (O.M.) for the partial financial support.

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SSRSE 02

Pechini method synthesis of Ho_2O_3 nanoparticles and its applications as a extremely sensitive electrochemical sensor for Diuron detection in tap water, apple and strawberry juice samples

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Industrialization and intensive agricultural practices, which are connected to problems with flora and fauna and cause decrease in water quality owing to pollution by persistent and dangerous pesticides, have been encouraged by population increase[1].In the current study, a new electrochemical sensor for Diuron (DU) detection was developed using a carbon paste electrode (CPE) enhanced with Ho_2O_3 nanoparticles. Rare earth elements, such as Ho, are increasingly being employed to create novel electrode nanocomposites with improved electrocatalytic performance. Holmium has been regarded a major lanthanide element with higher redox reaction characteristics[2].The synthesis of Ho_2O_3 was carried out using the Pechini method for the first time, and the morphology and nanostructure of the material were confirmed by the use of X-ray powder diffraction (XRPD), scanning electron microscopy (SEM), and transmission electron microscopy (TEM). To develop an analytical method for DU identification and measurement, the electrocatalytic properties of the proposed Ho_2O_3 modified CPE were investigated. The electrochemical behaviour of DU at the Ho_2O_3 sensor was examined using the CV and SWV methodologies. The electrochemical sensor that was suggested had a remarkable response to DU, displaying a broad linear range of 0.25 to 200 µM, a detection limit of 0.03 µM, and a sensitivity of 2,14 $\mu A\ \mu M^{-1}\ cm^{-2}$. The method's strong selectivity is confirmed by the minimal influence of potential interfering substances. Additionally, the sensor demonstrated outstanding stability, repeatability, and sensitivity. Furthermore, the Ho_2O_3-CPE sensor showed good recovery results when used to detect DU in water, apple, and strawberry samples. Also, its efficacy was validated by its successful use in the accurate measurement of DU levels in real samples, which was compared with conventional DU detection methods including UV-VIS detection.

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SSRSE 03

Dual dynamic voltammetry for the investigation of ferrate ion production

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Ferrate ions can be produced electrochemically with the transpassive dissolution of iron containing anodes. During this process, the parasitic oxygen evolution is inevitable. The oxygen evolution decreases the current efficiency of ferrate production and makes the characterisation of the ferrate ion formation process difficult. Usually, the electrochemical ferrate production is characterized by the accumulated ferrate ion concentration. Since ferrate ions are highly unstable and their decomposition rate depends on many circumstances (including cell design) that are difficult to control, most characterization for electrochemical ferrate synthesis are inadequate, leading to uncertain and sometimes misleading results.

Dual Dynamic Voltammetry (DDV) is a novel method that can be used for Rotating Ring Disk Electrodes (RRDE)[1] experimental setups. DDV makes the simultaneous, independent polarization of the two electrodes (ring and disk) possible. The fast polarization of the Platinum ring and the slow polarization of the Iron disk makes the characterization of the ferrate ion production possible with high resolution, and indifferent to the decomposition of ferrate ions. DDV measurement with non-dissolving disk (Platinum) made the investigation of the separate effect of oxygen evolution possible. Spectrophotometric measurements confirmed the ferrate ion detection at the Platinum ring. Using this setup the formal separation of ferrate ion production and oxygen evolution could be executed, and the ferrate ion formation reaction could be investigated alone.

