Association of
South-East European
Electrochemists


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8th Regional Symposium on Electrochemistry of South-East Europe

together with the

9th Kurt Schwabe Symposium

https://www.aseee.eu/index.php/rse-see-home
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Graz University of Technology, 11-15 July 2022

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Preface

RSE-SEE 8

The 8th Regional Symposium on Electrochemistry of South-East Europe is held in Graz, Austria on 11-15 July 2022. Since their inception, the RSE-SEE meetings have provided a forum for the scientific community of South-East Europe closely related to the fields of electrochemistry and electrochemical engineering. This forum has proven to be a place for fruitful debates and personal exchange necessary for the further development of the field. Seven RSE-SEE symposia were already held (Croatia, Red Island 2008, Serbia, Belgrade 2010, Romania, Bucharest 2012, Slovenia, Ljubljana 2013, Bulgaria, Pravets 2015, Hungary, Balatonkeneze 2017, Croatia, Split 2019) and have always been places where people could come together and present their latest findings, share experiences and challenges in a warm and stimulating atmosphere. We are convinced that the RSE-SEE 8 will take place in the same positive environment.

The specific objective of the RSE-SEE 8 is to address the most advanced directions and new achievements in fundamental and applied electrochemistry underlying almost all research activities aimed to enhance knowledge and develop novel and/or improved materials and processes.

The RSE-SEE meeting is fully reconciled with the mission of the ASEEE society boosting further activities towards:

- establishing a regional network of scientists working in all aspects of electrochemistry and electrochemical engineering fields,
- supporting cooperation among countries in the region and between countries of South-East Europe and the rest of the world.
- advancing science, spreading and disseminating knowledge.
- educating students and younger colleagues.
- transferring knowledge and technology.
- helping sustainable development of society and fostering economic growth.

Kurt Schwabe Symposium

The 9th Kurt Schwabe symposium (9KSS) is organized jointly with RSE-SEE 8 July 11-15, 2022, in Graz, Austria. It took place on Wednesday, July 13, at the Graz University of Technology.

The symposium was established in 1993 by Erika Kálmán in memoriam of Kurt Schwabe, a well-known German scientist working in the fields of electrochemistry and corrosion. He was particularly interested in the development of electrochemical analytics for different research areas as well as of equipment for customer applications. Beside his professorship at Dresden University and several other academical positions, Kurt Schwabe was the founding director of a research institute on applied sensor technologies.

Committees

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Ralf Moos	University Bayreuth, Germany
Winfried Vonau	Kurt-Schwabe-Institut Meinsberg, Germany
Claudia Weidlich	DECHEMA Forschungsinstitut, Frankfurt, Germany

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Alfred Kick	Kurt-Schwabe-Institut Meinsberg, Germany
Winfried Vonau	Kurt-Schwabe-Institut Meinsberg, Germany
Janek Weißpflog	Kurt-Schwabe-Institut Meinsberg, Germany

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Kurt Mayer	Graz University of Technology, Austria
Magdalena Pauritsch	Graz University of Technology, Austria
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Conference Program

Introductory student program

		Monday - 11th of July
08:30	13:00	**Registration and Exhibitor Set-up, Inffeldgasse 25D**
13:00	13:45	**Plenary Talk - Julia Kunze-Liebhäuser** Bare and Modified Cu(111) Electrocatalysts: Interfacial Structure and Reactivity
		Student Satellite Symposium (HS i7) (Chair Bodner / Kunze Liebhäuser)
13:45	14:05	Talk 1 - Julian Hörndl: Increased photocatalytic activity of BaTaO2N particles by morphology design and cocatalyst deposition
14:05	14:25	Talk 2 - Jakob Praxmair: Increased photocatalytic activity of BaTaO2N particles by morphology design and cocatalyst deposition
14:25	14:45	Coffee Break
14:45	15:05	Talk 3 - Verena Lipic: Electrochemical characterization of self-assembled monolayers on nanoporous copper
15:05	15:25	Talk 4 - Ana Rebeka Kamšek: Structural Analysis of Twinned Metallic Alloy Nanoparticulate Electrocatalysts
15:25	15:45	Talk 5 - Marcel Simhofer: Charge compensation processes in LiNi0.80Co0.15Al0.05O2 cathodes studied by operando SQUID magnetometry
15:45	16:05	Coffee Break
16:05	16:25	Talk 6 - Annika Just: Investigating the catalytic activity of gold-palladium nanoparticles for oxygen reduction reaction by single nanoparticle electrochemistry
16:25	16:45	Talk 7 - Mario Kircher: The Production and Characterisation of Membrane Electrode Assemblies
16:45	17:05	Talk 8 - Gabrijela Radić: Photoelectrochemical degradation of amoxicillin using $BiVO_4$ as photoactive material
17:05	18:05	**Student Satellite Symposium Poster Session**

		Tuesday - 12th of July	
8:00	8:30	Registration and Exhibitor Set-up, Rechbauerstraße 12	
08:30	09:00	**WELCOME** **Harald KAINZ, Rector TU Graz** **OPENING OF RSE-SEE8** **Viktor HACKER & Bernhard GOLLAS** TU Graz, Chairs of the Organizing and the Scientific Committee of the ASEEE	
09:00	09:45	**Plenary Talk - Peter Strasser** The Electrocatalytic Dark Side of Solar Fuels and Solar Chemicals	
09:45	10:05	Coffee Break	
10:05	10:50	**Plenary Talk - Csaba Janáky** Challenges and opportunities of electrochemical CO_2 conversion: from nanoscale catalysis to industrial implementation	
11:00	13:00	Lunch	
		Session 1 - Batteries and Electrochemical Energy Storage (HS II) (Chair Kraljic / Rokovic)	**Session 2 - Electrochemical Energy Conversion & Catalysis (AULA)** (Chair Strasser / Mayrhofer)
13:00	13:30	**Keynote - Daria Vladikova:** An Insight into the Potential of Proton Conducting Ceramic Cells	**Keynote - Rui Gusmão:** 2D layered MPX3 and electrochemical energy conversion reactions
13:30	13:50	Talk 1 - Christian Kuss: Applicability of conducting-polymer matrices in composite battery electrodes	Talk 1 - Karl Mayrhofer: Evaluation of Electrocatalyst Activity, Stability and Selectivity during dynamic operation – Online Coupling of Analytical Techniques to Electrochemical Flow Cells
13:50	14:10	Talk 2 - Zoran Mandic: Simultaneous testing of positive and negative electrodes in carbon supercapacitors	Talk 2 - Mohammed Azeezulla Nazrulla: Electronic structure manipulation of atomic copper quantum clusters for the CO activation with IIIA group elements
14:10	14:30	Talk 3 - Miglena Slavova: Optimized zinc electrode for rechargeable zinc-air batteries	Talk 3 - Marcin Opallo: Electrocatalysis at lithium batteries waste powders
14:30	14:50	Talk 4 - Daniel Rettenwander: The mechanism of lithium dendrite formation and propagation under pulsed charging conditions in solid state lithium batteries	Talk 4 - Verena Theußl: Influence of the carbon substrate on the electroreduction of CO2 to formate using various gas diffusion layers
14:50	15:10	Talk 5 - Florian Flatscher: Dendrite prevention in solid-state batteries by engineering the surface-near properties	Talk 5 - Blagoy Burdin: Artificial Aging via Chemical Redox Cycling for Accelerated Stress Tests of SOFC
15:10	15:30	Coffee Break	
15:30	15:50	Talk 6 - Qamar Abbas: Investigations of carbon/electrolyte interface in hybrid iodine-supercapacitors	Talk 6 - Eveline Kuhnert: Accelerated Stress Test Development based on Degradation Phenomena in PEMWE Cells
15:50	16:10	Talk 7 - Stefan Breitenbach: Comparison of Viscose-Based Supercapacitor Electrodes Activated by KOH, H2O, and CO2	Talk 7 - Svenja Baues: Combinatorial Screening of Cu-W Oxide-Based Photoanodes for Photoelectrochemical Water Splitting
16:10	16:30		Talk 8 - Monika Charążka: Ni(OH)2 type nanoparticles derived from poly(NiSalen)s to remediate urea-rich wastewater
18:00	-	**City Walk**	

		Wednesday - 13th of July	
		Registration and Exhibitor Set-up, Inffeldgasse 25D	
08:15	08:30	**Opening of Kurt Schwabe Symposium** **Michael Mertig & Winfried Vonau** Kurt-Schwabe-Institut, Meinsberg	
08:30	09:15	**Plenary Talk - Kristina Tschulik** Advanced understanding of electrocatalysis at nanoscale materials by spectro-electrochemistry and single entity electrochemistry	
		Session 9 - Kurt Schwabe Symposium (HS i7) (Chair Weidlich)	**Session 5 - Organic Electrochemistry & Bioelectrochemistry (HS i3)** (Chair Hromadova)
09:15	09:45	**Topic A - Gas Detection / H_2: Keynote - Olaf Kiesewetter:** H2 sensors for industrial and automotive applications	**Keynote - Yolina Hubenova:** Extracellular electron transfer through the cell wall of Gram-positive bacteria
09:45	10:05	Talk 1 - Jens Zosel: Miniaturized hydrogen gas sensor system for safety monitoring	Talk 1 - Sascha Morlock: Direct Electron Transfer from Indium Tin Oxide to Photosystem I in Mediator-free Photobiocathodes
10:05	10:25	Coffee Break	
10:25	10:45	Talk 2 - Sebastian Wohlrab: Impedimetric spillover sensing for hydrogen detection in reducing media	Talk 2 - Mario Mitov: Recovery of the metals from Group IB of the Periodic Table by Microbial Electrochemical Snorkel
		Session 9 - Kurt Schwabe Symposium (HS i7) (Chair Howorka)	**Session 2 - Electrochemical Energy Conversion & Catalysis (HS i3)** (Chair Opallo)
10:45	11:15	**Topic B - Bio-electrical sensors: Keynote - Ulrich Rant:** Versatile biosensing with electrically actuated DNA adaptors on a chip	**Keynote - Nejc Hodnik:** Towards Electrocatalysts' Structure-Stability Relationship
11:15	11:35	Talk 1 - Adam Dorey: Electrochemical sensing of single molecules using nanopores	Talk 10 - Sigrid Wolf: Graphene derivative supported palladium-based catalysts for the ethanol electrooxidation in alkaline media
12:00	13:00	Lunch	
13:00	13:20	Talk 2 - Fred Lisdat: Advancements in photobioelectrodes based on photosystem I	Talk 11 - Kamila Łępicka: Energy transport improvement in Ni2+salen polymer semiconductors by chains confinement inside vertical silica nanochannels
13:20	13:40	Talk 3 - Margaux Frigoli: Indirect Detection of Pseudomonas Aeruginosa using Molecularly Imprinted Polymers	Talk 12 - Mila Krstajic Pajic: Electrodeposited NiSn at Ni foams as electrodes for hydrogen production
13:40	14:00	Talk 4 - Manilo Caldara: Thermal detection of glucose in urine using a molecularly imprinted polymer as a recognition element	Talk 13 - Christoph Bondue: H2 Evolution During the Electrochemical Oxidation of Aliphatic Aldehydes: The Effect of the Electrochemical Double Layer
14:00	14:20	Talk 5 - Soroush Bakhshi Sichani: Study of DNA hybridization using a novel thermal biosensing platform as a proof-of-concept	Talk 14 - Kaur Sukhjot: Designing of electrocatalysts for Zn-CO2 battery – From CO2 utilization to energy storage
14:20	14:40	Coffee Break	
		Session 9 - Kurt Schwabe Symposium (HS i7) (Chair Rant)	**Session 2 - Electrochemical Energy Conversion & Catalysis (HS i3)** (Chair Mardare)
14:40	15:10	**Topic C - Environmental monitoring and smart farming:** **Keynote - Moritz Schlagmann:** Development of Sensor Nodes and Sensors for Smart Farming	**Keynote - Marco Bogar:** In-situ GISAXS-Revealed Interplay Among Dealloying, Ostwald Ripening and Coalescence of PtXNi100-X Bimentallic Alloy Under PEMFC Simulated Operational Conditions
15:10	15:40	Talk 1 - Sven Voigt: Environmental friendly and low cost monitoring system for plant and agriculture fields	Talk 15 - Elena Davydova: Amorphous Ni-B-based Materials for Electrochemical – Thermally-Activated Chemical (E-TAC) Water Splitting
15:40	16:00	Talk 2 - Michelle Brandão Silva de Assis: Development of a miniaturized electrochemical sensor for on-site nitrate monitoring	Talk 16 - Sebastian Rohde: Robust fuel cells and electrolysers for lunar energy systems
16:00	16:20	Talk 3 - Janek Weißpflog: Approaches to voltammetric detection of As(III) and As(V) in mining waters for in-situ application	Talk 17 - Ambrož Kregar: Unified model of hydrogen peroxide production and transport in LT-fuel cell membrane-electrode assembly
16:20	16:40	Talk 4 - Anastasiya Svirepa: Preparation and applications of biopolymer-modified electrochemical sensors	Talk 18 - C. Nagaiah Tharamani: H2S from environmental pollutant to new form of energy
16:40	17:00	Talk 5 - Jose Vigil: Indoor Air Quality (IIAQ) and Infection Probability Rate (IPR): Developing better spread risk models	Talk 19 - Kurt Mayer: Monitoring the disintegration of the catalyst layer in the PEFC with Total Harmonic Distortions
17:00	17:20	Coffee Break	
		Session 9 - Kurt Schwabe Symposium (HS i7) (Chair Vonau)	**Session 2 - Electrochemical Energy Conversion & Catalysis (HS i3)** (Chair Vladikova)
17:20	17:50	**Topic D - Advanced electrochemical detection methods:** **Keynote - Claudia Weidlich:** Electrochemical Monitoring of Vanadium Redox Flow Batteries	Talk 20 - Evelina Slavcheva: Electrochemical hydrogen compressor – novel cell design and electrodes structure
17:50	18:20	Talk 1 - Mariola Brycht: The effect of surface pre-treatment of a planar boron-doped diamond electrode on the electrochemical response of fenhexamid	Talk 21- Max Grandi: Influence of electrode composition and operating conditions on the performance and EIS of polymer electrolyte fuel cells
18:20	18:40	Talk 2 - Jens Zosel: Measurement of hydrogen peroxide vapour with mixed potential solid electrolyte sensors	Talk 22 - Iosif Fromondi: Material performance characterization in electrocatalysis: the role of the electrochemical instrument and measurement techniques in your discovery
18:40	19:00	Talk 3 - Rocio Arreguin Campos: Imprinted polydimethylsiloxane-graphene oxide composite receptor for the biomimetic thermal sensing of Escherichia coli.	

		Thursday - 14th of July	
08:30	09:15	**Plenary Talk - Göran Lindbergh** Limiting processes in Anion Exchange Membrane Fuel Cells	
		Session 7 - General Topics and Physical Electrochemistry (HS i7) (Chair Janaky)	**Session 6 - Electroanalytical Chemistry and Sensors (HS i3)** (Chair Lisdat)
09:15	09:45	**Keynote - Ivana Zrinski:** Forming free anodic memristors in hafnium-tantalum system	**Keynote - Piyush Sindhu Sharma:** Nanostructured polymers for chemosensing of proteins and biomolecules
09:45	10:05	Talk 1 - Mahnaz Azimzadeh Sani: Anomalously High Capacitance of the Metal /Water Interface: Revealed by Nano-Impact electrochemistry, Explained by Molecular Dynamics Simulations	Talk 1 - Sabine Kuss: Bacterial Drug Susceptibility Assessment by Electrochemical Quantification of Antibiotic Retention
10:05	10:25	Coffee Break	
10:25	10:45	Talk 2 - Lena Harms: Analysis of Multi-layer Thin Film Structures of Metal Hexacyanometallates	Talk 2 - Vasko Jovanovski: Amperometric gas sensor for detection of gaseous H2O2 based on redox mediators
10:45	11:05	Talk 3 - Soumyadip Mondal: Heterogeneous electron transfer with redox active insulating solid	Talk 3 - Guth Ulrich: Nano structured and pyrolytic deposited carbon electrodes for detection of nitroaromates – a comparison
11:05	11:25	Talk 4 - Győző G. Láng: Impedance analysis of polymer modified electrodes – the effects of thickness distribution and non-stationarity	Talk 4 - Oleksandr Vasylkevych: Electrochemical study of the kinetics of synthesis of antioxidants by the Mannich reaction
11:25	11:45	Talk 5 - Tamás Pajkossy: Analysis of quasi-reversible CVs and dEIS data: transformation to potential-program independent forms	
11:45	13:00	Lunch	
		Session 7 - General Topics and Physical Electrochemistry (HS i7) (Chair Lang)	**Session 4 - Corrosion Science and Protection (HS i3)** (Chair Hassel)
13:00	13:30	**Keynote - Marijana Kraljic Rokovic:** Influence of ascorbic acid on photoelectrochemical hydrogen evolution	**Keynote - Ingrid Milosev:** Cast aluminium-silicon alloys for marine exposure
13:30	13:50	Talk 6 - Jun Huang: Modelling of Electrocatalytic Double Layers with Refined Treatment of Metal-Water Interactions and Chemisorption	Talk 1 - Peter Rodič: Corrosion protection of AA2024-T3 using siloxane-silica sol-gel coating modified with various fluorinated (meth)acrylates
13:50	14:10	Talk 7 - Jesús Tartaj: Preparation and Characterization of La0.6Sr0.4Fe(Co)O3-δ Ceramic Materials for Cathodes of Intermediate Temperature SOFCs	Talk 2 - Shaukat Ali Lone: Crystal structure, nano mechanical and electrochemical properties of Co based alloys containing various Cr and Mo content
14:10	14:30	Talk 8 - Eva-Maria Steyskal: Porosity evolution and oxide formation during the formation of nanoporous copper via electrochemical dealloying	Talk 3 - Barbara Burnat: Comparative corrosion studies of co-doped TiO2 sol-gel coatings for biomedical applications
14:30	14:50	Talk 9 - Martin Vrlić: Model based state estimation of internal states distribution of a fuel cell using principal component analysis	Talk 4 - Dominik Knapic: Electrochemical characterisation and bioassessment of anodically oxidized and femtosecond laser treated Ti6Al4V for dental and bone implants
14:50	15:10	Talk 10 - Magdaléna Hromadová: Single Molecule Junctions Containing Parallel Aliphatic Bridges	
15:10	17:30	**Coffee Break & Poster Session**	
19:00	-	**"High Voltage" Conference Dinner Party featuring "Styrian Songbook" and "Shuffle Truffle"**	

		Friday - 15th of July	
09:00	09:45	**Plenary Talk - Martin Winter** Electrochemical and Chemical Analysis as Powerful Complement for Battery Diagnostics	
		Session 4 - Corrosion Science and Protection (HS i7) (Chair Pajkossy)	**Session 3 - Electrochemical Processing & Engineering (HS i3)** (Chair Lindbergh)
09:45	10:15	**Keynote - Liana Anicai:** Cathodic electrodeposition of cerium-based conversion coatings using deep eutectic solvents formulations for corrosion protection of AA7075 aluminum alloys	**Keynote - Davide Cademartori:** The Freeze Tape Casting Technique for the Manufacturing of Graded Porous Scaffolds for Solid Oxide Cells: Experimental Activities and CFD Modelling
10:15	10:35	Talk 5 - Achim Walter Hassel: beta-Phase Niobium Titanium Alloys and their Passivity in Medical Applications	Talk 1 - Michaela Roschger: New anode flow field design for alkaline direct ethanol fuel cells
10:35	10:55	Coffee Break	
10:55	11:15	Talk 6 - Ivan Spajić: Single-layer and multi-layer ALD thin films for the protection of titanium for biomedical applications	Talk 2 - Philipp Aldo Wieser: In operando monitoring templated electrodeposition of Pt films with hexagonal pore structure by GISAXS
11:15	11:35	Talk 7 - Anton Kokalj: Penetration of Cl− ions from solution into an organic self-assembled-monolayer on a metal substrate: Trends and modeling aspects	Talk 3 - Andrei Ionut Mardare: Electrical equivalent of Rayleigh-Taylor effect for engineering of composite anodic memristors
11:35	11:55	Talk 8 - Dževad Kozlica: Revealing the formation of corrosion protective films on copper through the role of chloride ions	Talk 4 - Antonio Maria Asensio: Effective calcium doping of the double perovskite SmBaCo2O5+δ as promising oxygen electrode for Intermediate-Temperature Solid Oxide Cells
		Conference End	
13:00	17:00	**Excursion to Zotter chocolate factory**	

Plenary Speakers

Csaba Janáky

Csaba Janáky is an Associate Professor at the Department of Physical Chemistry and Materials Science, University of Szeged, Hungary. He is the principal investigator of the MTA-SZTE „Momentum" Photoelectrochemistry Research Group, supported by the Hungarian Academy of Sciences and the European Research Council (ERC-Starting Grant). Csaba is also responsible for Green Economy and Climate Policy at the university and Chief Scientific Advisor of ThalesNanoEnergy Inc. He is an emerging expert of materials science oriented electrochemistry and photoelectrochemistry. He has developed new electrode materials for energy applications, such as CO2 reduction, water oxidation, and H2 evolution. He has published over 100 articles in peer-reviewed journals with an overall impact factor of 850. He is member of the Editorial Advisory Board of ACS Energy Letters and the Young Academy of Europe. In the last 5 years, 4 patent applications, the R&D 100 Award (the "Innovation Oscar"), the Hungarian Environmental Innovation Award, and the Gábor Dénes Award indicate the innovativeness of the applied research activity.

Julia Kunze-Liebhäuser

Julia Kunze-Liebhäuser is Professor at the University of Innsbruck and Head of the Institute of Physical Chemistry and the Materials- and Electrochemistry Group that has its focus in materials and surface science combined with electrochemistry. Her group characterizes materials for electrochemical energy conversion and storage with application in electrocatalysis and (post) lithium-ion batteries. One important focus is on the investigation of the solid/liquid interface at model systems. She graduated from the Chemistry Department at the Heinrich Heine University Düsseldorf with a University Degree in 1999 and pursued her Ph.D. study as a collaborative work between the Institute for Physical Chemistry und Electrochemistry at the University of Düsseldorf and the Laboratoire de Physico-Chimie des Surfaces at the Ecole Nationale Supérieure de Chimie de Paris. She was awarded her Ph.D. degree in 2002. From 2003 to 2005, she worked as a postdoctoral fellow at the University of Guelph in Canada. She accepted a position at the University of Erlangen, Germany, in 2005 where she joined the Institute of Surface Science and Corrosion. In 2009, she became a Junior Fellow of the Institute for Advanced Study at the Technical University of Munich, where she received her venia legendi in 2012.

Göran Lindbergh

Göran Lindbergh, Professor in Electrochemical Process and System Engineering and Head of Applied Electrochemistry at the Department of Chemical Engineering, KTH Royal Institute of Technology in Stockholm, Sweden. He holds a Master of Science in Chemical Engineering and a PhD in Applied Electrochemistry and Corrosion Science, at the same university. He has been a post-doctor at Tohoku University, Sendai, Japan. He is today working with electrochemical power sources and electrolytic processes within the field of electrochemical engineering. A common theme in the on-going research projects is the mathematical modelling and electrochemical characterisation of batteries, electrolysers and fuel cells. He has more than 230 published journal papers, and has been the principal advisor of 35 graduated doctoral students. He is coordinating the SSF Agenda 2030 Research Centre PUSH (Production, use and storage of hydrogen) and the energy storage activities in the Swedish Electromobility Centre, and is a member of The Royal Swedish Academy of Engineering Sciences (IVA).

Peter Strasser

Peter Strasser studied chemistry at the University of Tübingen, Germany, at Stanford University and at the University of Pisa and obtained his “Diploma” degree in Chemistry. He obtained his PhD in “Physical Chemistry and Electrochemistry” from the ‘Fritz-Haber-Institute of the Max-Planck-Society’ in Berlin. He then joined “Symyx Technologies Inc.” as a postdoctoral associate and was later promoted Senior Member of staff and served as project/group leader in Electrocatalysis and Heterogeneous Catalysis. He then assumed the position of Assistant Professor at the Department of Chemical and Biomolecular Engineering at the University of Houston before he became the chaired professor of “Electrochemistry and Electrocatalysis” in the Chemical Engineering Division of the Department of Chemistry at the Technical University Berlin. He is a Visiting Professor at the Department of Material Science at Tongji University, China. Since 2018, he has continuously been listed in the annual worldwide Web of Science list of “Highly Cited Researchers” documenting the significant and broad influence of his scientific work. Peter Strasser is a named inventor on 17 U.S., Japanese, and European patents. He has authored or co-authored more than 350 scientific papers that have appeared in refereed journals, as well as the book High-Throughput Screening in Chemical Catalysis Concepts, Strategies and Applications, Wiley-VCH, New York.

Kristina Tschulik

Kristina Tschulik holds a ‘Diplom’ in Chemistry from TU Dresden (Germany), and performed her doctoral studies on magnetic field-assisted structured electrodeposition at IFW Dresden (Germany) until 2012. Afterwards, she joined the University of Oxford (UK) as a Marie Skłodowska-Curie IEF postdoctoral researcher, working on single nanoparticle electrochemistry and quantitative physicochemical analysis of electrochemical reactions. In 2015, Kristina moved to Ruhr University Bochum (Germany) as a Junior Professor, where she was promoted to Full Professor in 2018 and currently holds the Chair of Analytical Chemistry II – Electrochemistry and Nanoscale Materials. Her research focuses on characterizing the physical properties and intrinsic chemical (re-)activity of functional nanomaterials for renewable energy technologies. To this end she develops advanced electrochemical tools including single entity electrochemistry and spectro-electrochemical methods. Her contributions to these fields have led to more than 130 journal publications and were highlighted by numerous prices and awards, including the Hellmuth Fischer Medal (2018), an ECR starting grant (2020) and a Max-Planck Felllowship (2021).

Martin Winter

Martin Winter has been researching in the field of electrochemical energy storage and conversion for more than 30 years. His focus is on the development of new materials, components and cell designs for lithium ion and lithium-metal batteries as well as alternative battery systems. Winter currently holds a professorship for “Materials Science, Energy and Electrochemistry” at the Institute of Physical Chemistry at the University of Münster, Germany. The full professorship developed from an endowed professorship funded by the companies Volkswagen, Evonik Industries and Chemetall (today Albemarle) from 2008 to 2012. Winter is the founder and scientific director of MEET Battery Research Center at the University of Münster. MEET stands for "Münster Electrochemical Energy Technology". A team of 150 scientists, engineers and technicians work there on the research and development of innovative electrochemical energy storage systems with higher energy density, longer durability and maximum safety. Since 2015, he is also the founding director of the Helmholtz Institute Münster HI MS “Ionics in Energy Storage”, an institute branch of Forschungszentrum Jülich. MEET and HI MS are internationally leading institutions in the research and development of innovative electrochemical energy storage systems.

Keynote Speakers

Liana Anicai	Politehnica University of Bucharest, Center of Surface Science and Nanotechnology, Romania
Marco Bogar	Università di Trieste, Italy
Davide Cademartori	University of Genoa, Department of Civil, Chemical and Environmental Engineering, Italy
Rui Gusmão	University of Chemistry and Technology Prague, Inorganic Chemistry, Czech Republic
Nejc Hodnik	National Institute of Chemistry, Slovenia
Yolina Hubenova	Bulgarian Academy of Sciences, Institute of Electrochemistry and Energy Systems, Bulgaria
Olaf Kiesewetter	UST Umweltsensortechnik GmbH, Germany
Marijana Kraljić Roković	University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia
Ingrid Milosev	Jožef Stefan Institute, Department of Physical and Organic Chemistry, Slovenia
Ulrich Rant	Dynamic Biosensors GmbH, Germany
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Oral Presentations

Investigations of carbon/electrolyte interface in hybrid iodine-supercapacitors

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In order to reach high energy values, commercial supercapacitors use organic electrolytes e.g., tetraethylammonium tetrafluoroborate (TEABF4) in acetonitrile to obtain cell voltage 2.7 V-2.8 V. However, acetonitrile-based supercapacitors are prone to catching fire and produce toxic gases under emergency situation.

Aqueous electrolytes (e.g., NaNO3 in water) are non-toxic, low cost, and carbon/carbon supercapacitor using them display voltage up to 1.5 V that leads to rather low energy value [1]. Iodide-based aqueous electrolyte in such supercapacitors are more adapted since one of the electrode works as battery-like, thus a hybrid supercapacitors is realized that displays high energy owing to high capacitance as a result of hybridization of battery and capacitor electrodes in one device [2-3].

In this presentation, we look at the state of aqueous sodium iodide (NaI) electrolyte in the nanopores of carbon electrode beside investigating its surface properties. The impact of initial charging of carbon/carbon cell and cycling as well as simple soaking of carbon electrode in the electrolyte has been elaborated by using electrochemical quartz crystal microbalance (EQCM), in situ Raman spectroscopy and X-ray photoelectron spectroscopy (XPS). Apart from the iodine electrodeposition in the nanopores that expels solvated sodium ions during charging, irreversible oxidation of the carbon surface has been confirmed. Once, the carbon surface is passivated during initial cycles, reactive sites are consumed and a stable cycling regime is reached. In addition, the iodine confined in the nanopores causes changes in the carbon lattice by charge transfer and mechanical strain.

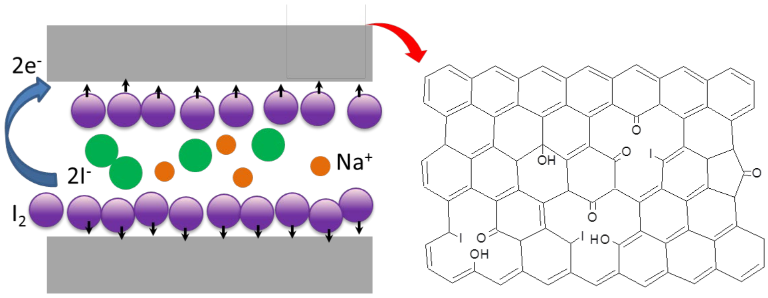

Figure 1. Schematic of iodine electrodeposition in the pore and functional groups of carbon electrode.

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Cathodic electrodeposition of cerium-based conversion coatings using deep eutectic solvents formulations for corrosion protection of AA7075 aluminium alloys

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An attractive route to replace chromate conversion coatings on Al and Al alloys is based on the use of rare-earth compounds [1]. Usually, they act as cathodic inhibitors. Cerium compounds are generally the most active ones. Cerium based conversion coatings can be applied to Al alloys by a large range of procedures, including electrolytic deposition, spray, swabbing and immersion.

A quite novel approach to form Ce-based nanostructures takes into consideration the use of deep eutectic solvents (DESs). They have recently attracted great interest in various fields due to their unique properties as new green solvents, efficient dispersants, and as large-scale media for the chemical and electrochemical synthesis of advanced functional surfaces and nanomaterials. These novel ionic media also known as “ionic liquid analogues-ILAs” are based on ammonium (i.e. choline chloride) and phosphonium based salts combined in different molar ratios with varieties of hydrogen bond donors such as: alcohols, carboxylic acids, esters, ethers,amides, and hydrated metal salts of chlorides, nitrates and acetates[2]. Hammond et al. [3] quite recently reported the formation of nanostructured ceria involving various DESs. Marin-Sanchez et al. [4] investigated the electrodeposition of Zn-Ce layers using choline chloride:urea eutectic mixture.

The present paper presents some preliminary experimental results regarding the cathodic electrodeposition of cerium-based conversion coatings onto AA7075 aluminium alloys involving different DES based formulations. Electrolytes containing $Ce(NO_3)_3.6H_2O$ dissolved in choline chloride-glycerine (1:2 molar ratio) and choline chloride-urea (1:2 molar ratio) have been investigated. The influence of the operating parameters (i.e. the applied current density, process duration and temperature) on the quality of the formed Ce containing conversion layers was studied.

A brief description of electrochemical conversion procedures, as well as of some characteristics, from appearance, composition, morphology viewpoints, is presented. The influence of a second sealing step also providing a certain level of hydrophobicity is also discussed.

To evaluate the corrosion performance, several accelerated corrosion tests have been performed, respectively: (i) continuous immersion in 0.5M NaCl for 720 hours with intermediary visual examinations and recording of corrosion potential; (ii) potentiodynamic polarization curves and (iii) impedance spectra at open circuit potential, in 0.5M NaCl, using a PARSTAT 4000 potentiostat controlled by VersaStudio software., as well as (iv) salt mist test, K_a method (in accordance with CEI 68-2-11) for 240 hours.

Different corrosion performances are discussed taking into account the used DES based systems and electrodeposition parameters.

Acknowledgements

The financial support for this work was under the ECOCCEALPROT project 311PED/2020.

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Imprinted polydimethylsiloxane-graphene oxide composite receptor for the biomimetic thermal sensing of *Escherichia coli*.

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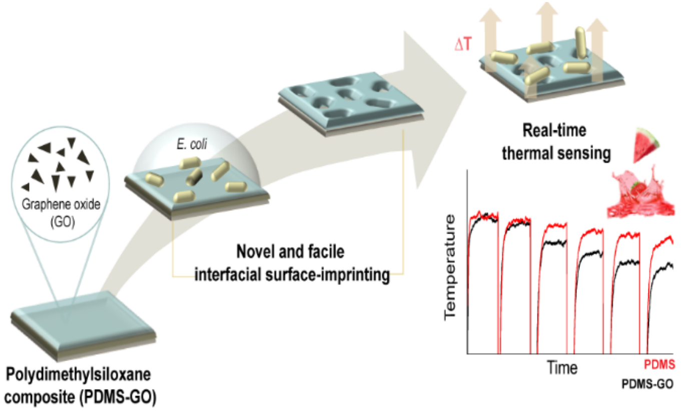
This work presents an imprinted polymer-based thermal biomimetic sensor for the detection of *Escherichia coli*. A novel and facile bacteria imprinting protocol for polydimethylsiloxane (PDMS) films is investigated and these receptor layers are functionalized with graphene oxide (GO) in order to improve the overall sensitivity of the sensor. Upon the recognition and binding of the target to the densely-imprinted polymers, a concentration-dependant measureable change in temperature is observed. The limit of detection attained for the sensor employing PDMS-GO imprints was 80 ±10 CFU/mL, a full order lower than neat PDMS imprints (670 ±140 CFU/mL), illustrating the beneficial effect of the dopant on the thermo-dynamical properties of the interfacial layer. A parallel benchmarking of the thermal sensor with a commercial impedance analyser was performed in order to prove the possibility of using the developed PDMS-GO receptors with multiple readout platforms. Moreover, *S. aureus* was employed as an analogue species for the assessment of the selectivity of the device. Finally, due to the potential that this biomimetic platform possess as low-cost, rapid and on-site tool for monitoring *E. coli* contamination in food safety applications, spiked fruit juice is analysed as real sample. Reproducible and sensitive results fulfil the limit requirements of the applicable European microbiological regulation.



Schematic of the interfacial imprinting procedure for the preparation of PDMS-GO synthetic receptors and their use as sensing surface for the thermal detection of Escherichia coli.

Effective calcium doping of the double perovskite $SmBaCo_2O_{5+\delta}$ as promising oxygen electrode for Intermediate-Temperature Solid Oxide Cells

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Despite the remarkable carbon emission reduction due to COVID-19 pandemic during 2020, a reckless energy demand has compromised the 2050 agenda. In this scenario, reversible-Solid Oxide Cells (rSOC) present an enormous potential on a decarbonized energy scenario as a result of its fuel flexibility and versatility to operate as a fuel cell (power generation), electrolyser (hydrogen production) or even in coelectrolysis mode (syngas production). Regardless its high versatility and efficiency their potentialities are however not yet fully exploited due to stability issues and component compatibility.

In this contribution the authors present an excellent electrochemical performance of the co-doped double-perovskite structure $SmBa_{1-x}Ca_xCo_2O_{5+\delta}$ used as an oxygen electrode material. As a symmetrical cell, the partial substitution of the Ba-site by calcium proved a remarkable improvement in the studied temperature range (450 – 700 °C), achieving at 700 °C a reduction of the polarization resistance from 0.082 $\Omega\cdot cm^2$ to 0.018 $\Omega\cdot cm^2$ for the pristine undoped powder to the best composition of Ca doped material, respectively. In addition, the synthesized material integrated into a conventional anode-supported cell allowed the achievement of current densities at 0.7 V ranging from ~1.4 $A\cdot cm^{-2}$ at 850 °C to ~0.4 $A\cdot cm^{-2}$ at 700 °C in SOFC mode. The behavior as SOEC oxygen electrode and reversibility between both modes is under investigation.

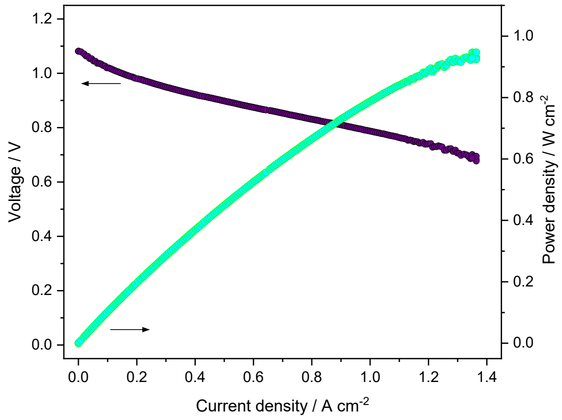

Figure: Cell potential and power density as function of current density for SBCCO|GDC|YSZ|NiO-YSZ single cell at 850 ºC.

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Combinatorial Screening of Cu-W Oxide-Based Photoanodes for Photoelectrochemical Water Splitting

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Since hydrogen has been considered as one possibility to replace fossil fuels in the near future, there has been an extensive research on solar water-splitting cells started by Fujishma and Honda by first titanium dioxide watersplitting photoanode [1]. Transition metal-oxides are promising materials from perspective of bandgap and abundance, but no single material fulfills all necessary criteria. Doping such oxides can dramatically improve the performance by modifying band gaps, band edge positions, conductivities, or catalytic activity of the material. Combinatorial testing is a fast and effective way to identify suitable materials for further improvement by batch experiments [2-4].

Here, we present a scalable high throughput method for preparing and testing photoactive anode materials. Photocatalyst metal oxide libraries were prepared by inkjet-printing onto fluorine-doped tin oxide (FTO) with different compositions. After calcination, the photoactivity of the metal-oxides libraries were investigated via scanning photoelectrochemical microscopy (SPECM) [4].

This study based on ternary Cu-W oxide systems, where the third component represents Cr, Mn, Fe, Co, Ni, Zn, Ga and Bi in different overall atomic ratios [5]. Array elements with promising performance were printed in more detail with smaller increment steps. Improved performance on the basis on $CuWO_4$ was found for Ga, Co and Ni as the third element.

The most promising compositions $Cu_{48}Ga_3W_{49}O_x$, $Cu_{44}Ni_9W_{47}O_x$ and $Cu_{44}Co_9W_{47}O_x$ were printed over larger area and are further characterized by X-ray photoelectron spectroscopy (XPS), ultraviolet photoelectron spectroscopy (UPS), X-ray diffraction (XRD), scanning electron microscopy (SEM), chopped light voltammetry (CLV) and SPECM and scanning electrochemical microscopy (SECM) for oxygen evolution reaction (OER).

For the best composition $Cu_{48}Ga_3W_{49}O_x$ from all screened mixed metal oxides, currents were 36 times higher than for the binary parent system $Cu_{50}Cu_{50}O_x$ ($CuWO_4$).

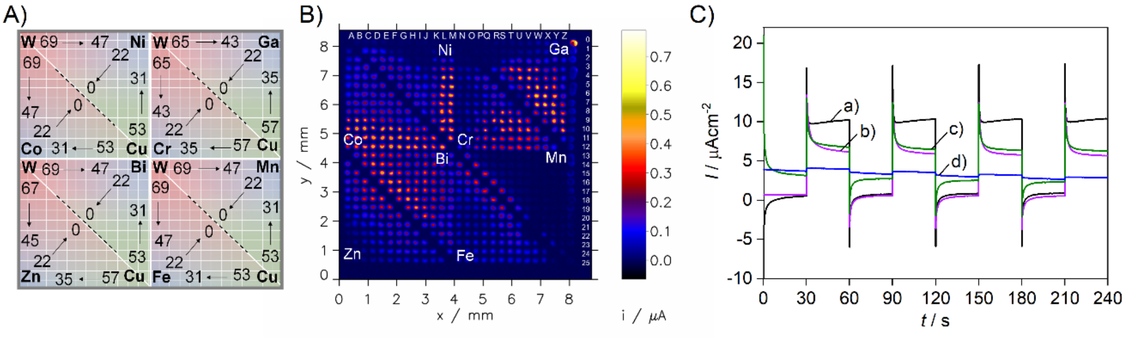

Figure 1. *All-in-one library of the Cu-W-M oxide system for a direct comparison of photocurrents. (A) Schematic layout of the library with Cu (green) and W (red) in the diagonal and the M (blue) element. The library was printed with increment mole fraction steps of 2%. (B) SPECM image from all-in-one library in 0.1 molL^{-1} NaOH with an applied bias from 1.2 V vs RHE. (C) Photocurrent transients from the most active hits a) $Cu_{48}Ga_3W_{49}O_x$, b) $Cu_{44}Co_9W_{47}O_x$, c) $Cu_{44}Ni_9W_{47}O_x$ and d) $Cu_{50}W_{50}O$ at E_S = 0.24 V vs Ag/AgCl that corresponds to 1.2 V vs RHE.*

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Artificial Aging via Chemical Redox Cycling for Accelerated Stress Tests of SOFC

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This work presents a procedure for accelerated stress tests (AST) based on *ex situ* artificial aging of Ni cermet anode of solid oxide cell (SOC) via chemical redox cycling. The procedure is performed on cells before the operation thus eliminating the influence of the degradation mechanisms coming from other components. The level of oxidation was selected experimentally by impedance measurements of bare anode subjected to oxidation/reduction cycles. The selected test configuration (Fig. 1a) gives direct information about the Ni network resistance and its increase due to partial oxidation (Fig. 1b). The proposed procedure ensures reproducibility and fine-tuned level of oxidation. It is combined with *in situ* impedance monitoring of the Ni network during the reduction and oxidation.

