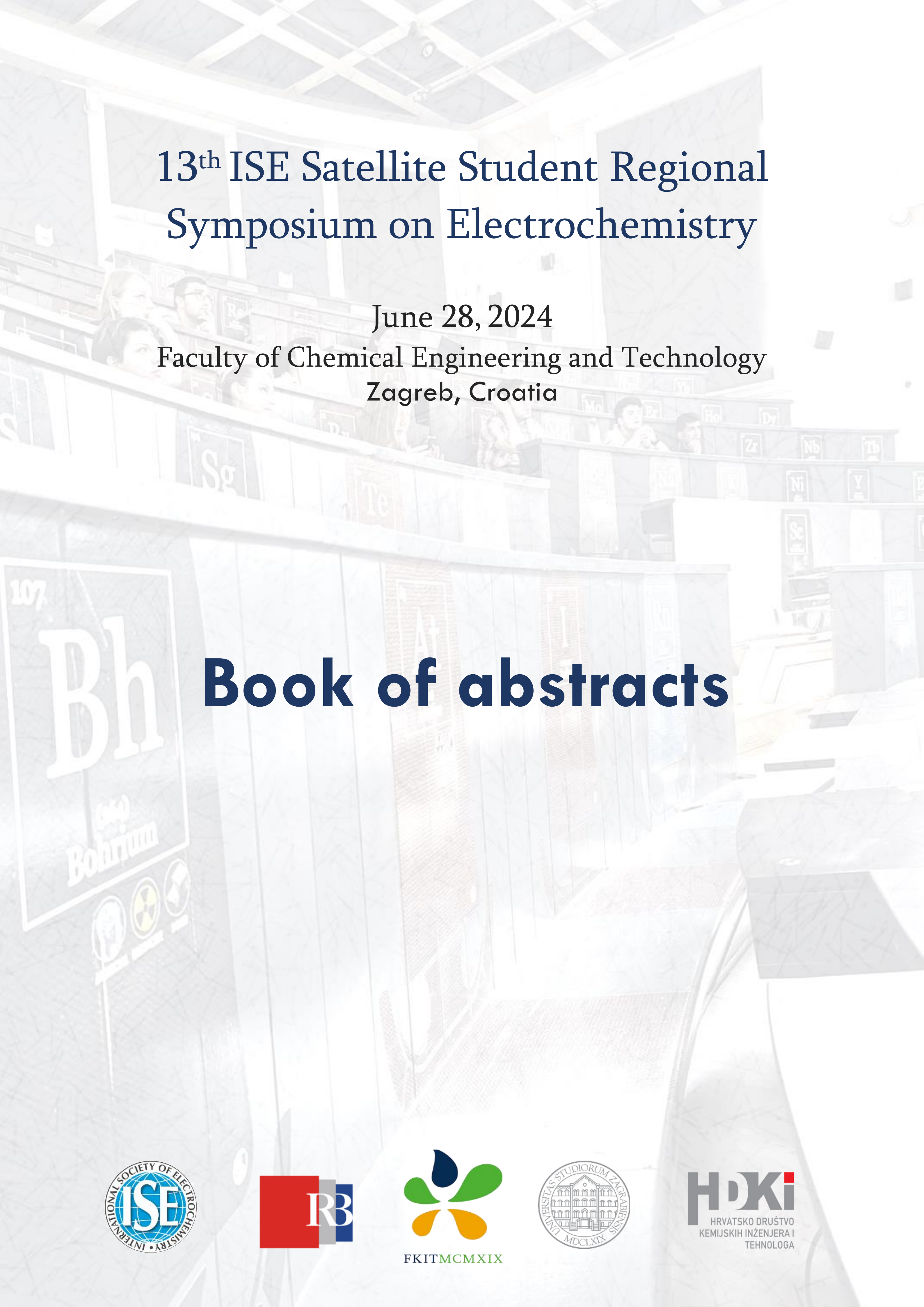

13th ISE Satellite Student Regional Symposium on Electrochemistry

June 28, 2024
Faculty of Chemical Engineering and Technology
Zagreb, Croatia

Book of abstracts

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July 28, 2024
Faculty of Chemical Engineering and Technology
Zagreb, Croatia