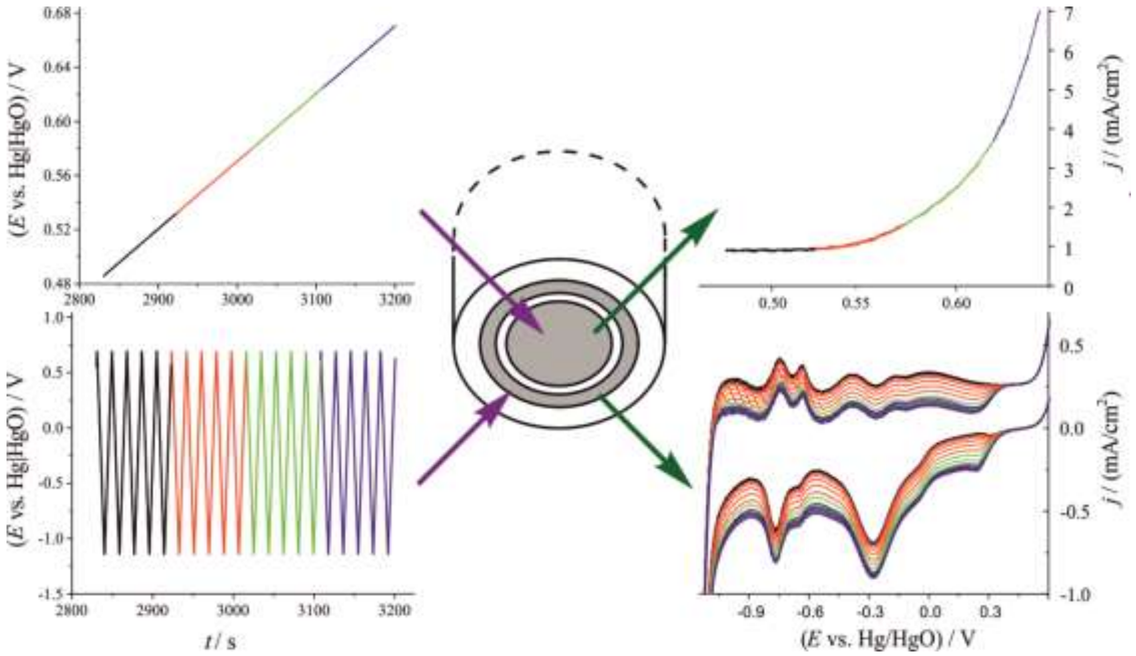

Figure 1. Potential program and voltammogram of the Disk and Ring during a Dual Dynamic Voltammetric (DDV).

Acknowledgement: Financial support from the National Research, Development, and Innovation Office (NKFIH, grant nos. K129210, FK135375, VEKOP-2.3.2-16-2017-00013) is gratefully acknowledged. Parts of this work was performed in the frame of the 2018-1.1.2-KFI-2018-00123 project, implemented with the support provided by the National Research, Development and Innovation Fund of Hungary, financed under the 2018-1.1.2-KFI funding scheme.

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SSRSE 04

Modifying composition of the SEI layers of calcium electrodes

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The structure and composition of the SEI layers formed on metal anodes is a key factor enabling fast and reversible anodic reactions in battery technologies. This is especially important for the multivalent battery technologies, which despite their high energy content and promising performances, still lack a sufficiently conductive layers for calcium or magnesium ions. Therefore, it is necessary to achieve an optimal ion conductive layer that will acquire desirable performances of the next generation multivalent batteries. The formation these layers depend on many operational parameters and conditions, most common being the composition of the electrolyte and the electrochemical approach of formation.

In this study, various approaches were employed in order to construct SEI layers on calcium electrode. Formed layers were electrochemically examined their ability to support reversible calcium deposition and stripping in previously selected organic electrolytes. The structural characterization of the formed layers was conducted by standard methods such as FTIR, XRD and SEM, providing comprehensive insight into the morphology and composition.

The results showcased a considerable influence of the electrolytes on the electrochemical behaviour of calcium electrode. It was found that it is possible to obtain a conductive SEI layer enabling reversible calcium deposition and stripping. This specific result expands the potential of possibilities for advancing the understanding and development of preferred SEI layer for highly reversible calcium electrode.