The selected on bare anode experimental redox-cycling conditions were applied on full cell configuration. The level of aging was monitored by periodic measurements of the cell impedance and current voltage (i-V) curves (after selected number of redox cycles), as well as by SEM microstructural characterization. The degree of aging was controlled by the deepness of oxidation and the number of redox cycles. The developed algorithm for AST confirms the applicability of the approach. It shall be used for the development of AST protocol.

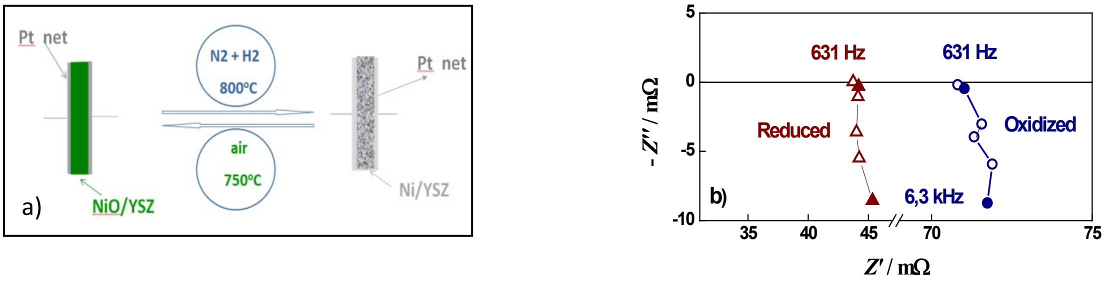

Figure 1. Redox cycling of bare anode: a) schematic presentation of the redox cycling; b) impedance diagrams after reduction and after partial oxidation

Acknowledgements

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In-situ GISAXS-Revealed Interplay Among Dealloying, Ostwald Ripening and Coalescence of PtXNi100-X Bimentallic Alloy Under PEMFC Simulated Operational Conditions

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Platinum-based bimetallic alloys demonstrated to be a promising and cheaper alternative to bare Pt as catalysts for the cathode electrode of Proton Exchange Membranes Fuel Cells (PEMFCs). Among them, PtNi was found to have a very good mass activity and a competitive catalytic activity[1,2]. The main drawback in applying Pt-based bimetallic alloys relies in their reduced stability, which is still under investigation. Being able to clearly describe Pt-based bimetallic alloy at a fundamental level is essential to shed light on the entire chain of interconnected degradation mechanisms taking place in catalyst model systems, which would help in interpreting catalyst degradation in real complex fuel cells. Here (Figure 1), we have combined *in situ* Inductively Coupled Plasma Mass Spectroscopy, *in situ* Grazing-Incidence Small-Angle X-ray Scattering, and *ex situ* Scanning Electron Microscopy, we have studied the morphological evolution of Pt_XNi_{100-X} model catalysts with different Ni contents (ranging from 0 to 75%) undergoing potentiodynamic cycling to two different upper potentials (1.0 and 1.3 V), selected to mime different operational conditions of a PEMFC. Data analysis allowed to develop a methodology for distinguishing among Ni dissolution, particle coalescence, and Ostwald ripening and their effects on both particle size distribution and interparticle distance. Finally, time-dependent interplay maps were realized to highlight the timeframe in which the aforementioned phenomena are prevailing or coexisting.

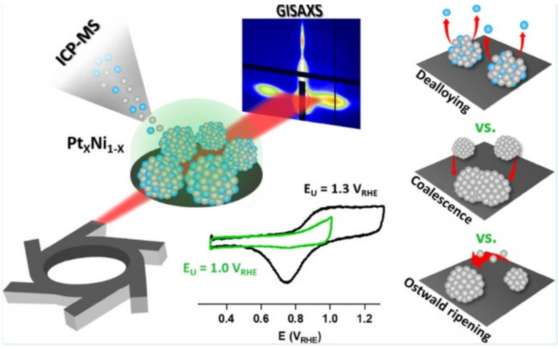

Figure 1. Graphical Abstract[3]

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Hydrogen Evolution During the Electrochemical Oxidation of Aliphatic Aldehydes: The Effect of the Electrochemical Double Layer

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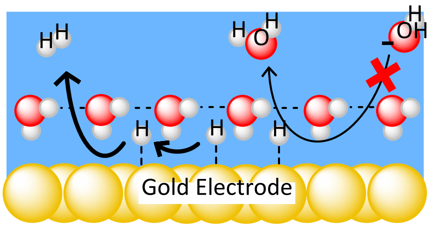
The electrochemical oxidation of aldehydes to carboxylic acids at coinage metal electrode has raised great attention[1] because it provides means to utilize renewable energy to transform sugar based, renewable resources (biomass) into value added products. Here we present our results on the electrochemical oxidation of aliphatic aldehydes at gold electrodes as model reaction for electrochemical aldehyde oxidation. The focus of our contribution lies on peculiar mechanistic aspects of these reactions: the oxidation of aldehydes at gold proceeds via hydrogen evolution. That is, the splitting of the C-H bond between hydrogen and carbonyl carbon leads to adsorbed hydrogen at the gold electrode[2], which can desorb reductively as H_2[1,2]. Formally, his poses the reduction of hydrogen at potentials that should favor oxidation of H_2 to water (E > 0 V vs. RHE).

In our contribution we will present differential electrochemical mass spectrometry (DEMS) results which allow us to trace the evolution of hydrogen online. Quantification of the DEMS data show that the share of aldehyde that reacts via the hydrogen evolution pathway increases as the potential decreases with respect to the potential of zero charge (PZC). We achieve this either by a potential sweep at constant pH or by changing the pH while maintaining the potential. In addition, we find that strongly adsorbing anions (Cl^-, SO_4^{2-}, PO_4^{3-}) inhibit the hydrogen evolution pathway of aldehyde oxidation.

Since oxidative desorption of hydrogen as water has a higher thermodynamic driving force than the reductive desorption as H_2, the latter reaction must be favored kinetically due to a high activation barrier for water formation. We argue that this is due to the water structure at the electrode|electrolyte interface: Due to the high interfacial electric field very negative of the PZC, water is highly ordered and points with one of its hydrogen atoms towards the electrode surface, while the oxygen atom points towards the bulk electrolyte[3]. In this configuration interfacial water cannot form an H-bond to solvate OH^-. Hence, OH^- must go through a high energy transition state when penetrating through the first water layer. Since the latter process is the precondition for the oxidative desorption of hydrogen, this reaction is inhibited. Because the combination of two adsorbed hydrogen atoms to H_2 does not require a charge transfer through the electrochemical double layer, the reductive desorption of hydrogen proceeds as the kinetically more viable reaction. This notion is supported by the finding that strongly adsorbing anions inhibit the hydrogen evolution pathway of aldehyde oxidation: Anions disturb the water layer and lower therefore the kinetic barrier for water formation.

Our results highlight that the solvent structure at the electrode|electrolyte interface can determine the product distribution and the selectivity of electrocatalytic reactions (i.e. H_2 versus water formation).



Graphical Abstract: Oxidative desorption of hydrogen as water requires the transfer of OH^- through the first water layer. At potentials negative of the PZC the latter is highly oriented and cannot provide hydrogen bonds for the solvation of OH^-. Hence, the transfer of OH^- from the bulk electrolyte to the electrode surface and therefore oxidative desorption as water comes along with a high kinetic barrier. Instead, hydrogen desorbs reductively as H_2, which does not require a charge transfer through the double layer. The reaction is therefore kinetically more viable

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Development of a miniaturized electrochemical sensor for on-site nitrate monitoring

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Agriculture and its increasing intensification play an essential role in our society. But at the same time, it has led to the overuse of fertilizers and pesticides, and thus, to environmental pollution. Nitrate is an important nutrient for many crops, passing from the soil to groundwater through leaching processes. Excessive nitrate contamination of ground and surface water has harmful effects on the environment and human health. Therefore, monitoring nitrate levels in soil and surface water are fundamental in agriculture [1]. Nitrate selective sensors are already available on the market. However, these sensor systems are either not suitable for on-site in field use or require time and laboratory intensive for sample preparation steps. The goal of this work is to overcome these difficulties by developing a miniaturized, screen-printed sensor in an all-solid-state configuration for potentiometric determination of nitrate in aqueous samples and for *in-situ* use in soil.

Here we present the results of the development of this sensor, which has the potential to be used for *in-situ* determination in soil. The sensor consists of an ion-selective electrode and a reference electrode integrated on a common ceramic substrate. The composition of the electrode structures is being optimized to achieve stability and reproducibility for long-term measurements, even with influence of different physico-chemical interferences.

The graphite-based nitrate sensor modified with polypyrrole layer as a conducting polymer showed, under preliminary conditions, important characteristics for the performance of these sensors in the environment. Electrochemical characterization of the sensor in aqueous samples features stable and reproducible potential values in the nitrate concentration range from 10^{-4} mol/L to 1 mol/L with an average sensitivity of > 50 mV/decade. With this wide detection range, the sensor will be able to monitor nitrogen fertilization processes on agricultural land, as well as the EU Commission's maximum legal limit of 50 mg/L nitrate in drinking water. Furthermore, the storage conditions between the measurements hardly affected the lifetime and the performance of this sensor during the investigations.

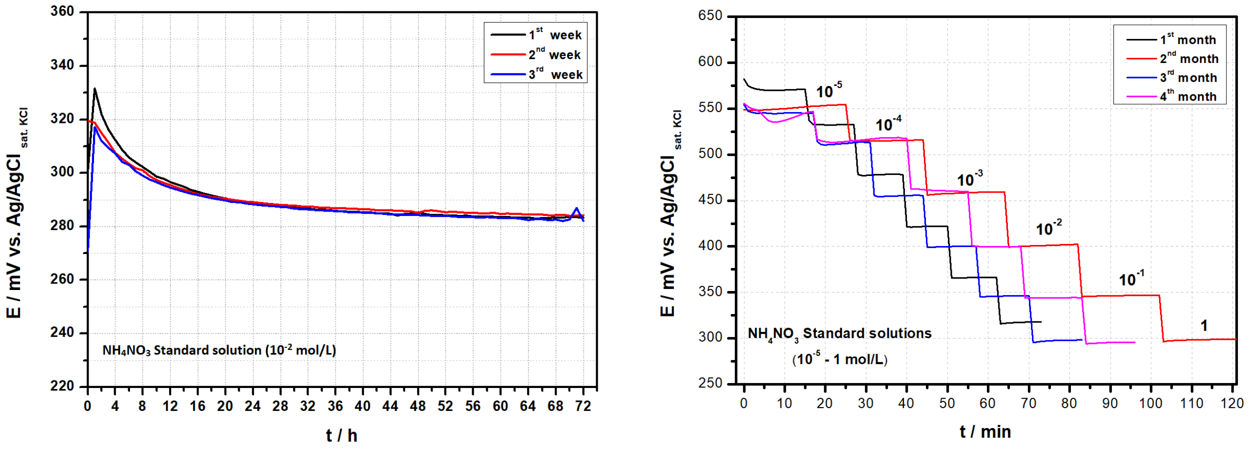

Figure 1: Potentiometric response behaviour of a screen-printed graphite paste modified electrod at different time intervals - in the conditioning steps repeated over weeks (left); and in the calibration steps repeated over several months (right).

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Comparison of Viscose-Based Supercapacitor Electrodes Activated by KOH, H_2O, and CO_2

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Activated carbons derived from viscose fibers were prepared using potassium hydroxide, carbon dioxide, or water vapor as activation agents. The produced activated carbon fibers were analyzed via scanning electron microscopy and energy dispersive X-ray spectroscopy, and their porosity (specific surface area, total pore volume, and pore size distribution) was calculated employing physisorption experiments. Activated carbon fibers with a specific surface area of more than 2500 $m^2\ g^{-1}$ were obtained by each of the three methods (Figure 1). Afterwards, the suitability of these materials as electrodes for electrochemical double-layer capacitors (supercapacitors) was investigated using cyclic voltammetry, galvanostatic measurements, and electrochemical impedance spectroscopy.

By combining CO_2 and H_2O activation, activated carbon fibers of high purity and excellent electrochemical performance could be obtained. A specific capacitance per electrode of up to 180 F g^{-1} was found. In addition, an energy density per double-layer capacitor of 42W h kg^{-1} was achieved. These results demonstrate the outstanding electrochemical properties of viscose-based activated carbon fibers for use as electrode materials in energy storage devices such as supercapacitors.

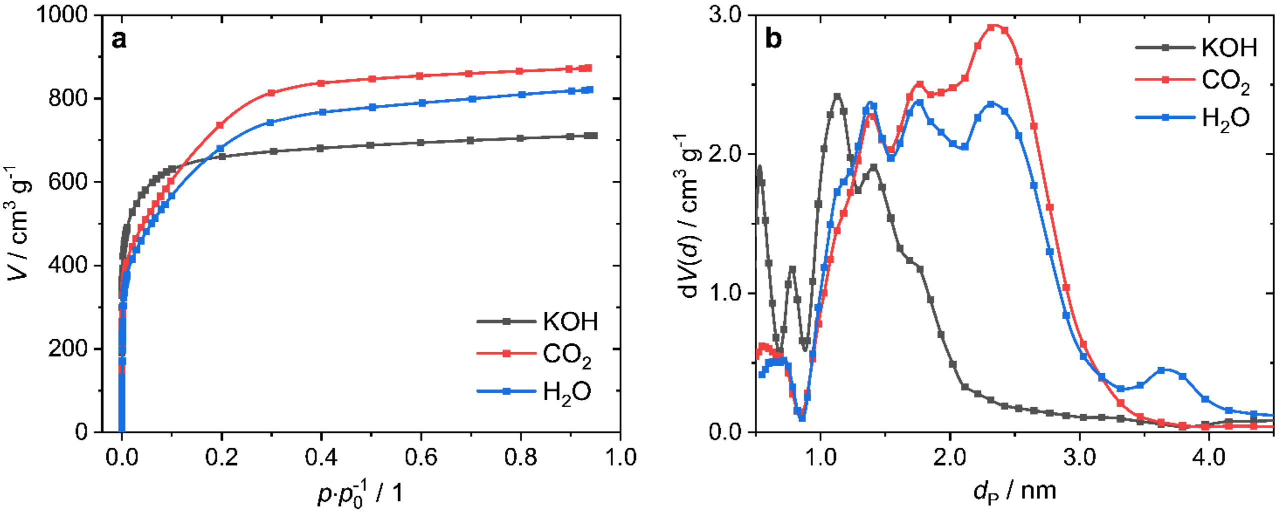

Figure 1: Isotherms (a) and pore size distribution (b) of the ACFs activated with KOH, CO_2, and H_2O (N_2; 77 K; NLDFT; slit-pore model).

Funding

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The effect of surface pre-treatment of a planar boron-doped diamond electrode on the electrochemical response of fenhexamid

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Fenhexamid (FH) is a hydroxyanilide fungicide used to prevent fungal diseases in strawberries, blueberries, and grapes. In our previous work[1], FH determination was carried out by square-wave voltammetry (SWV) on various carbon-based electrodes, *i.e.*, glassy carbon electrode, graphite-and glassy carbon-based paste electrodes, and graphite paste electrode modified with multi-walled carbon nanotubes. However, FH oxidation on these electrodes led to the formation of undesirable oxidation (by)products. Thus, labor- and time-consuming surface cleaning between each scan had to be performed.

Boron-doped diamond (BDD) electrode can be used as an alternative to the above-mentioned electrodes as its use for sensing purposes is widely recognized due to its unique properties including wide electrochemical potential window in aqueous solutions, low and stable background current, long-term stability, resistance to electrode fouling, and low sensitivity to dissolved oxygen[2,3]. BDD surface pre-treatment has been identified as a crucial factor which determines performance of BDD electrodes. Hydrogen-termination (H-BDD) leads to non-polar, hydrophobic BDD surfaces with considerable surface conductivity and negative electron affinity, whereas oxygen-terminated BDD (O-BDD) electrodes possess hydrophilic, polar surfaces with decreased conductivity and positive electron affinity. It is also worth mentioning that untreated (as-received) BDD surface (both commercially available and lab-made) is mainly H-terminated as deposition of BDD films is carried out in hydrogen atmosphere, and it is initially free of oxygen-containing functionalities. However, H-BDD electrode surface ages, *i.e.*, becomes gradually oxidized. One of the most common ways how to perform re-hydrogenation of progressively oxidized H-BDD electrode surface or conversion from H- to O-termination is *in situ* electrochemical activation[3].

In this work, manual mechanical polishing of a planar BDD electrode surface as well as different electrochemical activation programs, *i.e.*, the application of highly positive (+2.4 V) and highly negative (−2.4 V) potentials for 300 s in a 0.1 mol L^{-1} H_2SO_4 solution, were tested towards FH oxidation peak in Britton-Robinson buffer of pH 2.0 by SWV.

It was found that tested activation programs significantly influenced the heights of FH peak and the peak potential: lower peak currents were obtained for cathodic and mechanical activation when compared to anodically pre-treated surface, and cathodic activation lead to negative shift of peak potentials compared to positioning of the peaks of FH when mechanical or anodic activation was applied. For anodic pre-treatment, the highest FH signal with the lowest RSD ~2% was obtained. Therefore, anodic pre-treatment was found to be the most successful strategy how to re-activate a fouled electrode surface by FH oxidation (by)products.

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Comparative corrosion studies of co-doped TiO_2 sol-gel coatings for biomedical applications

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Nowadays, studies on orthopedic biomaterials are focused mainly on enhancing their bioactivity and giving them new properties, *i.e.* antibacterial properties. It is well known that antimicrobial biomaterials prevent post-operative infections by reducing the ability of adhesion and permanent attachment of microorganisms and thus the development of biofilm, which is the main reason of the infections. Within the numerous methods used for the preparation of biomaterials with the desired properties, covering their surfaces with functionalized coatings appears to be particularly interesting and of high capabilities. The sol-gel TiO_2 coating was proven to be a versatile platform for surface functionalization of stainless steels and other biomedical metals. The improvement of biocompatibility, bioactivity (related to osseointegration), and antibacterial properties of biomaterials can be obtained by means of ion doping procedure.

In the present study, we applied the possibility of incorporating more than one dopant into the sol solution in order to achieve a multifunctional biomedical coating with bioactive and antibacterial behavior, and what is the most important exhibiting corrosion protection capability towards biomedical stainless steels. We intended to combine anticorrosion properties of titanium dioxide, with the bioactive effect of Ca ions and the potential antibacterial effect of Ag and Ga ions widely reported in the literature. For that purpose, TiO_2 coatings co-doped with Ca/Ag and Ca/Ga were deposited by the dip-coating technique onto M30NW biomedical steel and subsequently annealed at 450°C in air. Our previous studies have shown that under these thermal oxidation conditions an effective crystallization of titanium dioxide occurs and formed anatase exhibits good corrosion protection ability in case of biomedical steels [1]. In other study we have reported that Ca/Ag-doped TiO_2 coatings are biocompatible and do not reduce the proliferation ability of the osteoblasts cells [2]. In the presented study, the influence of different molar ratios of Ca/Ag and Ca/Ga dopants on morphology, surface structure, wettability, bioactivity, and corrosion resistance of the TiO_2-based coatings was investigated and compared. Comprehensive measurements were performed including AFM, SEM, XRD, XRR, contact angle, immersion test and corrosion tests in PBS solution (pH 7.4, temperature 37°C). The obtained results confirmed that anatase-based coatings co-doped with Ca/Ag and Ca/Ga, independently on their molar ratio in the coating, are anticorrosive, hydrophilic and bioactive.

Acknowledgement

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The Freeze Tape Casting Technique for the Manufacturing of Graded Porous Scaffolds for Solid Oxide Cells: Experimental Activities and CFD Modelling

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Reversible Solid Oxide Cells (rSOCs) hold the potential of becoming a key technology in a new energy scenario based on renewable sources, finding significant applications into several industrial sectors (grid balancing, seasonal renewable energy storage, synthetic e-fuels), thanks to their fast reaction kinetics, high fuel flexibility and conversion efficiency [1], [2]. The state-of-the-art rSOCs, however, still suffer from issues related to chemical and mechanical instability, which often originate from poor reactants and products diffusion within the electrodes. The delamination of the air electrode from the electrolyte under the electrolysis operating mode has been repeatedly reported as a failure cause during their operation [3]. The high tortuosity of the percolating porosity within the air electrode leads to the pO_2 buildup at the interface with the electrolyte and makes gas diffusion a possible rate determining step of the overall electrochemical process. Freeze tape casting (or ice-templating) is a manufacturing technique which enables the production of hierarchical electrodes, characterized by large porosity, permeability and low tortuosity, thus boosting gas diffusion. The purpose of this contribution is the introduction of the benefits provided by the freeze tape casting method and its potential process advantages compared to the conventional ceramic production routes. In particular, this work goes through the main steps included in the processing procedure and underlines the major parameters affecting the resulting electrode properties. The suspension additives and the freezing conditions were especially optimized. The physical and electrochemical properties of button rSOCs, including at least one hierarchical porous electrode, have also been investigated by means of Computational Fluid Dynamics (CFD) simulations. Particular attention has been posed on the comparison between standard and ice-templated electrodes morphologies, pointing out the benefits provided by open porous structures.

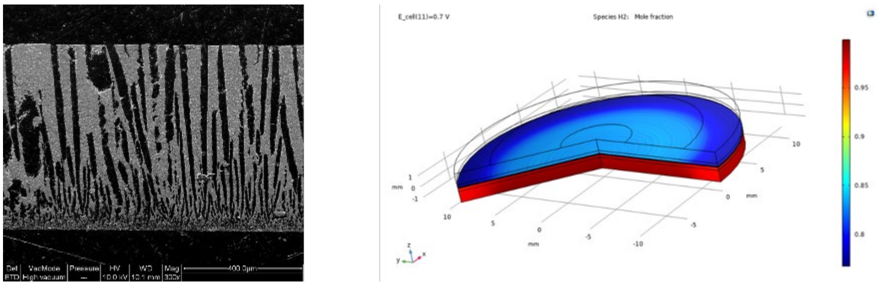

Figure 1: Cross Section of a 8YSZ freeze tape casted scaffold, on the left, and simulation of the H_2 molar fraction profile in a CFD model of a freeze tape casted button cell, on the right.

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Thermal detection of glucose in urine using a molecularly imprinted polymer as a recognition element

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Glucose bio-sensing technologies have received increasing attention in the last few decades, primarily due to the fundamental role that glucose plays in diseases (e.g., diabetes)[1]. Molecularly imprinted polymers (MIPs) could offer an alternative means of analysis to a field that is traditionally dominated by enzyme-based devices[2], posing superior chemical stability, cost-effectiveness, and ease of fabrication[3,4]. Their integration into sensing devices as recognition elements has been extensively studied with different readout methods. In this work, a dummy molecularly imprinted polymer is synthesized and optimized toward the sensing of glucose. Integration of this polymer into a thermally conductive receptor layer was achieved by micro-contact deposition. In essence, the MIP particles are pressed into a polyvinyl chloride adhesive layer using a polydimethylsiloxane stamp. The prepared layer is then evaluated with the so-called heat-transfer method, allowing the determination of the specificity and the sensitivity of the receptor layer (Figure 1). Furthermore, the selectivity was assessed by analyzing the thermal response after infusion with increasing concentrations of different saccharide analogues. The obtained results show a linear range of the sensor of 0.0194−0.3300 mM for the detection of glucose in PBS. Finally, a potential application of the sensor was demonstrated by exposing the receptor layer to increasing concentrations of glucose in human urine samples, demonstrating a linear range of 0.0444−0.3300 mM. The results obtained in this paper highlight the applicability of the sensor both in terms of non-invasive glucose monitoring and for the analysis of food samples.

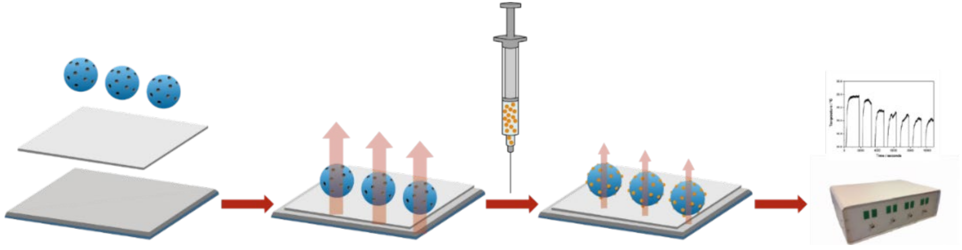

Figure 1: Schematic representation of the deposition of the MIP particles and rebinding analysis with HTM.

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Ni(OH)$_2$ type nanoparticles derived from poly(NiSalen)s to remediate urea-rich wastewater

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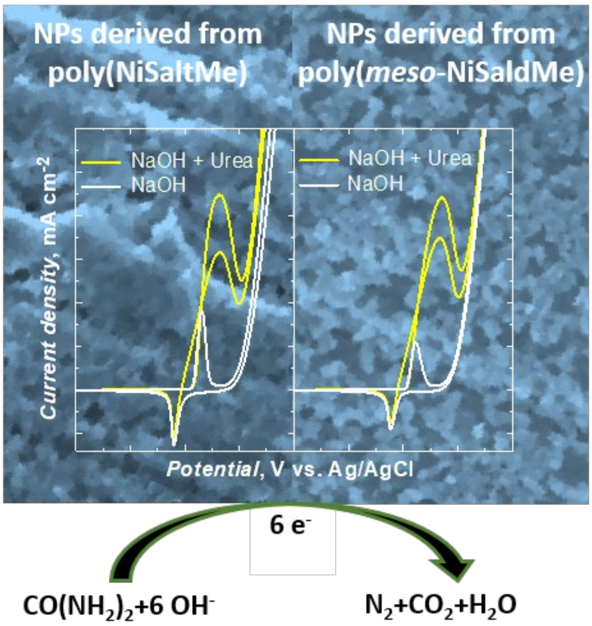
In recent years urea started to be considered a possible energy source for fuel cells because of its wide attainability. Two nickel salen polymers, named poly[2,3-dimethyl-*N,N'*-bis-(salicylidene)-2,3-butanediaminonickel],[1,2] and poly[*meso-N,N'*-bis-(salicylidene)-2,3-butanediaminonickel],[3,4] abbreviated as poly(NiSaltMe), and poly(*meso*-NiSaldMe), respectively were transformed in alkaline media into Ni(OH)$_2$ type electrocatalytically active nanoparticles (NPs), by the potential driven electrochemical process.

These poly(Salen) matrix embedded NPs undergoing potential triggered reaction:

$$\text{poly[SalenNi}^{2+}\text{(OH)}_2\text{]} + \text{OH}^- \rightleftharpoons \text{poly(SalenNi}^{3+}\text{OOH)} + \text{H}_2\text{O} + \text{e}^-$$

This reaction was used to electrocatalyze urea electrooxidation.



In order to prepare the possibly best performing heterogeneous NPs catalysts for urea electrooxidation, electrodeposition conditions of poly(NiSalen) precursors were optimized. Deposition of polymer precursor films, under potentiostatic conditions, performed at different times influenced the thickness of poly(NiSalen) films. Moreover, the influence of NaOH$_{aq}$ concentration on the catalytic transformation process of poly(NiSaltMe) and poly(*meso*-NiSaldMe) into Ni(OH)$_2$ type NPs was extensively investigated. Transformation of potentiostatically deposited poly(NiSalen) films was investigated in 0.2, 0.5, 1, and 2 M of NaOH$_{aq}$. Scanning electron microscopy (SEM) imaging revealed that different concentrations of NaOH$_{aq}$ influenced polymer matrix architecture and Ni(OH)$_2$ NPs distribution. Catalytic properties of Ni(OH)$_2$ type NPs derived from poly(NiSaltMe) and poly(*meso*-NiSaldMe) were also examined in artificial urine to prove that these catalysts can be used in biological samples to remediate urea rich wastewater. Further, a catalytic retention experiment confirmed these NPs catalysts' long-term use for artificial urine electrooxidation.

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Challenges in the Electrocatalytic Benchmarking of Complex Solid Solutions for Energy Conversion Reactions

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High entropy alloys (HEA) and, more generally, Complex Solid solutions (CSS) have emerged as promising new types of electrocatalysts for energy conversion reactions. Their exceptional properties, large number of degrees of freedom available, and anticipated stabilizing effects make CSSs a promising prospect for overcoming the limitations of "traditional" catalysts imposed on them by the scaling relations [1]. CSS have been tested for a wide veriety of electrocatalytic reactions, such as: the oxygen reduction and evolution reactions, carbon dioxide reduction, methanol oxidation, and hydrogen evolution reaction. However, significant experimental challenges need to be addressed and widely applied standards need to be implemented in order to understand and correctly asses the electrocatalytic behaviour of CSSs. The understanding of the state of the surface under reaction conditions, the identification of active sites, the electrochemically active surface area determination, and the ohmic drop correction are some of the most important experimental challenges in the benchmarking of CSSs [2]. Traditional methods used to evaluate model systems (e.g. noble metal electrodes) are discussed in relation to their use in CSS evaluation.

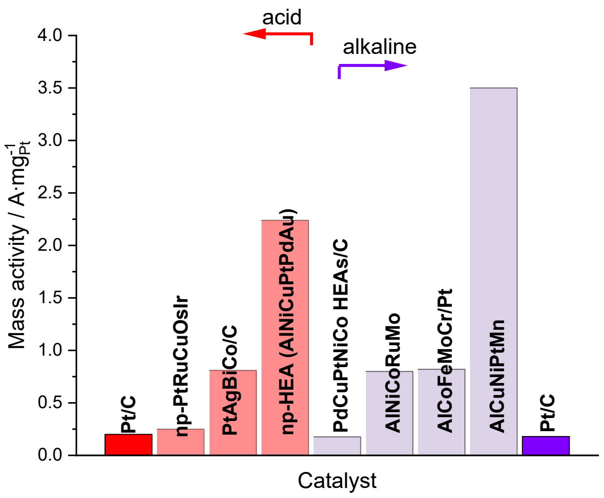

Figure 1: The mass activity of recently reported CSSs for ORR in 0.1 M HClO4 or 0.1 M KOH.

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Amorphous Ni-B-based Materials for Electrochemical – Thermally-Activated Chemical (E-TAC) Water Splitting

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Electrochemical–thermally-activated chemical (E-TAC) water splitting, invented in the Technion [1, 2] and further developed by H_2Pro (Caesarea, Israel), is a membraneless technology for the "green" H_2 stationary production based on abundant materials. Conventional E-TAC anodes are based on the reversible β-$Ni(OH)_2$↔β-NiOOH transition between the crystalline hydroxide/oxyhydroxide phases. High crystallinity and, consequently, slow phase transition could be one of the main reasons of the kinetic hindrances and decrease in active mass utilizations in the E-TAC process.

The aim of our research is to experimentally reveal the possibility to facilitate the E- and TAC-kinetics, to increase the capacity of the anodes and to improve the active mass utilization via the introduction of amorphous (or poorly crystalline) anode materials. In this study, we develop amorphous Ni-based material capable to perform in the E-TAC cycles and investigate its properties. Towards this end, a facile one-step chemical reduction method was applied to synthesize nickel-boron-based agglomerates directly on the surface of the Ni/Ti/carbon substrates or to obtain powder of the particles in the solution. As expected, the X-ray diffractograms confirmed that the applied synthetic technique results in amorphous material. TEM imaging of the as-synthesized powders showed that the powder consists of core-shell-like near-spherical nanoparticles (ca. 10-20 nm) interconnected in chains. HR-EDX mapping of the intact powder revealed that the shell is enriched by oxygen, whereas the core mainly consists of Ni and B. Galvanostatic charge/discharge measurements were used to study the rate capability of the material and the evolution of the capacity in time. We assumed that the slow charging and discharging of the electrodes results in the increase of the oxide shell thickness followed by the shrinking of the particle core. To provide an experimental prove, the as-synthesized material was exposed to slow potential cycling within the range of 1.13-1.48 V vs. RHE. HR-EDS mapping of the oxidized material clearly illustrated the growth of spongy, crystalline, layered structures around the cores which are fully or partially depleted, dependent of the particle sizes.

Series of electrochemical galvanostatic charges followed by thermally activated chemical (5M KOH, 95C) discharge tests have proven the feasibility of the developed amorphous Ni-B-based material for the anodes of the E-TAC process. The capacity values of the electrodes currently reach ca. 600 C g^{-1} (vs. theoretical capacity of 1400 C g^{-1}). The further investigation is needed to elucidate the effect the initial crystallinity degree of the material, as well as light needs to be shed on the crystallinity evolution of the material during the E-TAC process itself.

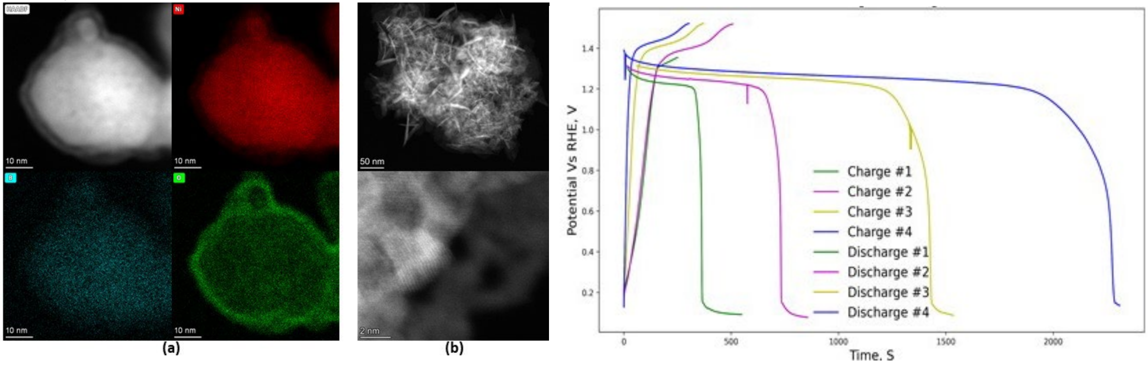

Figure 1. (a) TEM images of intact NiB; (b) TEM images of oxidized NiB; (c) E-TAC cycles on NiB.

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Electrochemical sensing of single molecules using nanopores

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Electrochemical sensing with nanopores is a generic approach to detect single molecules in a highly-selective and label-free manner[1]. In the approach, molecules are registered when they pass through a nanoscale hole and temporarily block the ionic current flowing through the pore. Nanopore sensing has been commercialised for fast and portable DNA sequencing, to speed up Covid-19 sequencing and genomics research[2]. The commerical hand-held sequencing kits feature advanced nanopore arrays, low-noise circuits, and intelligent data analysis for highly accurate DNA readouts. The next generation nanopore devices will focus on the sensing of larger proteins and other molecules of biological relevance[3–5]. Towards this aim, protein nanopores, solid-state nanopores and DNA-origami based nanopores are being used. An ultimate aim is full length protein sequencing to advance biological discovery and clinical biomedicine.

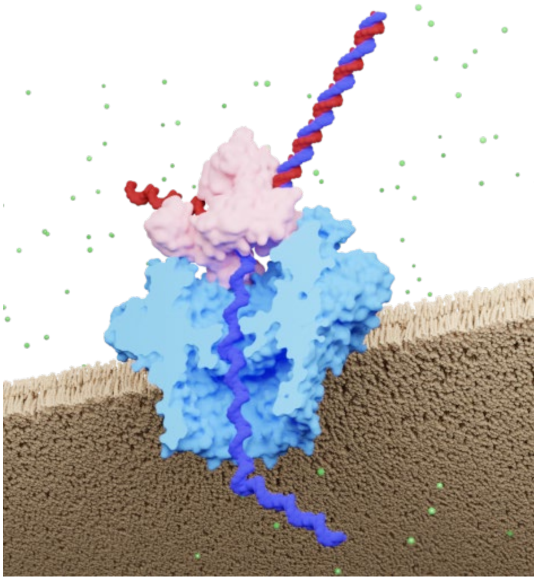

Figure 1: A protein nanopore used in the electrochemical sequencing of a single strand of DNA

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Dendrite prevention in solid-state batteries by engineering the surface-near properties

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For future energy storage the conventional lithium metal would be desired as the anode material, promising a tenfold increase in capacity and the lowest possible anode potential.[1] Its propensity to form dendritic structures during cycling and the subsequent safety issues have hampered its use. Solid electrolytes like $Li_7La_3Zr_2O_{12}$ (LLZO) with reasonable room temperature conductivities, wide electrochemical stability window, and no flammability allow for the resurgence of the lithium metal anode.[2]
The issue of dendrites remains, able to crack and penetrate the solid electrolyte even at low current densities.[3] Avoiding the formation or propagation of cracks is therefore of great interest to enable faster charging of batteries and to increase their longevity.
Previous results show that compressive stresses, induced by foreign ions inserted into the ceramic crystal structure via ion bombardment, can inhibit crack propagation.[4]
Herein, we show that the introduction of silver ions into the near surface region of LLZO has significant impact on the local mechanical properties leading to the deflection of cracks with potential large implications on the ability to withstand Li dendrites. We used a large portfolio of techniques such as FIB SEM, dark field TEM, impedance spectroscopy, cross sectional nano XRD, atom probe tomography and nanoindentation to investigate the alterations in the near surface region and to correlate it with the stresses in the material, the changed crack behaviour and electrochemical performance.

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Indirect Detection of Pseudomonas Aeruginosa using Molecularly Imprinted Polymers

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Pseudomonas Aeruginosa is an opportunistic ubiquitous bacterium commonly found in soil and water, capable of causing serious infections, for instance in the blood, lungs or other parts of the body. In 2017, multidrug-resistant P. Aeruginosa caused an estimated 32,600 infections among hospitalized patients and 2,700 deaths in the USA. This project is focused on the development of sensors for the indirect detection of P. Aeruginosa in the environment using Molecularly Imprinted Polymers (MIPs). This versatile and low-cost method exploits the selective recognition of pyocyanin, the most produced toxin of P. Aeruginosa. Pyocyanin is a small molecule and a secondary metabolite secreted by the bacterium itself, responsible for quorum sensing and biofilm formation of the bacterium. The backbone structure of pyocyanin falls into the category of phenazines, namely molecules small enough to be imprinted using the MIPs technology. In this project, MAA-based polymers were imprinted with pyocyanin. After removal of the template, these synthetic receptors were immobilized onto planar aluminum chips by means of an adhesive layer. These MIP-covered chips were used for thermal resistance measurements at the solid-liquid interface. The results of this experiments show that it is possible to construct a dose-response curve, relating the concentration of pyocyanin in the flow cell to a change in the transmitted temperature. Finally, we have developed a first model to translate the measured pyocyanin concentration into a bacterial concentration. The results of this study demonstrate that the indirect detection of P. Aeruginosa using MIP-based sensors offers a cheap and easily scalable technology that overcomes the drawbacks associated with classical laborious sensing techniques based on the identification of the whole microorganism.

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Material performance characterization in electrocatalysis: the role of the electrochemical instrument and measurement techniques in your discovery

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The electrochemical instrument (i.e. potentiostat/galvanostatt) is an important part of the experimental setup used to investigate electrochemical processes and to characterize a new electrocatalyst, in particular. During the electrochemical measurements, a disturbance is applied to the electrochemical cell (e.g. potential applied on the working vs the reference electrode) and the resulting response is measured and analysed (e.g. the current flowing between the working and the counter electrode is measured). Therefore, to have the most accurate experimental results and data interpretation, it is crucial to know all the parameters and specific characteristics of both the applied and measured signal.

In this presentation, the important particularities of the typical techniques used in the characterization of the electrocatalytic materials such as **analog vs staircase** scan[1] and monitoring the potential of the counter electrode with a **second potential sense**[2]**,** supported by experimental examples and comparison of results are shown. Additionally, the importance of **seamless measurements** (i.e. no gap or delay in the applied and/or measured signal) in new discoveries and in avoiding possible errors is presented.