13th ISE Satellite Student Regional Symposium on Electrochemistry

Book of abstracts

Croatian Society of Chemical Engineers

13th ISE Satellite Student Regional Symposium on Electrochemistry

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Preface

It was a great pleasure and honor to host the "13th ISE Satellite Regional Symposium on Electrochemistry" (13th ISE-SRSSE) on July 28, 2024. The symposium was held on-site at the Faculty of Chemical Engineering and Technology in Zagreb, Croatia. It was supported by the International Society of Electrochemistry (ISE) and aimed to encourage young scientists, postgraduates and PhD students to present their research results to their peers in a friendly atmosphere. For the first time, it was also supported by the companies BioLogic, Emus, ReCorrTech and Franck.

Another novelty was the creation of a conference website, which increased the recognition value of the conference and simplified the process of registering and submitting abstracts. The symposium was attended by 19 young scientists from Croatia, Austria, Slovenia and Serbia with a total of 17 presentations which covered broad aspects of electrochemical fields: electrochemistry of materials, corrosion, environmental, electroanalytical and electro-organic chemistry. This year, for the first time, three of the best speakers were awarded cash prizes.

The organizing committee would like to sincerely thank all participants for their contributions and gratefully acknowledge all sponsors, but especially the International Society of Electrochemistry for the given support and giving young researchers the opportunity to share their work experiences in different areas of electrochemistry and to establish contacts that may lead to future collaboration.

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Contents

ORAL PRESENTATIONS

The use of coupled multi-electrode array for long-term monitoring of galvanic currents of copper-steel coupling

Klara Prijatelj[1,*], Miha Hren[1], Tadeja Kosec[1]

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Many countries are faced with the problem of storing highly radioactive waste and spent nuclear fuel, for which the international solution is a deep geological repository. The critical component is a closed container surrounded by an additional engineering barrier (bentonite, cement mix). In countries such as Sweden, Finland, and Canada, copper is the proposed material for the outer barrier of steel containers and it is an absolute barrier to preventing radionuclide release in the environment. If the copper coating is damaged during the deposition process, galvanic corrosion between copper and steel may occur. A coupled multi-electrode array (CMEA) method was introduced for long-term monitoring of corrosion currents of copper-steel coupling. CMEA enables temporal and spatial monitoring of anodic and cathodic currents in contact with different electrolytic environments on the surface. [1, 2]

The present work focuses on the long-term monitoring of corrosion currents during 80 days of exposure to dense bentonite slurry with simulated groundwater in an oxic environment. The main focus was on developing anodic and cathodic currents of 25 electrodes. The pattern mimics a damaged cooper container where the steel is exposed to the environment and is galvanically coupled to copper (1 steel and 24 copper electrodes). For comparison, we monitored the development of corrosion currents on a sample of 25 copper electrodes. On the CMEA's samples, different anodic and cathodic electrodes can be distinguished. After the exposure, the surface of the electrodes was analyzed using various microscopic and spectroscopic techniques. Electrodes that behaved anodically have visible significant damage on the surface and presence of more accumulated corrosion products. Less corrosion products were observed on the surface of electrodes that behaved cathodically.

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Bronze patina protection by polymer nanocoatings

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One of the most popular metals used for works of art and cultural heritage objects like sculptures and architecture is bronze. Bronze is often covered by a thin layer of corrosion products, known as patina, which is intentionally applied to the surface to enhance the aesthetics of the object and protect it. Such objects are exposed to environmental pollution present indoors and outdoors on a daily basis. Under the influence of acid rain or other forms of precipitation, the patina can easily be washed off, leaving damage in the bronze and exposing it to new unwanted and uncontrolled corrosion processes. These processes can lead to changes in appearance and stability, resulting in a change in the color of the original surface and the appearance of localized corrosion, as well as chronic material deterioration, which in turn leads to loss of the original sculptural details and the loss of the aesthetic quality of the artwork, as well as the cost of repairing or replacing the material.

The aim of this work was to investigate the possibility of protecting bronze and its patina from corrosion caused by acid rain using cross-linked self-assembled molecular layers of behenic acid. Behenic acid, $C_{21}H_{43}COOH$, is a long-chain saturated fatty acid that was cross-linked by gamma irradiation. The stability of the obtained coatings was investigated in a solution simulating acid rain at pH 5 using electrochemical methods (Tafel extrapolation method and electrochemical impedance spectroscopy (EIS)). The results showed that the corrosion resistance of bronze covered with patina increased with the application of the self-assembled molecular layers of behenic acid.