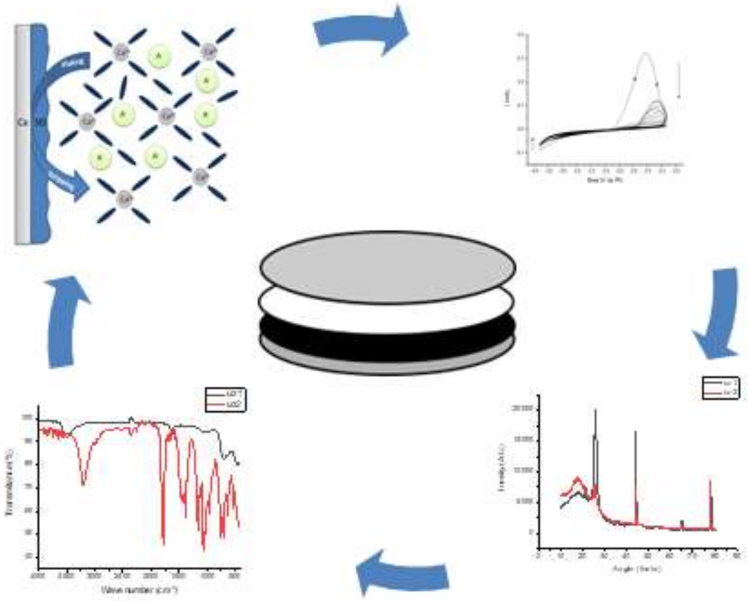

Figure 1. *Schematic representation of modification procedure for calcium anode*

SSRSE 05

The impact of a newly synthesized zwitterionic additive on the electrolyte performance of lithium-ion batteries

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Lithium-ion batteries (LIBs) have emerged as a crucial technology for powering sustainable transportation systems in the future. However, their large-scale application is hindered by serious safety concerns, particularly when LIBs are exposed to thermal, mechanical, or electrical abuse conditions [1,2]. The high energy density of LIBs, which is attributed to the use of volatile and flammable organic solvents in the electrolyte, poses significant safety risks [3,4]. Since the electrolyte is a critical component that interconnects all vital parts of the battery, it notably impacts numerous technological and chemical aspects of LIBs. To address these safety challenges, researchers have proposed several modifications to the electrolyte, including substituting the organic solvent or adding functional additives such as ionic liquids (ILs).

These modifications offer promising solutions for enhancing the safety and reliability of LIBs, thereby paving the way for their wider application in sustainable transportation systems.

The current demand for lithium-ion battery electrolytes entails developing electrolytes that can perform multiple functions simultaneously, such as stabilization and functionalization of the electrode materials such as stabilizing the electrode materials and functionalizing the electrode. In this context, electrochemical testing was conducted to compare the stability of the electrolyte containing the newly synthetised zwitterionic compound 1-butylsulfonate-3-methylimidazole ($C_1C_4imSO_3$) as an electrolyte additive. The study utilized electrolytes 1.0 M $LiPF_6$ in EC/DEC = 50/50, battery-grade solutions of lithium hexafluorophosphate salt in ethylene carbonate, and diethyl carbonate mixture. The results were evaluated based on the electrochemical performance of the electrolyte with the additive and compared to those of commercially used electrolytes. In addition to voltammetric results, molecular dynamic (MD) simulations and density functional theory (DFT) calculations were employed to reveal the essential mechanism between selected additive and electrolyte.

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Atomic adsorption on graphene from first principles: influences of defects and dispersion interactions

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This study presents a comprehensive analysis of atomic adsorption on graphene, focusing on pristine and defective graphene structures using Density Functional Theory (DFT). We compiled a complete database of atomic adsorption energies for elements up to atomic number 86 on pristine graphene, calculated using projector augmented wave (PAW) methods and dispersion corrections like PBE+D2, PBE+D3, and vdW-DF2. Significant findings include the importance of dispersion interactions, especially for elements with low atomic weights and high cohesive energies. Additionally, we explored the impact of single vacancies and Stone-Wales (SW) defects on graphene's chemical reactivity. We observed enhanced binding at vacancies, with elements higher in cohesive energy showing stronger bonds, suggesting that defect engineering could tailor graphene's properties for advanced applications. Furthermore, the SW defect not only increased adsorption strength but also, under mechanical deformation, led to significant reorganization within the graphene structure, impacting its reactivity and potential utility in materials science. This comprehensive analysis underscores the nuanced interplay of atomic structure, defects, and adsorbate characteristics in defining the properties of graphene, revealing ways for its optimized use in technology and material science.