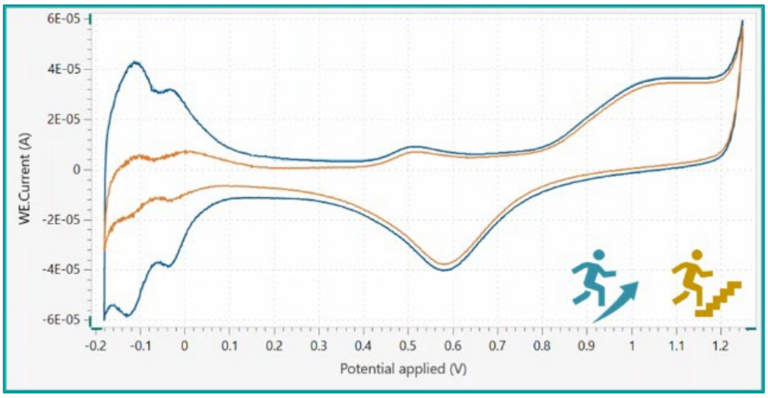

Figure1: Cyclic voltammetry of poly-Pt in 0.1M H_2SO_4 obtained by using staircase (brown) and analog (green) scan.

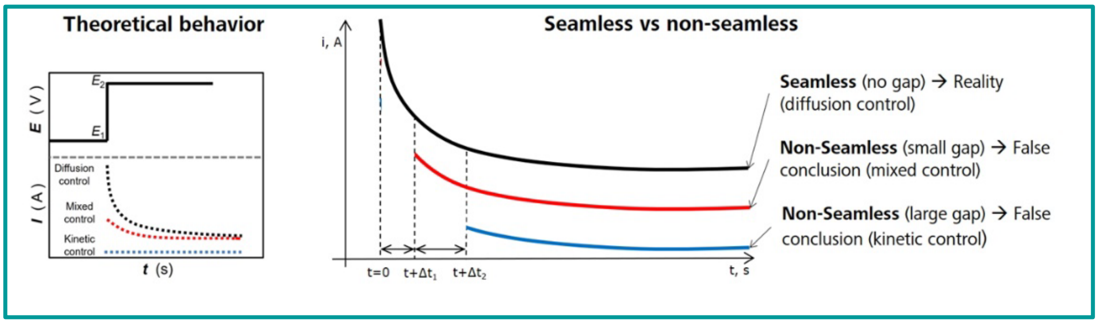

Figure2: Importance of Seamless measurements: example of possible errors in data interpretation due to gaps in applied and/or measured data.

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Influence of electrode composition and operating conditions on the performance and the electrochemical impedance spectra of polymer electrolyte fuel cells

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The cost-effective mass production of high-performance catalyst coated membranes (CCM) for use in polymer electrolyte fuel cells (PEFCs) is a major challenge for economic viability of this promising clean and sustainable technology. Highly scalable coating methods for the manufacturing already exist for other technologies and are in the process of implementation for fuel cell manufacturing. Thereby, speed and volume of production has already been vastly increased in the last decade and a reduction of the production costs by economy of scale is in reach [1,2].

However, another major cost contribution are raw materials, which are barely affected by upscaling. It is thus crucial to achieve high performance with as little platinum as possible and at high voltages[3–8]. This leads to considerable developmental effort towards developing advanced catalysts[7,8] combined with extensive parametric studies aiming at determining the effect of ionomer type and content as well as carbon microstructure on polarization performance[3–5].

While polarization curves are irreplaceable for the characterization of PEFCs, the nature and extend of the voltage losses at various current densities cannot always be determined without performing time consuming additional experiments, screening various combinations of catalyst coated membranes, operating conditions and even experimental setups[3,4]. Electrochemical impedance spectroscopy (EIS) on the other hand can give an extensive insight into the nature and extent of voltage loss mechanisms with very fast scan rates without the need to interrupt fuel cell operation[9,10] and can therefore accelerate material development efforts. There are however still some unanswered questions about the interpretation of the EIS signals for PEFC.

To address this lack of understanding, we performed an extensive experimental campaign examining the influence of gas pressure, gas relative humidity, gas flow rate, catalyst layer ionomer content and catalyst layer thickness. Thereby, the impact of reactant concentration, water concentration, supply and removal of reactants and products to and from the active sites is quantified. These are all processes that can be seen in the impedance spectrum. By variation of the controlling parameters a better understanding of the spectrum can be obtained. We continued the experimental and empirical modelling work based on previously published work that was mainly concerned with the influence of catalyst layer thickness and ionomer content[9] and added important experimental data from a variation of operating conditions. In the present work, we delve deeper in the experimental results obtained and present an equivalent circuit model that facilitates EIS data interpretation.

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2D layered MPX_3 and electrochemical energy conversion reactions

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Due to their unique physical and chemical properties, layered two-dimensional (2D) materials have been established as the most significant topic in materials science for the current decade. This includes layers comprising mono-element (graphene, phosphorene), di-element (TMD, MXene), and even multi-element. The 2D layered materials are currently one of the most explored materials for developing efficient and stable electrocatalysts for energy conversion applications. A distinctive class of 2D-layered materials is the metal phosphorous trichalcogenides (MPX_3, X=S, Se), which have unusual intercalation. [1] Some 2D MPX_3, have been reported to be useful catalysts for water splitting,[1,2] although the results have been less promising for the sluggish oxygen evolution reaction (OER) due to insufficient activity or compromised stability.

We report on the water splitting performance of a series of MPX_3 (M^{2+} = Mg, Mn, Fe, Co, Zn, Cd; X = S, Se). For the MPX_3 series, $CoPS_3$ yields the best results with an overpotential within the range of values typically obtained for IrO_2 or RuO_2 catalysts.[3] The liquid phase exfoliation of $CoPS_3$ improves the OER activity due to the abundant active edges of the downsized sheets, accompanied by the presence of surface oxides. The influence of the OER medium and the underlying substrate electrode is studied, with exfoliated $CoPS_3$ reaching the lowest overpotential and able to sustain high current densities, with excellent stability after multiple cycles or long-term operation.

The photoelectrochemical (PEC) responsivity of MPX_3 was also tested in the OER region, with excitation wavelengths from 385 to 700 nm. [4, 5] The experimentally determined optical band gaps of the MPX_3 materials range from 1.5 eV for $FePSe_3$ to 3.7 eV for $ZnPS_3$. At +1.23 V *vs* RHE, the PEC activity in the OER region of $MnPSe_3$ exhibits superior performance, while $CoPS_3$ exfoliation of $CoPS_3$ improves its PEC activity by up to double in contrast with its bulk counterpart. The influence of the substrate and applied potential is also optimized.

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Nano structured and pyrolytic deposited carbon electrodes for detection of nitroaromates – a comparison

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Nitroaromatics like 2,4,6-trinitrotoluene (TNT) and 2,4-dinitrotoluene (DNT) are long-lasting organic pollutants in natural water and soil caused mainly by the military usage. Nano structured electrodes are established in detection of such compounds in water by linear sweep voltammetry (DP) [1]. On the other hand, it could be shown that screen printed carbon electrodes [2] and such made of pyrolytic deposited carbon are also suited for that purpose [3]. Both kind of electrodes were investigated regarding the determination of nitroaromatic compounds in aqueous solution. Electrodes using carbon nano-tubes and gold nano-particles on printed carbon are commercially available (DropSens, Spain DRP-110CNT-GNP). Screen printed electrodes (SPCE) of 3mm in diameter were industrially like produced on an alumina substrate with a commercial carbon ink carbon paste. Pyrolytic graphite layer were deposited by high temperature decomposition (1050 °C) of aromatic vapor for 15 min with high reproducibility (PyGE). Solid state analyses as XRD and SEM analysis show crystalline carbon with a sp^2 hybridization.

The potentials of the single reduction peak of nitro-aromates can be clearly separated for both kind of electrodes, SPCE and PyGE. The nitroaromates trinitrotoluene (TNT) and dinitrotoluene (DNT) are reduced in DPV mode. The peak currents are proportional to the TNT concentrations with a sensitivity of 2.7 nA/ppb for SPCE (Fig.1) and 0.78 for PyGE (Fig. 2) at the characteristic peak potential of -0.59 V (R^2=0.99). Commercial electrodes DRP-110CNT-GNP made of carbon with gold nano particles require a special treatment in cyclo-voltammertic mode up to stable measuring conditions. The sensitivity of 2.8 nA/ppb is high compared to PyGEs. The relative errors in measuring cycles (35 %) are very much higher than those for PyGEs (5 %). PyGE do not need a special pretreatment before use.

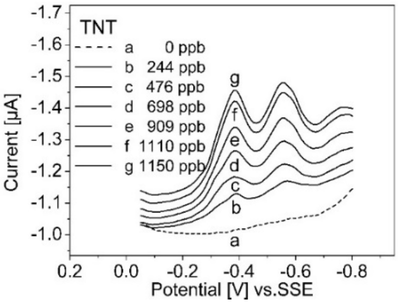

Fig. 1 Determination of TNT at bare SPCE in 0.1 M acetate buffer solution with increasing TNT-concentration; DPV conditions: scan rate: 15 mV·s^{-1}

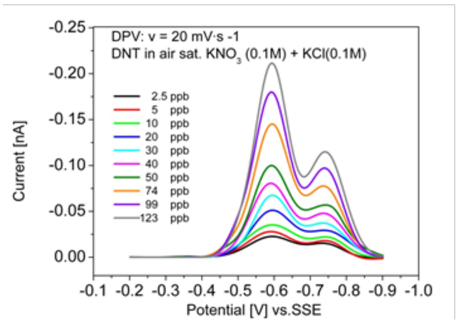

Fig. 2 Peak current vs. potential for pyrolytic deposited carbon electrode at different TNT concentration in air saturated aqueous solution. (peak current increases with increasing TNT-concentration)

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Analysis of Multi-layer Thin Film Structures of Metal Hexacyanometallates

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Transition metal hexacyanometallates (M-HCMs) represent an interesting group of redox-active coordination network compounds with electronic and ionic conductivity. Cyanide ligands (CN^-) bridge the transition metal centers, whereby a mixed valence character can arise in the material.[1,2] Redox transitions of many M-HCMs have been studied by voltammetry and complementing spectroscopic, microscopic and diffraction studies.[1,3] The overall charge of the compound is balanced by the ingress or ejection of alkali metal ions (or NH_4^+). These ions can migrate through the channels of the structure. By layering of M-HCMs, electrical transport processes can be manipulated, and directional charge transport can be achieved and controlled.[4]

In this work, multi-layer films of different M-HCMs are constructed and their redox switching behavior is analyzed. In order to obtain well defined interfaces between the materials, different (electro)chemical deposition techniques are combined to produce thin multilayers of M-HCMs.[5] They include electrodeposition but also layer-by-layer modification and casting of bulk-synthesized colloids.[5] Cyclic voltammetry is used to observe the electrochemical properties of the materials, such as the directional charge transport (Figure 1b). X-ray diffraction is used to analyze the crystallinity of the deposited materials. Scanning force microscopy and scanning electron microscopy are applied to study the morphology of the films (Figure 1a). X-ray photoelectron spectroscopy is used to investigate the chemical composition as well as the redox state of the metal centers in the structure before and after redox transitions. Current-voltage curves were recorded in the dry state between the substrate electrode and a conducting tip of the scanning force microscopy demonstrated the rectifying behavior of the wet-processed layered system (Figure 1c).

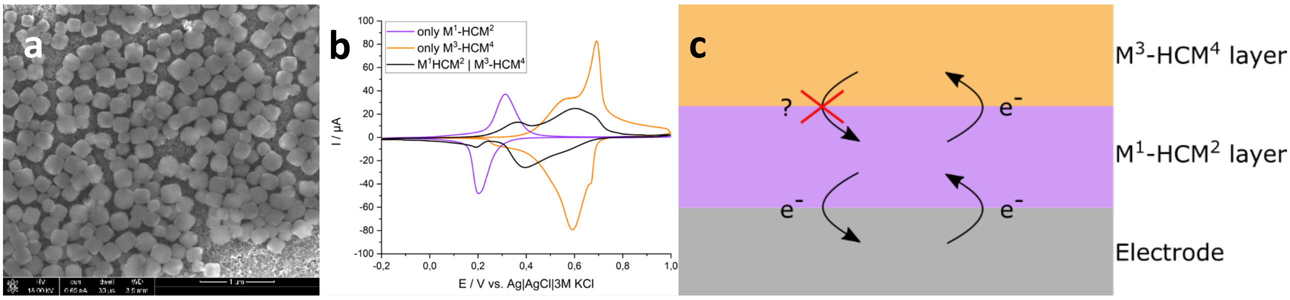

Figure 1: Two-layer M-HCM system. a) SEM image of the morphology of a composite of an electrodeposited smooth M^1-HCM^2 film coated with a second layer of bulk-synthesized crystalline M^3-HCM^4 colloids; b) Cyclic voltammogram of bilayer system revealing rectifying behavior; c) schematic illustration of proposed electronic mechanism in bilayer system.

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Crystal structure, nano mechanical and electrochemical properties of Co based alloys containing various Cr and Mo content

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This work focuses on the preparation of Co-Cr-Mo alloys with various Cr and Mo concentration. The heat treatment was done in evacuated ampoule followed with quenching. The final composition was tested with X-ray dispersive spectroscopy and showed corroboration to the added content. X-ray diffraction and light microscopy analysis confirmed that the a sigma phase was particularly precipitated along the grain boundaries as the Cr and Mo increased from a certain concentration. The effect of the sigma phase on the hardness and reduced modulus is pondered in this work. Moreover, the electrochemical experiments in the chloride rich solution at 37 oC are discussed.

β-Phase Niobium Titanium Alloys and their Passivity in Medical Applications

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Niobium and Titanium are forming dense stable oxide films which protect them from further corrosion. For this they are called valve metals. Both, the lower price and the higher availability are the reasons for using mainly titanium in medical applications such as endoimplants. The room temperature structure of Titanium is hexagonal, is vcalled α-Ti and has mechanical properties that deviate form that of human bones. While it shows high biocompatibility the high mechanical load to the bone connection point brings a high load to any joint.

The cubic high temperature β-phase of Titanium can be stabilised with Niobium even down to room temperature. Its anisotropy is much lower due to the highre symmetry of the crystal and thus it yields mechanical properties which align well with those of the human bone. In between the two pure phases a mixed metallurgy is fiund in a compositional transition range. They need to be considered besides the pure β-phases for high Niobium contents.

The first part of this study is based on a combinatorial approach in which Niobium Titanium material libraries are produced by co-sputtering. Scanning energy dispersive x-ray is used to map the composition and the scanning x-ray diffraction allows determining the contribution of the phases as function of the composition.

A systematic microelectrochemical study using scanning droplet cell microscopy (SDCM) gives a comprehensive overview about the passivity of these alloys.

Selected alloys are then prepared as bulk samples and studied concerning their microstructure by means of EBSD. Also, here SDCM is used to study the differences and similarities between grains of different orientation and the influence of grain boundaries. This behavior is quantitatively described by film formation factors, electrochemical impedance spectroscopy and AFM measurements.

Niobium Titanium alloys are a very promising material class for bone replacement as well as in dental application to avoid periimplantitis.

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Towards Electrocatalysts' Structure-Stability Relationship

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Investigating the Structure-Activity Relationship (SAR) is a popular approach designed to establish relationships between the chemical structure (or structural-related properties) and activity of studied compounds (in present case electrocatalysts). Accordingly, the Structure-Stability Relationship (SSR) should also be explored, as it is paramount for a good electrocatalyst to sustain the necessary activity for the time of the operation of the device.

In my talk, I will present our methodological approach, namely a concept of atomically resolved identical location transmission electron microscopy (IL-TEM) [1] (Fig. 1) and how it provides us with unique insights into SSRs of the electrocatalysts. I will argue that IL-TEM gives an objective evaluation and certainty of observed events compared to randomly executed *ex-situ* TEM where the information about the exact history of the observed location before an electrochemical treatment is not known and the choice of the imaged locations is purely subjective, namely chosen by the operator. Thus, in *ex-situ* microscopy, evaluating numerous locations only provides us with general statistical descriptive insights.

To complement the *ex-situ*-obtained atomically resolved local structures before and after electrochemical bias, the so called *in-situ* or even operando information is needed. A few advanced characterization techniques will be introduced, relevant to the interpretation of electrocatalyst stability, such as an electrochemical flow cell, coupled to an ICP-MS detector and modified floating electrode. These information is an important feedback to the synthesis where electrocatalysts can be tuned and improved. In a perspective, the concept of understanding the electrocatalysts' SSRs will be extended to theoretical and computational approaches.

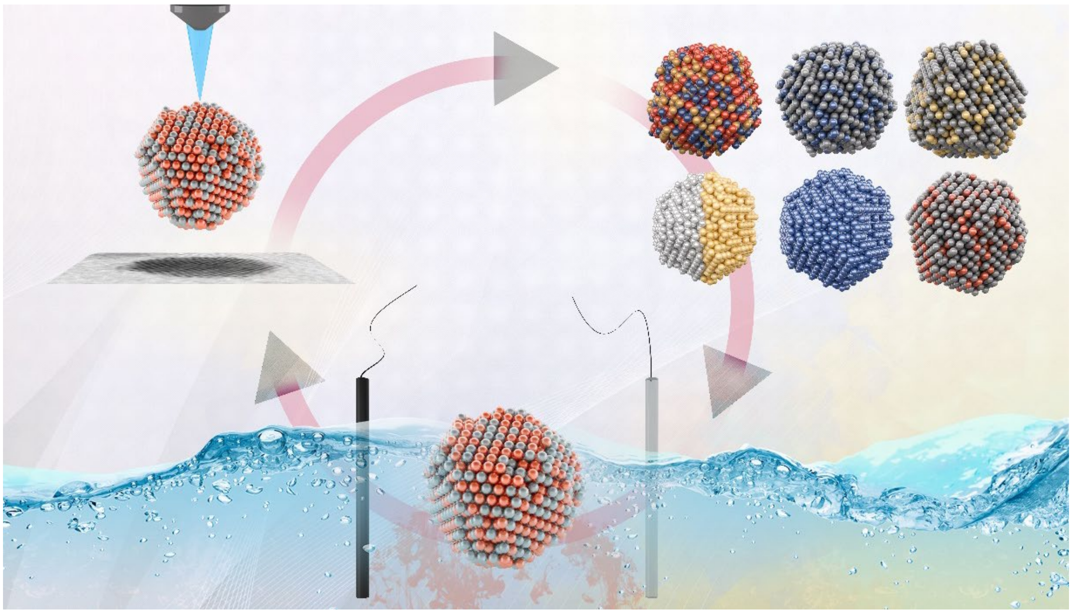

Figure 1: A schematic representation of the electrochemical and microscopy studies revealing structure-stability relationships of nanoparticulate electrocatalysts.

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Increased photocatalytic activity of $BaTaO_2N$ particles by morphology design and cocatalyst deposition

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Sustainable fuel production based on solar energy conversion could make a significant contribution to cover the energy demand in the future. Due to its simple setup, photocatalytic water splitting could provide a very cheap way for the generation of the fuel hydrogen. However, to make it industrially applicable further improvement regarding efficiency, scalability, and stability is needed. [1]

In order to perform photocatalytic water splitting, a photoactive material is needed which has a suitable band gap and proper band edge positions regarding the water splitting half reactions. Another important requirement for a photoactive material is its resistance to corrosion and photodegradation. [1, 2]

Oxides like TiO_2 can be used for solar water splitting, however the efficiency is limited by their large band gap (3.2 eV for TiO_2). By thermal ammonolysis, oxynitrides can be synthesized, which have a reduced band gap due to the partial replacement of oxygen by nitrogen [3]. Perovskite-related oxynitrides with the common formula of $ABO_{3-x}N_x$ show great potential as photocatalysts for solar water splitting. One example for this group is $BaTaO_2N$ which has a bandgap of 1.9 – 2 eV and has proven to be photocatalytically active for the oxygen and the hydrogen evolution reaction. Its photocatalytic activity can be increased by the addition of cocatalysts. In this context cobalt oxide (CoOx) can be used to promote the oxygen evolution reaction (oxygen evolution cocatalyst, OEC) and platinum (Pt) can be used to promote the hydrogen evolution reaction (hydrogen evolution cocatalyst, HEC). [4, 5]

In this work, $BaTaO_2N$ particles with different morphologies are prepared by thermal ammonolysis of the precursor $Ba_5Ta_4O_{15}$ and one-pot synthesis of $BaCO_3$ and Ta_2O_5 under NH_3 flow [6, 7]. Cocatalyst particles (CoOx as OEC/Pt for HEC) are deposited on the photoactive material by using deposition methods such as impregnation and/or photodeposition. X-ray diffraction is used to verify the phase purity of the prepared samples. The band gap is determined by UV-vis spectroscopy. By scanning electron microscopy, the morphology of the particles is investigated. Photocatalytic measurements are used to compare the photocatalytic activity of $BaTaO_2N$ particles with different morphologies, with and without cocatalysts. An aqueous particle dispersion containing either electron donor or acceptor is illuminated in order to investigate the activity for HER and OER, respectively. Gas chromatography is used to quantify the evolving gases.

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Single Molecule Junctions Containing Parallel Aliphatic Bridges.

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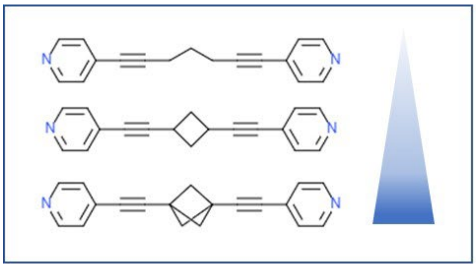
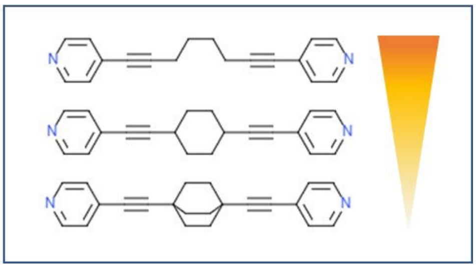
Quantum interference is an important concept in single molecule electronics.[1] The constructive interference is preferred since in one molecule of the same length a significant augmentation of the conductance *G* is achieved. For molecules with multiple conductance pathways (branches) *G* is higher than the sum of conductances of individual branches.[2–4] In this work we studied two sets of molecules with single, double and triple connectors in parallel. They differ in the number of carbon atoms in the conducting bridge. The first set contains -CH_2- and the second set contains -CH_2-CH_2- units in the bridge connected to a common carbon on both sides of the bridge.





The single molecule conductance was obtained by STM break junction technique in trimethylbenzene solvent. Density functional theory combined with the non-equilibrium Green's function formalism was used to understand charge transport properties and provide most probable metal-molecule-metal junction geometries. In general, the conductance is about one order of magnitude higher for molecules with -CH_2- bridging units compared to -CH_2-CH_2- bridges. This observation is in accord with recent studies on σ-bonded silanes with increasing backbone length.[5] The single molecule conductance in -CH_2- containing bridges increases with increasing number of bridging units (one to three). The opposite trend was observed experimentally for molecular bridges with -CH_2-CH_2- units. Experimentally obtained conductance values are discussed in terms of the available molecular configurations and conformations within the molecular junction. Quantum chemical calculations were able to reproduce the experimental results and provided an understanding of the essential features of the electron transport in these systems.

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Modelling of Electrocatalytic Double Layers with Refined Treatment of Metal-Water Interactions and Chemisorption

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The double layer at metal-aqueous interfaces in electrocatalytic systems has two features that are inadequately described by classical double layer models, namely, metal-water chemical interactions and chemisorption of partially charged adsorbates. A modified model is developed herein to encompass these two features. Specifically, the first-layer water molecules are treated statistically, considering chemical interactions and a continuous spectrum of water orientational states. In the latter aspect, this model improves over the often-used two-state water models. In addition, the chemisorption processes are assumed to have distributed equilibrium potentials, and the partially charged chemisorbates form dipole moments. With these modifications, the present model provides insights into how the potential of zero charge and the double-layer capacitance are influenced by behaviors of the first-layer water molecules and partially charged chemisorbates. The model is then employed to fit recent experimental capacitance data of Pt(111)-aqueous interfaces that are calculated from cyclic voltammetry (CV).[1] Quantitative agreement between experiments and the model is obtained, based on the assumption that the CV-based capacitance data are not the pure double-layer capacitance but include chemisorption capacitances. This assumption is supported by the observation that the CV-based capacitance values are several fold higher than the values obtained using electrochemical impedance spectroscopy, a technique that can separate pure double-layer charging and chemisorption processes. The model and the explanation of experimental data are critically discussed.

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Extracellular electron transfer through the cell wall of Gram-positive bacteria

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The extracellular electron transfer (EET) of bacteria has attracted attention with the development of the microbial fuel cells. While the electron transfer systems of Gram-negative bacteria are intensively investigated, the components responsible for the electron transfer of the Gram-positive bacteria, possessing tick cell wall instead of outer membrane, are not well-recognized till today. Recently, we established that new bacterial species belonging to the genera *Paenibacillus* are capable of transferring electrons extracellularly to an electrode surface [1,2]. We identified them by 16S rRNA technology and further we sequenced the whole genome of *Paenibacillus profundus* [3] and looked into its annotated genome in the NCBI data base (https://www.ncbi.nlm.nih.gov/nuccore/JAJNBZ000000000) for possible participating redox compounds. Along with the molecular biology and bioinformatics work, by applying electrochemical approach including CA, CV, DPV and EIS it was proved that multiple heme cytochromes are probably responsible for the EET through the cell wall and the extracellular polymer matrix of the natural biofilms covering the anodes of the bioelectrochemical devices (Fig. 1). In addition, electrodes covered by bacteria entrapped in artificial polymer were also examined. The EET mechanisms of Gram-positive and Gram-negative bacteria are compared and discussed.

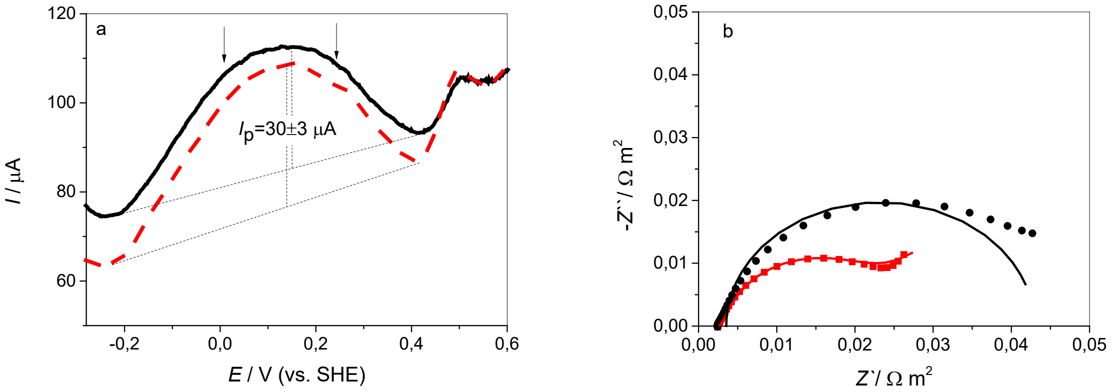

Fig. 1. a) DPVs recorded on the third (solid line) and fifth day (dashed line) of culturing at polarization; b) Nyquist plots obtained at the 15th (squares) and 120th h (circles) of poising for biofilm formation, dots - measured data, lines –fitted data.

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Challenges and opportunities of electrochemical CO_2 conversion: from nanoscale catalysis to industrial implementation

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Electrochemical reduction of CO_2 is a promising method for converting a greenhouse gas into value-added products, utilizing renewable energy. Novel catalysts, electrode assemblies, and cell configurations are all necessary to achieve economically appealing performance. In this talk, I am going to present a zero gap electrolyzer cell, which converts gas phase CO_2 to products without the need for any liquid catholyte. This is the first report of a CO_2 electrolyzer cell, where multiple cells are connected into a stack, thus scaling up the electrolysis process. I will show how proper cell components and operational conditions result in unprecedentedly high partial current densities in zero-gap cells ($j_{CO} > 1.0$ A cm^{-2}), while maintaining high conversion (20-45%), selectivity (up to 90%) and low cell voltage (2.6-3.2 V).

In the second part of my talk, I will show that while precipitate formation in the cathode gas diffusion electrode is detrimental for the long-term stability, the presence of alkali metal cations at the cathode improves performance. To overcome this contradiction, we develop an operando activation and regeneration process, where the cathode of a zero-gap electrolyzer cell is periodically infused with alkali cation-containing solutions. This enables deionized water-fed electrolyzers to operate at a CO_2 reduction rate matching that of those using alkaline electrolytes (CO partial current density of 420 ± 50 mA cm^{-2} for over 200 hours).

Finally, I will I will discuss the role of anode catalysts in CO2R cells. The urge to substitute Ir is driven by its high- and steeply rising market price as well as its limited stability in alkaline media. Although Ni is a ~ten thousand times cheaper, active, and stable oxygen evolution reaction (OER) catalyst in alkaline media, I will demonstrate that there are factors, which hinder its application in CO_2 electrolysis. As an outlook, I will show the key attributes what an anode catalyst needs to possess, to be applied in CO_2 electrolyzers.

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Amperometric gas sensor for detection of gaseous H_2O_2 based on redox mediators

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The determination of gases and other volatile compounds using electrochemical gas sensors remains a challenge with respect to sensitivity and selectivity. Many real-life situations require fast, sensitive, and yet easy-to-operate sensors for gaseous hydrogen peroxide (H_2O_2) that can operate at room temperature. Here, we will present an H_2O_2 gas sensor based on polyacrylic acid gel electrolytes comprising redox mediators together with commercially available screen-printed carbon electrodes. Aqueous polyacrylate gel electrolyte containing Cu(II) provided for sensing material that enabled the accumulation and stabilization of the gaseous analyte and via redox interaction with Cu(II) its fast and sensitive detection. The designed sensor exhibited good sensitivity in the low mg m^{-3} range with a wide linear response in the examined concentration range of 10-100 mg m^{-3} after only 10 min accumulation under ambient conditions. Sensors' relatively simple setup and solid electroanalytical performance have strong application potential in emerging fields such as clinical diagnostics [1], explosive detection [2], environmental monitoring [3] and occupational health and safety [4].

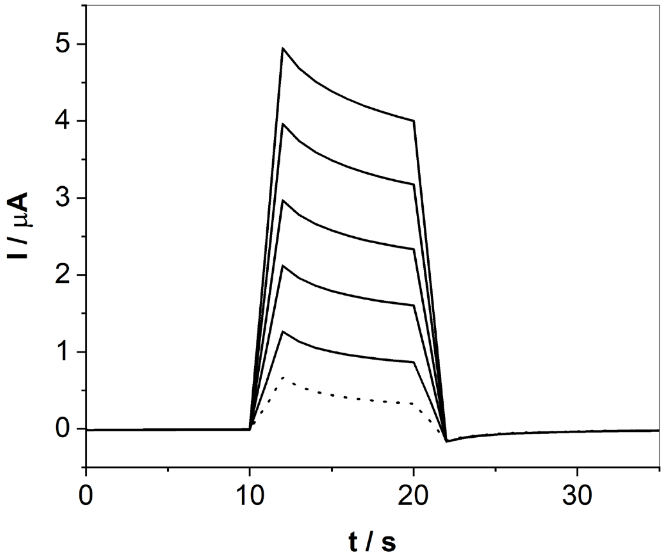

Figure: responses of the gas sensor while altering accumulation time measuring 20 mg m^{-3} $H_2O_{2\,(g)}$

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Investigating the catalytic activity of gold-palladium nanoparticles for oxygen reduction reaction by single nanoparticle electrochemistry

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Our society is confronted with serious problems related to energy supply and conversion, ranging from lacking access to fossil resources to global warming and climate change. Therefore, new technologies are necessary to lower the consumption of fossil fuels and the amount of greenhouse gas emission, which are mainly caused by the transport sector and electric power generation. High-capacity energy systems, such as fuel cells and metal-air batteries are highly promising to reliably supply humankind with renewable, green energy. Nowadays, these environmentally friendly systems are still cost-intensive because of the sluggish oxygen reduction reaction (ORR) kinetics as their cathode reaction, which is tried to be overcome with a high loading of precious and rare metal-containing catalysts like platinum [1].

Employing nanoparticles (NPs), instead of bulk materials, is a promising approach for decreasing the amount of precious metals required in these technologies. Due to their high surface-to-volume ratios, nanoparticles are favourable catalysts and using bimetallic systems, to reduce the amount of precious metals, is a promising route to further reduce catalyst cost. We explore this for gold-palladium NPs as catalyst materials. It has been reported that the epitaxial growth of a Pd layer on a Au NP can enhance the electrocatalytic performance of Pd towards ORR by downshifting its d-band center and, hence, adjusting the adsorption of the reactants and the desorption of the intermediates [2].

To study the ORR electrocatalytic activity of the bimetallic NPs and to delineate their intrinsic properties, we propose single particle electrochemistry instead of conventional ensemble measurements. This promising electrochemical characterization method allows to study the intrinsic properties of nanocatalysts without overlaying effects of neighboring particles [3]. Due to their random motion, freely diffusing catalytically active NPs collide with a potentiostated micro-electrode and mediate the reaction of interest (Figure 1) [4]. In the present study the ORR catalytic activity of bimetallic gold-palladium nanoparticles is characterized by using NP impacts at a carbon fiber micro-electrode. The associated cathodic current is measured, which provides valuable insights into the oxygen reduction reaction.

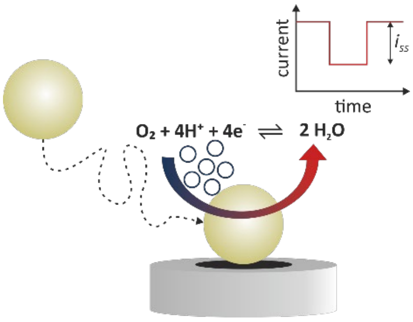

Figure 1: Shematic illustration of a catalytic impact at a potentiostated electrode.

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Structural Analysis of Twinned Metallic Alloy Nanoparticulate Electrocatalysts

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To lower the electrocatalyst cost in proton exchange membrane fuel cells (PEMFC) and water electrolysers, commonly containing scarce and expensive metals, synthesizing nanoparticles and alloying them with more abundant transition metals is a common strategy[1]. A typical representative is a PEMFC catalyst used for oxygen reduction reaction (ORR), consisting of supported Pt-alloy nanoparticles. Real-world batches of electrocatalysts contain unimaginably large numbers of nanoparticles that exhibit a wide variety of atomic-scale structural differences which can influence their catalytic behaviour[2,3].

A deeper understanding of the influence of the catalyst structure on its properties would lead to a more informed synthesis strategy, which is a good motivation for performing advanced characterization. Among different characterization techniques, X-ray powder diffraction and atomically-resolved scanning transmission electron microscopy (STEM) are especially valuable when evaluating nanoparticulate electrocatalysts. Additionally, simulated datasets and advanced data analysis can serve as tools to reveal structural subtleties that can be used to interpret electrocatalyst activity and stability.

This work encompasses a comprehensive structural analysis of thermally treated carbon-supported $PtCu_3$ nanoparticles. Specifically, we investigated ensembles of disordered or partially ordered nanoparticles, and nanoparticles exhibiting a large number of parallel twin boundaries. The goal of this work is to provide an accurate description of the twin boundary manifestation in electron micrographs and diffraction patterns as well as establishing a link to synthesis conditions. This study is a step towards a thorough understanding of the formation and influence of structural defects in nanoparticulate electrocatalysts, paving the way towards smart design of advanced functional materials.

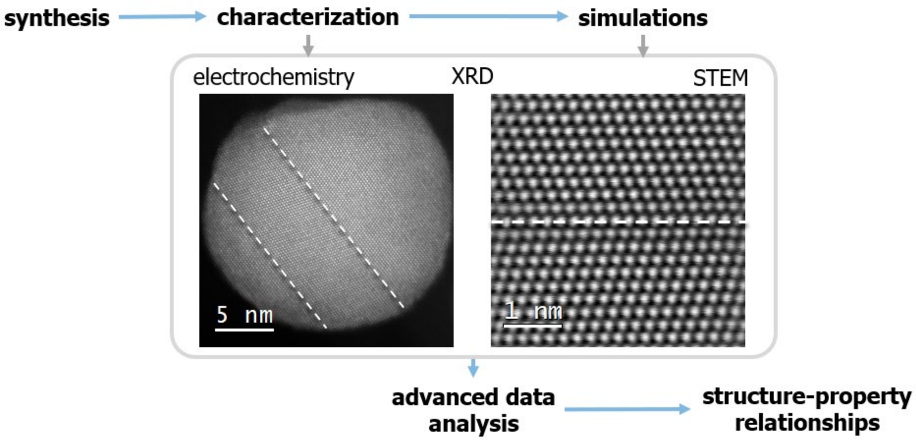

Figure 1: A pipeline for the structural analysis of alloyed nanoparticles including atomically resolved high-angle annular dark field STEM images showing polysynthetic twinning in a $PtCu_3$ nanoparticle.

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H_2 sensors for industrial and automotive applications
- Technical, safety and cost aspects of customized and scalable sensor systems -

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For the hydrogen measurement several sensing principles will be used, e.g. catalytic, electrochemical, thermal conductivity, resistive, optical principles as well as combinations of these. A benchmarking of selected used H_2 sensor principles regarding, e.g. selectivity, sensitivity, cross sensitivities, accuracy, response time, power consumption, safety aspects, long-term stability, life-time and costs shows their advantages and disadvantages. Their application-related weighting is an important basis for the selection of the appropriate sensor principle and ultimately the sensor type.

With the intelligent integration of the two functional principles in a sensor system a combination of their advantages and a compensation of their disadvantages are possible. The combination of a selective metal-oxide(MOX) semi-conductive gas sensor element (figure 1) and a thermal conductivity detector element makes customized H_2-sensor systems with high sensitivity, selectivity, stability and safety possible [1]. Both sensor principles, which are integrated in this sensor system, are used successfully in a large number of market-proven applications, e.g. detection of fire / combustion gases in lignite power plants, sub-ways, H_2 process engineering and H_2 leak detectors for many years. Furthermore the application-specific scalability of the sensor system and its economical production from small to large series especially of the components gas sensor elements, electronics and housings enables the realization of customized, highly reliable H_2 detection solutions for users in industry, public sector and research.

Based on these platform-concept selected examples of products and projects are H_2-monitoring of electrolysers at the H_2- and the O_2-side up to 100% H_2 and 100bar pressure (figure 2), the H_2 detection in ambient (figure 3) and exhaust of fuel cell systems (vehicles and stationary systems), the leak detection in high-pressure lines, in underground cables / cable pipes and the leak detection with forming gas (95% N_2/5% H_2) in climate systems (automotive and buildings) with H_2 handheld gas leak detectors (figure 4) also in ATEX environments.

Figure 1: H_2 MOX gas sensor elements

Figure 2: H_2 Semicon® gas sensors

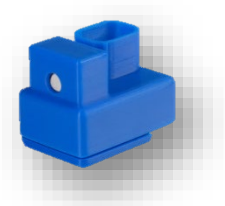

Figure 3: H_2 ambient gas sensor - laboratory sample, NIP2-project H2D4EV

Figure 4: H_2 handheld gas leak detectors

Figures: UST Umweltsensortechnik GmbH

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The Production and Characterisation of a Membrane Electrode Assembly

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About 90 % of the energy demand in the transport sector is provided by petroleum products. A viable way to reduce greenhouse gas emissions in this sector is to use hydrogen as a fuel for polymer electrolyte membrane fuel cell (PEMFC) vehicles. The widespread commercialisation of fuel cell electric vehicles (FCEVs) demands an increase in reliability and durability as well as a reduction in costs [2,3].

The work focuses on the core unit of the fuel cell, the membrane electrode assembly (MEA) in the with the aim of presenting a pathway for reproducible, highly automated MEA production on an industrial scale for novel catalyst systems and optimising the manufacturing, including the catalyst/ionomer interfaces.

First, the process engineering challenges for MEAs e.g., the risks and costs for catalyst materials, will be discussed. The degradation of catalyst ink under different manufacturing and storage conditions and for different compositions will be investigated. The influence of the degradation products on the fabrication of a MEA and on the performance and lifetime of a PEMFC will be explored. The experimental results will provide recommendations for the storage and fabrication of MEAs and provide suitable techniques for in-line quality control of MEAs on an industrial scale. A mechanistic understanding of the performance determining parameters through single cell tests with advanced characterisation techniques (e.g., cyclic voltammetry, electrochemical impedance spectroscopy, polarisation curves) will be obtained.

This work was enabled and financed in cooperation by Graz University of Technology and Darmstadt University of Technology. We, Mario Kircher and Adrian Baumunk, would like to thank Viktor Hacker and Bastian Etzold for arranging this joint project and giving us the opportunity to work on this topic.