ACKNOWLEDGMENTS:

The authors would like to acknowledge financial support through the project HRZZ IP-2020-02-4344.

The Novel Paste Electrolyte Cell Used for Testing Protective Layers on Bronze

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Bronze is the predominant material for outdoor sculptures and monuments, which requires effective conservation and inspection techniques. Electrochemical impedance spectroscopy (EIS) is widely recognized for the assessment of bronzes, patinas and coatings in the conservation of metallic cultural heritage. However, its adoption as a standard tool for on-site measurements is hampered by the difficulties associated with adapting conventional electrochemical cells to non-flat, complex surfaces.

Recent advances have led to new electrolytes and cell concepts. In this study, the paste electrolyte cell was applied to various bronze systems, investigating both natural and artificial patinas. The effect of different coating numbers was evaluated and comparative studies were carried out on widely used and newly developed coatings for bronze preservation. The laboratory results were compared with in-situ measurements on real bronze sculptures. These results underline the potential of the paste electrolyte cell to improve conservation strategies for bronze artworks.

ACKNOWLEDGMENTS

This work has been fully supported by Croatian Science Foundation under the project Development of new solutions for characterization and protection of bronze cultural heritage exposed to outdoor environment IP-2019-04-5030.

Multilayered polymer nano-coatings of fatty acids on copper cross-linked by ionizing radiation

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New materials with improved properties are being developed daily to achieve better quality protection and enhanced material stability. The aim of this study was to examine the possibility of forming self-organizing coatings using four fatty acids with 4, 6, 18, and 22 carbon atoms. After formation, the coatings were crosslinked using gamma ionizing radiation. In this study, simple SAMs (Self-Assembled Monolayers) were formed by exposing samples to a solution of one fatty acid for a period of 24 hours. For layered samples, they were immersed first in the solution of one acid, and then in the solution of another fatty acid for 24 hours.

The protective properties of the obtained coatings were examined using the Tafel extrapolation method and electrochemical impedance spectroscopy (EIS). For the characterization of the formed SAMs, goniometry was used, while thermogravimetric analysis (TG) determined changes in sample mass and the degree of degradation.

The obtained results indicate that the coating consisting of the combination of C_6-C_{22} and pure C_{22} acid provides the best protection and is thus the best choice. Furthermore, the results for the C_{rot}-C_{22} acid yield satisfactory outcomes, suggesting that the length of the short chain (crotonic acid with 4 carbon atoms) ensures better alignment compared to C_6 in SAMs.

The implications of MXene surface chemistry beyond the electrochemical response

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MXenes are a rapidly growing family of 2D transition metal carbides and nitrides that are promising for various applications. The surface chemistry of MXenes plays a key role in the electrochemical response of MXenes.[1] Thus, tuning the MXene surface chemistry and electrolyte allows MXenes to function as electrode materials for either electrochemical double-layer capacitors, pseudocapacitors, or batteries. While the synthesis of MXenes through molten salt etching or dry selective extraction[2] and chemical scissor-mediated structural editing of MXenes[3] enables tuning of the surface chemistry of MXenes beyond oxygen and fluorine, the chemical space of these surface terminations remains severely underexplored. Here, we report a comprehensive density functional theory screening for thermodynamically stable MXenes that accounts for the diverse surface chemistry of MXenes.[4] This work will rationalize experimental efforts on the synthesis of new MXenes and their applications in devices for electrochemical energy storage and conversion.