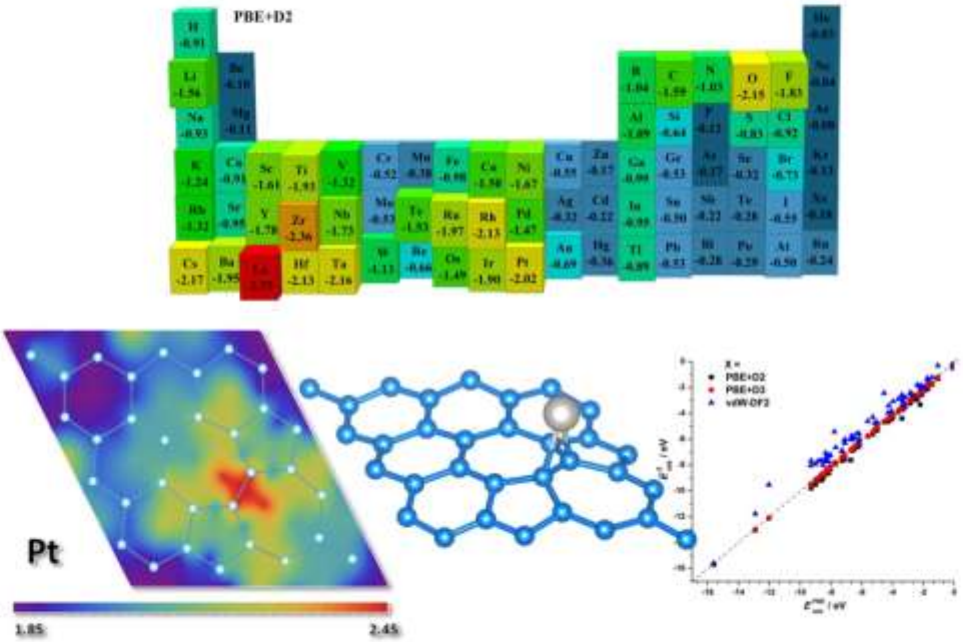

Figure 1. Adsorption energy of the elements of PTE on pristine graphene (top), heatmap of Pt adsorption on SW-graphene (bottom, left) and a structural model of the most stable adsorption configuration (bottom, center), correlation of adsorption energy for different computational schemes on monovacant graphene (bottom, left)

Acknowledgement: I.A.P, A.S.D and A.Z.J acknowledge the support provided by the Serbian Ministry Science, Technological Development, and Innovation (451-03-65/2024-03/200146). The computations and data handling were enabled by resources provided by the National Academic Infrastructure for Supercomputing in Sweden (NAISS) at the NSC center of Linköping University, partially funded by the Swedish Research Council through grant agreements no. 2022-06725 and no. 2018-05973.

A redox activity of the diazo dye acting as an exogenous mediator of electron transfer

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Microbial fuel cells (MFCs) are devices that can convert the chemical energy of naturally available organic substrates directly into electricity by using different microorganisms as bio-microreactors. The organic matter is oxidized through the catabolic processes of the microorganisms and a part of the gained electrons are transferred to the anode. The number of electrons transferred and/or the rate of their transmission can be adjusted using artificially added substances passing through the membranes, which is supposed to improve the theoretical thermodynamic limitations. In this study, the photophysical (Fig. 1A) and electrochemical properties (Fig. 1B) of the diazo dye Ponceau S were investigated. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) energy levels of the dye were estimated based on experimental data. The putative mechanism of electrochemical oxidation/reduction of Ponceau S is proposed based on the established data that HOMO is equal to -3.87 eV, LUMO is equal to -1.73 eV, and E_g^{opt} = 2.14 eV.

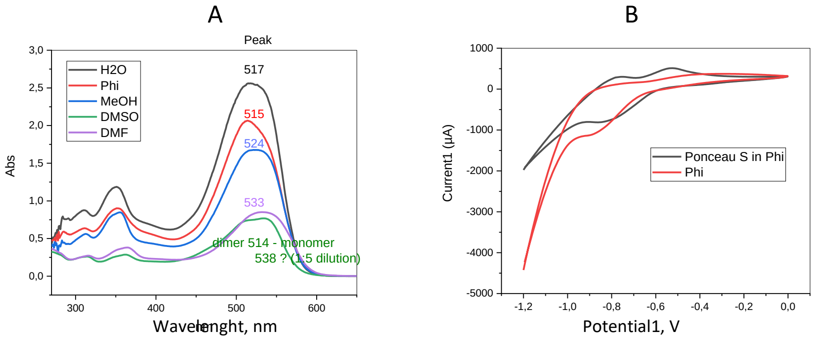

Figure 1. A- absorption measured in different solvents
B - CV of Ponceau S diluted in phosphate buffer (Phi) compared to the buffer as control