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Electrochemical characterisation and bioassessment of anodically oxidized and femtosecond laser treated Ti_6Al_4V for dental and bone implants

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Ti6Al4V (Titanium grade 5) alloy is commercially used biocompatible material for dental protheses and medical bone implants. Since some implants have to be taken out after the implantation, the osteo repellent surface is a crucial property for the bone implants such as bone plates and screws. In contrast, the dental protheses requires increased osseointegration. Femtosecond laser treatment produces LIPSS ("laser induced periodic surface structures") that consist of micro-cones and nano-ripples, which mimic roughness and structures of a bone. Therefore, surface modifications by femtosecond laser and electrochemical anodization could be promising methods for improving both osseointegration and osteo-repellence in dental protheses and bone implants. The aim of this work was bioassessment and electrochemical surface characterization of the femtosecond laser treated and anodically oxidized Ti6Al4V alloy. Following the potentiostatic anodization of Ti6Al4V alloy, samples were structured with femtosecond laser. As a final stage, laser structured spots were anodized potentiodynamically by self-developed SDCM (Scanning Droplet Cell Microscopy) setup. Influence of different electrochemical parameters such as different electrolytes, scan rates and potentials were studied. Topography and morphology were determined by Atomic Force Microscopy (AFM) and Scanning Electron Microscopy (SEM), while X-Ray Diffraction (XRD) was used to examine the crystallography. Additionally, the composition of the oxide layer was determined by X-ray photoelectron spectroscopy (XPS). Electrochemical surface area (ECSA), a relative permittivity ε_r and an oxide forming factor (k_{ox}) were obtained. Finally, bioassessment was done with osteoblast. In conclusion, obtained results indicate that femtosecond laser treated and anodized samples could be used as both, dental and medical bone implants.

Penetration of Cl⁻ ions from solution into an organic self-assembled-monolayer on a metal substrate: Trends and modeling aspects

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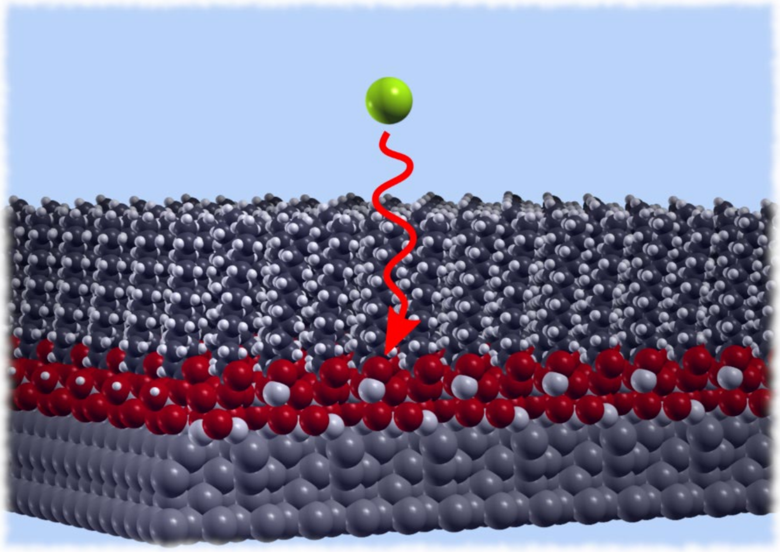
Organic molecules that form self-assembled-monolayers (SAMs) on metal substrates may provide efficient corrosion protection. A possible mechanism by which SAMs inhibit corrosion is to hinder the transport of ions to/from the metal substrate, e.g., chlorides from solution toward the metal substrate and metal cations from the metal substrate to the solution. For this reason, the mechanism by which SAMs hinder the penetration of ions from aqueous solution toward the metal substrate was studied. A simple scheme was developed that describes the activation barrier for penetration of ions into SAM as a function of the electrode potential [1]. For chlorides, the activation barrier decreases as the electrode potential increases, as would be intuitively expected; however, for thick SAMs, the barrier remains sizable even at rather positive potentials, which may be one of the reasons why dense and sufficiently thick SAMs efficiently inhibit corrosion. By utilizing a simple model where metal substrate, organic layer, and aqueous solvent are described implicitly by dielectric continuum slabs, two important effects by which SAMs hinder the penetration of Cl^- ions toward the metal substrate are identified. The first effect is due to inferior solvation of ions in the organic layer compared to that in an aqueous solvent, and the estimated difference is larger than 1 eV for Cl^-. This effect is independent of the thickness of the organic layer, provided that the layer is thicker than about 10 Å. The second effect is due to the electric field at the electrochemical interface and the extent to which it affects the penetration of Cl^- depends on the electrode potential and the thickness of the organic layer.

The developed scheme [1] is not specific to Cl^- ions, but can also be applied to the anodic dissolution of metals, i.e., diffusion of metal cations from the metal substrate through SAM toward the solvent, irrespective of whether metal dissolves in the form of bare cations or coordinated to ligands in metal–ligand complexes, provided that the complexes are charged. Indeed, the model is based on electrostatic arguments and applies to any charged species.



A schematic illustration of a Cl^- ion penetrating through an organic SAM toward an oxide layer on a metal substrate.

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V_2O_5 doped with Conducting Polymer PEDOT for Cathodes of Aqueous Zinc-Ion Batteries

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Aqueous zinc-ion batteries (AZIBs) have received much attention recently as alternative power sources, owing to the advantages of high theoretical capacity, low cost, environmental friendliness, and good safety. Among the various possible cathode materials for AZIBs, V_2O_5 is considered as a promising cathode material due to its rather stable open structure facilitating zinc ion insertion. Recent studies have shown that pre-insertion of conducting polymers into the layered structure of V_2O_5 results in better electrochemical performance of the cathode materials [1,2].

In this work we have investigated the electrochemical performance of different kinds of V_2O_5-based electrodes, with pristine and electrospun V_2O_5, and V_2O_5 doped with poly(3,4-ethylenedioxythiophene) (V_2O_5/PEDOT). The structure and morphology of all materials were studied by high resolution X-ray diffraction, energy dispersive X-ray spectroscopy, scanning electron microscopy, optical microscopy, and X-ray photoelectron spectroscopy. Electrochemical performance was studied in CR2032 coin cells with aqueous 3 M $ZnSO_4$. Electrochemical tests were performed by galvanostatic charge/discharge (GCD) and cyclic voltammetry (CV) in the (0.3–1.4) V potential range vs. Zn/Zn^{2+} at room temperature (20±2 °C). GCD tests were performed in the (0.3–20) A g^{-1} current range using CT-4008 battery testing system (Neware Co., China), CV measurements were carried out at a scan rate of 0.1 mV s^{-1} using a BCS-805 potentiostat (Biologic, France).

The activation process of V_2O_5 material structure and the corresponding evolution of electrochemical performance and enhancement of capacity was observed at initial several cycles. It is related to interlayer expansion taking place due to co-insertion of counter ions and water molecules with gradual transformation of V_2O_5 layered structure. After the transformation, two pairs of stable peaks appear at 0.78 V / 0.58 V, and 1.05 V / 0.88 V, which probably correspond to the consecutive redox process of V^{5+} to V^{3+}, forming $Zn_xV_2O_5$ phases with different degrees of Zn^{2+} intercalation. Alternatively, both Zn^{2+} and protons intercalation may occur. The maximal values of specific capacities for initial and nanostructured forms of V_2O_5 were found as 260 mAh g^{-1} at 0.1 A g^{-1} and 350 mAh g^{-1} at 0.1 A g^{-1}, respectively.

At the in situ oxidative polymerization/intercalation of 3,4-ethylenedioxythiophene, the V_2O_5 framework was partly reduced, so that the mixed valence compounds with increased overall electrical conductivity of V_2O_5/PEDOT were formed. Accordingly, this modification improved the cycle performance of the material. V_2O_5/PEDOT electrodes reach high steady-state capacity values without long activation processes commonly proceeding with pristine V_2O_5 electrodes. V_2O_5/PEDOT electrodes provide high specific capacity 380 mAh g^{-1} at 0.3 A g^{-1}, improved C-rate capability (274 mAh g^{-1} and 102 mAh g^{-1} at 5 A g^{-1} and 20 A g^{-1}, respectively, and better stability during long-term cycling (7% capacity loss during 200 cycles at 5 A g^{-1}).

Detailed analysis of electrochemical performance of electrodes and the reasons of improved electrochemical performance will be discussed in the report.

Acknowledgements

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Revealing the formation of corrosion protective films on copper through the role of chloride ions

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Based on previous literature data [1-3], the role of chloride ions remains a subject of profound debate – with doubt as to whether they act as a catalyst, an intermediate or a promoter in the formation of corrosion protective films on copper. Herein, unambiguous evidence is presented that the Cl^- ions act simultaneously as promoters and reactants, thus revealing their dual role in the formation of polymerized Cu-Cl-MBI chains, as confirmed by time-of-flight secondary ion mass spectrometry (ToF-SIMS) [4]. Hence, the pure catalytic role of chloride ions is excluded since they are consumed in the reaction. This occurs when the copper is exposed to 3 wt.% NaCl solution containing 1 mM of the mixture of inhibitors 2-mercaptobenzimidazole, MBI, and octylphosphonic acid, OPA, in the molar ratio MBI:OPA of 9:1 [5]. We believe that such a scenario can also be expected for other metal-organic inhibitor systems. The energy-dispersive X-ray spectroscopy analysis at the cross-section of the thick polymerized film revealed the formation of a Cu_2O film under the Cu-inhibitor film. The Cu_2O underlayer, together with the porous straw-like morphology of the $[Cu\text{-}Cl\text{-}MBI]_n$ overlayer, is believed to be responsible for the excellent corrosion protection of copper, even in a chloride environment without the reservoir of MBI+OPA. We also report a new insight into the mechanism of degradation of the Cu-MBI/Cu-Cl-MBI film, obtained by a combination of Tof-SIMS, X-ray photoelectron spectroscopy and cyclic voltammetry, that results in the formation of $(MBI)_2$ dimers. The inhibitor layer, formed in chloride solution containing a synergistic mixture of MBI and OPA, showed outstanding resistance to degradation.

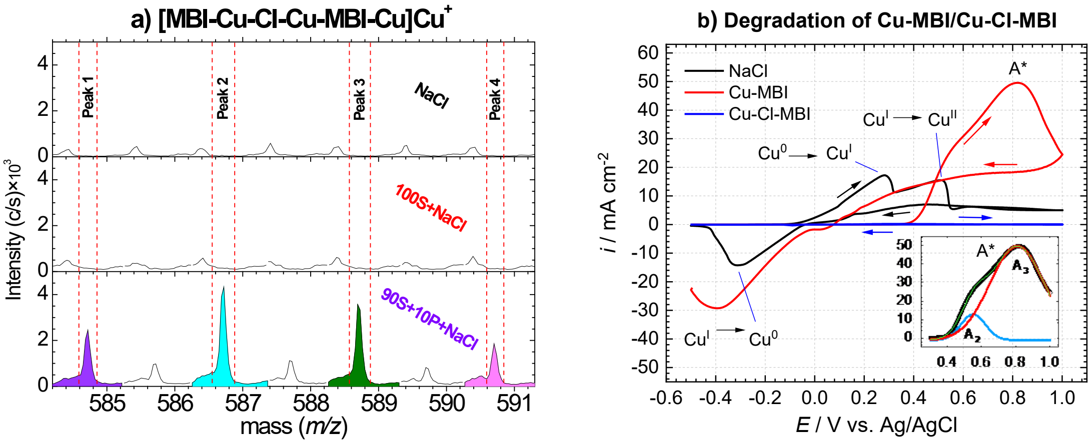

Figure 8. a) The evidence for the chlorine-bridge in the fragment of the polymer chain consisting of two inhibitor molecules in the surface layer. These are formed on Cu immersed for 24 h in 3 wt.% NaCl containing 1 mM 2-mercaptobenzimidazole, MBI, and octylphosphonic acid, OPA, in the ratio 9:1 (90S+10P+NaCl). Peak 1 corresponds to $[C_{14}H_{10}N_4S_2Cu_4Cl]^+$. *Other fragments with* ^{65}Cu *isotope, such as* $[C_{14}H_{10}N_4S_2Cu_3{}^{65}CuCl]^+$, $[C_{14}H_{10}N_4S_2Cu_2{}^{65}Cu_2Cl]^+$ *and* $[C_{14}H_{10}N_4S_2Cu^{65}Cu_3Cl]^+$, *assigned to peak 2, 3 and 4, respectively, are also present; b) Cyclic voltammograms recorded for copper in 3 wt.% NaCl solution (NaCl) and in 3 wt.% NaCl containing 1 mM of MBI (Cu-MBI) and in 3 wt.% NaCl containing 1 mM MBI and OPA, in the ratio 9:1 (Cu-Cl-MBI) after 24 h of immersion. The scan rate was 10 mV* s^{-1}.

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Unified model of hydrogen peroxide production and transport in LT-fuel cell membrane-electrode assembly

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Low-temperature fuel cells are one of promising devices for future transition to clean, carbon emission free energy production. However, their wider adoption is currently still limited by relatively fast degradation of some of their key components, such as catalyst layer and proton exchange membrane.

Chemical degradation of the membrane is initiated by the presence of hydrogen peroxide, formed as a by-product of electrochemical reaction between oxygen and protons, which would ideally result only in water. The hydrogen peroxide further decays into reactive radical groups in the presence of transition metal ions in a series of Fenton-like reactions, recycling the metal ions between different states of ionization. The reactive radical, formed in reactions, attack various points of perfluorinated polymer chains, forming the membrane, causing the loss of membrane conductivity and its mass, eventually leading to membrane thinning and pinhole formation. [1]

The rate of hydrogen peroxide formation and especially its location in the fuel cell have long been debated. Abundance of oxygen in cathode catalyst layer suggest its production there, but high electric potential strongly promotes water production via 4-electron oxygen reduction reaction (ORR) with equilibrium potential 1.23 V, and supresses hydrogen peroxide via 2-electron ORR with far lower equilibrium potential of 0.65 V. In terms of electric potential, the anode side catalyst layer is therefore better suited for peroxide production. However, low concentration of oxygen on anode side, present only due to gas crossover through the membrane, limits the hydrogen peroxide production on anode side. Another possible source of hydrogen peroxide is also the platinum band in the membrane, formed from diffusion flux of platinum ions, originating from dissolution of platinum catalyst particles in the cathode. Electric potential of these particles is determined by the rates of electrochemical reactions between hydrogen and oxygen membrane crossover fluxes on their surface, resulting in conditions which can promote formation of hydrogen peroxide. [2]

This complex interplay between various conditions, promoting the hydrogen peroxide formation, suggest that the prevailing mechanism and position of its production strongly depends on both fuel cell operating conditions as well as the state of its degradation, determining the position and concentration of platinum particles in the membrane. To quantitively investigate different possibilities, we propose a comprehensive mathematical model of hydrogen peroxide production, which consistently calculates its production throughout the entire membrane-electrode assembly (MEA) based on the local concentration and diffusion fluxes of relevant species and electric potential on cathode and anode catalyst layer. Relevant boundary conditions are obtained from state-of-the-art fuel cell performance model, capable of calculating spatially and temporarily resolved concentration and potential fields inside the fuel cell MEA during its operation [3].

Preliminary results of the model indicate that anode catalyst layer is the main source of hydrogen peroxide in the fresh fuel cell when operated at low current densities and high voltages, while high current densities and consequently lower voltages can cause significant production also on cathode side. For aged fuel cells, when significant amount of platinum is deposited as Pt band in the membrane, the crossover oxygen reacts on these particles rather than diffuses into the anode, thus reducing hydrogen peroxide production in the anode and increasing its production inside the membrane.

These results indicate that mitigation of chemical membrane degradation requires different fuel cell operation strategies, which depend on the state of its degradation. The proposed model thus represents an excellent tool for further study of degradation processes in the fuel cells as well as the development of appropriate strategies for their mitigation.

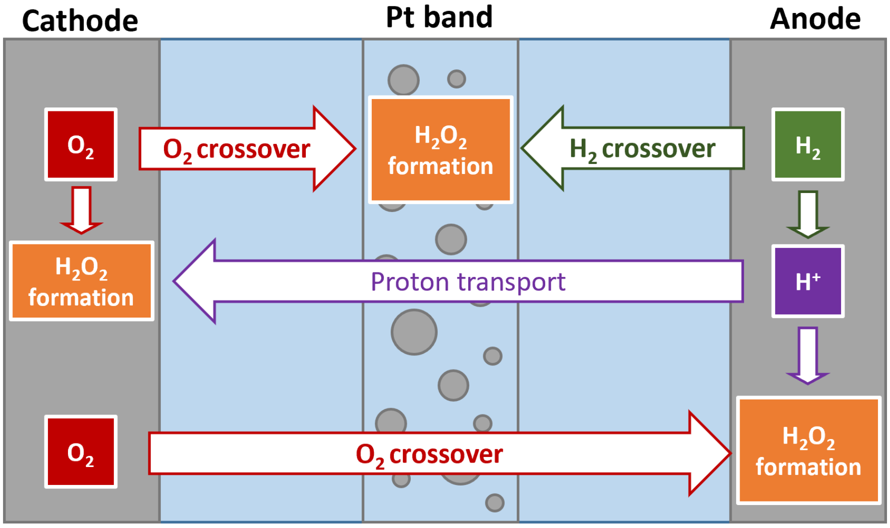

Figure 1: Schematic overview of modelled processes

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Accelerated Stress Test Development based on Degradation Phenomena in Proton Exchange Membrane Water Electrolysis (PEMWE) Cells

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Proton exchange membrane water electrolysis (PEMWE) is a highly efficient technology for the large-scale production of green hydrogen. Yet, the comparability and reproducibility of scientific results is not always straight forward. A deeper understanding of the degradation mechanisms is needed to further advance this technology for its market penetration. Several scenarios like the high current density operation or shut-down procedures have a major impact on the performance of the PEM water electrolysis cell[1]. The most affected PEMWE components, including the catalyst/catalyst layer, membrane, gas diffusion layer (GDL), porous transport layer (PTL) and bipolar plates are presented in Figure 2[2].

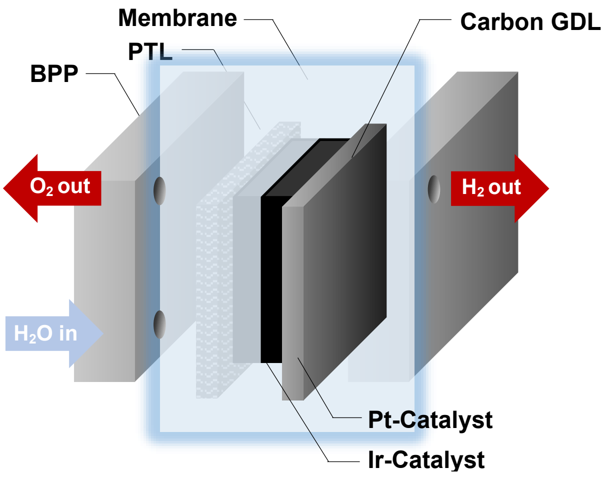

Figure 2. Scheme of a PEM water electrolysis cell.

In this work, a characterisation and accelerated stress test (AST) protocol has been designed based on the main degradation effects in PEMWE components**.** Therefore, sources of degradation for individual components in a PEMWE single cell are investigated by various techniques, including in-situ and ex-situ cell tests. The 5 cm^2 PEMWE single cell is electrochemically analysed in means of polarization behaviour and impedance spectroscopy throughout a range of currents (0.01 A cm^{-2} to 2.0 A cm^{-2}) at 40°C. This complementary investigation enables the benchmarking of baseline components in terms of their durability and performance.

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Bare and Modified Cu(111) Electrocatalysts: Interfacial Structure and Reactivity

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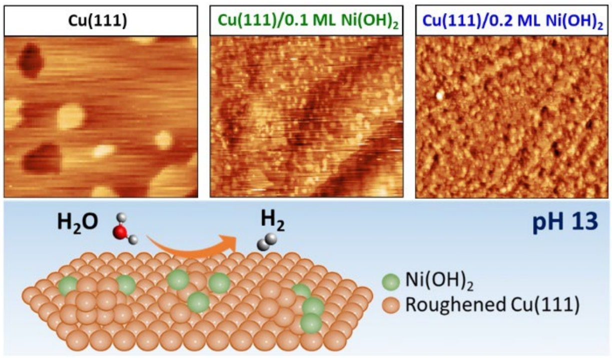
A very important parameter for the electrocatalytic performance of a material is its potential of zero free charge (pzfc). For Cu(111) at pH 13 it was identified at −0.73 V_{SHE} in the apparent double layer region. It shifts by (88 ± 4) mV to more positive potentials per decreasing pH unit.[1] At the pzfc, Cu(111) starts to restructure. At higher potentials, full reconstruction and electric field dependent OH adsorption occur, causing a remarkable decrease in the atomic density of the first Cu layer.[1] It is this restructuring that enables Cu(111) to efficiently oxidize CO and to reduce water. Therefore, knowledge of the surface structure and the position of the pzfc is of paramount importance for the understanding of copper's catalytic properties and for the rational design of electrocatalysts.

CO is a key intermediate in the electro-oxidation of energy carrying fuels and known to act as a catalyst poison. Single-crystal Cu(111) model catalysts can efficiently electro-oxidize CO in alkaline media,[2] where strong surface structural changes are observed under reaction conditions with electrochemical scanning tunneling microscopy (EC-STM). Supported by first-principles microkinetic modelling, we have shown that the concomitant presence of high-energy undercoordinated Cu structures at the surface is a prerequisite for the high activity.



In water electrolyzers, it is possible to produce H_2 in the course of the hydrogen evolution reaction (HER), which was studied with $Ni(OH)_2$ and $Co(OH)_2$ modified Cu(111) electrodes in alkaline media.[3] Strong morphological changes upon adatom modification lead to a significant HER rate enhancement. Intriguingly, this is induced through a decrease of the electric field strength negative of the pzfc. This implies an easier reorganization of the interfacial water molecules facilitating charge transfer through the double layer, and thus enhancing the efficiency of electrocatalytic reactions. The tendency of Cu(111) to restructure is found to dominate its electrochemical properties. The structural changes of the electrode surface are intimately related to the electric field at the solid/liquid interface and to its electrocatalytic activity, in general.

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Applicability of conducting-polymer matrices in composite battery electrodes

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Though Lithium-ion batteries are currently the best performing battery technology for most performance measures, they are limited in energy density and specific energy by the need for active materials to maintain a rigid structural framework for the storage of lithium ions. This framework represents weight and volume that cannot be avoided, if charge storage is to rely on intercalation. As these frameworks have been optimized over the last two decades to store as much lithium in as little volume and mass as possible, it is unlikely that step-changes in specific energy and energy density in lithium-ion technology will be observed. Instead, 'beyond lithium-ion' technology has become the target for drastic improvements, using a charge-storage chemistry based on conversion, displacement and alloying reactions. However, different from intercalation chemistry, these are accompanied by significant morphological and volume changes of the active material. For many of the most promising materials, the polyvinylidene fluoride (PVDF) and conductive carbon electrode matrix, that has been successful for lithium-ion technology cannot accommodate such significant microstructural changes[1,2].

In this presentation, we are exploring the properties of single-component electrode matrices that are based on conducting polymers[3]. These matrices include a conducting polymer, as a flexible conductor, doped by a anionic polymer, which serves to ease processing and as adhesive component. As such, these matrices offer much increased adhesion of the conductive component to active materials, with the goal to maintain electronic connection over cycling. We present a demonstration of the performance of batteries that use such one-component matrices, a description of their dynamic changes during cycling and an attempt to elucidate the complex conduction in these materials. Among others, our work shows that such nano-composites require an initial activation step to operate, but can subsequently sustain current rates above 250 mA g^{-1} with a 10 wt.-% single-component electrode matrix.

Our work shows that electrode matrix innovations are possible and can significantly impact battery performance. It provides insights into the operation of conducting polymer-based single-component matrices. This understanding forms a foundation for the development of composite electrodes that can sustain the reversible operation of high energy density materials beyond the current lithium-ion technology.

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Bacterial Drug Susceptibility Assessment by Electrochemical Quantification of Antibiotic Retention

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Drug resistance in bacteria and cancer is a growing problem that severely increases the number of deaths from bacterial infections and cancer.[1,2] According to the World Health Organization, drug resistance is present in every country, and various national and international health organizations have called for the urgent development of new treatment and diagnostic strategies.[3] Cellular resistance mechanisms are at the root of drug resistance, which include cell membrane protein modifications, intracellular drug target alterations, and the over expression of efflux pumps.[4]

This presentation outlines innovative and interdisciplinary approaches to recognize and quantify drug resistance in bacteria and cancer cells by electrochemistry. Electroanalytical techniques are cost efficient, sensitive and the transparency of a liquid sample is irrelevant, allowing direct in vitro analysis of blood, urine, and saliva samples. This presentation covers the characterization of some of the most important commercial drugs, and new investigational antibiotic hybrids by electrochemistry.[5] Building on this exploration of drug electrochemistry, the quantification of drug influx and retention in biological cells will be presented. This research forms the basis for the development of a point-of-care biosensor to identify drug resistance in patient samples. Such technology would advance clinical treatment from the current trial-and-error approach to the prescription of evidence-based personalized drug regimens.

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Impedance analysis of polymer modified electrodes – the effects of thickness distribution and non-stationarity

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The benefits of using electropolymerization reactions to modify electrode surfaces is the ability to change the properties of the polymer film by changing the experimental conditions, and the ability to tailor the electrodes for specific applications. In the present study we report the electrochemical preparation and characterization of poly(3,4-ethylenedioxythiophene) (PEDOT) modified electrodes before and after overoxidation. Cyclic voltammetry (CV) and electrochemical impedance spectroscopy (EIS) were used for the electrochemical characterization of the system.

According to the results, the impedance response of the overoxidized films differ considerably from those measured for freshly prepared films. The decreasing capacitance of the double layer region and the increasing charge transfer resistance suggest that during overoxidation the electrochemical activity of the film decreases and the charge transfer process at the metal/film interface becomes more hindered than in the case of pristine films. The results of electro-chemo-mechanical measurements showed that the mechanical properties of a PEDOT layer and its resistance against the consequences of overoxidation could be significantly improved by the electrochemical deposition of poly(bisphenol A) (poly(BPA)) [1] on its surface and in its pores, i.e. by the combination of the two polymers [2]. It is known that pure poly(BPA) has low electrochemical conductivity and poor electrochemical activity, therefore, it was expected that its presence would not affect considerably the electrochemical properties of the PEDOT layer, even after its overoxidation.

When modeling the impedance response of the polymer modified electrodes, we encountered two difficulties: thickness distribution of the film and time evolution of the state (properties) of the system after overoxidation. The latter observation indicates that the system is non-stationary or unstable.

To reduce the effect of non-stationarity [3], we used the four-dimensional (4D) analysis method for the calculation of the impedances corresponding to different time instants. One of the most important results of the present work is that in case of PEDOT and poly(BPA)/PEDOT modified electrodes the deviations of the impedance responses from the purely capacitive behavior predicted at low frequencies by the theoretical models (i.e. the frequency dispersion of the low frequency capacitance [4]) can be well explained solely by the assumption of uneven film thickness. It has been found that the impedance model, which considers the film thickness distribution (by assuming regions of different film thicknesses on the basis of SEM micrographs) gives a good description of the impedance data, both before and after overoxidation. By using this model reasonable values for the different parameters characterizing the polymer film electrodes could be obtained by CNLS fitting the impedance function to the experimental data.

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Energy transport improvement in Ni^{2+}salen polymer semiconductors by chains confinement inside vertical silica nanochannels

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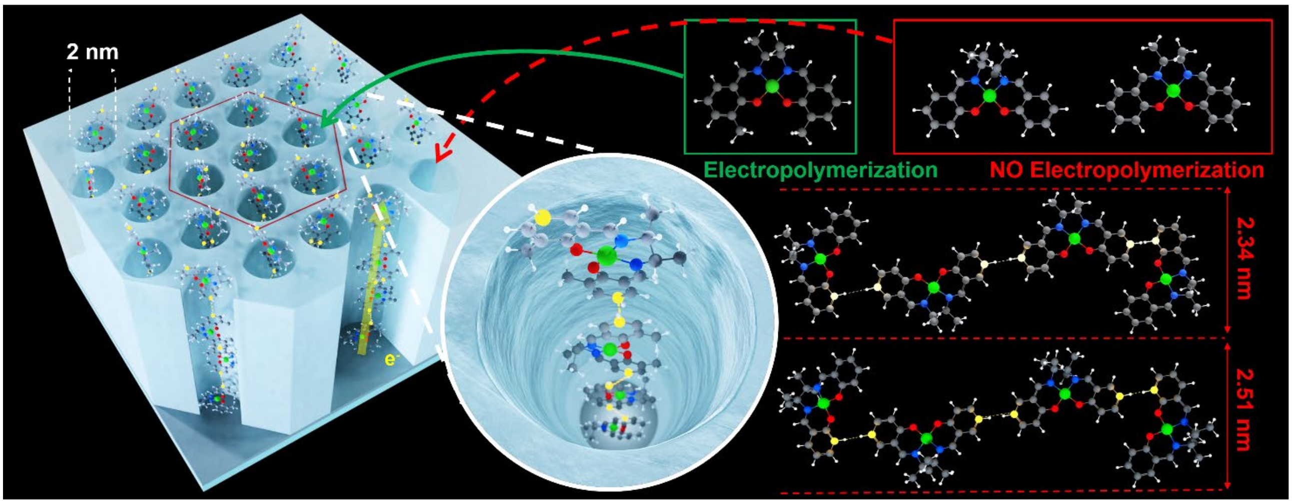
The scientific problem we addressed aims to improve energy transport in Ni^{2+}salen conducting polymers by isolating individual polymer chains inside the silica matrix of vertical nanochannels used to suppress charge carrier trapping observed in the continuous Ni^{2+}salen polymers. With that respect, we prepared molecular wires based on structurally privileged ortho substituted Ni^{2+}salen conducting polymer, offering the molecular structure facilitating its linear electropolymerization growth inside the confined space of silica matrix containing 2 nm in diameter channels.

Moreover, we noticed that analogical embedment of *ortho* unsubstituted Ni^{2+}salen polymers was not possible. Thus, we engaged quantum chemical calculations utilizing the density functional to explain this phenomenon. Hence, we succeeded in recognizing structure–property relationships of Ni^{2+}salens governing the local electropolymerization ability inside vertical nanochannels. Isolation of polymer chains allowed us to get insight into the intrinsic properties of Ni^{2+}salen polymers creating a better understanding of their charge transport and polymerization mechanisms.

Prepared molecular wires indicated improved energy transport properties evidenced by the electrochemical measurements revealing the energetically favoured charge transport components and the increased ratio between anodic and cathodic charge. These results highlight its promising application in molecular electronics as molecular interconnections transport energy to desired locations with minimum loss.

Furthermore, we applied a holistic physicochemical methodology to evidence a molecular level deposition of the polymer inside the silica nanochannels. Our approach revealed the necessity of using high-resolution X-ray photoelectron spectroscopy combined with a very low-energy argon ion beam sputtering for direct evidence of polymer wires inside silica channels combined with nanomaterial components visualization by atomic force microscopy and transmission electron microscopy.



Limiting processes in Anion Exchange Membrane Fuel Cells

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The anion exchange membrane fuel cell (AEMFC) is under rapid development. However, it is in many aspects still inferior to the more mature proton exchange membrane fuel cell (PEMFC). This presentation will focus on some of the limiting processes related to the oxygen reduction reaction, the hydrogen oxidation reaction, the ionomer and water transport in the AEMFC.

When experimental polarisation curves for electrodes with different platinum catalyst loadings and oxygen partial pressures are fitted to a physics-based porous electrode model, a good fit for the oxygen reduction reaction is obtained with a first order dependency on oxygen partial pressure, and a charge transfer coefficient of 0.8[1]. At higher current densities losses at the anode must also be accounted for. The experimental data from a symmetrical anion exchange membrane (AEM) hydrogen cell indicate a two-step reaction pathway of the hydrogen oxidation reaction and hydrogen evolution reaction[2]. The fit of a model shows that the Tafel-Volmer pathway describes the kinetics better than the Heyrovsky-Volmer pathway. The reaction rates of the adsorption and charge transfer steps are similar in magnitude implying that both need consideration during modelling and evaluation of the hydrogen electrode. Furthermore, the performance is limited also by the ionic conductivity in the electrode.

Sufficient water transport through the membrane is necessary for a well-performing AEMFC. When the water flux through a membrane electrode assembly (MEA) is quantified using humidity sensors, the flux during fuel cell operation shows that the transport rate of water in the membrane is strongly affected by an applied current[3]. The water content increases on both the anode and cathode side. These results implicate that flooding, on one or both electrodes, is a larger concern than dry-out in an AEMFC. There is also an increasing demand for high-performing polymers stable under alkaline conditions. A poly(p-terphenylene piperidinium)-based ionomer was synthesised and applied in membrane electrode assemblies (MEAs), with porous gas-diffusion electrodes based on Pt catalysts supported by VULCAN® and high surface area carbon, respectively4. Mass transport limitations at higher current densities were observed for high surface area carbon electrodes, leading to an overall higher performance with the use of VULCAN®. Properties of the ionomer related to water uptake capabilities were observed to inhibit performance. A higher water uptake of the ionomers appears to be a key property for increasing electrode performance.

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Electrochemical characterization of self-assembled monolayers on nanoporous copper

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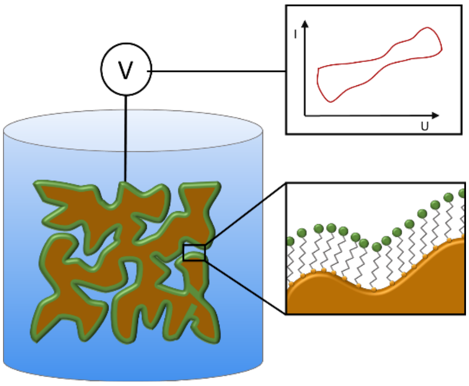
Offering a free-standing structure with a very high surface-to volume ratio, nanoporous metals prepared by selective etching, so-called "dealloying" [1], are highly interesting electrode materials for a broad variety of applications. Among them, nanoporous copper (npCu) has recently become a major research interest due to its mechanical and electrical properties as well as low cost and mild fabrication conditions. For tailored surface functionalization, copper surfaces can be modified with self-assembled monolayers, offering not only functional groups but also oxidation protection [2].

However, direct transfer of available literature knowledge for SAM formation and functionality on planar copper to the curved, defect-rich surface of npCu is impossible. Moreover, a precise analysis of surface modifications is challenging for nanoporous metal electrodes, as their inner surfaces are not directly accessible for many typical techniques, such as microscopy (SEM and TEM) or spectroscopy (XPS and Raman).

Here, we investigate the electrochemical performance and stability of self-assembled monolayers on nanoporous copper which is synthesized from a CuMn alloy [3]. 16-Mercaptohexadecanoic acid (MHDA), a long chain SAM with a carboxylic terminal group, is afterwards adsorbed on the porous carrier by immersion of the carrier in an organic solvent containing the respective molecules. Cyclic voltammograms are recorded in varying potential ranges, providing information on the electrochemical stability and change in active surface area. In the first cathodic scan, loosely bound molecules desorb from the npCu (similar to finding on nanoporous gold [4]). Afterwards, the SAMs are stable in the investigated potential regime and a shielding of npCu from further oxidation is observed. Furthermore, the influence of solvent type (ethanol and isopropanol) is investigated revealing that, incubation in ethanol result in a significantly enhanced adsorption.



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Advancements in photobioelectrodes based on photosystem I

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Learning from nature is a basic principle when constructing biohybrid devices. In photobiovoltaics the combination of photoactive biocomponents with electrode materials has become in the focus. Photosystem I is an a rather large, but very stable protein complex with a very high energy conversion efficiency. We have coupled it to several electrode structures. Here the focus is clearly on 3D approaches in order to maximize the interaction with light. This can be realized by the construction of multiple layers of PSI [1] or the application of 3D electrode materials [2,3]. Template based approaches are highly suited to such conditions, however, care has to be taken that sufficient light interaction can be ensured by increasing the electrode thickness. Transparent materials such as indium tin oxide (ITO) are particularly suited and have been used in our research.

It can be shown that the surface of such 3D electrodes can be fully used for electrochemical conversions and protein immobilisation when the pore size is properly adjusted. Scalability can be demonstrated with respect to the preparation by a simple spin coating procedure and also with respect to the performance of a photobioelectrode with immobilized photosystem I. The system can be further improved by application of precursors during the preparation since here transparency benefits from thinner wall structures. Thus, photocurrent densities up to 270 µA/cm2 can be obtained for an electrode prepared by 15 spin coating steps [5].

Communication of the large protein supercomplex with the electrode material is not trivial. Mostly we have used the small redox protein cytochrome c which can be stably immobilised within such 3D electrodes and which can work as a shuttle molecule despite its surface-fixed state. We have also exploited the use of small nanoparticles [4]. Alternatively, we have studied the direct electron transfer of PSI. Here we can show that solution composition is one key parameter for obtaining functional systems of reasonable current values. An attractive feature here is the start of the cathodic photocurrent already at rather high potential.

Furthermore, it can be shown that such approaches are also valuable for the coupling of enzyme reactions to the light directed current generation.

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Anomalously High Capacitance of the Metal /Water Interface: Revealed by Nano-Impact electrochemistry, Explained by Molecular Dynamics Simulations

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Understanding the electrical double-layer (EDL) structure is of high importance for the development of sustainable technologies, from catalysis to energy storage. Despite of many investigations on the EDL, no general model exists, yet, that describes all experimental findings, as the EDL structure and capacitance are ruled by several factors, such as electrode material and morphology, the presence of surface adsorbed species, and the interaction and orientation of water molecules at the interface. To improve our understanding of solid/liquid interfaces and extract new physico-chemical information on the capacitance and structure of the EDL at the molecular level we have employed nano-impact electrochemistry and rationalized our experimental findings by molecular dynamics simulations.

In the nano-impact technique, individual nanoparticles, dispersed in the electrolyte, randomly collide with an ultramicroelectrode.[1,2] During capacitive nano-impacts, the EDL of colliding nanoparticles is perturbed resulting in transient current-time events.[3] Analyzing these signals provides direct insights into the electronic properties of the impacting particles such as their EDL capacitance and their potential in solution.[3] Our nano-impact experiments of platinum and gold nanoparticles in aqueous solutions showed that the EDL capacitance is larger by about one order-of-magnitude than predictions by the traditional models of the EDL including the Gouy–Chapman–Stern model.

Employing solvent density fluctuations analysis from classical MD simulations, we investigated the possible relationship between the measured high capacitance and adsorption strength of the water adlayer formed at the metal surface. These investigations suggest that strong interactions between the metal surface and the water adlayer result in a lack of donor sites in the adlayer for hydrogen bonding with its adjacent water layer. This induces local hydrophobicity as surface-adsorbed water with respect to adjacent water layers, resulting in local density fluctuations,[4, 5] which leads to ion accumulation near the interface and, thus, to the large capacitance measured for platinum and gold surfaces. Based on these simulations, a weaker binding of the water adlayer to gold vs. platinum surfaces is predicted. Therefore, a lower capacitance for gold with respect to platinum is expected, which matches well with obtained results by nano-impact experiments and recent literature reports on single crystalline surfaces.[6]

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Simultaneous testing of positive and negative electrodes in carbon supercapacitors

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The testing of supercapacitors is routinely done by electrochemical methods in a two-electrode system. With such methods, the overall properties of supercapacitors are obtained. However, in order to make further improvements to supercapacitors properties, it is of key importance to separate the processes occurring at both electrodes during charging/discharging reactions. Such measurements would reveal electrodes of limiting capacitance, the potential distribution through the supercapacitor as well as the occurrence of various resistances within different parts of the cell.

In this presentation, we will address the results obtained on self-assembled supercapacitors in different electrolytes by inserting a Pt wire as a reference electrode inside the separator.

Electrical equivalent of Rayleigh-Taylor effect for engineering of composite anodic memristors

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Anodic oxides of valve metals (Al, Hf, Ta, Ti, Nb, Zr) have shown remarkable performances as memristive elements, in which the resistance state of a device can be switched between two or more levels by externally applied electrical fields. This generally impacts the conductive pathways (filaments) formation, which is mediated by oxygen vacancies and/or cations, and their field-activated movement inside the oxide. Studies on Hf- and Ta-based memristors reported excellent electrical and memory properties, such as multi-level switching, high endurance and data retention. These can be further tuned by carefully selecting the anodization electrolyte or other electrochemical parameters, e.g. allowing an in-situ doping with electrolyte species. Such process may play a crucial role in positioning and sizing of conductive filaments within the memristive oxide. Another possibility for spatial pinning of conductive filaments relies on controlled nanostructuring of the memristive film.