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Exploring Mechanochemistry for Fluoride-Free MXene Synthesis Surface characterisation

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MXenes are a new member of the 2D materials family and this study aims to characterise new 2D nanomaterials for scientific application. The scientific question that's been addressed throughout this study is addressing the challenges of HF synthesis such as environmental and safety concerns because of the hazardous nature of fluoride and emphasizing the importance of new synthesis techniques for fluorine-free MXene production. Specifically, the study investigates whether mechanochemical synthesis is a successful alternative. The results demonstrate successful partial etching of MXene on the surface of Ti_3AlC_2. Surface characterisation using Raman spectroscopy confirms the presence of new rovibronic states in the newly formed structure with the appearance of characteristic MXene Raman shift at 120 cm^{-1}. Scanning electron microscopy (SEM) distinguishes the morphology of MXenes from that of the MAX phase. Energy dispersive X-ray spectroscopy (EDX) affirms the etching of Al, corroborated with the newest Low energy ion scattering spectroscopy (LEIS) technique confirming the delamination of a few nanometres of aluminium on the surface. Atomic force microscopy (AFM) implies the formation of a monolayer MXene structure. In conclusion, the study successfully achieved partial delamination of MXene on the surface, validating the efficiency of the mechanochemical approach in producing fluorine-free MXenes, applicable in various fields.

The determination and importance of Li^+ transport number in lithium metal batteries with fluorinated ether-based electrolytes

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Lithium (Li) metal batteries (LMBs) are perceived to be limited in their performance due to a low cation transport number (t_{Li+}) of non-aqueous liquid electrolytes. Therefore, electrolytes with a high t_{Li+} have gained enormous attention in the battery research community. This study investigated the determination of the t_{Li+} of fluorinated ether (1,2-(1,1,2,2-tetra fluoroethoxy) ethane, TFEE) based electrolytes with 1,2-dioxolane (DOL) and dimethoxy ethane (DME) as a co-solvent. We explored different methods for the t_{Li+} determination including the Bruce-Vincent's method, nuclear magnetic resonance spectroscopy, four electrode measurements, and low-frequency electrochemical impedance spectroscopy (EIS). We showcased that the electrolyte mixture with TFEE-DOL solvents was found to have a high transport number of 0.42. This electrolyte mixture, on the other hand, exhibits a low electrolyte coulombic efficiency (<90%) and poor stability when tested with Li metal. The same fluorinated ether with DME as a co-solvent showed high coulombic efficiency (97%) and stability despite its low t_{Li+} of 0.14. A significant migration resistance through the porous solid electrolyte interface (SEI) in the case of TFEE-DOL electrolyte is suspected to explain the observed discrepancy, as revealed by EIS assisted by scanning electron microscopy and X-ray photoelectron spectroscopy. We propose that the interfacial properties of the Li anode are more crucial for LMBs' performance than the ionic transport through the bulk liquid electrolyte. Importantly, since it enables the characterization of the interphase layer(s), more focus should be made on the measurements of full impedance spectra of Li metal in contact with electrolytes rather than the t_{Li+} of LMB electrolytes.

ACKNOWLEDGMENTS

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Transport and Interfacial Properties of Polymer Coatings in Solid-State Lithium Metal Batteries

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Metallic Li anodes are the best choice for advancing the current state-of-the-art LIB systems. Unfortunately their use is limited by high surface area lithium deposits, which affect interfacial and transport properties in the battery[1]. Solid-state polymer electrolytes present one of the solutions for this issue, though they often struggle to achieve a good compromise between ion-conduction and mechanical properties. Additionally, the lack of suitable characterization techniques hinders the ability to fully understand the interface that is formed between the electrode and the electrolyte.

Our approach involves designing a polymer-based coating compatible with both Li metal and polymer-based electrolyte[2], aiming to improve electrode-electrolyte interface properties. This is achieved by exploiting film-forming additives and stable SEI-forming lithium salts. The impact of these coatings is studied through galvanostatic cycling with time/potential limitation and electrochemical impedance spectroscopy. A three-electrode measurement approach using a microreference electrode[3] is also employed to monitor the contributions of individual electrodes under dynamic conditions. Further insights are obtained through *ex-situ* characterization with scanning electron microscopy and X-ray photoelectron spectroscopy.

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Influence of V_2O_5 addition on the structure and conductivity of Li_2O-Fe_2O_3-P_2O_5 glasses

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The widespread use of portable electrical devices as well as the electrification of the transportation sector require the development of advanced batteries with high energy density. However, today's lithium-ion batteries do not achieve high enough energy density and have a relatively short service life. Also, due to the use of liquid electrolytes, the risk of battery ignition due to damage is at an unacceptable level. One approach to overcome the shortcomings of modern ion batteries in general is directed towards the research and development of new glass and ceramic materials suitable for solid electrolytes and electrode material. The mentioned materials show a whole range of advantages compared to the standard ones used, such as a wide range of composition, isotropic conductivity, a wide temperature range of operation, etc.