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SSRSE 08

Electrochemical quartz crystal microbalance studies of inert electrolyte cation roles during the electrochemical reduction of thin graphene oxide films

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The electrochemical reduction of graphene oxide films offers a promising method for precise control of the graphene oxide properties, important for applications in electrochemical capacitors, sensors, and electrocatalysis. While the primary role of an inert electrolyte is to maintain sufficient electrical conductivity, the choice of electrolyte can significantly influence the reduction behavior of graphene oxide films [1,2]. Notably, this effect appears to correlate with the size of the cation in the electrolyte, with trends in peak potential and other parameters following the Li -> Na -> K sequence. To better understand the influence of cation size in inert electrolytes, electrochemical quartz crystal microbalance (EQCM) measurements were conducted simultaneously with cathodic potential sweeps. The EQCM results reveal substantial differences in gravimetric behavior depending on whether the electrolyte contained Li, Na, or K cations. These variations can be explained by differences in the solvation and charge densities of the cations.

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SSRSE 10

Electrochemical assessment of stem cell viability for application in regenerative medicine

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Stem cell research has emerged as a promising avenue for regenerative medicine, offering potential solutions for various medical conditions, particularly wound healing, such as burns, where conventional treatments often fall short. Central to this field is the exploration of stem cells and stem cell-conditioned media, which have shown remarkable therapeutic potential and contain a complex array of bioactive molecules, including growth factors, cytokines, and extracellular vesicles [1,2]. These factors play critical roles in modulating cellular behaviour, promoting tissue repair, and stimulating regeneration. One of the major concerns in the investigation and application of stem cells is the assessment of their viability. Usual methods for cell viability testing include morphological assessment, cell counting, viability staining, metabolic activity, apoptosis, and functional assays, which are time-consuming and expensive.

Electrochemical methods are fast and do not require special preparation of samples. This study focuses on the utilization of cyclic voltammetry and electrochemical impedance spectroscopy methods for rapid cell viability assessment. Dental pulp stem cells (DPSC) were grown in culture until they achieved appropriate confluence. To be able to compare the electrochemical response of viable cells to non-viable cells, DPSC were subjected to several cycles of freezing and heating. All electrochemical experiments were performed using aliquots of DPSC in its condition media as applied to a screen-printed electrode and immediately recorded.

Cyclic voltammograms did not show a predictable trend that could be used for the confirmation of cell viability. On the other hand, electrochemical impedance spectroscopy, which has the advantage of probing processes across a wide range of frequencies and resolving slow and fast processes, was more successful. The obtained Nyquist plots for viable and non-viable cells (Figure 1) shows a clear distinction.

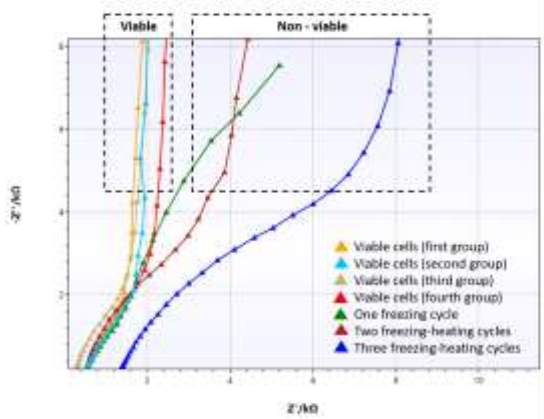

Figure 1. Nyquist plots of stem cell samples as received and conditioned by freezing-heating cycles

Viable cells show characteristic capacitive behaviour at lower frequencies, which can be attributed to the capacitive behaviour of the intact cell membrane. On the other hand, treated samples of cells showed deviations from this behaviour. The degree of deviation is in correlation with the number of freezing-heating cycles, i.e., the number of non-viable cells; a smaller number of viable cells results in a greater deviation from the capacitive behaviour.