In this work, the Rayleigh-Taylor effect is exploited for nanostructure control in composite anodic oxides and its impact on the final memristive behavior is observed. Concomitant anodization of two superimposed metallic films (e.g. Hf/Ta) intrinsically leads to a columnar growth of one oxide within the other, if the metal in direct contact with the electrolyte produces an oxide more insulating as compared to the oxide produced by the underlaying metal. This results from the ionic current preferring the less resistive paths, enhancing the growth of the correspondent oxide. The obtained oxide fingers (e.g. Ta_2O_5 within HfO_2) and especially their interfaces are responsible for conductive filament easier formation and spatial pinning. Oxide resistivities and structures, transport numbers, Pilling-Bedworth ratios are all considered as determining factors for the anodization process of such superimposed systems. Predicting the position and shape/thickness of a conducting filament may eventually lead to enhanced device stability and resistive states control. The boundary between Hf and Ta oxides may influence the conductive pathways required for the memristive effect, thus being most relevant for fabrication of highly stable and forming-free memristors. Additionally, the use of superimposed films with gradient but complementary thicknesses allows investigating the ideal Hf/Ta ratios for which the best memristive behavior is obtained. One pronounced zone relevant for memristive applications is found for Hf/Ta thickness ratios between 4 and 5. Here, unipolar and bipolar memristors are identified, with remarkable endurance and retention capabilities.

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Monitoring the disintegration of the catalyst layer in the PEFC with Total Harmonic Distortions

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Catalyst layer disintegration is a prevalent degradation mechanism in fuel cells. It includes catalyst degradation as well as carbon corrosion and ionomer degradation. Especially during load cycling [1] and at start up and shut down [2], catalyst layer degradation increases significantly. In order to prevent substantial performance losses and assess the lifetime of fuel cells, a fast-online detection method is required.

A polymer electrolyte fuel cell with a 25 cm^2 electrode area was subjected to US DoE stress tests [3] in which either the catalyst, the carbon support or the ionomer was degraded, as well as slightly modified stress tests in which all three components were degraded. After certain numbers of cycles, comprehensive electrochemical characterisations were performed, and during the stress tests, the exhaust gas on the cathode side was analysed for degradation products like CO_2.
Firstly, the electrochemical active surface area was calculated from cyclic voltammetry measurements in order to quantify the degradation of the catalyst. Secondly, linear sweep measurements were performed to analyse the degradation of the membrane and ionomer content in the catalyst layer. Thirdly, polarization curves were measured to investigate the performance at certain stages of degradation. Fourthly, electrochemical impedance spectra were recorded at different operating points and with the help of a newly developed small signal equivalent circuit [4] the different losses inside the fuel cell and their trends during degradation were investigated. Lastly, total harmonic distortion (THD) spectra were recorded in order to identify a specific frequency range for each degradation mechanism (catalyst, carbon support, ionomer) where the THD peaks get bigger with continuing degradation. In addition, the located frequencies were correlated with the findings of the other electrochemical measurements. Exciting the cell with these frequencies can give information about the stage of degradation and can be used for lifetime estimation.

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Evaluation of Electrocatalyst Activity, Stability and Selectivity during dynamic operation – Online Coupling of Analytical Techniques to Electrochemical Flow Cells

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The investigation of novel catalyst materials for applications in fuel cells and electrolyzers, as well as the assessment of operation regimes, demands fast and highly informative characterization methods. Standard electrochemical approaches are often insufficient in information depth particularly when it comes to studying dynamic processes with high time resolution, so in-situ or online coupled analytics are necessary to enhance knowledge on catalytic materials. In this presentation I will demonstrate the portfolio of coupled analytical techniques that have been developed over the last decade in our team, and which help obtaining complementary data on particularly stability versus dissolution and selectivity towards gases and liquid chemical products. Starting out from an advanced high-throughput screening approach as the electrochemical platform, namely the Scanning Flow Cell (SFC), various coupled mass spectrometry tchniques with second time resolution provide novel insights into electrocatalytic processes. Hopefully these insights aid in the further technical developments of novel catalysts and improved reaction conditions for fuel cells and electrolyzers, which are so desperately required for the successful implementation of the Energiewende.

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Cast aluminium-silicon alloys for marine exposure

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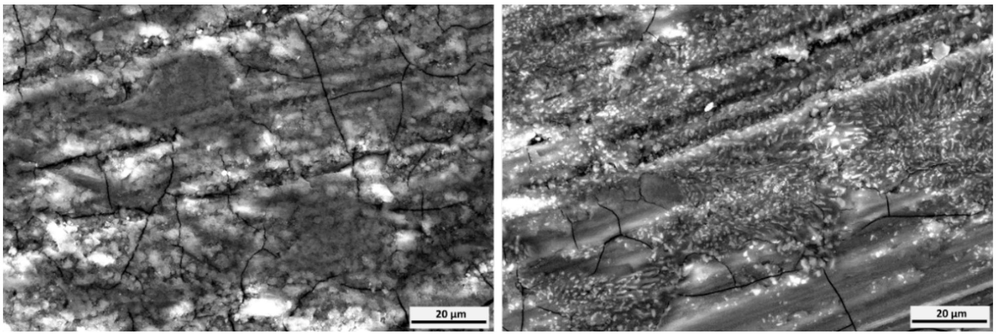
Due to their structural integrity, enhanced mechanical properties and other properties, wrought alloys account for around 63% of total sales of aluminium alloys. However, cast aluminium alloys have been growing mainly because of their excellent castability and high specific strength. Compared with wrought Al alloys, casting alloys have clear economical advantages due to their shorter processing cycle and assembly costs.[1] Therefore, market demands are high, and the need for aluminium alloys with suitable materials properties is increasing.

For Al-Si7-Mg0.3, we studied its corrosion behaviour in artificial seawater in the presence of sodium sulphide.[2] The surface-analytical analysis of metals exposed to artificial seawater and bacteria was explored in our previous studies on stainless steel.[3,4] In this study, we focus on two cast alloys: EN AC 42100 (Al-Si7-Mg0.3) and EN AC 46000 (Al-Si9-Cu3(Fe)). We investigated the microstructure, composition, and electrochemical corrosion characteristics of bare Al-Si9-Cu3 and Al-Si7-Mg0.3 alloys before and after immersion in seawater. The samples were characterized by surface composition, surface layer thickness and microstructure (using FE-SEM/EDXS, XPS and GDOES), and electrochemical and protection properties. Both alloys are suitable for use in seawater, with magnesium-containing alloys showing superior corrosion resistance.



SEM images of Al-Si9-Cu3 (left) and Al-Si7-Mg0.3 (right) samples after immersion for 8 months in the Adriatic sea.

Acknowledgement

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Recovery of the metals from Group IB of the Periodic Table by Microbial Electrochemical Snorkel

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Microbial electrochemical snorkel (MES) was introduced ten years ago [1] as a novel bioelectrochemical approach for accelerating COD removal from wastewaters. Recently, we provided for the first time the Proof-of-concept for metal (copper) recovery by MES [2]. Later on, we demonstrated the applicability of MES technology for silver [3] and gold recovery [4]. In this report, we summarize the data collected for the recovery of the three metals from Group IB of the Periodic Table obtained by MES. The experiments were performed in dual-chamber bioelectrochemical reactors using bioanodes from well-acclimated Sediment microbial fuel cells (S-MFC). The metals were recovered on the cathodes of various types placed in a compartment separated from the anodes by PEM. While the removal efficiency is approaching 100% for all metals studied, the recovery efficiency increases with the increasing of the atomic number (Table 1). When the used catholyte consisted of Ag- or Au-dithiosulfate complexes, simulating industrial effluents, the cathodic efficiency was higher than that achieved with the respective free metallic ions. All results obtained by MES are compared with those achieved at operation in MFC mode and discussed.

Table 1. Metal removal, recovery, and cathodic efficiency achieved with MES by using different catholytes.

Metal recovered	***COPPER***	***SILVER***		***GOLD***	
Catholyte content	$CuSO_4$	$AgNO_3$	$Na_3[Ag(S_2O_3)_2]$	$HAuCl_4$	$Na_3[Au(S_2O_3)_2]$
Removal efficiency, %	*97.8±4.5*	*97.8±2.4*	*88.2±5.8*	*95.2±1.8*	*94.0±5.6*
Recovery efficiency, %	*42.4±4.9*	*78.9±2.7*	*55.8±3.8*	*94.5±1.7*	*79.2±3.8*
Cathodic efficiency, %	*44.7±5.6*	*79.6±3.4*	*127±15*	99.5±1.7	*109±17*

Acknowledgment

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Direct Electron Transfer from Indium Tin Oxide to Photosystem I in Mediator-free Photobiocathodes

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Humanity tries to mimic the natural photosynthesis for the conversion of light into an electrical current in biohybrid systems called photobioelectrodes. These semi-artificial systems are based on biocomponents that also play a role in photosynthesis, e.g., photosystem I or II (PSI or PSII).1–6 Advances in materials chemistry have led to a large variety of synthetic electrode materials.1–3 Of special interest are conductive materials that are transparent in the visible region as it enables the fabrication of 3D setups. These architectures offer higher current densities per geometrical area since they provide a larger interface for the interaction between artificial and biological component.2,3 For efficient communication between both partners normally a redox molecule is applied to shuttle the electrons. Yet, a less complex system is obtained for mediator-free photobioelectrodes. Due to its simplicity this direct electron transfer (DET) enables many options such as enzyme-coupling. However, it has been seldom used as the photocurrents have been found to be small.3–5

For the present study photobiocathodes based on the well-established electrode material indium tin oxide (ITO) were prepared.2,5,6 Thereto, a mixture of ITO nanoparticles and latex beads were spin-coated to build up a 3D structure as reported previously.5 Photobioelectrodes were prepared by drop-casting of PSI solutions. Then, for the first time, systematic examinations were conducted on different factors regarding their influence on the DET from ITO to PSI. The photocurrent output was selected as measure for the quality of the interaction. It could be shown that the incubation method in general plays only a minor role for the performance. However, the solution composition during the measurement strongly influences the photocurrent output. By increasing the buffer concentration from 5 to 100 mM the photocurrent doubles from 1.4 to 3.3 µA/cm² for a 10 µm thick electrode at an applied overpotential of -100 mV vs. Ag/AgCl under illumination with white light at 100 mW/cm². The pH application window for this photobioelectrode spans from pH 5 to 8 with its maximum at pH 6, which coincides with the natural pH within the lumen of the thylakoids. The addition of salts to the measurement buffer is favorable. Interestingly, the best results were obtained for the monovalent KCl, when the photocurrent is almost doubled to 6.3 µA/cm² under the same measurement conditions. The spin-coating process allows for the preparation of thicker electrodes. Yet, the performance does not scale linearly as the transparency of the structure is limited. Thus, up to 10.1 µA/cm² have been achieved for these photobiocathodes based on DET.

The properties of the biohybrid system enable the coupling to enzymes. While the mediator cytochrome c requires low ionic strength for good functionality, here, high buffer concentrations can be used. This is practical for the enzymatic conversion of some educts. The pH as well as the presence of detergents and various salts can be adapted to the demands of the enzyme. The stability of the system is noteworthy. Hence, it enables measurement times that are sufficiently long to obtain enough product for its detection.

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H_2S from environmental pollutant to new form of energy

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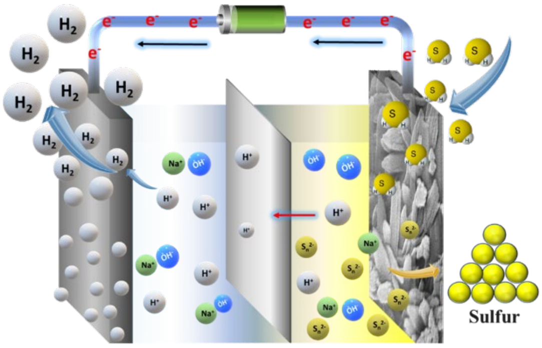
Highly efficient and cost-effective hydrogen production (H_2) promises to play a vital role in green energy production due to its high energy density, low-pollution, and renewable nature. The electrocatalytic decomposition of H_2O to H_2 and O_2 considered to be the most sustainable method for pure H_2 production, unfortunately, it stumbles due to potentially uphill and energy-consuming sluggish anodic oxygen evolution reaction (OER).[1] Contrary to H_2O isostructural hydrogen sulfide (H_2S) possesses lower bond dissociation energy. Therefore, anodic sulfide oxidation reaction (SOR) will be more energy-efficient than OER. Presently, the Claus process is the most popular industrial technology for removing H_2S, but energy wasted in the form of steam. Therefore, electrochemical conversion of environment pollutant H_2S into H_2 and S provide a way to remove pollutant H_2S and also emerges as new energy source.[2] However, the industrialization of such energy-efficient technology never meets the expectation in reality in the absence of cost-effective and robust electrocatalyst. Herein we have designed $CoFeS_2$ based catalyst that exhibited lower onset potential of 0.23 V *vs.* RHE towards SOR, which is 1.25 V lower than OER (Scheme 1).[3] Notably, only a 1.2 V commercial battery easily derives H_2S electrolysis, which is impossible for H_2O splitting demonstrating the tremendous future prospective of H_2S for cheaper hydrogen production for a sustainable economy.



Scheme 1. Schematic representation of H_2S electrolysis into cathodic H_2 and anodic S by $CoFeS_2$.

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Electronic structure manipulation of atomic copper quantum clusters for the CO activation with IIIA group elements

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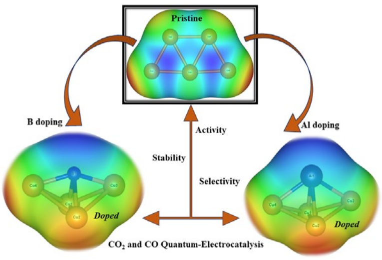
EU climate action and the European Green Deal[1] signifies the gravity of environmental measures to be taken to reduce the greenhouse gas emissions, to have cutting-edge research and innovation to become the first climate-neutral continent. CO$_2$, a greenhouse gas, has attracted significant attention from researchers to circumvent global warming as well as to have chemical feed-stock (value-added liquid oxygenates and hydrocarbons).[2] (Photo)Electrochemical technologies offer promising solutions if powered with renewable electricity. Copper, the noblest among 3d transition metals and the only mono-metallic electrocatalyst which has a unique ability for C-C coupling, severely endure from surface passivation, restructuration and other degradation mechanisms during long-term electrolysis.[3] Nonetheless, there exists plethora of very fine research reports addressing the issues on structure-activity-selectivity. However, only recently countable research is gradually making headway with the associated surface-sensitivity of copper-based electrocatalysts (CBE) towards structure-activity-selectivity-stability aspects.[4-7] In addition, reports regarding the identification of real-active sites during CO$_2$ reduction reaction conditions are still very few.



Herein, we evaluate the electronic structure manipulation (by doping) of copper with IIIA group elements viz, boron, aluminum and gallium to improve the selectivity-stability of copper towards better CO$_2$/CO electrocatalysis. The study begins with dispersion-corrected, spin-polarized density functional theory-based calculations on boron-aluminum-gallium-doped copper nanoclusters. Precisely, pristine and doped (one B/Al/Ga atom per cluster) of size range from three to six atoms have been considered (Cu$_3$ to Cu$_6$ to study in detail with G16 suite of program. Later on, the study will be extended to the bigger clusters of specific shape and size, and eventually at the surface and sub-surface level in the periodic copper lattices. To describe and corroborate our findings we have used conceptual DFT based reactivity descriptors such as Fukui functions, chemical hardness and potential, global electrophilicity index, electronegativity, spin density distribution, electrostatic potential mapping, change in enthalpy of adsorption and free energy along with binding energies and relative energies wherever necessary. The activation of CO is further confirmed by IR stretching frequency, bond length, and extent of charge transfer. Moreover, to better understand the proton coupled electron transfer (PCET) at the electrochemical interface we have also considered few reactive intermediates (RIs) such as *COOH, *H, *COH, and *CHO. All these RIs are selected to better understand the interfacial phenomena where product selectivity, HER suppression, and bifurcation pathways for liquid oxygenates and hydrocarbons. In summary, IIIA group elements-doped copper nanoclusters are better in activating CO$_2$/CO, and in stabilizing RIs compared to pristine nanoclusters. Thus, we can design better electrocatalysts by fine-tuning the electronic structure of copper for efficient, selective and stable electrocatalysis in near future.

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Electrocatalysis at lithium batteries waste powders

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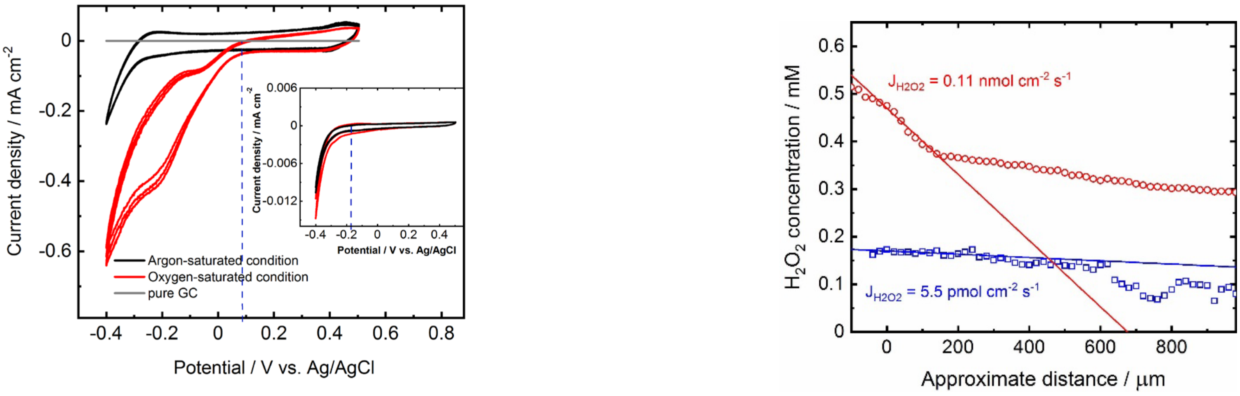
Lithium-ion battery (LiB) waste powder is a valuable source of various materials including carbon and metals. It is obtained as a by-product of the processing of electrodes of lithium batteries to recover lithium and transition metals [1-3]. Its composition and morphology depends on the way of processing. As this material exhibits electric conductivity, nanostructured morphology, and may contain metal oxides, it can be applied as an electrocatalyst. Recently, we have demonstrated that such a sample, when deposited on the electrode surface or assembled at the liquid|liquid interface it exhibits electrocatalytic properties towards oxygen reduction reaction (ORR) and in both configurations 2 electron stoichiometry was confirmed [4]. Therefore it can be considered as potential catalyst towards H_2O_2 generation [5-7].



(Left) Cyclic voltammograms recorded at GC modified with LiB waste powder, 5 mV s^{-1}. (Right) H_2O_2 concentration gradient at unmodified (blue) and modified (red) trifluorotoluene|0.1 M $HClO_4$ aqueous interface. From Ref. [4].

Here, we would like to present results of more systematic studies of electrocatalytic properties of this material in ORR and hydrogen evolution reaction (HER). The studies were performed with a sample deposited on the electrode surface or assembled at liquid|liquid interface with cyclic voltammetry, rotating disc electrode voltammetry, scanning electrochemical microscopy and UV-vis spectroscopy. For example, the effect of material processing and therefore its structure and composition determined by scanning electron microscopy and surface spectroscopies on ORR stoichiometry (2 vs. 4 electrons) will be demonstrated.

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Electrodeposited NiSn at Ni foams as electrodes for hydrogen production

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Nickel based materials are often used as non-noble, low cost, abundant and quite stable alternative to noble metals for hydrogen evolution reaction (HER) in alkaline media. Increasing the activity of Nickel towards HER is done by two approaches [1]– using porous materials with large electrochemically active surface area (EASA), or by coating Nickel with more active alloys, in this case NiSn, a good HER catalyst [2].

In this reasearch Ni foams with different pore sizes (450 to 1200 µm pore diameters) were used as HER electrodes. In addition, they were coated with NiSn by electrodeposition using controlled potential coulometry, and tested for HER in 1 M KOH at 25°C. The electrodes were characterized electrochemically and by scanning electron microscopy (SEM) coupled with energy dispersive X-ray spectroscopy (EDS). Ni foams have demonstrated higher HER activity then Ni mesh 40 (30 mV lower η at 100 mA cm^{-2}) due to higher surface area. As for the coated samples, the foams were completely covered by NiSn, with homogenous coating composition of roughly 70 % Ni and 30 % Sn, and significantly improved HER activity (Fig 1.) compared to bare Ni foams (up to 300 mV lower η at 100 mA cm^{-2}), showing that NiSn@Ni foam electrodes could be tested as industrial scale electrodes for HER.

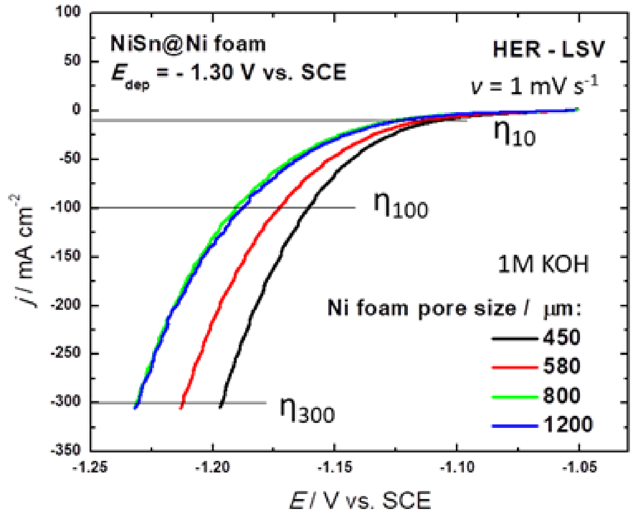

Fig. 1. HER polarization curves at NiSn@Ni foam

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Analysis of quasi-reversible CVs and dEIS data: transformation to potential-program independent forms

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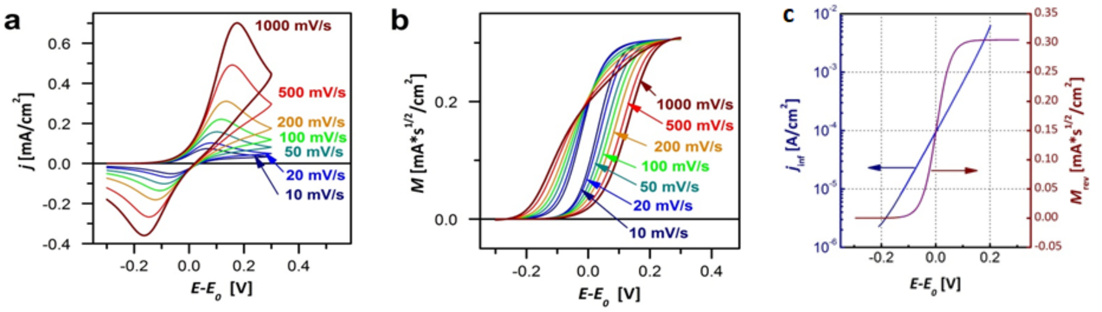
Recently a numerical procedure has been suggested by which the $j(E)$ cyclic voltammograms, CVs, pertinent to partially diffusion controlled charge transfer reactions can be analyzed [1]. Using this procedure, from a set of "quasi-reversible" CVs taken at varied scan-rates v, two scan-rate independent, hysteresis-free functions can be calculated. One of them is the diffusion-free polarization curve, $j_{\mathrm{inf}}(E)$, the other is the semiintegrated form of the reversible CV, $M_{\mathrm{rev}}(E)$.

As this has been discussed in Ref.2, the resulting $j(E) = j_{\mathrm{inf}}(E) - [j_{\mathrm{inf}}(E) / M_{\mathrm{rev}}(E)] \times M(E)$ equation is a general and exact solution to the problem of charge transfer coupled with semiinfinite diffusion. Various cases have been illustrated by numerical simulations; one is shown below.



Simulated CVs (a), their semiintegrals (b), and the calculated j_{inf} and M_{rev} functions (c). Simulation parameters: D_{red}= D_{ox} =10^{-5} cm^2/s, c_{red} =10^{-6} mol/cm^3, c_{ox}=0 mol/cm^3, E_0=0, k_0=0.001 cm/s, α=0.5.

Separating the contributions of charge transfer and diffusion to electrode kinetics can be done also by measuring and analyzing electrochemical impedance spectra (EIS). Parameters characterizing charge transfer and diffusion are R_{ct}, the charge transfer resistance and σ_{W}, the Warburg coefficient. These can be calculated from impedance spectra measured under *dc* conditions and also from spectra recorded during potential scans. This latter method, the combination of (sufficiently low scan-rate) CV and (sufficiently high frequency) EIS is called dynamic EIS (dEIS).

Both R_{ct} and σ_{W}, obtained from dEIS, depend on the scan-rate. However, the scan-rate dependence can be eliminated using the linear equations derived in [3]. As a result, we have the following set of equations connecting the measured j, M, R_{ct} and σ_{W}; the coupling parameter H (= $k_{\mathrm{ox}}/\sqrt{D_{\mathrm{red}}} + k_{\mathrm{red}}/\sqrt{D_{\mathrm{ox}}}$) is composed of rate and diffusion coefficients only. Note the simplicity and symmetry of the equations.

	charge transfer	**coupling**	**diffusion**
CV	$j = j_{\mathrm{inf}} - H \cdot M$	$H = j_{\mathrm{inf}}/M_{\mathrm{rev}}$	$M = M_{\mathrm{rev}} - 1/H \cdot j$
DEIS	$\frac{1}{R_{\mathrm{ct}}} = \frac{\mathrm{d}j_{\mathrm{inf}}}{\mathrm{d}E} - \frac{\mathrm{d}H}{\mathrm{d}E} \cdot M$	$H = \sigma_{\mathrm{W}}/R_{\mathrm{ct}}$	$\frac{1}{\sigma_{\mathrm{W}}} = \frac{\mathrm{d}M_{\mathrm{rev}}}{\mathrm{d}E} + \frac{1}{H^2}\frac{\mathrm{d}H}{\mathrm{d}E} \cdot j$

The theory opens a new route for the high-accuracy, fast determination of charge transfer rate coefficients of quasi-reversible redox systems by employing dEIS.

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Photoelectrochemical degradation of amoxicillin using $BiVO_4$ as photoactive material

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The widespread use of antibiotics, pesticides, and other organic pharmaceuticals results in their accumulation in the aquatic environment as they are regularly detected in surface and wastewaters. Environmental policies regarding the quality of discharged wastewater are tightening; demanding new solutions for water treatment in all water-intensive industries as well as municipal wastewater. Among the antibiotics, amoxicillin is one of the frequently used ones. Since its impact on human health and the environment is uncertain it is considered an emerging contaminant. Wastewater treatment plants do not remove amoxicillin efficiently, which contributes to its presence in drinking water and water bodies. To decompose organic contaminants in an aquatic system, photoelectrochemical processes might be employed. In this work, photoelectrochemical (PEC) degradation of amoxicillin was investigated using $BiVO_4$ as a solar light-activated material. The photoactive material was deposited onto FTO glass electrodes and characterized using various electrochemical methods including linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Moreover, the effect of combining $BiVO_4$ and reduced graphene oxide (rGO) in PEC degradation of amoxicillin was studied.

Versatile biosensing with electrically actuated DNA adaptors on a chip

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Biosensors have become indispensable tools for the diagnostics of biomarkers, in drug discovery, and in fundamental research of molecular interactions. Electrochemical and optical methods were successfully established over the last decades to detect analytes, quantify their concentrations, and to analyse affinities and binding rate constants.

Future challenges pertain to the analysis of complex molecular interactions, such as multi-specific binding between three or more interactants, the real-time analysis of enzymatic activity, or binding induced conformational changes in proteins.

I will describe a novel electro-optical sensing modality that can be adapted easily to investigate multifaceted interactions, and previously unattainable biophysical data concerning the binding and structural properties of molecules of interest. The switchSENSE principle utilizes fluorescently labelled DNA nanolevers tethered to gold microelectrodes, which are manipulated by electric fields. The nanolevers can be actuated at high frequencies to infer the size or conformation of bound proteins, and the association and dissociation of interaction partners can be analysed in real-time by fluorescence detection. Applications that are relevant to current challenges in drug discovery will be discussed, including RNA/DNA binding proteins, multi-specific antibodies, and ternary complexes between small molecules and proteins.

The mechanism of lithium dendrite formation and propagation under pulsed charging conditions in solid state lithium batteries

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To this date lithium dendrites remain one of the key challenges in solid-state Li-batteries (SSLB).[1,2] The formation and growth of these dendrites cause an inevitable failure at charge rates far below the threshold set by industry (>3mA/cm^2) and are believed to be driven by stress accumulation stemming from the deposited lithium itself. Upon reaching a critical pressure, the solid-state electrolyte (SSE) starts to crack, which propagates until the cell short-circuits.[3] Herein, we propose that this fracturing is not of mechanical origin but can rather be related to an increased Li activity in the SSE near the protrusion, caused by the diffusion-controlled Li deposition. This destabilizes the local structure of the SSE and weakens it within a certain time frame. If current is applied for shorter durations than is required for the Li activity to reach critical values, as is with high frequency pulses, the structural destabilization of the SSE can be delayed, and higher critical current densities (CCD) can be reached. Applying 1 MHz current pulses, a sixfold increase of the CCD, compared to DC operation and a maximum value of around 6.3 mA/cm² was reached in this work. Since an adaption of the applied current waveform can be combined with other reported measures like interlayers, alloys or structured interfaces, the fast-charging goal set for electric vehicles, appears to become feasible.[4,5,6] Hence, the application of pulsed currents represents a crucial step toward realization of SSLBs for electric vehicles and other emerging applications.

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Corrosion protection of AA2024-T3 using siloxane-silica sol-gel coating modified with various fluorinated (meth)acrylates

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Aluminium alloy (AA) 2024-T3 is commonly used in aviation due to its lightweight, high mechanical strength, and low cost. The limitation of this alloy is susceptibility to corrosion in chloride-containing solutions due to alloying elements such as Cu, Fe, Mn, etc. To enhance the corrosion protection of this alloy, chromium (VI) compounds have been used. These compounds have been strictly regulated in various countries due to their harmful effects on humans and the environment. Among possible environmentally acceptable surface treatments, the siloxane-silica sol-gel coating is considered an alternative.

In this study, the corrosion performance was studied for the coated AA2024-T3. The synthesis of the siloxane-silica sol-gel was performed using methyl methacrylate (MMA), 3-(trimethoxysilyl)propyl methacrylate (MAPTMS), and tetraethyl orthosilicate (TEOS), [1,2] and the addition of various fluorinated (meth)acrylates with different chain length, Figure 1.

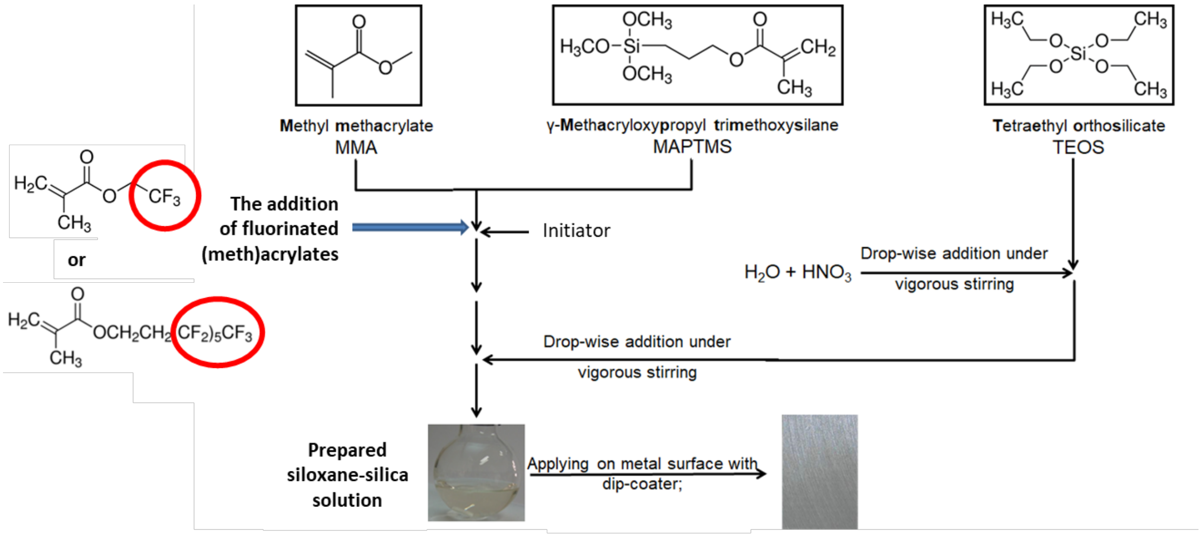

Figure 1: Flow chart of the siloxane-silica sol-gel preparation.

The reactions during preparation were characterized using real-time Fourier transform infrared spectroscopy. Once deposited on AA2024-T3 samples, the coatings were evaluated using a field emission scanning electron microscope coupled to an energy dispersive spectrometer (FIB-SEM/EDS) to determine surface morphology, topography, composition, and coating thickness. The corrosion characterization was performed in 0.1 M NaCl using electrochemical impedance spectra (EIS) and salt spray test according to the ASTM B117-07A standard.

The results revealed the importance of the addition of fluorinated (meth)acrylates to obtain a few micrometres thin coating that evenly covers the alloy surface. Such coatings present durable barrier corrosion protection (EIS values remain unchanged for one year).

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Robust fuel cells and electrolysers for lunar energy systems

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The space proven fuel cell and electrolyser technology will likely play a crucial role in the infrastructure of a remote lunar outpost. Excess energy can be stored by splitting water, which is potentially derived from In-Situ Resource Utilization (ISRU) processes, while formed hydrogen and oxygen can be turned back to electricity on demand. However, this technology needs to be optimized to cope with the harmful constituents found in ISRU derived water. According to a publication by Colaprete et. al [1], large amounts of sulfides and ammonia, as well as smaller quantities of hydrocarbons were spectroscopically detected alongside water in an ejecta plume of a permanently shadowed crater. These compounds are well known impurities causing reversible but also irreversible damage to the platinum catalyst and other components of the membrane electrode assembly [2]. Commercially available proton exchange membrane (PEM) fuel cells, on the other hand, require highly purified fuels with acceptable contamination levels of only a few ppb. To avoid damages caused by these impurities, energy intense multi-step purification processes are required before water and the fuel gases are in a useable condition – a process that might be too costly in the extreme environment of a lunar outpost. Hence, this work aims to study and improve electrolyser and fuel cell resilience against ISRU derived impurities. This will be attempted by incorporating catalysts with a protective polyaniline coating into a nanofiber electrode layer that is fabricated with electrospinning, a method which has recently been employed to produce high performance and durable electrodes. Optimized fuel cells will be compared to conventional fuel cells under accelerated stress tests with conventional but also heavy lunar conditions, where the feed gases are contaminated with said impurities. The outcome of this study aims to support the exploration community in developing robust energy systems on the moon by investigating ISRU process output interactions with PEM fuel cell and electrolyser technology.

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Influence of ascorbic acid on photoelectrochemical hydrogen evolution

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Hydrogen (H_2) evolution, through solar water splitting, triggered wide interest after the publication of Fujishima and Honda in 1972 about photoelectrochemical water splitting on a titanium dioxide electrode. In general, photoelectrochemical water splitting implies a process where photons are used to break water molecules. The process is assisted by a photocatalyst which generates photoexcited charge carriers, electron and hole pairs (e^-/h^+), which are then transferred to the solid-liquid interface where redox reaction takes place. In order to make this process sustainable, it is important to develop photoactive materials that harvest visible-light irradiation. SnS_2 is an attractive material for this purpose due to a small band gap, as well as the position of the conduction band that is more negative than the standard reduction potential of H_2O/H_2 [1].
Because of the high recombination rates of photogenerated holes and electrons the efficiency of the photocatalytic process is low. The efficiency can be increased by voltage application or by the usage of a sacrificial agent such as ethanol, methanol and ethylene glycol [2]. For a sacrificial agent to be successful and supress electron-hole pair recombination, its oxidation potential must be lower than that of water. Denisov et al. [2] found that organic sacrificial agents on TiO_2 nanotubes enhance photocurrent conversion efficiency up to three times and lead to 10 to 28.8 times higher H_2 production.
The aim of this work was to investigate the possibility of photoelectrochemical hydrogen production by using SnS_2 photocatalyst and ascorbic acid as the sacrificial agent. The low oxidation potential and easy availability make this sacrificial agent a promising candidate for increasing the efficiency of hydrogen production. In this work photoelectrochemical process was carried out in a three-electrode system using visible-light irradiation. The influence of pH, ascorbic acid concentration, and potential on the efficiency of H_2 production was investigated.

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New anode flow field design for alkaline direct ethanol fuel cells

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The use of ethanol, a fuel sustainably produced from biomass with high energy density for power generation in alkaline direct ethanol fuel cells (ADEFCs) was investigated. This technology offers several advantages, such as the ease of transport and storage of the liquid fuel ethanol and the alkaline environment that enhances electrode reactions, leading to a reduction in ethanol crossover and allowing the use of cost-effective anion exchange membranes. Although many studies have been performed on ADEFCs, there are still barriers to overcome, such as the optimal supply and distribution of the liquid reactant over the entire active electrode surface.

In this study, a new flow field design is developed and the effect on the performance in a new in-house fabricated ADEFC (Figure 1) is investigated. Hence, membrane electrode assemblies (MEAs), consisting of a self-prepared PdNiBi/C[1], a commercial PtRu/C catalyst and a commercial fumasep® FAA-3-50 membrane, are fabricated with an ultrasonic spray coater. The single cell tests were performed with 1 M KOH and 1 M EtOH solution as anode fuel and dry or humidified oxygen as cathode fed gas at different operating temperatures. This new developed flow field showed an increase in the maximum power density in comparison with the previously used one[2,3].

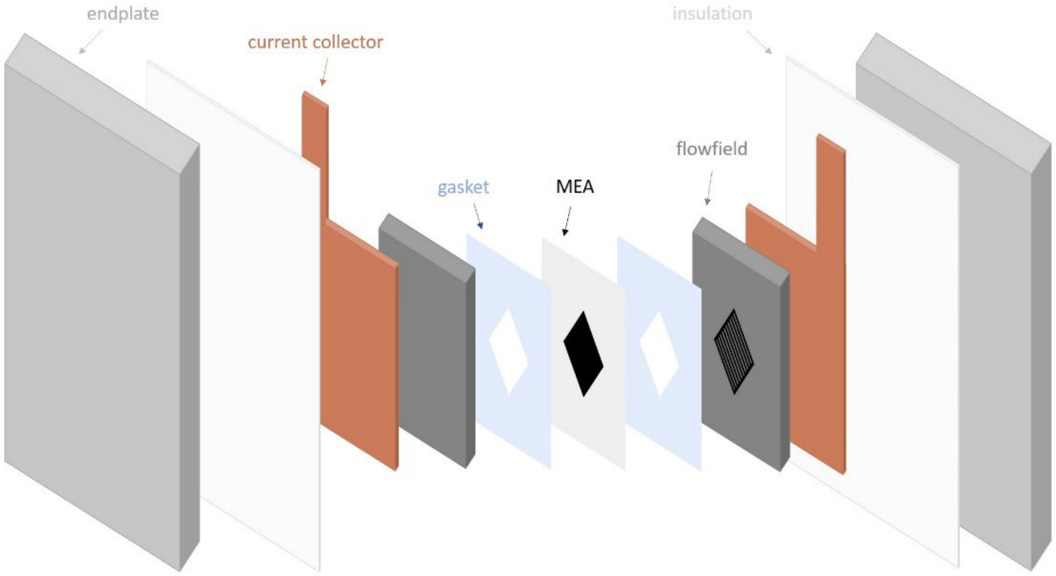

Figure 1: Simplified exploded view of the utilized in-house fabricated ADEFC.

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SAN-PMMA Blend as Polymer Gel Electrolyte for Dye Sensitized Solar Cells

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Electrolyte is considered as one of the crucial components in the performance of dye sensitized solar cells (DSSCs). This work reports blending of poly(styrene-co-acrylonitrile) (SAN) with poly(methylmethacrylate) (PMMA) to be used as gelator. The composition of the constituent polymers was varied while incorporating the fixed amount of triiodide/iodide (I_3^-/I^-) as redox couple and the resultant polymer gel electrolyte (PGE) was analyzed alone as well as in the DSSC device. The absorption edge for the PGE lies close to 400 to 410nm having high transparency of more than 80% in the visible and NIR region. The maximum ionic conductivity (8.90 mS/cm) of the PGE was recorded for the 50% SAN in SAN/PMMA (1:1) blend with the triiodide diffusion coefficient of 7.74×10^{-5} cm^2s^{-1} indicating highly favorable environment for the mobility of the charge carriers. The electrochemical impedance analysis evidently validated the performance of the blend, with optimal composition, indicating the decreased charge transfer resistance and increased recombination resistance which accelerated the charge transportation across the electrolyte/dye/semiconductor interface(s). Exceptionally large electron lifetime values were recorded having values 0.06 to 0.16s. Similarly, very good charge collection efficiencies, 33 to 66% were recorded for different compositions showing a fair conduction to the external circuit. The photoconversion efficiencies of the resultant devices (Fig.1 below) were recorded between 5.48 to 6.66% with good reproducibility. The incident photon to current efficiency (IPCE) was found to be 48% for the SAN/PMMA blend.