In this research, a series of glasses from the Li_2O-Fe_2O_3-V_2O_5-P_2O_5 system, in which Fe_2O_3 is gradually replaced by V_2O_5 in a wide range, was prepared by the rapid melt cooling method. The ratios of individual oxides were maintained to correspond to the LiFePO4 system, and the preparation conditions were investigated in order to obtain optimized samples with specific target characteristics. Electrical transport in glasses containing alkali and transition metal oxides (TMO) is ionic-polaronic. Namely, depending on the amount and mobility of Li^+ ions, they show ionic conductivity, while polaronic conductivity depends on the concentration of a small polaron, i.e. the proportion of TM ions in lower oxidation states. The thermal and structural properties of the obtained samples were examined using DTA analysis and using PXRD and FTIR methods, while insight into the electrical characteristics was obtained using the impedance spectroscopy (IS) method. This research aims to show how the addition of another TMO (V_2O_5) results in structural changes in the dominant amorphous matrix which consequently affects the electrical transport, in order to optimize and maximize conductivity for potential application in solid ion batteries, which will be discussed in detail.

Green hydrogen production using nickel and platinum as electrocatalyst materials

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Green hydrogen is obtained using renewable energy sources, making it a clean, sustainable fuel with zero pollution index. As such, it represents a key component for decarbonizing the energy sector and reducing greenhouse gas emissions. [1] Typically, it can be obtained from water electrolysis process [2-4].

In this work, the process of water electrolysis under alkaline conditions was explored, and the performances of platinum and nickel metals as electrocatalysts were examined. Measurements were conducted using the method of electrochemical impedance spectroscopy (EIS), allowing for a detailed analysis of the electrochemical properties of materials and processes.

The results provide deeper insights into the correlation between electrocatalyst material employed and kinetic parameters obtained, contributing to the optimization of water electrolysis system performance. The conclusions of this research offer valuable insights into reaction mechanisms and potential process adjustments aimed at improving the efficiency and cost-effectiveness of green hydrogen production.

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Application of electrochemical measurements in justifying hydrogen embrittlement resistance of surface and heat-treated tempered martensitic steels

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In recent years, hydrogen appears to be a promising alternative to fossil fuels, therefore evolvement of materials for hydrogen transportation and storage facilities is of high importance. Exposure of high-strength steels to hydrogen can deleteriously influence their performance due to elevated susceptibility to hydrogen embrittlement (HE). The addition of carbide-forming elements such as Mo can be beneficial for the material since certain carbides serve as hydrogen trapping sites. On the other hand, modifying the steel with surface treatments is another possible route to improve the mechanical behaviour of the steel and simultaneously increase its resistance to HE. Shot peening (SP) as mechanical modification technique introduces compressive residual stresses to the material as well as the formation of hydrogen trapping sites in the deformed layer. Although SP is well-known method for improving the mechanical properties of engineering materials, implementation of this method in terms of HE of tempered martensitic steels has not been investigated.

In this study, the effect of Mo carbides and surface modification on HE susceptibility of two tempered martensitic steels will be compared from the electrochemical viewpoint. Hydrogen trapping behaviour of the steels was elucidated via Thermal Desorption Spectroscopy (TDS) combined with electrochemical charging. The influence of carbides and surface treatment was further justified using Electrochemical Permeation. In addition, Slow Strain Rate Tests (SSRT) were conducted to examine mechanical properties of the steels subjected to hydrogen environment.

The results implied that steel with higher Mo content, finer Mo carbides and lower dislocation density exhibited superior resistance to HE. SP-induced trapping sites in plastically deformed layer and grain refinement resulted in a decreased effective diffusion coefficient. Electrochemical charging experiments indicated higher hydrogen uptake and a low-temperature peak for both SP steels.