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SSRSE 11

The fumarate reductase is not related to the extracellular electron transfer at polarization

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After whole genome sequencing and genome annotation of newly established Gram-positive bacteria *Paenibacillus profundus* YoMME [1] we began to study the putative role of important enzymes participating in the processes of respiration and acting as alternative electron acceptors and donors in the lack of oxygen. Under anaerobic conditions, it is supposed that fumarate reductase participates in the process of respiration in bacteria and can be reduced by electrons originating from H_2, sulphide, and formate used as electrons` donors. Although gene for fumarate reductase flavoproteins exists in the genome of *P. profundus* YoMME [1], the expression analyses showed that at three different polarization potentials: -200, +155 and +220 mV *vs.* SHE the fumarate reductase is not represented by more than copies (Fig. 1A), which means that this enzyme is nor expressed under polarization. The registered current when using graphite electrodes covered with bacterial biofilm show that this bacterial strain is capable of transferring electrons extracellularly (Fig. 1B) but the rate of this transfer depends on the applied potential.

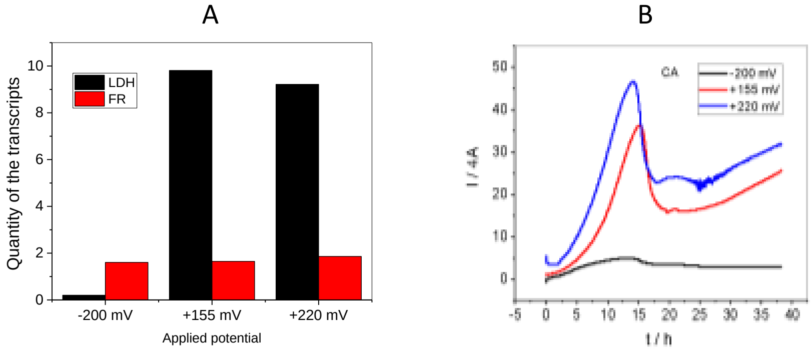

Figure 1. A - quantity of the transcripts calculated from the microliter of the cDNA (results from RT-PCR normalized toward ddPCR) in the total RNA extracted from bacterial biofilm after two days' cultivation at polarization at -200 mV, +155 mV, and +220 mV
B - CA of bacteria cultivated in medium consisting of MPB and fructose under polarization using different potentials

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SSRSE 12

Exploring noble metal modifications: enhanced electrocatalytic activity of cobalt and nickel electrodes in alkaline environments

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This research focuses on the development and comprehensive analysis of novel electrocatalysts for energy conversion applications, particularly for the hydrogen evolution reaction (HER) and oxygen evolution reaction (OER) in alkaline media.[1,2,3] We investigated the electrocatalytic activity of nickel and cobalt electrodes modified with noble metals such as rhodium, ruthenium, iridium, and platinum. Modified polycrystalline electrodes were prepared via facile galvanic displacement from a highly concentrated acidic solution of noble metals.[1,2,3] Our findings show that nickel-based electrodes, especially those modified with rhodium and platinum, demonstrate superior performance, making them promising candidates for alkaline water electrolysis.[1,2] Because of its high efficiency, we investigated further the rhodium-modified nickel polycrystalline electrodes.[1] This surface modification led to a significant enhancement in both HER and OER activities, although hydrogen oxidation (HOR) and oxygen reduction reaction (ORR) activities were reduced compared to those of polycrystalline platinum. The presence of semiconducting Rh_2O_3 was found to adversely affect HOR and ORR performance, while metallic Rh and conductive RhO_2 were beneficial for the HER and OER.[1] The research further elucidates the mechanisms underlying the enhanced electrode kinetics on these Rh-modified nickel electrodes and highlights the role of rapid galvanic changes in improving electrocatalytic activity. Overall, the studies provide insights into engineering advanced, efficient, and cost-effective electrocatalysts for clean energy applications, critical for achieving energy security in modern society.