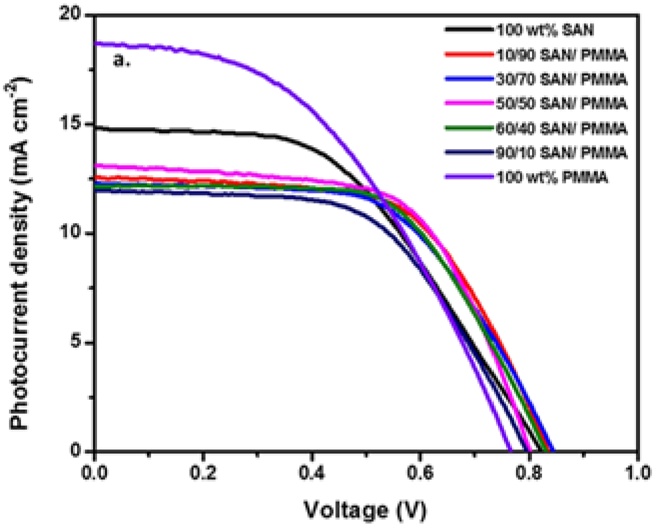

Fig.1. J-V curve of the DSSC device employing various compositions of SAN/PMMA polymeric gel electrolyte.

Development of Sensor Nodes and Sensors for Smart Farming

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The United Nations expects to reach 8 billion humans on earth within the next three years. In order to provide food for the growing world population, while reducing the use of fertilizers and biocides, smart farming is one of the emerging megatrends. The foundation of this development are sensors and the data of these sensors.

But how do we get from stimulus to electrical signal, from electrical signal to digital value and from digital value to the measurement data? What is needed to turn a sensor to a sensor node?

A sensor can be described as following: “A sensor is a device that receives a stimulus and responds with an electrical signal.” [1] Where a sensor node is a system, consisting of a microcontroller, a power source, a communication interface and a sensor.

The source of an electrical signal is a sensor. Through suitable pre-processing of a signal, e.g. by filtering and amplification, it is conditioned for analog to digital conversion. Continuous advancements in the analog to digital conversion (ADC) technology open new opportunities, whether it is a higher sampling rate for more precise timing, higher impedance for better potential measurements, or lower noise for detection of the tiniest sensor signals. Additionally with further optimization and miniaturization, semiconductor chips are getting more energy efficient, too.

After an analog to digital conversion, a digital signal is available and ready to be processed by a microcontroller. A microcontroller is the brain of a sensor node. It is responsible for the storage, calculation, communication and is even capable to use artificial intelligence. There are various choices of microcontroller, which can be selected depending of the requirement and the complexity of a sensor system. A suitable choice has enough computational power, input output interfaces and storage capabilities for sensor data and firmware, but also considers that additional features go along with higher cost and more energy consumption, which is often limited in portable devices.

The available energy budget can be provided from a variety of sources, from coin cells to lithium ion batteries to solar power, energy harvesting and biodegradable batteries. Different batteries have different key properties, like energy density, internal resistance, self-discharge, voltage level and rechargeability. For example, coin cells provide a low self-discharge, high energy, but are usually not rechargeable. Still, these properties make them a good fit for low power nodes, with runtimes of up to several years. In contrast, for high power sensors and extensive microcontroller computations often more power is required. For this application rechargeable lithium ion batteries are widely used. A recent battery trend is the usage of biodegradable materials. This opens up the opportunity for a step towards mostly biodegradable sensor nodes.

Another key consumer of the available energy budget is communication. Energy consumption correlates with bandwidth and covered distance. Optimized communication protocols allow a coverage of up to 40 km.

Various low-power wide-area networks are available, like narrow band internet of things (NB-IoT), LoRaWAN or Sigfox. They differ in the quality of service, energy consumption, latency, scalability, payload length and deployment model. There is no perfect fit for all use cases. E.g. temperature and humidity change slowly, therefore a higher latency in measurement and communication is acceptable.

A novel smart farming sensor node is developed by a suitable combination of new sensors, with higher sensitivity, selectivity and miniaturization, appropriate analog to digital conversion, digital processing, with reduced power consumption, and IoT technology, with wide coverage to monitor large farms and fields.

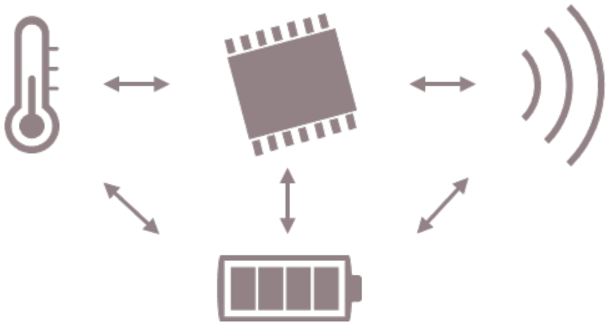

Figure 3 Sensor Node with components: microcontroller, power source, communication interface and sensor.

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Nanostructured polymers for chemosensing of proteins and biomolecules

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Molecularly imprinted polymers (MIPs) represent an excellent example of synthetic systems that mimic the recognition encountered in nature. MIPs are synthetic materials prepared by co-polymerization, in a porogenic solvent, with functional and cross-linking monomers in the presence of a template. This template can be similar to the target substance or be the target itself- the analyte - that the polymer should subsequently selectively recognize. This templating induces three-dimensional binding sites in the polymer that are complementary to the template in size, shape, and chemical functionality. This synthetic antibody-mimicking polymer can recognize and bind its target with an affinity and selectivity similar to a natural antibody.

Preparation of imprinted polymer in the form of nanoparticles has received a great deal of consideration because of their excellent binding efficiency compared to a polymer synthesized in the form of film or bulk. Several research efforts have been made to prepare polymer with a high surface area to achieve binding efficiency in the current research. Additionally, we intended to synthesize electrochemically active nanoparticles. The electrochemically active polymer prepared that way could transduce any recognition event efficiently.

To prepare nanostructured polymer film, we adopted inverse opal structure, developed via silica molding, together with surface imprinting technique for preparation of a hierarchical structure that provides control in the synthetic receptor structure at three-size scale levels for selectively determining protein. This control ensures deposition of a synthetic receptor in the form of poly(2,3'-bithiophene) based inverse opal crystal with pores of five hundred nanometers in diameter, with a few nanometer-size molecularly imprinted cavities located directly on the inner surface of the polymer pores, and, on the molecular level, with recognition sites located complementarily to binding sites of molecules of the target protein analyte. With such a highly developed surface area, the recognition layer strongly affected the sensitivity of the final chemosensor.

In another such example, imprinted nanoparticles were synthesized. Adopted approaches helped us to synthesize uniform size polymeric nanoparticles below 100 nm size. Purified MIP or NIP nanoparticles were, after template removal, immobilized via suitable techniques on the carbon electrodes for fabrication of chemosensors. The binding of analytes to the MIP structures was manifested by the turn on/off signal from a DPV peak current. Importantly, changes observed on the NIP nanoparticles modified electrode were much lower. In the presence of interferents, the MIP nanoparticle-based chemosensor response was minimal, confirming the high selectivity of the chemosensor.

Acknowledgements

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Study of DNA hybridization using a novel thermal biosensing platform as a proof-of-concept

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In this study, a single sensing element as a thermal biosensing platform can detect analytes based on a change on thermal interface conductance. The core of this sensor is a 30 µm aluminium micro-wire serves as an immobilization platform for receptors, a heat source, and a temperature sensor together. For this proof-of-concept, we studied the heat-transfer efficiency between the wire and the surrounding medium (PBS buffer and air) for four different coatings including the native oxide layer, a self-assembled silane monolayer, single stranded DNA linked covalently to the silanes, and complementary duplexes of oligonucleotides [1]. As a readout method, the highly sensitive 3ω principle has been used. In this method the voltage at the third harmonic of the triggering frequency ($U_{3\omega}$) is a direct measure for the thermal interface resistance between the wire and the ambient [2]. Interestingly, $U_{3\omega}$ alters systematically with the coating type and the effect sizes are large in relation to the very low noise levels. As a practical result, we found that silane monolayers enhance heat transfer from the wire to the buffer considerably due to an overlap in the molecular vibration modes of the silanes' carboxyl group with water molecules. Single-stranded DNA layers with their entangled morphology strongly impede thermal transport while hybridization to stiff double helices makes heat transfer again more efficient. Starting from this proof-of-concept, we are currently exploring whether this 3ω-based "hot-wire" technique offers the same functionality as the heat-transfer method (HTM) with its static temperature gradient [3].

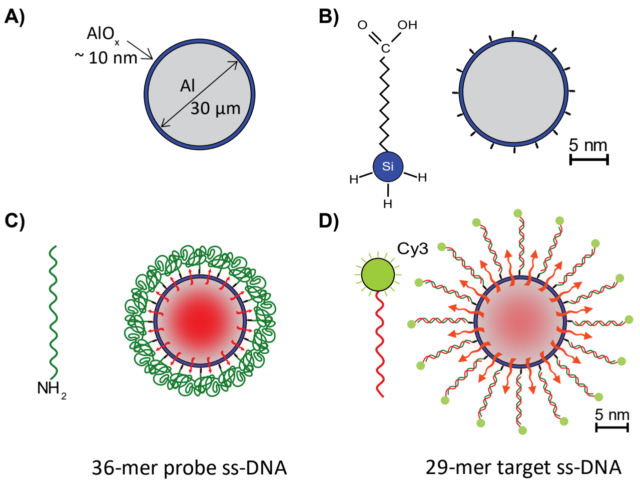

Figure 1. A) Scheme of the aluminium wire cross section. B) Functionalization with the silanes used as the cross linker. C) Attachment of single-stranded probe DNA. D) Hybridization with complementary target DNA.

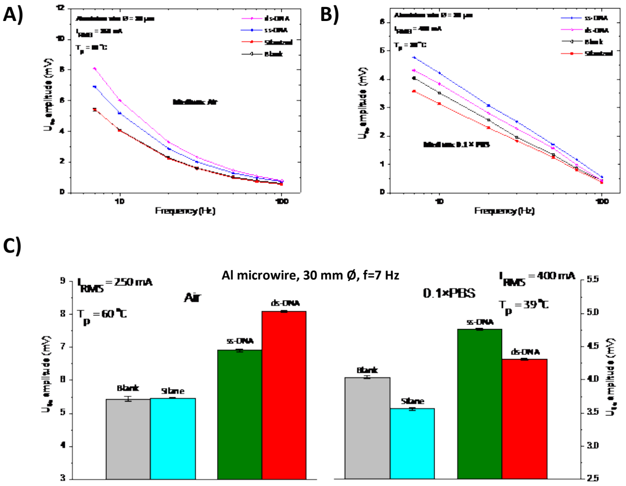

Figure 2. Frequency dependence of $U_{3\omega}$ A). B) Functionalization with the silanes used as the cross linker. C) Attachment of single-stranded probe DNA. D) Hybridization with complementary target DNA.

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Charge compensation processes in $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ cathodes studied by operando SQUID magnetometry

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Since the magnetic properties of the technologically important Li-ion battery electrode materials are sensitive to phase composition, structural disorder, defects and the oxidation state of the transition metals ions [1], magnetic studies can be used to provide insights into the electronic and chemical processes occurring during charging and discharging. By developing an operando SQUID magnetometry technique, a method was established, which enables a continuous monitoring of the oxidation states of the transition metal ions and, therefore, an identification of the redox active ions [2,3]. Here, the first results of the application of this method to study the charge compensation processes in $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ cathodes will be presented.

With the electrochemical cell enabling the operando measurements in a SQUID magnetometer the magnetic susceptibility χ of the cathode material is continuously recorded during charging and discharging. The changes of χ can be used to discern between the different oxidation processes taking place in the cathode material. For $LiNi_{0.80}Co_{0.15}Al_{0.05}O_2$ the observed steady decrease of χ with charging, which exhibits an almost constant slope for the majority of the charging time, indicates that the same charge compensation mechanism is taking place over a wide range of delithiation. Surprisingly, the slope is higher as it is expected for a change of the spin states for the transition between Ni^{3+} and Ni^{4+}. A possible explanation for this deviation could be the presence of Ni^{2+} ions in the initial state that are oxidized to Ni^{3+} upon charging. However, as will be outlined in this presentation, an unrealistic high amount of Ni^{2+} would be necessary to describe the magnetic susceptibility variation solely by the simultaneous oxidation of Ni^{2+} and Ni^{3+}. Thus, it is highly likely that the deviation arises mainly from an additional contribution of an orbital magnetic moment to the magnetic susceptibility. Furthermore, it will be shown that the magnetic susceptibility variation indicates that for higher degrees of delithiation additionally to the oxidation from Ni^{3+} to Ni^{4+} the oxidation from Co^{3+} to Co^{4+} sets in.

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Electrochemical hydrogen compressor – novel cell design and electrodes structure

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The electrochemical hydrogen compression is a highly efficient, low-maintenance, and silent technology, which is considered a potentially viable and cost-competitive alternative to the traditionally used mechanical piston compression. The technology is still under development and encounters problems such as high catalytic loading of the commonly used Pt catalyst for both partial reactions and insufficient performance stability under high differential pressure. Herein, a newly developed laboratory prototype of electrochemical hydrogen compressor, operating with proton conductive membrane is presented. The working temperature range of the device is up to 120 °C and it could sustain pressure up to 160 bar. The cell can be operated in open mode, e.g. at atmospheric pressure, or it can be hermetically closed so that the differential pressure between anode and cathode can be precisely adjusted. The research performed demonstrates the flexibility of the cell for studying the processes of the electrochemical hydrogen compression. Membrane electrode assemblies with Nafion 117 polymer membrane electrode and thin magnetron sputtered platinum (Pt) catalyst deposited over commercial gas diffusion electrodes were prepared and integrated in the cell. The efficiency of hydrogen conversion and compression was investigated at varying pressure and temperature by means of steady state polarization curves and cell voltage measurements (U/j and U/p_{diff} characteristics). The achieved current density at a cell voltage of 0.5 V, an atmospheric pressure of the input hydrogen gas, and a temperature of 60 °C, was more than 1.3 Acm^{-2}, while the registered increase of the cell voltage with the increasing pressure was only 0.05 mVbar^{-1}. The effects revealed an enhanced efficiency of both electrode reactions on the sputtered Pt compared to those observed on commercial E-TEK electrodes with four times higher platinum loading. The results obtained demonstrated the feasibility of the constructed hydrogen conversion device as well as the superior performance and cost efficiency of the sputtered platinum catalyst.

Acknowledgment

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Optimized zinc electrode for rechargeable zinc-air batteries

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Due to the numerous advantages as high energy density, high capacity, work in humid environments and aqueous electrolytes with low self-discharge, the Zn-Air batteries have great developmental potential. Extensively studied as primary batteries since many years, nowadays, they attract both science and industry with development of electric rechargeable zinc-air batteries which will play an important role at integrating and optimizing the consumption of energy from renewable sources. The main problem for the commercialization of zinc-air batteries is their life (number of discharge/charge cycles) which is related to the degradation of the electrodes during cycling and leads to a rapid decrease of their capacity. Concerning the Zn-electrode, the main reasons are dissolution of Zn and passivation of the electrode with ZnO. This study presents the effect of the addition of various metal oxides to the initial zinc paste in order to prevent the formation of dendrites and thus inhibit degradation processes. The typical zinc electrode pasta was prepared as a mixture of Zn/ZnO, which ratio was previously optimized to be 30/70 wt. % [1-3] and painted on both sides of the tinned copper mesh as current collector. The experiments were carried out by charge/discharge tests using a KOH-based electrolyte in three electrodes cell configuration with reference hydrogen electrode and stainless steel as counter electrode. The effect of different contents of oxide additives (Bi_2O_3, In_2O_3, Al_2O_3 and/or Ga_2O_3) on the electrode performance was examined. The results showed that the additives have a significant effect (more than 30%) the real discharge capacity of the Zn electrode and increased its stability. It was found that the replacement of Al_2O_3 with Ga_2O_3 increases the total electrochemical performance of the Zn electrode.

Acknowledgement

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Single-layer and multi-layer ALD thin films for the protection of titanium for biomedical applications

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One of the most commonly used materials for the production of biomedical implants is Ti-based alloys [1]. Due to the complex environment in the human body, different strategies have been employed to protect them and improve the functionality of Ti alloys in vivo [2]. In this work, a novel atomic layer deposition method (ALD) was used [3-5].

Ultrathin barrier films of alumina (Al_2O_3) of different thicknesses were deposited on commercially pure titanium (cp-Ti) to estimate the critical thickness for their stability in simulated body fluid (SBF). Multi-layered ALD thin films were also deposited and compared with the protective properties of the single-layer thin films. Single-layer alumina thin films were prepared in 20 nm and 60 nm thicknesses. The thickness of the multi-layer thin film was 60 nm and composed of 20 nm alumina + 20 nm hafnia (HfO_2) + 20 nm alumina. Several specimens of each type were prepared to analyse the layers' cross-section. All specimens were properly ground and polished to high smoothness before deposition.

FE-SEM/EDS was used for chemical and morphological analyses. For 20 nm thin alumina films, defects or pinholes may occur in the film and later be reflected on electrochemical measurements. Thicker films of 60 nm achieved complete coverage of the substrates.

Potentiodynamic polarization and electrochemical impedance spectroscopy tests during 30-days immersion were carried out in SBF at 37°C. 20 nm thick films showed significantly weaker protective properties than 60 nm thick films. Single-layer and multi-layer achieved almost the same level of protection, but after long-term measurements, the porosity of the multi-layer was slightly lower than the single-layer. Further, the multi-layer film was prone to defects due to agglomerates in the hafnia intermediate layer, and these defects can significantly affect the protective properties of the layer. X-ray photoelectron spectroscopy depth profiles confirmed that the upper alumina layer of the multi-layer film was dissolved during immersion.

Atomic force microscopy combined with scanning Kelvin probe force microscopy (AFM-SKPFM) was used for thickness measurements of the thin films. The differences in the Volta potential between the bare metal surface and ALD thin films were also measured. Summarising, the results show that the thickness of ALD thin films is critical for achieving sufficient barrier protection under simulating physiological conditions.

Acknowledgement

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Heterogeneous electron transfer with redox active insulating solid

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Redox mediation is the key process in electrochemistry with insulators. Mediators shuttle charge between the electron-conducting electrode and the surface of the insulating storage material to drive the discharge or charge reaction by reducing or oxidizing the surface of the redox active insulator. Mediation is now widely accepted to be key to high efficiency, rate capability, and lifetime. It may on the one hand involve external mediators that are added as an electrolyte additive and which have been studied in a wide variety for metal-O2 cells and a few examples for metal-sulphur. On the other hand, there is inherent mediation, where soluble intermediates act as mediators, such as lithium polysulphides in lithium-sulphur batteries. However, surprisingly little attention has been devoted to quantitatively assessing heterogeneous reaction kinetics between mediator and storage material. Work so far clearly shows that the kinetics of this electron transfer step is overall rate limiting and decisive to understand and to control reaction mechanisms towards improving energy efficiency, rate capability, capacity, and cycle life, which underscores the urgency to measure them and to identify governing factors.

Here we systematically assess heterogeneous electron transfer at redox active insulators and identify governing factors. Particular systems we present to investigate are twofold. First, mediated kinetics of (su)peroxide oxidation. Our previous work has strikingly discovered decreasing electron transfer rate as the driving force (mediator redox potential) increases beyond a certain value, which represents a first example of Marcus inverted-region behaviour for heterogeneous reactions[1]. We are leveraging the predictive value of this finding regarding possibilities to impact maximum kinetics and the occurrence of a separate kinetic parabola for singlet oxygen evolution. Second, mediated kinetics of S_8 reduction and Li_2S oxidation[2]. Major tools to assess kinetics include following species concentration over time using UV-Vis-NIR spectroscopy. Doing so requires deconvoluting spectra of mixtures of mediator oxidation/reduction states even if pure substance spectra cannot be obtained. Particularly, obtaining kinetics in S chemistry requires assessing dynamic equilibria of multiple species, for which we develop chemo-metrics tools. The results afford detailed insights into kinetics, thermodynamics, and reaction mechanisms, allowing them to influence in an informed way.

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Porosity evolution and oxide formation during the formation of nanoporous copper via electrochemical dealloying

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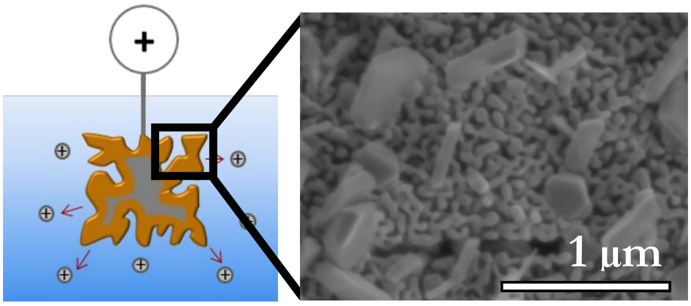
Dealloying is a selective etching process [1], which removes the less noble component(s) from an alloy, resulting in a free-standing, nanoporous structure of the more noble component(s). A high surface-to-volume ratio together with an enormous freedom of design, makes the conductive "nano-sponges" resulting from this process very interesting electrode materials for a broad variety of applications, such as sensing, bio- and electro-catalysis, energy storage or as functional materials. By far, the most intensively studied dealloyed material is nanoporous gold (np-Au), produced from Ag-Au precursor alloys, but also a variety of other systems is known in the literature, e.g., nanoporous Pt, Pd, Ag, or Cu. Besides low cost, np-Cu is particularly interesting due to its mechanical and electrical properties as well as mild fabrication conditions and a broad range of pore sizes (20-100nm) directly accessible via dealloying parameters. However, the (electro-)chemistry and in particular the oxide formation on the porous structure are not yet fully understood.

Here, we provide a comprehensive study of the formation of np-Cu by dealloying a Mn-Cu precursor alloy [2] and compare it to dealloying of Al-Cu. In addition to classical electrochemical methods, the dealloying process of Mn-Cu is characterized by in-situ resistometry, employing a model description established previously by our group [3]. The analysis reveals that structure formation is strongly dominated by charge transfer directly at the progressing etch front, separating the precursor "backbone" from the already etched, porous structure. In contrast to more noble dealloying systems, contributions from processes in the porous network (lying already "behind" the sharp etch front) are suppressed stronger in the case of np-Cu due to pronounced oxide formation. This picture is supported by scanning electron microscopy (SEM) as well as energy dispersive X-ray spectroscopy (EDX) of the produced np-Cu structures, revealing a hybrid composite of copper and manganese oxide on top of the metallic surface. A controlled formation of these oxides, known for their energy storage capabilities (supercapacitors) as well as their strong catalytic activity, is of highest interest for future applications of np-Cu.



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The Electrocatalytic Dark Side of Solar Fuels and Solar Chemicals

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The rising share of renewable electricity is testament to the increasing importance of solar/wind-electric routes to harvest sun light in form of potential differences and free electrons. While some electricity is used directly or stored capacitively, an increasing portion calls for direct conversion into valuable molecular solar fuels or chemicals. This conversion in the dark is made possible by heterogeneous electrocatalysis on the surface of solid electrodes. Electrocatalysis at the electrode surface orchestrates the stepwise making or breaking of molecular chemical bonds by means of electronic charge transfer across the electrified solid electrode/electrolyte interface. Kinetic barriers of elementary reaction steps – associated with suboptimal chemisorption or stabilization of intermediates – typically limit the efficiency of the overall reaction process. Fundamental understanding of the origin of the kinetic barriers arising along the reaction coordinate aids in the design of more efficient, tailor-made electrochemical interfaces.

In this presentation, I will report on recent advances in our understanding of “dark” electrocatalytic materials, interfaces and mechanisms relevant to the conversion of solar energy into value-added molecular compounds, using in-situ/operando X-ray spectroscopic, microscopic, scattering or spectrometric techniques. Examples include the electrochemistry of small molecules as they occur in low-temperature water- and CO_2 electrolyzers, electrosynthetic processes, as well as low-temperature PEM fuel cells.

Designing of electrocatalysts for Zn-CO2 battery – From CO2 utilization to energy storage

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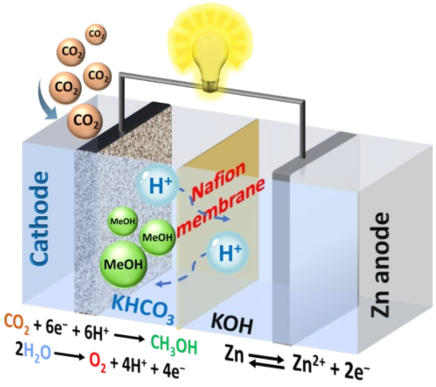
Being an important part of the carbon cycle, carbon dioxide (CO_2) is essential for sustaining life on Earth. However, in the practice of fulfilling the energy demands, CO_2 emissions have exceeded to a level which can prove to be life threatening in the coming years.[1] Therefore, the need of decarbonization and the use of renewable energy sources is expanding. In that regard, the electrochemical energy storage devices are considered to be a promising alternative to fossil fuels. Combining the electrochemical CO_2 reduction (e-CO_2R) with Metal-air batteries[2] is an effective way to target CO_2 utilization and energy storage and conversion through an aqueous rechargeable Zn-CO_2 battery.[3] The rechargeability depends on the ability of the electrocatalyst to show bifunctional activity for CO_2R and oxygen evolution reaction (OER) or the oxidation of the CO_2 reduction products.

Therefore, the bifunctional activity, selectivity and stability of the catalyst along with the kinetics of these reactions need to be improved for the growth of Zn-CO_2 batteries. Till date, a diverse range of transition metal-based catalysts have been explored for the e-CO_2RR. However, selectivity in the reduction to liquid fuels like alcohols and cost of these catalysts has been a matter of concern. In this aspect, metal-organic frameworks (MOFs) are known to be active for e-CO_2RR[4] and OER[5] owing to their unique structural properties. Also, carbonaceous materials possess the ability to reduce CO_2.[6] Thus, formation of MOF composites with carbon or formation of carbonaceous materials by post-synthetic treatment of MOFs can effectively enhance the stability and conductivity of MOFs and can prove to be a viable approach for use as bifunctional electrocatalysts in Zn-CO_2 batteries.



Figures: Schematic representation of Zn-CO_2 battery.

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Preparation and applications of biopolymer-modified electrochemical sensors

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Electrochemical sensors play a crucial role as tools for the quantitative determination of different ions from routine laboratory measurements to environmental monitoring. For the purpos of in-field analysis, there is an increasing demand for sensors with non-poisonous, nature-compatible components. In this context, “environmentally friendly” biopolymers can be considered as an important and promising functional sensor material. In particular, chitosan possesses biological properties such as biodegradability and biocompatibility, as well as interesting chemical features such as the presence of accessible hydroxyl and amine groups. The latter are protonated at acidic pH value, so that the chitosan molecule is positively charged under these conditions, making them an unique material for sensing applications.

The Lusatia Lake District is a result of former lignite opencast mining in Germany. As an effect of the rock weathering process, the region has actually to deal with a post-mining pollution of water bodies. As a consequence of the decomposition of sulfide minerals such as pyrite FeS_2 by atmospheric oxygen, both sulfate and iron ions appear in high concentrations in the water bodies, especially in the Spree River, and thus, the water color turns to ochre.

The main contribution of the presented work is the development and application of chitosan-modified electrodes for the determination of the sulfate and iron ions in ochre-colored surface water samples. Rod-shaped electrodes based on graphite paste were modified with chitosan and applied for determination of sulfate and iron ions in standard solutions and real water samples by the potentiometry and differential pulse voltammetry, respectively. The developed sulfate-selective electrodes exhibited a satisfactory sensitivity in sulfate containing standard solutions from 0.96 mg/l to 9600 mg/l. The lower detection limit of the examined voltammetric chitosan-modified electrodes amounts to 2.5 µg/l, whereas the maximum detected concentration of iron ions is about 300 mg/l.

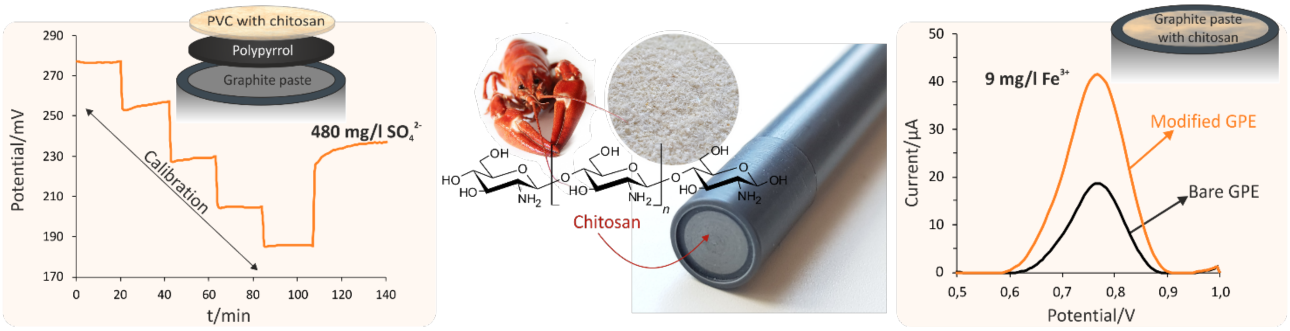

Figure 1: Modifications of graphite paste electrodes with chitosan for the potentiometric measurements of sulfate ions (left) and for the voltammetric determination of iron ions (right).

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Preparation and Characterization of $La_{0.6}Sr_{0.4}Fe(Co)O_{3-\delta}$ 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% 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) or $La(Sr)Ga(Mg)O_3$ (LSGM) and also is crucial the development of more effective cathode materials with increased electrocatalytic.

Many investigations have been performed to improve the perovskite-type materials based on lanthanum manganites. Different compositions with lanthanides and Sr or Ca on the A-site and with Mn, Fe, Co, Ni on the B-site have been proposed as alternative cathode materials. These cathode materials should be characterized by increased oxide ion transport in addition to high electronic conductivity. The mixed conductivity extends the active oxygen reduction site from the typical TPB to the entire exposed cathode surface, thus greatly reducing the cathode polarization at low operating temperatures. $La_{1-x}Sr_xFeO_3$ (LSF) has demonstrated higher electrical and ionic conductivity than $La_{1-x}Sr_xMnO_3$ (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. 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. 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. The new cathode materials also exhibit chemical stability with the electrolytes mentioned above.

Here we show that a synthetic route based on the auto-combustion of an ethylene glycol-metal nitrate polymerized gel precursor 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. We have therefore been able to determine on air-sintered samples how the electronic conductivity and thermal expansion coeficients change with the Fe, Co composition. 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.

Influence of the carbon substrate on the electroreduction of CO_2 to formate using various gas diffusion layers

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The increasing concentration of carbon dioxide (CO_2) from anthropogenic sources in the atmosphere is one of the major causes of climate change making carbon capture and utilization (CCU) a topic of great importance. In context of CCU, the electroreduction of CO_2 attracts particular attention, since it opens a way to use waste emissions for the production of value added products such as formic acid enabling its use as a green commodity in the chemical industry[1].

For the electroreduction of CO_2, the architecture of the gas diffusion electrode (GDE) plays a pivotal role[2], since the GDE carries the catalyst layer and promotes the reduction reaction. However, despite its importance, research in the field of electroreduction has mainly been focused on catalyst development and the investigation of cell designs, often neglecting the influence of the GDE on the cell performance. Therefore, aiming for an in-depth understanding of the underlying design principles, the influence of different gas diffusion layers (GDLs) on the electroreduction of CO_2 to formate was investigated. At this, our study with respect to formate shall be regarded as an exemplary investigation, which we expect to hold true for other dissolved reaction products as well.

In our study, the investigated GDLs differed in their composition regarding the presence of a microporous layer (MPL), the extent of the hydrophobic treatment and the thickness of the GDL. The electrodes for the investigation of the influence of the GDLs on the electroreduction of CO_2 to formate were prepared via spray coating and were investigated by several physicochemical- and electrochemical techniques such as BET, SEM, X-ray microtomography (Micro-CT), contact angle analysis, capillary flow porometry, PEIS, LSV and CP afterwards. The quantification of the emerging formate during the electroreduction was implemented via offline ion exclusion chromatography (IC), while gaseous side-products were determined by online gas chromatography. A micro-CT image of the GDE prepared with Toray Paper 120 with MPL can be seen in Figure 1. The bright layer on top of the GDE is the catalyst layer that exhibits extended stability for short-term testing based on the applied preparation procedure. As an overall result of our study, it was found that the GDEs with a MPL show the best electrode performance identified by the least negative electrode potentials and the highest amounts of produced formate in comparison to the electrodes without MPL. This effect is mainly ascribed to the enhanced wettability of the electrode and the resulting improvement of the electrode-electrolyte interface. Furthermore, we observed that for the electroreduction of CO_2 also a sufficiently high hydrophobic treatment of the GDLs is important in order to prevent electrode flooding. However, a too high PTFE content causes repulsion of the electrolyte and may impede the electroreduction of CO_2. The GDL thickness on the other hand seems to play no decisive role on the electrode performance. To conclude, the decisive parameters describing a suitable GDL for the electroreduction of CO_2, are an interaction for the presence of a MPL and the amount of hydrophobic treatment, with the most important aspect being the presence of a microporous layer.

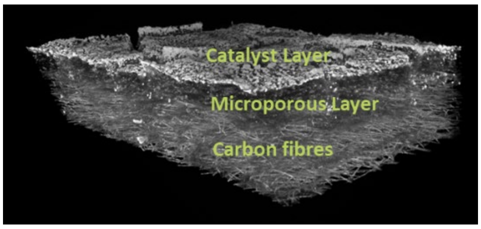

Figure 1: Micro-CT picture of Toray Paper 120 MPL coated with SnO_2 nanoparticles, after the electroreduction of CO_2 to formate. Bright spots identify the location of the nanoparticles after the experiment.

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Advanced understanding of electrocatalysis at nanoscale materials by spectro-electrochemistry and single entity electrochemistry

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Over the past two decades, electrochemistry transformed into a widely utilized toolbox for basic physicochemical studies, smart bio- and nanoparticle sensors, environmentally friendly synthesis approaches, and renewable energy technologies. The goal of sustainable conversion and storage of energy from renewable energy sources and non-fossil fuels is of particular relevance, as almost all technologies discussed for this purpose are based on electrochemical processes: Batteries, supercapacitors, photovoltaic cells, water electrolyzers, fuel cells, etc. Since electrochemical reactions always occur at an electrode, the transport of reactants and products to and from the electrode play a significant role in addition to reaction kinetics, which complicates quantitative understanding. Nanomaterials are often used to achieve large surface areas and high reaction rates. However, their reactivity and transformations are insufficiently described by traditional electrochemical concepts.[1] This inhibits the characterization - and thus the targeted further development - of nanocatalysts, as well as active materials and requires the development of novel electrochemical methods. As examples for such methods, single entity electrochemistry, i.e. electrochemistry of or at single nanoparticles, and electrochemical dark field microscopy coupled to hyperspectral imaging or Raman microscopy will be highlighted in this plenary talk (Figure 1).

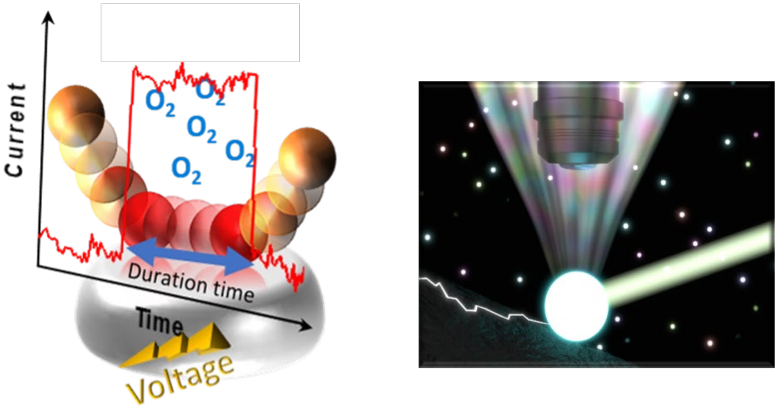

Figure 1.Schematic drawings of single particle electrocatalysis[2] (left), and spectro-electrochemical dark-field microscopy[3]; two examples of emerging electrochemical tools.

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Electrochemical study of the kinetics of synthesis of antioxidants by the Mannich reaction

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Electrochemically studied the kinetics of the reaction of hindered alkylphenols with hexamethylenetetramine according to the Mannich reaction.

The reaction products have antioxidant properties and are used as industrial antioxidants for lubricating materials. The reactions of hexamethylenetetramine with 2,6-di-tert-butylphenol and 4-iso-nonylphenol were studied. A chromatographic method of analysis is known, which is quite complex. In this work, we used coulometric analysis and the reaction of phenols with bromine for this purpose. This is an electrophilic substitution reaction. The bromine, necessary for its implementation, was obtained by electrochemical oxidation of HBr directly in the reaction mixture. The amount of electricity consumed is proportional to the amount of phenol that reacts with bromine. The electrochemical method gives good agreement with the chromatographic method.

Reactions of the interaction of hexamethylenetetramine separately with 4-iso-nonylphenol, 2,6-di-tert-butylphenol, as well as in a mixture of both alkylphenols were studied. The reactions were carried out in a melt, in a nitrogen atmosphere.

It was determined that 4-iso-nonylphenol reacts two orders faster than 2,6-di-tert-butylphenol. The rate constants of the second order for 2,6-di-tert-butylphenol is equal to 3*10 -3 l mol-1s-1, and for 4-iso-nonylphenol is equal 4*10-1 l mol-1s-1. Based on the electronic structure and ability to electrophilic substitution, this fact cannot be explained. The higher reaction rate for 4-iso-nonylphenol can be explained by the formation of a benzoxazine intermediate. Similar products are described for 4-methyl-2-tert-butylphenol. Such a product contains a six-membered ring. It is known that the more stable the intermediate, the faster it is formed. For 2,6-di-tert-butylphenol, the formation of such a product is not possible.

When studying the reaction in a mixture of 2,6-di-tert-butylphenol and 4-iso-nonylphenol taken in equimolar amounts, it was determined that p-iso-nonyl-phenol reacts first. Its concentration decreases to trace amounts. At the same time, a benzoxazine derivative is probably formed, which then reacts with 2,6-di-tert-butylphenol. it was determined that the reaction is accelerated in the presence of boric acid. Probably, boric acid catalyzes the decomposition of hexamethylenetetramine and the interaction of the benzoxazine intermediate with 2,6-di-tert-butylphenol.

The electrochemical method is fast and convenient, as it does not require additional processing of the sample of the reaction mixture. The technique can be used for research, as well as for control of the synthesis process and product quality control in industry.

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Indoor Air Quality (IIAQ) & Infection Probability Rate (IPR): Developing better spread risk models

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The Covid-19 pandemic has changed the perception of society about different aspects of life.

Human perception of air quality is subjective. Many gasses are odorless. We can only perceive the air quality by factors such as difficulty breathing, lack of concentration, or headaches.

Data-driven applications from real-time air quality sensors have been proposed in this paper as an effective solution to assess the healthiness of indoor air in public places.

The development and future use of two new indexes related to the risk of airborne disease spread are proposed in this paper:

- IIAQ or Indoor Air Quality Index. A new IAQ index created by the authors
- IPR or Infection Probability Rate. A new concept derived from the Wells-Riley mode

The Wells-Riley model is used by Martin Z. Bazant et al (1). and other previous work (Chung Min Liao et al. and Freja Nordsiek et al). The model was further developed to include additional variables beyond CO2.

$$IPR_{person} = \int_{t_{in}}^{t_{out}} 1 - e^{-ICkq(L+N')\beta t} \delta t$$

The authors have designed a new air quality multiple-sensor device that has been successfully tested where the new IIAQ and IRP indexes also are proven to be effective tools.

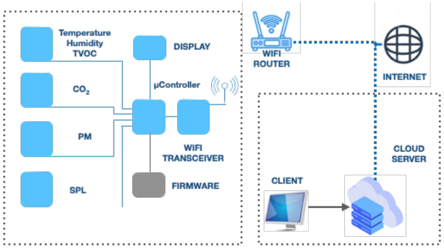
Research published up-to-date takes into account only the Carbon Dioxide concentrations.

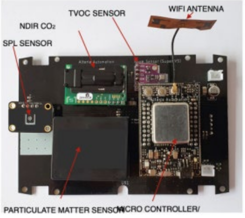
The new sensor device monitors other factors such as the concentration of aerosols (Particulate Matter), the speech sound pressure level produced by occupants, and the room occupancy rate.

Impact Statement: This paper has further developed the existing infection risk models going some steps beyond, taking into account the concentration of Aerosols with other relevant spread risks, and creating algorithms to interpret these variables into a meaningful at-a-glance simple factor conclusions.