Development of an inkjet-printed Prussian Blue based lactate biosensor

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The use of inkjet printing in electrochemical sensor development offers cost effective material deposition approach, as it is a completely digital, non-contact technique that requires little material and enables deposition of much thinner layers compared to current state-of-the-art printing methods, such as screen printing. However, fully inkjet-printed electrochemical sensors are not as common due to inability to deposit the sensing material, as the ink material needs to satisfy narrow windows for rheological properties to be printable. The fabrication is then supplemented with other deposition techniques such as drop casting [1].

In this work, Prussian Blue nanoparticle suspension was prepared according to [2]. Properties of the drop cast layer were examined via cyclic voltammetry on screen-printed carbon and inkjet printed graphene electrodes in 0.1 M KCl and phosphate buffer solutions of varying pH. Pretreatment procedure of inkjet printed electrodes and amount of deposited Prussian Blue were optimized to achieve minimal peak separation and enable use in biosensors at low potential vs. Ag/AgCl. Chronoamperometric detection of hydrogen peroxide was conducted to test the functionality of the nanoparticle layer. Lastly, lactate oxidase was immobilized on top of the Prussian Blue modified electrode and the functionality of assembled biosensors was evaluated via chronoamperometric detection of lactate.

ACKNOWLEDGMENTS

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Characterization of chemically deposited Prussian Blue layers on carbon electrodes

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Biosensors have been used for many years to determine the concentration of biomolecules. The most used configuration of biosensors is that involving the use of an oxidase enzyme. Oxidase enzyme oxidizes substrate and produces an oxidized form of substrate and hydrogen peroxide as a side product. The measurement of H_2O_2 concentration can provide information about concentration of the target analyte. High overpotentials are needed for oxidising hydrogen peroxide, which increases risk of interferences. Prussian Blue is used as an electrochemical mediator in the biosensor field because it can selectively catalyze hydrogen peroxide reduction at much lower potential (0 V vs. Ag/AgCl) [1].

In this work, Prussian Blue was deposited chemically by mixing equal amounts of 0.1 M solutions of $FeCl_3$ and $K_3[Fe(CN)_6]$ prepared in 0.1 M KCl and 0.01 M HCl solution. Deposition was conducted on glassy carbon, screen printed carbon and inkjet printed graphene electrodes in varying duration times. Deposited Prussian Blue layers were characterized via cyclic voltammetry scan from -0.2 V to +0.5 V in 0.1 M KCl or phosphate buffer solutions of varying pH level (5.4, 6.4 and 7.4). After deposition on printed electrodes, chronoamperometric detection of hydrogen peroxide was conducted to check the functionality of deposited layers as artificial peroxidase. The goal of this work is to determine optimal deposition conditions for biosensing applications on inkjet printed electrodes.

ACKNOWLEDGMENTS

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What's voltammetry got to do with it - interaction of trace metals and (micro)plastics from marine environments

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The increasing production and use of plastics have resulted in their widespread presence in marine environments, creating a significant environmental issue. Plastic debris can adsorb various ecotoxicants, including trace metals (TM), and serve as a vector for their transport in aquatic systems [1]. To investigate the interaction between plastics and TM, we conducted model adsorption experiments and sampled (micro)plastics along the eastern Adriatic coast. Metals adsorbed on plastic samples were leached using acidic solutions, and TM concentrations were measured using differential pulse anodic (Zn, Cd, Pb, Cu) and differential pulse cathodic (Ni, Co) stripping voltammetry. Voltammetry is a cost-effective, reliable, and relatively simple method with low detection limits, offering well-established techniques for measuring metals in environmental samples. Method modifications, challenges and surprises encountered during the analysis of marine and estuarine (micro)plastic samples will be discussed.

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Electrochemical synthesis of 1-(4-hydroxy-3-methoxyphenyl)propan-2-one