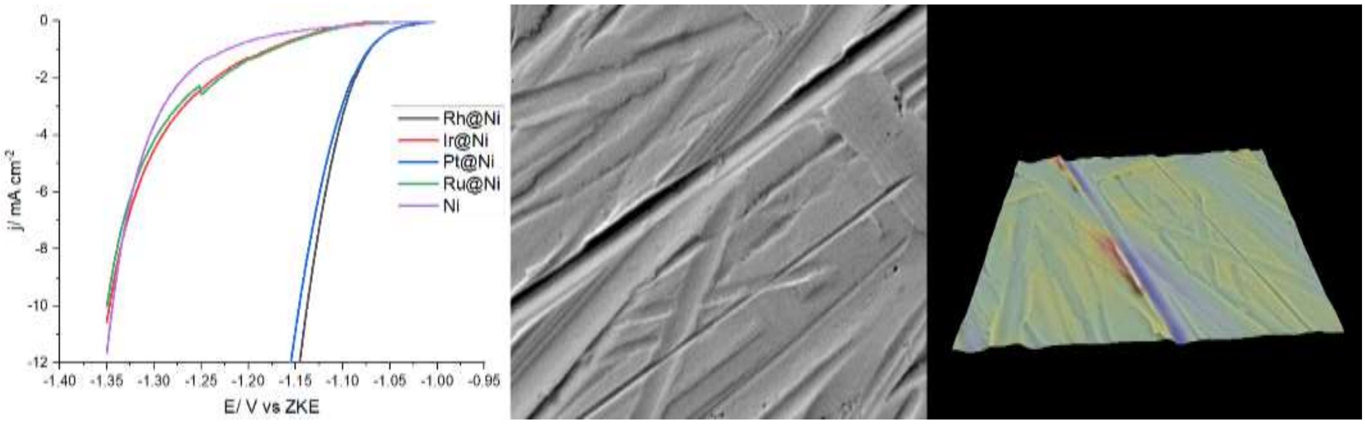

Figure 1. HER diagrams and scanning electron microscopy images

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SSRSE 13

Hydrothermal synthesis of novel $Sm_2(MoO_4)_3$ for selective electrochemical detection of pesticide metol in water samples

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The rapid advancement of technology over the past decade has resulted in significant transformations within the photography sector. In photographic processes, photosensitive materials are used by photographers to convert latent images into visible ones. Among other photographic developers, Metol has been used as a monochrome photographic chemical for more than 100 years in Europe. Metol (MTL), chemically N-methyl-p-aminophenol sulphate with formula $[HOC_6H_4NH_2(CH_3)]_2SO_4$, is also used as a corrosion inhibitor, antioxidant, and antimicrobial, and it serves as an intermediary for the medication diloxanide and dyes for fur and hair [1]. Since it is used in the photographic industry, it is released into the water, contaminating ground, and household water. It can be easily found in different water bodies such as rivers, lakes, ponds, and seas. MTL was found to be a cancerogenic organic pollutant with a significant impact on human health, the environment, animals, plants, and water sources [2]. MTL is non-biodegradable and can accumulate in biotic organisms. It is also related to numerous environmental issues, even in low concentrations. Nevertheless, a larger dose of MTL is necessary to have a substantial effect on several health problems, such as cancer, irritable eyes, slowed heartbeat, skin allergies, and harm to the body's internal blood supply [3]. Therefore, developing a straightforward, quick, affordable, sensitive, and practical method for ML detection in aquatic bodies is imperative.

In this study, a susceptible and selective sensor for the detection and quantification of nitrogen-organic pollutant Metol (MTL) was developed. For this purpose, samarium-molybdate ($Sm_2(MoO_4)_3$ nanoparticles were synthesized by organic solvent-free, eco-friendly, low-cost hydrothermal method and used as an excellent modifier with high catalytic efficiency for implementation into the carbon paste. Electrochemical measurements indicate that the developed electrode facilitates electron transfer processes and enriches the catalytic response. The fabricated $Sm_2(MoO_4)_3$/CPE sensor has a wide linear range of 0.1 to 100 and 100 to 300 µM of MTL with a low detection and quantification limit of 0.047 µM and 0.156 µM at pH 3 in a BRBS, as supporting electrolyte. The results of using this sensor to analyze real water samples from various sources were satisfactory, indicating that this approach can offer an inexpensive, quick, sensitive sensor for ambient MTL monitoring.

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