Some specific impacts from this study are:

1. SENSOR DEVELOPMENT. A practical sensor device was developed from scratch, monitoring air quality variables in real-time and providing data-driven insights.
2. INDOOR AIR QUALITY INDEX. A new indoor-specific index (IIAQ-polynomial algorithm) was developed.
3. INFECTION PROBABILITY RATE. A new airborne disease spread Index, called Infection Probability Rate index (IPR), using a modified time-baselined Wells-Riley model.
4. DATA-DRIVEN MITIGATION. Learning from data: Analyzing the air quality in real indoor case study scenarios and generating recommendations to minimize the airborne spread of disease risks.
5. TRACEABILITY. Using an on-the-cloud server to store air quality data provides traceability to public places





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An Insight into the Potential of Proton Conducting Ceramic Cells - Review

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Green hydrogen is crucial to meet the CO2 reduction objectives of the ambitious European decarbonization program which in the moment has a new challenge - to ensure the independence of our energy system from Russian gas. In this context, the demand of high-quality hydrogen regarding dryness, purity and pressure is steadily increasing. Although conventional methods like mechanical compressors, zeolites, and thermal drying cycles to clean, dry and compress hydrogen are economic and reliable at large scales, they have not been optimised to the scale of decentralised hydrogen production such as electrolysis. Electrochemical hydrogen pumping for drying, purification and compression presents a radically different approach to fulfil the high-quality requirements of fuel cell applications in various fields. The most advanced technology in this field is based on symmetric high temperature Polymer Electrolyte Membrane, however only marginal progress has been achieved over the last decade and the commercial maturity is yet to be reached.

Proton conducting Ceramic Cells (PCC) represent a promising alternative way to compress and purify hydrogen. They operate in a temperature range of 400°C – 700°C and allow seamless heat integration options. The use of noble metals is avoided, as these cells are based on inexpensive and abundantly available materials. Therefore, the technology is extremely attractive for an efficient thermal integration when coupled with other chemical processes (e.g. steam biogas reforming, methanation etc.). The current challenge is to overcome the limited understanding at the materials level and the lack of optimized stack/ reactor designs for energetically integrated downstream processing of hydrogen. The first part of this presentation gives a review of the potential application niches and current SoA of PCC.

In the second part recent developments of our team on PCC for improving electrochemical performance are discussed (Fig. 1).

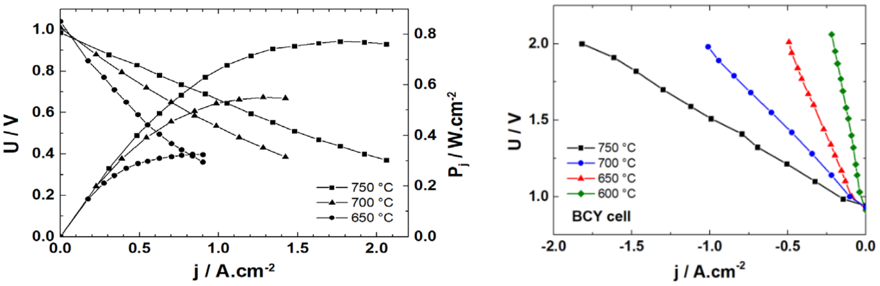

Figure 1. PCC in fuel cell (left) and electrolyzis mode with electrolyte yttrium doped barium cerate

Acknowledgements

Part of the testing is performed with equipment supported by the Bulgarian Ministry of Education and Science under the National Roadmap for Research Infrastructure 2017-2023 “Energy storage and hydrogen energetics (ESHER)”, approved by DCM No 354/29.08.2017.

Environmental friendly and low cost monitoring system for plant and agriculture fields

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The constantly growing global population is to be sustainably supplied with food. Due to climatic changes and increasing problems in protecting the environment, farmers are faced with great challenges.

In order to automate, specify and simplify processes, reliable decision-making bases for the control of irrigation, fertilisation and plant protection measures with a close-meshed database are required. This can be achieved with cost-efficiently produced and environmentally friendly sensor systems for monitoring cultivated areas.

Such a monitoring system is currently being developed, first laboratory samples are available and are being tested step by step in laboratory and field (Fig.1a). The single sensor devices consist of a miniaturised electronic module with single-chip radio system, sensors for measuring temperature, soil tension, in the near future leaf wetness and nitrate. The sensors and the electronic module are fabricated from materials that are biodegradable or inert with a minimum amount of metal and ceramic and allow for remaining them on the field when harvesting. The device is powered by a biodegradable zinc-manganese dioxide battery. For wireless communication a printed antenna on a wood carrier is used (Fig.1b). A gateway collects the data transmitted by the distributed sensor devices and brings it to the internet to a central server running an expert system. The advance of the new forecast system is that the sensors are cheap and degradable which make it possible to monitor micro-climate on an even significantly higher dense scale at lower effort and low price by the professionals. This allows for site-specific treatment, and thus makes it possible to lower the plant protection agents application even more within the field scale.

a) Sensor device on agriculture field for communication tests

b) Printed antenna on wood carrier

Figure 1: Environmental friendly and low cost monitoring system for plant and agriculture fields

Model based state estimation of internal states distribution of a fuel cell using principal component analysis

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Polymer electrolyte membrane fuel cell modelling and state observation are crucial for successful control and diagnostics. In this work, a state observer is developed to estimate the distribution of unmeasurable internal states of a fuel cell along the cathode/anode gas channels as well as across the gas diffusion layers and the membrane. The keyword is "distribution" – meaning that the whole profile of the internal states (e.g. concentration) is estimated, and not just an average value or the value at a single location. A state observer uses measurement signals from the system in combination with a simulation model and some correction algorithm (e.g. Extended Kalman Filter) to estimate the true system states. Evidently, an observer is more than just a simulation model running in parallel to the plant. The models used for fuel cell observers are usually zero-dimensional (0D), with no spatial distribution of the internal states [1]. In this work, however, a quasi 2D distributed fuel cell model is used, where the system is described with several hundred states [2]. In the observer, correcting every single of the several hundred states is not feasible as observability is not ensured and it also makes no physical sense. To understand this, one should consider the concentration distribution of hydrogen, for example. It is not realistic that during operation, the concentrations at all points should be independently corrected, as they are obviously strongly coupled. That kind of observer action could lead to unrealistic zig-zag distributions. Therefore, principal component analysis is performed to extract the dominant features of the system to obtain a reduced order model with only a few (10 to 15) states whose dynamics project the whole profiles of the internal states. Thus, the observer corrects the profile of the concentration distribution, instead of every single point resulting in a smooth and realistic estimation. The approach can of course, never be fully validated in reality as the internal states are not available. Therefore, a high-fidelity model is used as „reality", with a fine discretisation grid. The cell voltage is used as measurement and the obsever's task is to estimate the internal states' distribution from the available voltage. A uncorrected simulation is also run, for comparison. In Figure 1, the hydrogen mole fraction in the anode can be seen at different times where the observer pushes the model towards reality with the described approach, faster than the pure simulation is able to converge. In some cases, the pure simulation will not reach reality at all. Of course, all the internal states are estimated, Figure 1 is shown as an example of only one of the quantities. To sum up, several major topics are investigated: 1) modelling of the distribution of the internal states 2) principal component analysis of the model 3) observer design using the principal components as corrective action, and 4) validation of the observer against a high-fidelity model and compared to the uncorrected system.

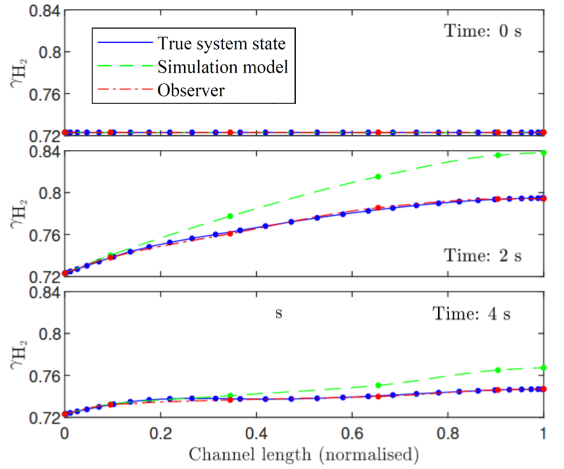

Figure 1 Hydrogen mole fraction in anode channel at different times. The observer (red line) converges towards reality (blue line) much faster than the, uncorrected traditional simulation model (green line), crucial for real time diagnostics. The reality model has a finer discretisation grid than the observer model

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Electrochemical Monitoring of Vanadium Redox Flow Batteries

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Redox Flow batteries gain increasing interest for the storage of renewable energies due to their independent scalability of power and capacity. Amongst a variety of chemistries Vanadium Redox Flow batteries (VRFB) are intensively studied and most common commercially applied.

Vanadium electrolytes in both battery half cells are advantageous because mixing of the half-cell electrolytes does not result in contamination of the electrolytes. Nevertheless, undesirable crossover of electrolyte components, especially active vanadium species, can be observed for commercially employed membranes and results in self discharge and capacity fading of the VRFB. For an efficient operation, the reliable detection of the state of charge (SOC) of the battery during charging and discharging is essential.

We present open circuit potential (OCP) measurements of the battery half-cell electrolytes as a monitoring method to determine continuously the SOC of VFRB [1, 2]. At a VRFB test station OCP monitoring using reference electrodes and glassy carbon rods has been investigated concerning an applicability to determine SOC during charging and discharging processes as well as identification of electrolyte crossover [3].

This simple and cost-effective monitoring method is discussed in comparison to established monitoring methods as coulomb counting and reference cell measurements.

Further electrochemical methods which have yet not been applied for VRFB as chronoamperometric measurements and Electrochemical Quartz Cristal Microbalance (EQCM) measurements will be presented and discussed concerning their applicability for SOC determination at VRFB half-cells.

Acknowledgements

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Approaches to voltammetric detection of As(III) and As(V) in mining waters for *in-situ* application

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As a result of mining, the water quality of former tin ore mines in former East Germany has been significantly affected for several decades due to increased arsenic content. Special all-solid-state electrodes have been developed and tested for the selective detection of As(III) + As(V) in aqueous samples. Screen-printed electrodes (SPEs) represent an elegant possibility for the sensitive and reliable determination of arsenic species by stripping voltammetry. In this presentation, novel SPEs are described, which consist of a three-electrode system: Au – working electrode, Pt – auxiliary electrode and Ag/AgCl – pseudo reference electrode. They are applied to *square-wave anodic stripping* voltammetry (SWASV) using a portable electroanalytical potentiostat. This not only enables arsenic ion detection under laboratory conditions, but also their *in-situ* application. The optimized measurement parameters allow for monitoring of mining-relevant As(III) + As(V) concentrations up to the drinking water limit of 10 µg/l with a short deposition time. In addition to the influence of interfering metal ions, the direct and simultaneous detection of As(III) + As(V) as a function of pH was investigated. The data obtained was interpreted using calculated Pourbaix diagram (Fig. 1).

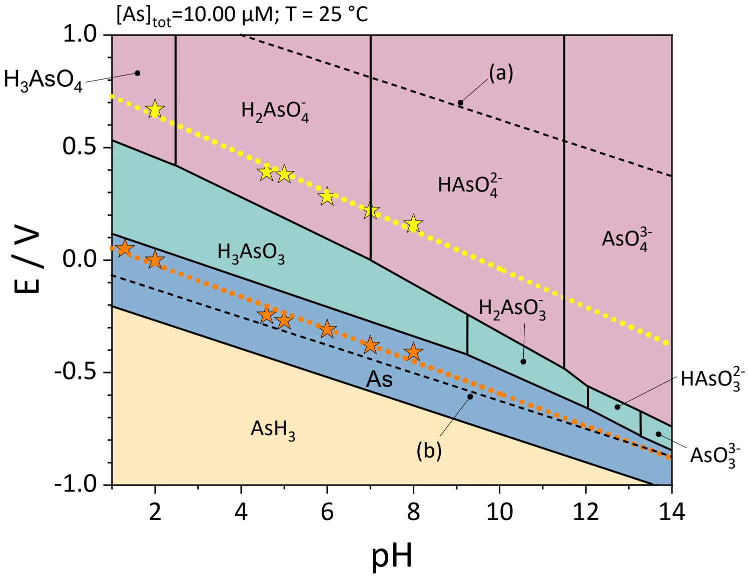

Fig. 1: Calculated Pourbaix diagram for a total arsenic content of 10.00 µmol/l at 25 °C. This represents the potential E depending on pH for red areas indicating As(V) species; turquoise areas indicating As(III) species, blue area – elemental As(0) and yellow area – gaseous AsH_3. The stars show the positions of the peak maxima from performed anodic stripping voltammetric measurements. The dotted orange line represents the linearization of the peak maxima at the transition from As(0) → As(III). The dotted yellow line represents the linearization of the peak maxima at the transition from As(III) → As(V). Dashed lines (a) $O_{2(g)} + 4\ H^+_{(aq)} + 4\ e^- \rightarrow 2\ H_2O_{(l)}$ and (b) $2\ H^+_{(aq)} + 2\ e^- \rightarrow H_{2(g)}$ enclose the theoretical region of stability of the water to oxidation or reduction.

These sensors represent an effective way for *in-situ* monitoring of arsenic ions in mining and surface waters. Furthermore, extensive hydrochemical monitoring is planned. Based on those, guidelines are proposed for an automatic *in-situ* monitoring system for the detection of As(III) + As(V) and an AI-based control of water treatment modules.

In operando monitoring templated electrodeposition of Pt films with hexagonal pore structure by GISAXS

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Liquid crystal (LC) templated electrodeposition is a facile and versatile method to electrodeposit metal films with highly structured mesopores. These mesopores are essential to increase surface area for electrocatalysis and sensing. Previous studies showed that LC templating allowed to tailor pore size[1,2], shape[3,4], and orientation[5] of the pores in the deposited film. Generally, these studies suggest that the pores in the film inherit the structure of the LC template.

However, little is known about the interplay between the kinetics of the templated deposition, i.e. the transition from the structure of the LC template to the resulting film. A better understanding of this interplay requires in operando monitoring structural changes during the templated electrodeposition process.

As a part of my PhD, we characterized the surface structure of Au substrates during templated electrodeposition of Pt with *operando* Grazing Incidence Small Angle X-Ray Scattering (GISAXS).

We were able to identify a series of structural changes at the film surface: A loss of preferential alignment of the LC, followed by the formation of vertically aligned pores. These findings potentially lead to more effective electrodeposition routines and films with higher surface area.

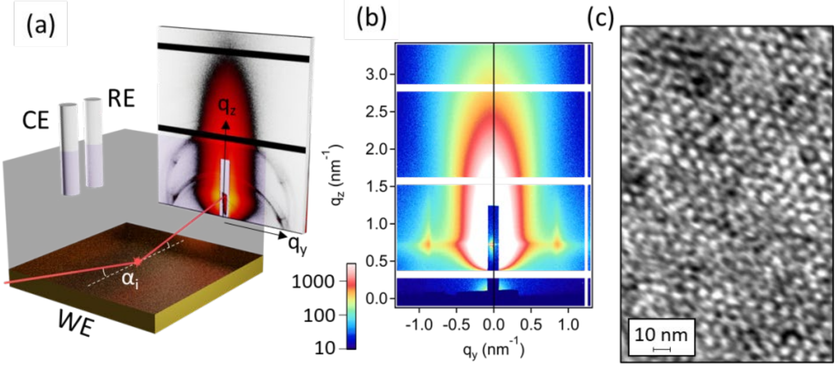

Figure 1: Operando GISAXS experiment during templated electrodeposition of Pt films: (a)Schematic experimental setup, (b) GISAXS pattern of mesoporous Pt film after deposition and removal of electrolyte. Vertical streaks at qy=±0.9nm-1 indicate vertical

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Electrochemical and Chemical Analyses as Powerful Complement for Battery Diagnostics

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From the very early findings of Galvani, Volta and Ritter until today, Electrochemistry has all times been a discipline that received most attention, when basic science could be well coupled to application. In fact, Electrochemistry has always been highly interdisciplinary, in particular in combination with materials science and materials analysis.

Electrochemical energy storage through batteries is considered as important enabler for mobility and energy transition. The lithium ion battery is the state-of-the-art battery technology. It is a very versatile technology as its performance can be designed for specific application scenarios by combination of various functional electrode and electrolyte materials. In addition, there are many battery systems beyond lithium ion, which also can benefit from the existing very broad material and component variety.

Understanding, improvement and further development of the numerous battery systems, components and materials require qualitative and quantitative chemical analysis as well as quantitative electrochemical diagnostics.

Results from conventional direct-current (galvanostatic) operation during charge and discharge provide important key performance indicators such cycle life, capacity retention and rate performance. Systematic and smart adaptation of this technique can reveal precious additional information and can uncover underlying operation mechanisms and possible failure sources. In parallel, chemical-analytical methods cannot only prove and validate the assumptions elaborated from electrochemical diagnostics, but is able to deliver complementary missing (“blank area”) information, beyond the possibilities of electrochemical techniques. This presentation will show selected examples of this complementary approach for high voltage/high capacity lithium ion batteries and lithium metal batteries, both being hot topics in actual battery R&D.

Impedimetric spillover sensing for hydrogen detection in reducing media

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Hydrogen sensing is a well explored field with various sensor concepts already available on the market. However, in reducing atmospheres the available sensor systems are limited. In this contribution, we show how a well-known catalytic principle - the so-called spillover - can contribute as the basis for hydrogen selectivity of such a demanded sensor concept.

The spillover of hydrogen species, which in turn is preceded by homolytic cleavage of H_2 preferably over a metal species, has already been described for numerous materials such as silica, alumina, metal oxides, activated carbon and zeolites. Roland et al. postulated that the spillover of hydrogen is correlated with a partial charge transfer to the support with atomic H* acting as electron donor [1]. This was explicitly shown for TiO_2 even when the active metal was separated from the point of measuring [2]. Moreover, Roland et al. were able to show the oxide support had also an influence on the measured effect [1]. Later, Karim et al. determined the ranges of the spillover hydrogen over different support materials.[3]

Applying this knowledge, we were able to fabricate and test catalytically active sensor layers that allow to exploit the H_2 spillover effect for the impedimetric measurement of H_2 concentration in gas mixtures of different compositions. As best material combination, an active component based on a noble metal (Pt) was introduced onto a support layer (TiO_2), which is itself inert to H_2 activation. The sensor principle can be traced back to the following mechanisms: homogeneous H_2 cleavage, H* spillover, electron transfer to the metal oxide conduction band and to oxygen vacancies (Fig. 1). The first transfer interaction can be followed by a change in resistance in the impedance spectrum. In addition to determining the H_2 concentration over a wide concentration range (from ppm to 20 vol% H_2 in N_2), the layers were successfully tested in mixtures of H_2 in CH_4 which demonstrated the potential suitability of the sensor system for gas grid monitoring.

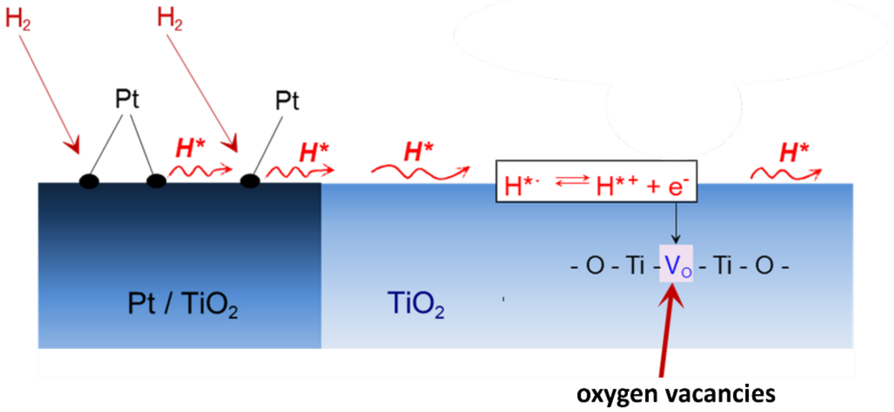

Figure 1: Elementary processes occurring at an impedance sensor for hydrogen detection.

The sensors were also shown to selectively detect hydrogen in the presence of classical interfering gases (presence of small amounts of oxygen) at relatively low temperatures (50 °C). Sensitivity is especially high at small hydrogen concentrations in the lower percentage range.

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Graphene derivative supported palladium-based catalysts for the ethanol electrooxidation in alkaline media

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Research on alkaline direct ethanol fuel cells has gained attention in recent years due to numerous advantages, such as ethanol being non-toxic, having a high energy density and being able to be produced from biomass such as sugar cane and agricultural waste. However, the biggest obstacle to commercialization of this technology remains its slow kinetics on the anode side. The cleavage of the carbon-carbon bond is not successful with known catalysts, making research on highly active, but also stable ethanol oxidation electrocatalysts an important research topic (Figure 1). Pd-based catalyst systems are considered the best materials for electrochemical ethanol oxidation. An effective method for improving catalytic activity and stability is the development of new catalyst supports for metal particles. Graphene derivatives are seen as prospective catalyst supports in fuel cells due to their superior electronic conductivity, large specific surface area, and their reasonable stability[1].

In this study, Pd-based anode catalysts are developed[2,3], characterized physicochemically and electrochemically tested. Ex-situ measurements like cyclic voltammetry and chronoamperometry are performed with a thin film rotating disc electrode (RDE-CV; RDE-CA) in 1 M potassium hydroxide solution. The electrochemical active surface area (ECSA), the maximum peak current density and the by-product tolerance are evaluated with these methods. The Pd-based catalysts have high activity and stability due to the large surface area and the introduction of oxophilic elements (bifunctional, electronic and synergetic effects).

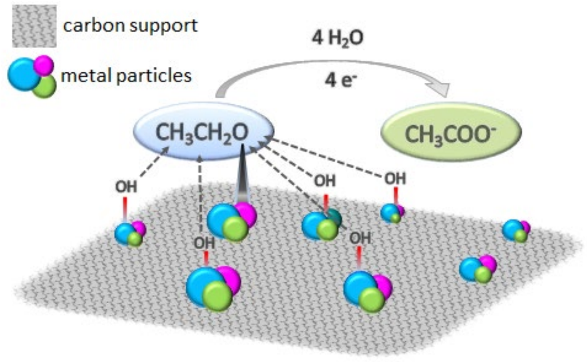

Figure 1: Ethanol oxidation reaction on carbon supported electrocatalyst.

Acknowledgements

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Measurement of hydrogen peroxide vapour with mixed potential solid electrolyte sensors

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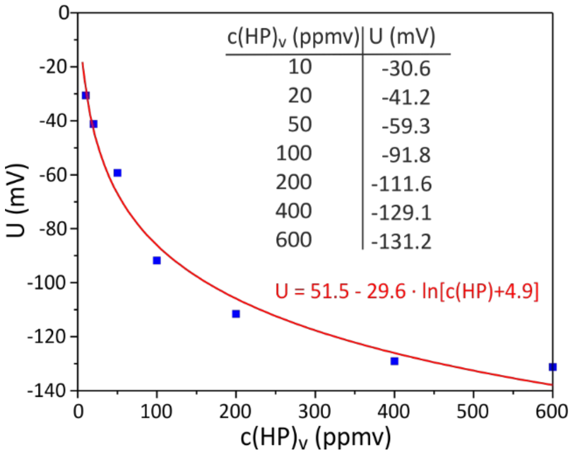
The sterilisation of technical systems by means of vaporized hydrogen peroxide (HP) solutions is used in many sectors of the chemical, pharmaceutical and food industry [1]. This process requires reliable and sensitive measurement of HP vapour concentrations (c(HP)$_v$) in a broad range to ensure product quality and to document decontamination/sterilisation. The reliable measurement of c(HP)$_v$ < 1 ppmv is carried out so fare with complex and expensive cavity ring-down spectrometers [2]. For diminishing the measuring effort significantly, a new approach was developed, which consists in the inline c(HP)$_v$ measurement by means of mixed potential solid electrolyte sensors (MPSES). These sensors are based on yttria-stabilized zirconia (YSZ) as oxygen ion conductor and use the effect of a mixed potential in non-equilibrated gas mixtures. To explore this application in detail, different electrode materials were screen printed on YSZ and tested in a chamber with different c(HP)$_v$ values established by nebulising HP solution with compressed air. Some of the electrode materials showed responses above 1 mV/ppmv, and therefore, can be used in a range between 0.1 and 600 ppmv. The signal curve provided in Fig. 1 suggested that the gaseous hydrogen peroxide at these conditions, contrary to its well-known effect as a strong oxidising agent [3], acts as a reducing agent and withdraws oxide ions from the lattice of the solid electrolyte, reacting to water and molecular oxygen, which desorb from the electrode subsequently. The remaining electrons charge the electrode negatively, and result in a negative potentiometric signal until the oxygen reduction is running at the same rate. Therefore, YSZ-based MPSES allow to monitor the process of HP discharge within a unit to be sterilized, before HP sensitive products are processed there.



c(HP)$_v$ (ppmv)	U (mV)
10	-30.6
20	-41.2
50	-59.3
100	-91.8
200	-111.6
400	-129.1
600	-131.2

Fig. 1: Signal dependency of a mixed potential sensor, operated at 450 °C in HP containing air.

Acknowledgments
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Miniaturized hydrogen gas sensor system for safety monitoring

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The extensive use of electricity from wind and sun for the economic production of hydrogen (H_2) via electrolysis on an industrial scale and its subsequent use as a chemical energy carrier, chemical base material and fuel for mobile applications, heat and electrical energy generation requires new approaches to H_2 application safety. The new quality of this application comes with the broad introduction of H_2 into the consumer sector. The new H_2 infrastructure to be created requires high-performance and future-proof innovative hydrogen sensors based on different measurement principles. Theses sensors are required to be much more flexible and cost-effective than before in addressing the needs of the H_2 value chain in terms of quality monitoring and ensuring maximum application safety. The paper presents a new approach for a highly selective hydrogen sensor system, which has been developed in the joint project "Process and Safety Sensors for Hydrogen Quality Management (HyProS)" of the HYPOS network.

This system is especially designed for leakage monitoring and suited to counter the risks resulting from the very low ignition energy and the invisibility of hydrogen flames. It is based on the coulometric detection of H_2 with a solid electrolyte detector in combination with a chromatographic pre-separation as shown in Fig. 1. The lower limit of detection ranges $c(H_2) < 100$ ppbv [1]. The system enables selective and calibration-free detection of oxidizable (H_2, CH_4) and/or reducible gas components [2]. This contribution describes the miniaturization all functional components of such a sensor system and their characterization under varying GC and detector parameters, and thus, enabling a systematic and insight-driven optimization.

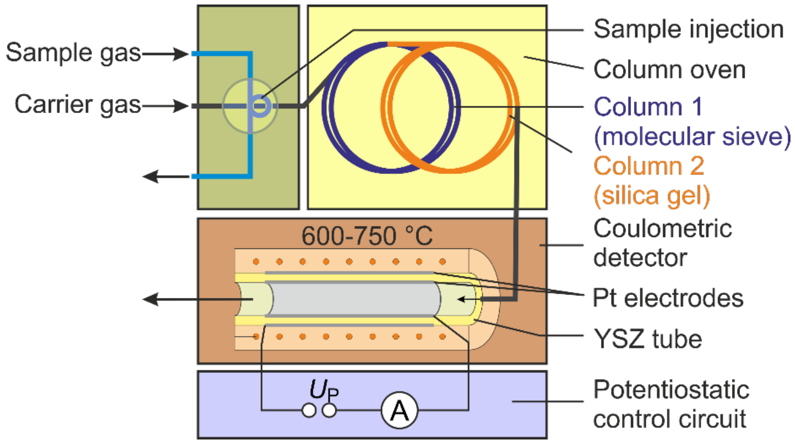

Fig. 1: Scheme of the highly selective chromatographic sensor system for H_2 trace concentrations.

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Forming free anodic memristors in hafnium-tantalum system

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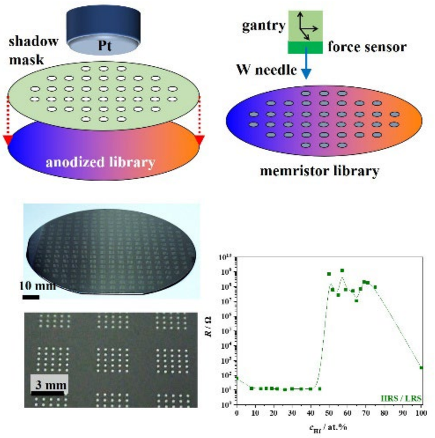
The conventional memory technology has already reached its technical and scaling limits, mainly due to architecture of von Neumann machines consisted of separated memory and processing units. Hence, a huge scientific attention has been drawn into the development of novel in-computing systems. Memristors are alternatives in the next generation of non-volatile memories promoting scalability and processing speed. The information storage mechanism of such metal-insulator-metal (MIM) structures is based on the resistance change. The selection of bottom and top electrodes with an insulating layer sandwiched between them, plays a crucial role in resistive switching based on conductive filaments formation. With this regard., high-κ dielectric materials such as Hf and Ta are promising valve metals with memristive properties. However, a memory window and device lifetime of memristors with HfO_2 and Ta_2O_5 active layers, is limited. Hence, the aim of this work was to improve the properties of devices formed on pure metals by mixing them. Hafnium-Ta thin film library was deposited by sputtering onto oxidized Si wafers with a total compositional spread ranging from 5 to 92 at.% Hf. Oxides were grown via electrochemical anodization process which is an inexpensive, fast and simple method, favoring industrial implementation. Memristive properties of devices were screened with 1 at.% resolution for a high number of alloys, while the switching mechanism was confirmed by depth profile investigation by XPS, HAXPES and imaging of CFs by HRTEM. Using the combinatorial approach, high performance forming free memristors were identified, with nanofilaments different in size, shape and position in the mixed oxides, for devices based on Hf, Ta and their alloys.



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Posters

Miniaturized pressure-resistant sensors for limnological applications

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A variety of problems related to the sustainable development of industrial and post-mining pit lakes require the establishment of an area-wide monitoring system.

As part of a European Eurostars project "HydroSense" [1], a vehicle was developed that can move autonomously in water and collect data concerning water quality. The partial task to be solved by the Kurt-Schwabe-Institute (KSI Meinsberg) consisted in the development and realization of a miniaturized, submersible measuring device for the determination of pH, redox potential and conductivity together with pressure and temperature. The base for the vehicle is the Sonobot®-catamaran developed by lead partner EvoLogic GmbH (D). The paper presents a complex measurement system with a miniaturized multiparameter probe including the electronics and data transmission concept (Fig. 1).

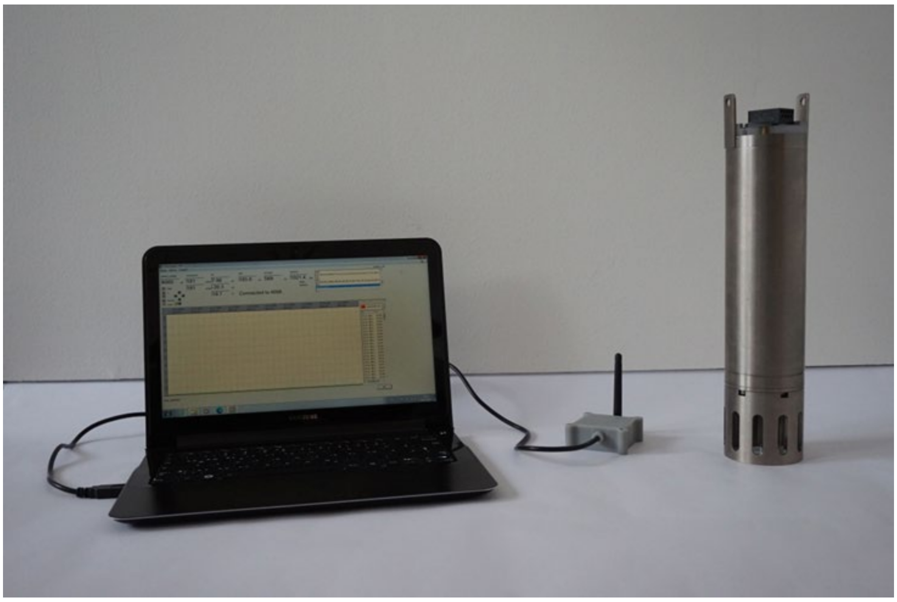

Figure 1: Measuring system with multiparameter probe, wireless transmission and evaluation software

In order to meet the requirement of miniaturization and robustness of the measurement system, sensors in thick-film technology and all-solid-state arrangements [2] have been developed in addition to sensors in conventional manufacturing processes. Among other things, design- and technology-specific features of sensors are considered and discussed with regard to their suitability for various practical applications.

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Composite coatings based on Zn-Co alloy and cerium with self-healing effect

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A great work has been carried out in the last decade on electrochemically deposited composite coatings with the aim of improving their properties: micro hardness, wear resistance, morphology, corrosion resistance, etc. The enhancement of all these features faces many challenges in deposition process, like particle agglomeration in the electrolyte, particle distribution within the metallic matrix and its content and size. In this work a novel protective Zn-alloy-composite coating was developed, based on Co as an alloying element, with an additional benefit of incorporation of cerium, as a well-known corrosion inhibitor [1-3]. Composite coatings were deposited galvanostatically, at a range of current densities, from additive-free chloride-based electrolytes, pH 5.5. Different sources were used as cerium particles, commercial CeO_2 and $CeCl_3$ powder. The particle agglomeration was minimized by mechanical stirring of the electrolyte for 2h before electrodeposition and during deposition. The effect of Ce source and its concentration in the plating electrolyte on morphology, coating composition and corrosion stability was analyzed. Morphology and chemical content were determined by SEM-EDS measurements, while corrosion behaviour of Zn-Co-Ce composite coatings was evaluated by polaryzation measurements and electrochemical impedance spectroscopy in 3% NaCl solution. This is a continuation of our earlier work on Zn-Co-CeO_2 coatings [3,4] when electrodeposition was carried out at low pH 3 and utilizing CeO_2 sol and commercial nanoparticles, agitated by ultrasound.

It was shown in this work that compact and homogenous coatings were obtained at current densities of up to 12 A dm^{-2}, for both Ce sources. Based on the chemical content of composite coatings the anomalous deposition was confirmed and that the smaller deposition current densities were beneficial for Ce incorporation for both types of Ce sources. The EIS data recorded during prolonged exposure to NaCl solution shown that electrodeposition at 2 and 3 A dm^{-2} was favorable for obtaining coatings with higher corrosion stability. The resistivity of all coatings decreased during initial exposure time, as a consequence of electrolyte penetration through the coating. However, the low impedance modulus increased during further exposure to corrosive agent and reached a plateau of almost constant values, suggesting self-healing effect. The phenomenon was more pronounced for composite coatings derived from electrolyte containing $CeCl_3$. The explanation for such findings will be offered.

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Effects of reactants stoichiometry ratios on current density distribution across the active area of the JRC ZERO∇CELL

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The aim of the JRC ZERO∇CELL, a single cell PEM fuel cell testing setup is to characterise the tested MEA (or its components) minimising the effects of the testing setup itself. Therefore showing the “true” characteristics of the tested specimen. For this purpose, a parallel pattern flow field was employed, while features of the testing hardware are supposed to ensure the same operating conditions (temperature, pressure and gas composition) at inlets of each equally long parallel channel.

In order to evaluate MEA performance gradients across the active area of the JRC ZERO∇CELL segmented current collectors were developed. The current collectors are associated with a single electronic load bank and allow to asses current and voltage distribution in two spatial dimensions, namely along as well as across the gas channels. The experiments using segmented current collectors were done at various reactants stoichiometry ratios, ranging from a16/c20 (anode/cathode) down to a1.5/c2.

Results show that current density gradient in the direction perpendicular to the gas channels is very small. Variations of the measured current density are at the same order of magnitude as the accuracy of measuring instruments. Therefore, it is experimentally confirmed that the JRC ZERO∇CELL provides uniform operating conditions at the inlets of each parallel channel and the channels work “independently”, irrespectively on the stoichiometry ratio within tested range. On the other hand, the longitudinal gradient of current density, what is expected, shows dependency on the applied stoichiometry ratio.

A modified Proton Exchange Membrane Fuel Cell for in operando SAXS and XAS

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Catalyst stability at the cathode side of Proton Exchange Membranes Fuel Cells (PEMFCs) is strongly affected from the harsh environment in which the Oxygen Reduction Reaction takes place and it is strongly limiting their commercial diffusion[1–3]. Significant improvements in this field could be achieved by a better understanding and discrimination among the several degradation processes which are overlapping during fuel cell operation[4,5]. Such a goal could lead to the development of new mitigation strategies for reducing catalyst degradation over time, thus increasing PEMFCs lifetime and reducing hydrogen consumption. In this framework, Small Angle X-Ray Scattering (SAXS) and X-Ray Absorption Spectroscopy (XAS) performed at synchrotron facilities can play a key role in providing complementary morphological and chemical information. In this framework, a modified PEMFC system is being designed for in operando analysis SAXS and XAS analysis to be performed at ELETTRA synchrotron in Trieste, for advanced catalyst characterization and is here presented.

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DFT analysis of quantum chemical reactivity parameters for electro-chemical applications of an azulene-phenyloxazolone based ligand

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The azulene derivative, namely 4-((5-isopropyl-3,8-dimethylazulen-1-yl)methylene)-2-phenyl oxazole-5(4H)-one (**L**) was electrochemically studied on glassy carbon using three methods: pulse-differential voltammetry, cyclic voltammetry (CV) and rotating disk electrode. The investigations were performed at different concentrations of **L** in 0.1M TBAP / CH_3CN. **L**’s films were obtained by successive cycling at different potentials or by controlled potential electrolysis (CPE). The formation of the films was proved by recording the CV curves of the chemically modified electrodes (CMEs) in ferrocene solutions. CMEs prepared for various charges or potentials were used to detect heavy metals (HMs) ions. Synthetic samples of HMs solutions (Cd (II), Pb (II), Cu (II), Hg (II)) at concentration ranging between $5x10^{-7}$ - 10^{-4} M were analyzed using these CMEs. The electrochemical study was supplemented by Density Functional Theory (DFT) theoretical approach using B3LYP/6-31 G^* density functional [1], aiming to obtain complete structural insights for further electrochemical properties estimations. Previous computational approaches showed pertinent results in terms of key parameters for designing novel ligands with enchanced electrochemical properties for HMs detection [2, 3]. Generally, the approach is based on the correlation of electrochemical oxidation and reduction potentials, with energy levels corresponding to the highest occupied molecular orbital (HOMO) or the lowest unoccupied molecular orbital (LUMO), respectively resulted from quantum computations [4]. The complexing capacity of **L** was disccused also based on electrosatic potential map (Figure 1) and charge distribution. It can be concluded that these methods afford access to new hybrid azulene ligands with promising characteristics as organic sensors materials for HMs recongnition.

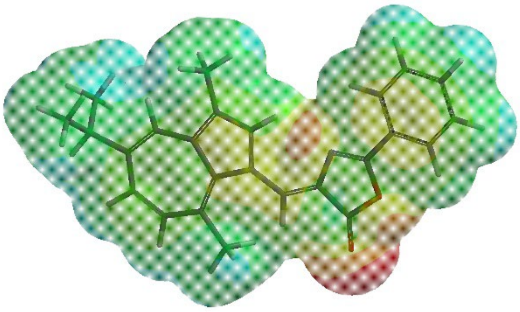

*Figure 1: Predicted molecular electrostatic potential map for **L**.*

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Prototype of a redox flow battery stack with tubular cell design

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A promising option for the conversion and stationary storage of renewable energy with rapidly growing research and development activities are all-vanadium redox flow batteries (VRFBs). By connecting single VRFBs to stacks, the power of the system is increased while the capacity of the system can be scaled independently by varying the separately stored vanadium electrolyte volumes. Using a VRFB cell with a tubular geometry instead of the prevalent planar geometry, offers several advantages: a cost-efficient production of cells by extrusion and reduced sealing-lengths [1]. Furthermore, cells within a stack can be connected not only in series but also in parallel, possibly reducing shunt currents.

We report on the recent progress of the research project StaTuR (stack of tubular redox flow batteries). The setup and extruded components of the tubular cell (cell length ~100mm, membrane diameter ~5mm) are described. Furthermore, the results of the characterisation of three generations of cells and corresponding assemblies/stacks with different electric connections are presented with the newest one reaching promising results (single cell $P_{max}/V > 500 W/l$ and $i_{max} > 600 mA/cm^2$). In addition, an overview of an accompanying design tool for the development of VRFB stacks with tubular cell geometry is provided.

Acknowledgements
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Voltammetric determination of plant growth regulator forchlorfenuron at carbon-based electrodes

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The use of agrochemicals has been critically important in increasing the yield of agricultural crops. However, their intensive use may lead to the presence of residues in foodstuffs when commodities reach the market. Accordingly, the use of agrochemicals in different crops is strictly regulated by international organizations and national governments. With the aim of protecting public health and the environment, maximum residue limits (MRLs) fixing the highest acceptable amount of a particular chemical in a certain crop have been established.