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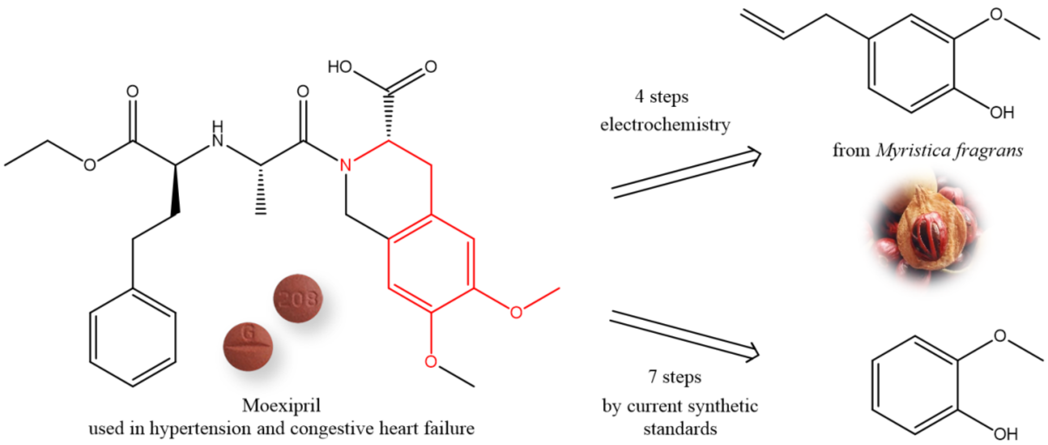
Development of an active pharmaceutical ingredient requires extensive studies on topic of its synthesis and possibility of process optimization. Not only yield and selectivity should be in focus while developing a synthetic pathway, but also the ecological impact of the future industrial process. For example, synthesis of guaiacylalkylamine moiety seen as pharmacophore in many medications including: drotaverine, moexipril, tofisopam and tetrabenazine could be optimized which is researched in this study. Current synthesis of said moiety includes low temperatures, Grignard reagents and a number of steps that build the molecule one atom at a time. With many steps, today's synthesis requires numerous extractions and evaporations maximizing the carbon footprint. Retrosynthetic analysis of the moiety proposes another, shorter, pathway that is yet to be researched and optimized. Natural source of starting material, simple electrochemical reactions and fewer steps mean that this synthetic pathway for intermediates of guaiacylalkylamine could boost the greenness score of the process.



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Exploring electrochemical performance of calcium anode with Ca(TFSI)$_2$-based electrolytes

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Multivalent batteries utilizing earth-alkaline metals represent a new direction of post-lithium battery technology. Among them, calcium possesses high abundance, low redox potential (-2,87 vs. SHE), and a high capacity due to the two-electron charge transfer (1,34 A h kg^{-1}), and high melting point (842 °C) for safe operations.[1] Despite these attractive characteristics, calcium batteries are far from the commercialization. The main reason for this is the passivation of calcium electrodes in organic electrolytes, which prevents further use of anode. To fully utilize calcium anode, developing and optimizing a calcium solid electrolyte interface (SEI) that enables calcium ion migration is necessary.

In this work, we examined Ca(TFSI)$_2$ salt in two different solvents: acetonitrile and ethylene carbonate-propylene carbonate mixture, on the electrochemical behaviour of calcium electrodes. The measurements were performed inside a Swagelok cell with Pt as a pseudo reference electrode, active carbon as a counter electrode, and calcium disc as a working electrode. Electrochemical characterization of calcium electrodes was performed by various techniques: cyclic voltammetry, electrochemical impedance spectroscopy, chronoamperometry, and quartz crystal microbalance. The composition and structure of obtained SEI layers were characterized using FTIR and XRD techniques.

We discovered that different solvents significantly influence the electrochemistry of calcium anode. Also, the composition of the SIE layer can be modified using different solvents and can severely influence plating/striping of calcium in organic electrolytes.

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The electrochemical methods cycle for corrosion testing

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Application of a electrochemical methods cycle enables easy and quick analysis of metals in terms of corrosion analysis. The possibility of combining non-destructive and destructive methods is shown in this paper. Successive methods achieve quick results, while the number of consecutive experiments reduces the number of polishing and electrode preparation. The open circuit potential measurement, electrochemical frequency modulation and potentiodynamic method were taken as a good combination of methods for the electrochemical cycle. An electrochemical system containing a three-electrode cell was used, where the corrosion effect of 0.5 M NaCl solution on copper was investigated. A Gamry instruments potentiostat and software were used to form an adequate cycle [1]. The electrochemical cell was placed in a Faraday cage to avoid external influences. As results, the values of current density, anodic Tafel slope, and cathodic Tafel slope were obtained. The CF-2 and CF-3 factor values confirm that the EFM results correspond to the EFM theory [2].

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