Forchlorfenuron, also referred to as CPPU, is a highly effective synthetic phenyl urea cytokinin which acts synergistically with natural auxins to promote plant cell division and lateral growth[1,2]. CPPU has been registered in many countries around the world, including EU and the USA, for the treatment of kiwifruits and table grapes. This relatively new plant growth regulator is extensively applied to improve berry/fruit size, fruit set, cluster weight, and cold storage[1]. Due to the increasing demand for high-quality fruits in the international market, CPPU has been widely used and it is possible that the residues of this pesticide could eventually reach the consumers. In this respect, CPPU residues in foodstuffs should be monitored and controlled. The MRL proposed by EU is set at 0.01 mg kg^{-1} for grapes and kiwifruit[3], while the U.S. Environmental Protection Agency (US EPA) establishes MRLs of 0.03 and 0.04 mg kg^{-1} for grapes and kiwifruit[4], respectively. Since the MRLs for CPPU in fruits are strictly controlled, there is an urgent need to develop sensitive analytical methods to detect trace level of this compound.

In this study, a quantitative determination of CPPU was performed using square-wave voltammetry on representative sp^2 and sp^3 carbon-based electrodes, *i.e.*, edge plane pyrolytic graphite electrode (EPPGE) and boron-doped diamond electrode (BDDE), respectively. Optimal conditions for CPPU quantification on EPPGE and BDDE were found in 0.04 mol L^{-1} Britton-Robinson buffer at pH 2.0. To determine linear dynamic ranges (LDRs), the wide CPPU concentration range from 1.0 to 100.0 µmol L^{-1} was measured. It was found that the CPPU current increased linearly with the CPPU concentration within two LDRs of 4.0–10.0 and 10.0–80.0 µmol L^{-1} (LOD of 0.86 µmol L^{-1}, LOQ of 2.60 µmol L^{-1}, sensitivity of 0.6073 µA µmol^{-1} L, RSD of I_p up to 8.6%) on EPPGE and 3.0–10.0 and 10.0–100.0 µmol L^{-1} (LOD of 0.80 µmol L^{-1}, LOQ of 2.43 µmol L^{-1}, sensitivity of 0.1631 µA µmol^{-1} L, RSD of I_p up to 3.8%) on BDDE. The results showed that wider LDRs with slightly lower linear response limit, slightly lower LOD and LOQ values as well as better repeatability of the peak current were achieved on BDDE. However, better sensitivity was obtained on EPPGE.

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Metal ions detection under photo-accumulation on a poly(azulene-EDTA) like modified electrode

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Metal ions detection using modified electrodes usually involves an accumulation step performed under imposed potential or sorption of metal ions in open circuit, followed by metal ion reduction and stripping. Another approach involves metal ions deposition under photoirradiation and quantified by stripping voltammetry [1]. By using this method, the accumulation and reduction of metal ions on the electrode surface is accomplished in a single step. Furthermore, Ma et al. [2] propose that by matching the potential of metal ions to the energy levels of the conduction band of a semiconductor could improve the selectivity and sensitivity of electrode materials for heavy metal ion electrochemical detection.

Thus, here we present sensing properties of previously developed glassy carbon modified electrodes with poly(2,2'-(ethane-1,2-diylbis((2-(azulen-2-ylamino)-2-oxoethyl)azanediyl)diacetic acid, (poly**L**) [3, 4] to metal ions detection under photo-accumulation. A Mott Schottky study was also performed to assess poly**L**'s semiconductor character and the impact of charge carrier density and flat band potential on photoreduction and electrode sensitivity.

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Titanium dioxide coating decorated with photodeposited silver nanostructures – corrosion behaviour in simulated body solution

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The modification of the surface of metallic biomaterials with ceramic coatings based on titanium dioxide (TiO_2) is widely applied to improve their mechanical, anticorrosive, and osteoinductive properties. To ensure the antibacterial properties of ceramic-based coatings, further modification with silver nanostructures is advantageous [1].

Many researchers have reported photocatalytic properties for TiO_2 coatings that are determined by several factors, including preparation method, crystallographic structure, coating thickness and roughness, surface density and size of TiO_2 isolated grains, and the type of substrate [2-4]. The photocatalytic activity of TiO_2 coatings in the form of anatase can be used for photoinduced deposition of silver nanoparticles (AgNPs) from a silver nitrate solution. This approach was successfully applied by Piwoński et al. [5] for TiO_2 coatings deposited on silicon wafers using two methods, *i.e.*, sol–gel dip-coating and magnetron sputtering.

The main goal of this study was to take the advantage of the photocatalytic activity of anatase to produce protective coatings decorated with nanosilver for biomedical purposes. In this work, TiO_2 coatings were prepared on M30NW biomedical alloy samples using the sol–gel dip–coating technique, and were heated at three different temperatures (400°C, 450°C, and 500°C). The obtained samples were characterized for phase composition, morphology and topography, and electrochemically tested to determine the optimal temperature for further studies on the photocatalytic deposition of AgNPs. As a result, the temperature of 450°C was selected. Further, three series of AgNPs were photochemically produced on the surface of M30NW biomedical alloy samples modified with a TiO_2 layer (450°C) of anatase structure using silver nitrate at different concentrations and using different UV exposure times. The influence of AgNPs on the properties of TiO_2 coating was determined by analysis of morphology, topography and corrosion properties in PBS solution that simulates body solution. It was found that the morphology and the amount of photochemically generated silver nanostructures differ depending on the concentration of $AgNO_3$ solution and the time of irradiation: higher concentration or longer-lasting irradiation allowed producing larger quantities of AgNPs with larger sizes and different shapes. Moreover, the deposition of AgNPs on the TiO_2 surface caused an increase in the electrochemical reactivity of the tested samples. The results showed a decrease in thepolarization resistance value and an increase in the calculated corrosion rate with the increasing amount of AgNPs. However, the embedded AgNPs did not change the pitting corrosion resistance of the tested samples in PBS solution.

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Poster about posters: How to make a good one - where we go wrong

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Usually, young researchers present their first results of scientific research work at the first scientific meeting they attend, through a poster. Unfortunately, they are very often left to themselves in the preparation, design and selection of information to present, and equally often they have neither the experience nor the skills to do it well. Not infrequently, older, and more experienced researchers also make many mistakes when creating a poster presentation.

This presentation aims to point out the good practice of creating clear, informative but also eye-pleasing posters. In addition to outlining the principles of well-designed posters, it will show what data and information a good poster should contain, and how to present it. Part of the presentation will be dedicated to some of the most common mistakes in presenting the results, how to avoid them and how to make the presented data clear and understandable to anyone who visits the poster.

Here are “10 golden rules” for preparing a good poster (Figure 1.):

1. Follow the **given dimensions** - the poster must be the size given in the Instructions for Authors.
2. The **title** is important: Short, sharp, striking - the visit to the poster depends on it!
3. The poster should answer the questions: **Why** the research was done, **what was done**, **what was obtained**, what was the **contribution** and what was **concluded**.
4. **The simpler the better** - avoid decorations, complicated pictures, bulky tables; **Minimum amount of text** (only necessary) arranged in small clear blocks.
5. **Text size**: minimum 18 pt; Recommended: Title - 85 pt, Authors - 56 pt, Affiliations - 48 pt, Subtitles 36 pt, text - 24 pr, Figs. and Tables captions - 18 pt.
6. **Order** of presented data: from top to bottom and/or from left to right, Figure 2.
7. No more than **3 colours**, dark on a light (not colourful and flashy) background.
8. **Illustrations**: photos - .png or. jpg format (150 dpi), line art (charts and diagrams) - .tif or .eps. format (minimum 300 dpi.).
9. **Personalization**: The poster reflects the author's personality - consider adding your own photo
10. Provide **contact** (E-mail) and **URL** for more information, prepare a **paper copy** of the poster and/or reprints (URL) of suitable articles.

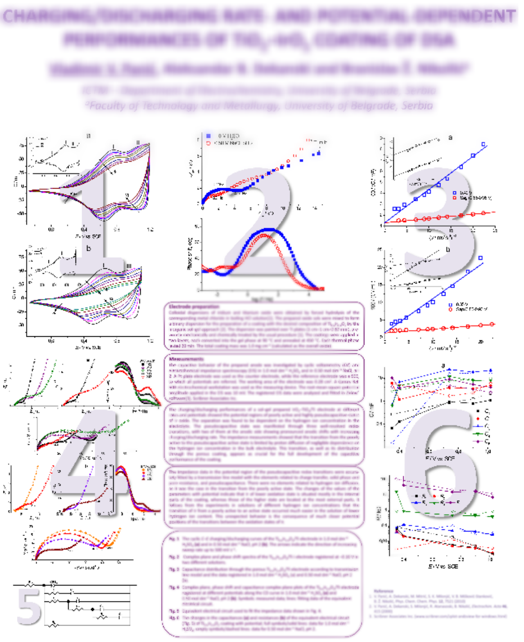

Fig. 1. A well-made poster

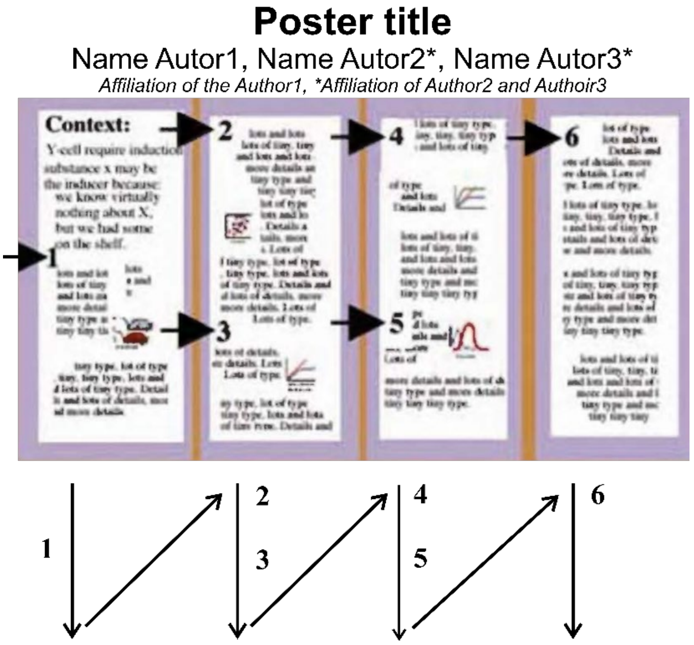

Fig 2. Good order of data presentation

Recycling Expired Midazolam Drug as Efficient Corrosion Inhibitor for Copper in Nitric Acid Solution

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The current work explores the potential of recycling unused or expired Midazolam (MID) drug, a benzodiazepine derivative, as an efficient corrosion inhibitor for copper in nitric acid solution. A quantitative assessment of the inhibition efficiency was made by several methods, including weight loss and polarization measurements, as well as electrochemical impedance spectroscopy. It was found that inhibition efficiency increases with inhibitor concentration, reaching a highest value of 92.9% for a concentration of 10^{-4} M MID. The potentiodynamic polarization curves clearly point to a significant decrease of the cathodic currents and a less important decrease of the anodic currents with increasing concentrations of MID, indicating that MID molecules inhibit preferentially the cathodic processes. Based on the E_{corr} shift, MID was classified as a mixed type inhibitor, meaning it can suppress both cathodic and anodic processes involved in copper corrosion.

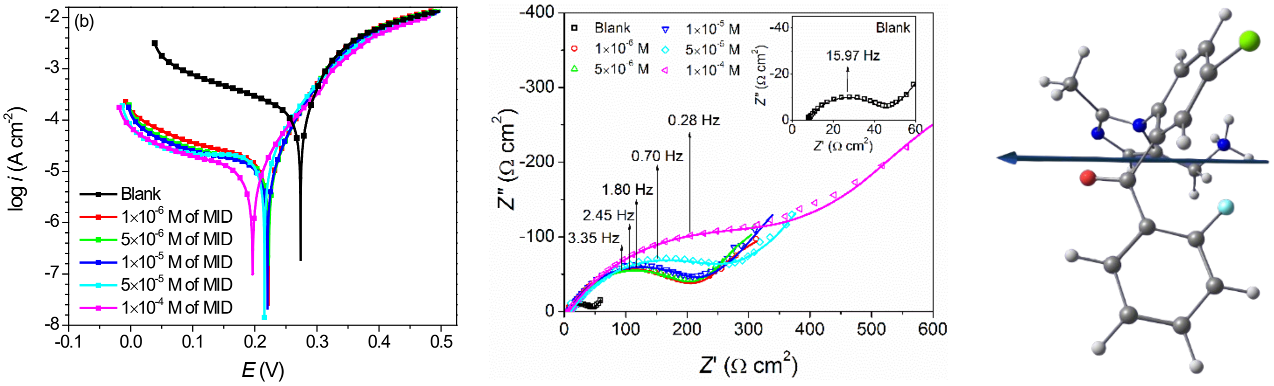

Figure 1. Potentiodynamic polarization curves (a) and electrochemical impedance measurements (b) of copper in 0.1 M HNO_3 in the absence and presence of different concentrations of MID. Optimized molecular structure of MID (c).

Electrochemical impedance measurements show that the charge-transfer resistance has an increasing tendency with the increasing MID concentration, which corresponds to a reduction of the corrosion rate. Furthermore, the diffusion resistance and the diffusion time constant have higher values in the presence of MID, as compared to the blank, meaning that MID molecules also interfere with the diffusion of ions from the solution the copper surface, by forming a barrier that slows down this process.

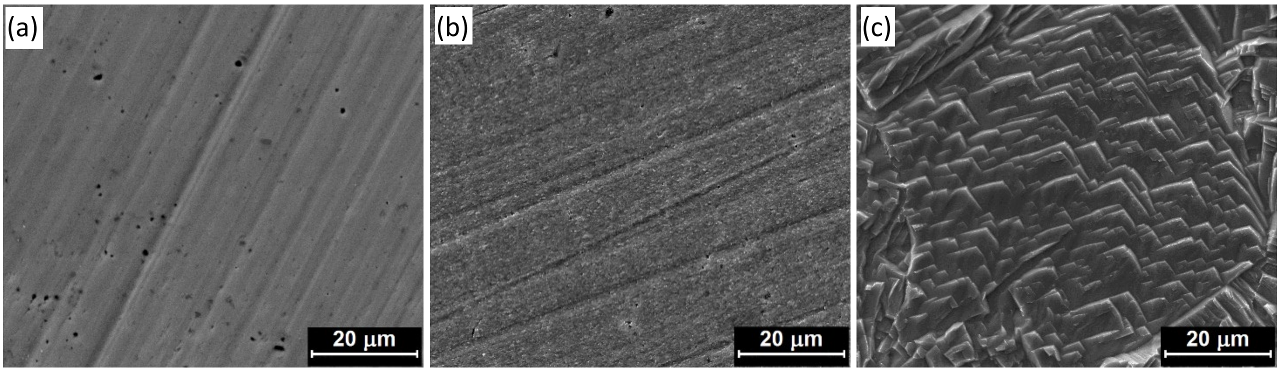

***Figure 2.** FE–SEM images of copper surface: (a) before and after potentiodynamic polarization measurements in 0.1 M HNO_3 solution with (b) 10^{-4} M MID and (c) without inhibitor.*

Quantum chemical parameters were computed and used to explain the inhibition efficiency of MID, such as the HOMO and LUMO energy levels, the HOMO-LUMO energy gap (ΔE) and the dipole moment (μ).

Moisture measurement in the partially saturated area of dyke structures using impedimetric soil sensors

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Due to the effects of climate change, dyke structures will be exposed to increasing demands on their stability. For example, long rainless periods accompanied by irreversible crack formation might be flanked by heavy rain events. Therefore, not only a more critical, prognostic view of the stability of dyke structures will become necessary in future, but also the identification of mechanisms for the early detection of impacts that go beyond the previous design values are desired.

Low-cost impedimetric sensors, embedded in critical areas of the dyke, enable a fast online monitoring of moisture penetration in the dyke construction material, and particularly, an early monitoring of the occurrence of saturation states. Corrosion-free carbon fiber mats are used as electrode materials for the new ground sensors. The practical and long-term suitability of the sensors has been verified with reference methods for moisture determination. The sensors are suited for practical use when installed during renovation or rebuilding of dykes.

The development of the measurement technology at the KSI Meinsberg is accompanied by tests in which the sensors are investigated in experiments on a test dyke at the TU Dresden with specified impounding scenarios up to the dyke failure. The results show that impedimetric sensors can qualitatively map the development water content of dyke construction materials in the partially saturated area in situ.

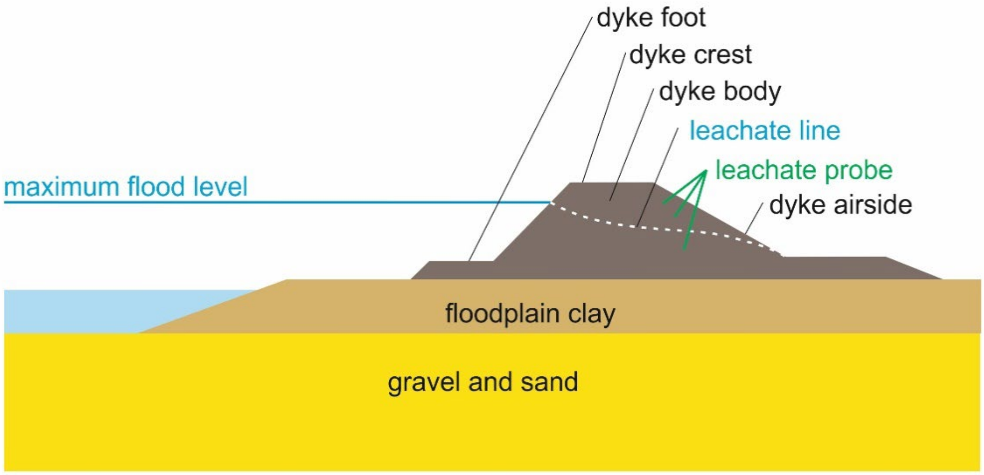

Figure 1: Schematic dyke cross-section.

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Sensor technology for variable, soil moisture-dependent seed placement

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The germination capacity of seeds depends essentially on the soil moisture in the upper layers of farm fields. Due to particular climatic situations or variations in soil composition and quality, significant local fluctuations of water content in soil can be observed. However, since the latter usually depends on the distance from the surface, germination processes can be influenced by the optimally setting of the seed placement depth in the ground.

Here we describe the construction of a sensor-actor system, which allows the measurement of soil moisture in situ during seeding, and thus, enables a local adjustment of the seeding depth dependent on moisture. The humidity degree is impedimetrically measured on site, while the tractor is moving over the farmland. This is possible, because impedance spectroscopy allows rapid measurement of soil moisture. The impedance measurement of soil moisture is accomplished in a tricycle, which is mounted in front of the tractor. In particular, electrically insulated drill discs act as electrodes for measuring the soil moisture. The in-situ determined data is transferred to the seeding machine moving behind the tractor, which facilitates fast adjustment of the seeding depth.

This contribution presents the measurement technique needed to record soil moisture in on-board operation and its field test. The sensors are integrated into an overall system, in which the associated actuators use an electric servomotor to set the optimum processing depth for the cross-plowed soil.

The investigations show, how smart farming methods can be used to create solutions for changed production conditions.

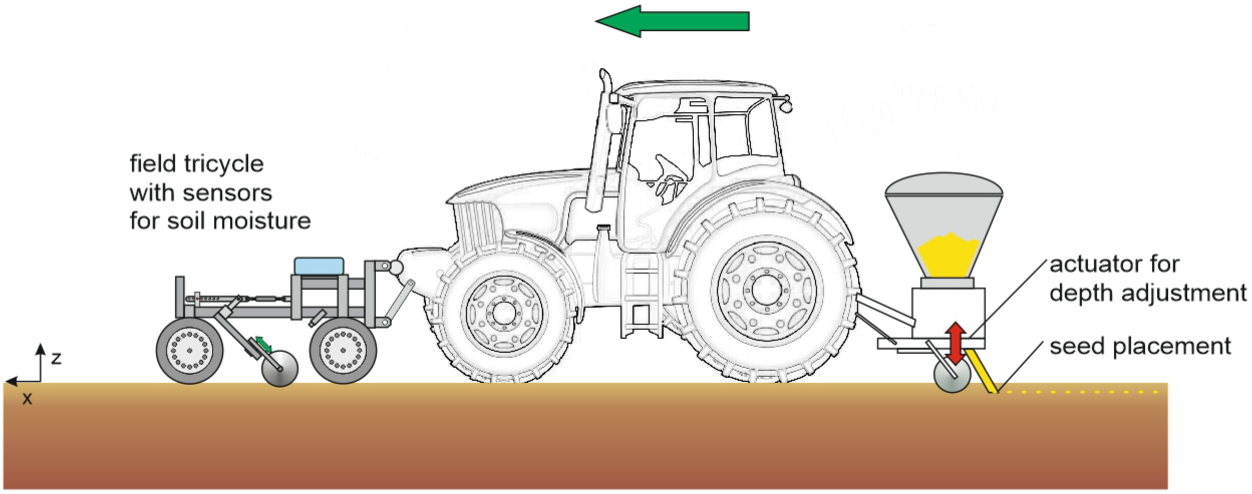

Figure 1: Combination of measuring vehicle for determining soil moisture, tractor and depth-controlled seeding machine.

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Colorimetric method for the determination of fluorine emission rates in PEFC

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The chemical degradation of the membrane leads to the premature end of the life of polymer electrolyte fuel cells (PEFCs). Hydrogen peroxide is a promoter of ionomer degradation, which can occur at the anode side and cathode side at lower or higher current densities, respectively [1,2,3,4,5]. Free radicals of hydrogen peroxide attack the side chains and the backbone of Nafion®, which leads to fluoride and fluorine emissions into the effluent water. Impurities in reactant gases are another source of chemical degradation of the membrane [6, 7]. Accurate determination of the fluorine emission rates indicates how much ionomer has been degraded.

A PEFC with an electrode area of 25 cm² was subjected to a JRC stress test [8]. After a certain number of cycles, comprehensive electrochemical characterizations were performed and effluent water samples were taken. Polarization curves and electrochemical impedance spectra were recorded to investigate the performance losses as well as the changes due to membrane degradation. In addition, linear sweep voltammetry measurements were performed to investigate the hydrogen cross-over current and the thinning of the membrane.

The effluent water was analyzed using a UV-vis spectrometer developed by AiDEXA GmbH. Zr(IV)-SPADNS2 [9] was added to the water samples and the absorption spectra were recorded which was used to determine the fluorine concentration. The results were correlated with the electrochemical measurements to obtain information on the power loss to a given amount of degraded membrane. These results can be used for lifetime estimates.

Acknowledgements

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Interlaboratory Comparison of the Novel Gas Diffusion Electrode Methodologies for Testing Nano-electrocatalysts at High Current Densities

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Low-temperature proton exchange membrane fuel cells (LT-PEMFC) showed great potential for efficient conversion of chemical energy stored in hydrogen to electrical energy. In the last couple of decades, immense progress has been made in the field of development of novel electrocatalysts for oxygen reduction reaction (ORR)[1]. However, most of the catalysts underperformed at the real-life device level. Development of novel methodologies is needed for the purposes of bridging the gap between current screening methods such as thin film rotating disk electrode (TF-RDE) and real-life devices such as fuel cells. We present interlaboratory comparison of several gas diffusion electrode (GDE) methods designed for the purposes of analysing the performance and durability of catalysts for electrocatalytical reactions. One of the methodologies presented is modified floating electrode (MFE), that is designed designed to test electrochemical properties of electrocatalysts at high current densities and scanning transmission electron microscopy (STEM)[2]. With this methodology, it is possible to obtain high-resolution TEM images of the same location of the nanoparticles before and after applying the electrochemical protocol.

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Development of a Co-Simulation Concept to Account for Multiphase Transport in Polymer Electrolyte Membrane Fuel Cells

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Polymer electrolyte membrane fuel cells (PEMFC) convert energy, which is stored in fuels to electrical energy, whereby the running redox processes are separated with an ion exchange membrane. A central challenge in optimizing PEMFC performance is the supply of the catalyst layer with gaseous fuels or oxidants and the removal of formed liquid products like water in the gas diffusion layers. For optimizing gas diffusion layer structure, on the one hand experimental assessment, on the other hand modelling the multiphase transport are needed to gain fundamental insights. Here, a concept for a co-simulation of detailed multiphase transport within a representative element of the gas diffusion layer coupled to an overall 1D simulation of the membrane electrode assembly (MEA) of a low temperature PEMFCs operated with hydrogen as fuel is introduced. A fast, 1D model of a MEA based on the groundwork of Vetter and Schumacher[1], is thus linked to a detailed multiphase transport model using the hybrid interface resolving two fluid model approach from Marschall and Hinrichsen.[2]

The co-simulation consists of three parts. First, a very fast, transient and one dimensional model for fuel cell performance is implemented. This pseudohomogenous approach accounts for electric losses in electrode and electrolyte, temperature profile, mass transport due to Fick-diffusion mechanisms and the water management in the membrane as well as in the gas diffusion layers. For the anode and cathode kinetics, Butler-Volmer equation is employed. Within this simulation a potential scan from the electrode potential (Nernst equation) to 0 V and the calculation of the resulting current density is realized. The resulting polarization curve shows all domains from kinetic losses at high potential, over the resistance losses due to mass and heat transfer, up to the mass and heat transfer limitation at low potential. Next, a modelling approach for multiphase flow is implemented. In this hybrid interface-resolving two fluid model by Marschall and Hinrichsen[2] the two-phase flow features are grouped in unresolved and resolved portions, like it is known from large eddy simulation for turbulence modelling, which leads to a stable method. This approach will be used to model two phase flow in cathodic gas diffusion layers in a PEMFC and investigate gas diffusion layer structure. The third part is the connecting process. Linking the two solvers with preCICE[3] enables us to let them communicate with each other and exchange parameters, data mapping or coupling schemes for each time step (Fig. 1). With that, a combined model for investigation of two phase flow in gas diffusion layer with a relative low calculation time can be achieved.

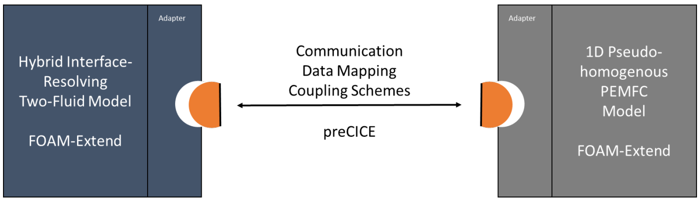

Figure 1 Co-Simulation Scheme.

Currently the 1D model has been successful implemented and validated in Comsol Multiphysics® and parameter variations to study transport and kinetic influences on fuel cell performance has been done. The model is translated currently to FOAM-Extend and validated against the Comsol model. Linking via preCICE the 1D Model in FOAM-Extend with the existing two fluid model will be carried out with simple model 3D mesh structures.

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Physicochemical and electrochemical characteristics of novel aqueous electrolytes for hybrid capacitors

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The application of aqueous electrolytes is advantageous in electrochemical technologies for their unique features like being eco-friendly, non-flammable and safe. Additionally, they have higher ionic conductivity than those of nonaqueous ones as well as low raw material and manufacturing cost [1, 2, 3]. However, one of the major shortcomings of aqueous electrolytes is their low operating voltage, which limits the energy density of device. Tuning the interactions among ions and solvents in electrolyte have been explored as one of the effective way for high voltage operation of electrochemical capacitors [4,5]. To this end, several water-in-salt, water-in-bisalt, bisalt-in-water, and hydrate melt, have attained a soaring attention very recently for electrochemical energy storage due to their enriched stability and much-enlarged electrochemical stability window [3]. However, the proper understanding of the fundamental ion-water interaction mechanisms and their correlation with supercapacitor performance has not been widely explored yet.

For that reason, we investigated several aqueous electrolytes for disclosing the fundamental ion-water interaction to correlate their physicochemical and electrochemical characteristics with supercapacitor performance. Firstly, electrolytes were prepared by varying the concentration of $NaNO_3$, NaI, $Na_2MoO_4{\cdot}2H_2O$, combination (bisalt-in-water) of $NaNO_3$ and 0.5M NaI, combination of $Na_2MoO_4{\cdot}2H_2O$ and 1M $NaNO_3$. Then, different fractions of ethylene glycol (EG) were added into 1M $NaNO_3$ into water (W) to explore the interaction of ion and solvents. Water-in-salt electrolyte was prepared from choline chloride. The ionic conductivity of electrolytes is determined by electrochemical impedance spectroscopy and compared with values obtained from conductometer. For different concentration of $NaNO_3$ the pH values were almost unchanged. At lower concentration both NaI and $Na_2MoO_4{\cdot}2H_2O$ was almost neutral which gradually turned into alkaline with increasing concentration. For varying concentrations of $NaNO_3$ into 0.5 M NaI the pH was almost unchanged. With increasing concentration of $Na_2MoO_4{\cdot}2H_2O$ into 1 M $NaNO_3$, the pH got higher. Interestingly, for water-in-salt electrolyte of choline chloride the pH level was also almost identical/neutral (pH of 0.5 mol/kg and 20 mol/kg solutions is 7.1 and 8.5, respectively). For all salt or/and bisalt-in-water electrolytes, conductivity was found to be increased with increasing concentration. With addition of EG fraction into 1 M $NaNO_3$ the conductivity was linearly decreased. Interestingly, for water-in-salt electrolyte of choline chloride, with increasing concentration, the conductivity firstly increased and then decreased with a maximum at 5 mol/kg (97.6 mS/cm). Forthcoming study includes the determination of iconicity, and electrochemical stability window of the electrolytes and correlating those with the hybrid supercapacitor performance.

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Development of a state of charge and state of health measurement sensor for vanadium redox flow batteries

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Vanadium redox flow batteries (VRFBs) are a promising technology for stationary long-term energy storage, because of their independent scalability of power and capacity and potentially high life cycle. VRFB operation is accompanied by capacity loss and half-cell imbalances caused by side reactions and crossover through the membrane [1]. In commercially operated VRFB systems the state of charge (SOC) is estimated using the Open-Circuit-Voltage or via coulomb counting. With these SOC monitoring methods electrolyte imbalances cannot be detected and states of high side reactions cannot be avoided. A sensor which measures the SOC of both half-cells independently and a thorough understanding of the crossover through the membrane is needed to reliably describe the state of health (SOH) of the VRFB.

In this work, we introduce our approach for the development of a SOC/SOH sensor for VRFBs and for the investigation of the electrolyte crossover. For the sensor development, we combine new and standard SOC and SOH related quantities in one test rig to identify the quantities most suited for this task. In preliminary works, we established two SOC and SOH monitoring methods, one based on electrolyte half-cell potentials and one via electrolyte density [2,3]. In addition to that, we implement in situ SOC monitoring for both half cells based on UV/VIS absorbance spectroscopy, electrolyte pH-value and electrolyte viscosity via pressure drop measurements. Imbalances will be measured based on a fill level measurement installed in the tanks and quantified via potentiometric titration. On this poster, we present first results of the SOC monitoring calibration.

Acknowledgements

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Electrochemical oxidation and superoxide radical scavenging activity of 2-hydroxy/methoxy phenylbenzothiazole derivatives

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Benzothiazoles are among the most important nitrogen heterocyclic compounds, frequently found in many molecules of interest in medicinal chemistry. Their derivatives are possessing diverse biological activities such as anticancer, cardio-protective, anti-inflammatory, anticonvulsant, antifungal, antibacterial, antiprotozoal activities, etc. Recently, amidino-substituted benzothiazole derivatives substituted with the variable number of hydroxyl and methoxy groups have shown to possess antioxidant activity, by using DPPH, ABTS and FRAP spectrophotometric methods [1,2]. As a continuation of the study reported by Racané et al., the present study was aimed to elucidate the redox chemistry behind the antioxidant activity of amino/amidino-substituted 2-hydroxy/methoxy phenylbenzothiazoles. The kinetics and mechanism of electrochemical oxidation of compounds of interest (compounds 1-4, Fig.1) were studied by means of square-wave voltammetry (SWV) in aqueous electrolyte solution (0.1 mol/L KNO_3) at a glassy-carbon electrode (GCE) over a wide range of pHs (pH 1–11) and SW frequencies (8-1000 Hz). We have shown that the studied compounds incorporate electron-transfer (ET) moieties which may play important role in their antioxidant activities. The oxidation mechanism of compounds 1-3 is related to an oxidation process taking place on the hydroxyl groups located at 2-phenyl ring. The electrochemical behaviour of compound 4 (without –OH groups on the phenyl ring) proved more complex and further studies are in progress to elucidate the functional groups responsible for electroactivity and antioxidant activity of 4. Furthermore, we studied the reactivity of compounds 1-4 against electrochemically generated superoxide anion radical by the means of cyclic voltammetry. The superoxide radical scavenging activities of compounds 1-4, determined by measuring the anodic current decay of the radical in the presence of increasing concentrations of compounds of interest, were expressed in terms of EC50 values, i.e. the concentration of compound needed to consume 50% of a superoxide radical. All four compounds showed a more or less pronounced superoxide radical scavenging activity, depending on their structural features. Superoxide radical scavenging activities of compounds correlated well with their electrochemical oxidation potentials, implying that the scavenging activity of investigated compounds is mainly governed by their redox properties.

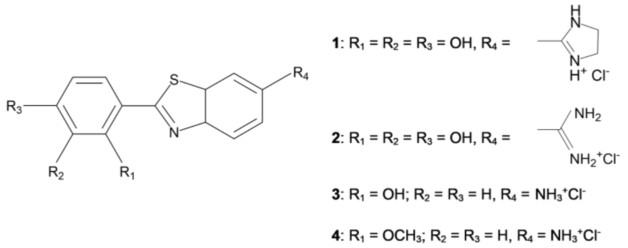

Fig. 1. Chemical structures of the investigated amino/amidino-substituted 2-hydroxy/methoxy phenylbenzothiazoles.

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Sol-gel coatings on cast aluminium-silicon alloys for marine exposure

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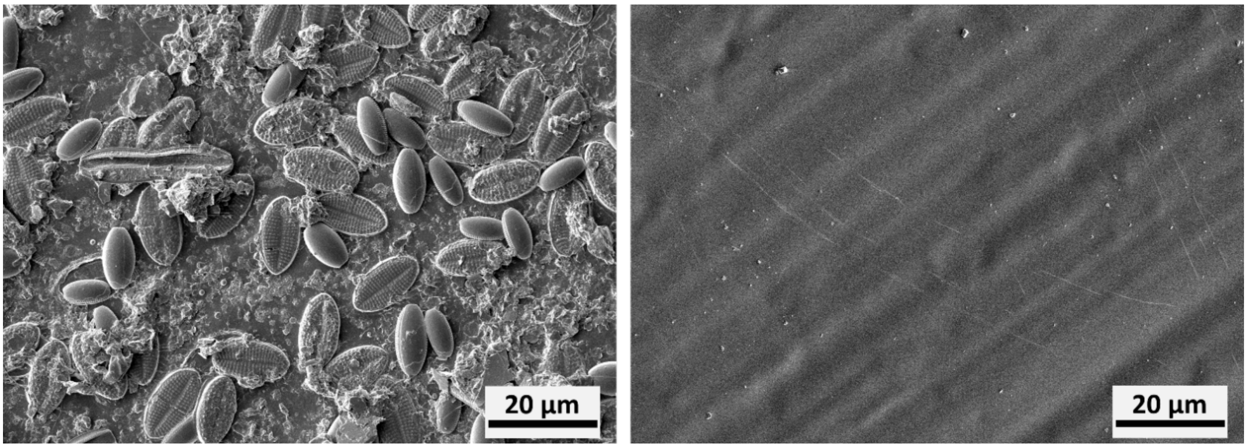
Biofouling refers to the accumulation of living organisms on submerged artificial surfaces immersed in seawater. It includes the formation of conditioning film, micro- and macrofouling.[1] This process is undesirable for ships in motion because it increases fuel consumption, reduces propeller power and top speed; for stationary fixed and floating structures, it reduces structural integrity, increases weight and causes corrosion damage. Therefore, artificial surfaces should be chemically protected by antifouling paints and coatings and cleaned mechanically to remove the biofilms. Design of new coatings with targeted properties of efficient antifouling and corrosion resistance, prolonged service lifetime and reduced ecological impact is essential for metal alloys aimed at marine applications.

This study focuses on two cast alloys: Al-Si7-Mg0.3 and Al-Si9-Cu3(Fe). Substrates were used coated with two types of synthesized sol-gel coatings: epoxy- and acrylate-based. After immersion for 8 months in seawater, the samples were characterized in composition, thickness and microstructure (FE-SEM/EDXS, XPS and GDOES), and electrochemical and protection properties. Sol-gel coatings act as a corrosion barrier and decrease the level of biofouling.



SEM images of Al-Si7-Mg0.3 coated with ZG coating after 1 month of immersion in the Adriatic Sea before (left) and after (right) sonication to remove the biofilm.

Acknowledgements

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Pencil Graphite Electrodes Decorated with Platinum Nanoparticles as Efficient Electrocatalyst for Hydrogen Evolution Reaction

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Platinum-based materials are state of the art electrocatalysts for the hydrogen evolution reaction (HER). However, due to the high cost and scarcity of platinum, strategies are searched to reduce the platinum amount. In our work, pencil graphite (PG) leads have been decorated with Pt nanoparticles (NPs) to obtain very efficient electrodes for HER. PG is an affordable carbon-based support, highly available and very cost-effective. The main challenge for developing Pt electrocatalysts is to achieve as low as possible catalyst loading, while still preserving the electrocatalytic properties. This can be realized by using suitable deposition methods, such as pulsed current electrodeposition, which enables the formation of NPs with a narrow size distribution, highly dispersed on the PG support. We investigated the effect of current density during pulsed current electrodeposition of Pt on the morphology and performance of the electrocatalyst for HER.

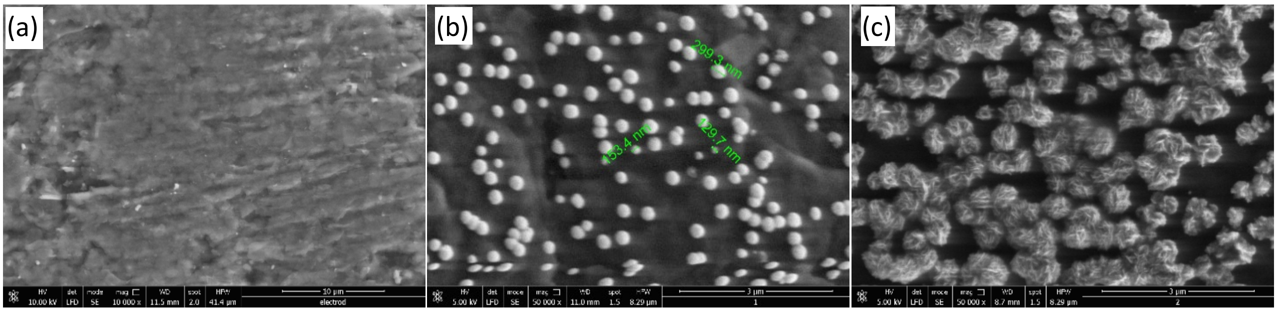

Figure 1. SEM micrographs of bare PG substrate (a) and of Pt-PG electrodes obtained by pulsed current deposition from 5 mM H_2PtCl_6 in 1 M HCl solution, at different current densities: 5 mA cm^{-2} (b) and 25 mA cm^{-2} (c).

The results showed that deposition at low current density leads to spherical nanoparticles, and then the morphology gradually changes to flower-like structures as the current density increases. The electrocatalytic activity towards HER is affected by both morphology and catalyst loading.

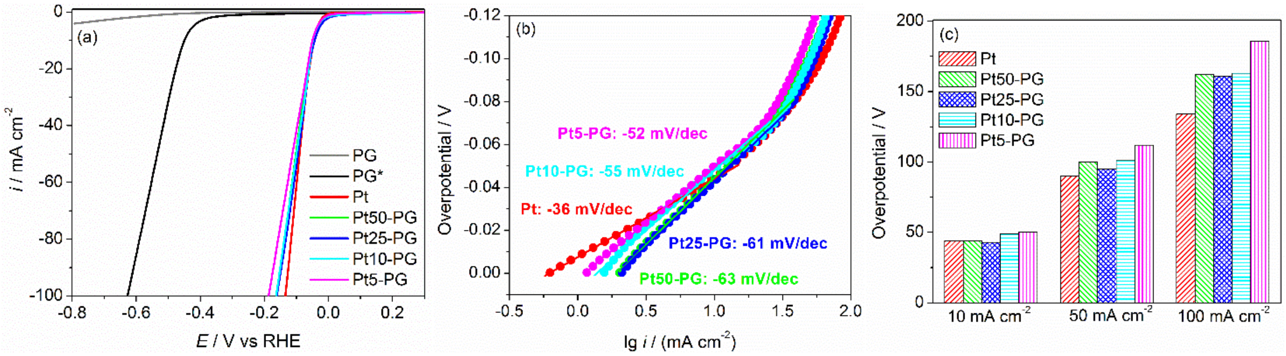

Figure 2. Polarization curves in 0.5 M H_2SO_4 solution at scan rate 50 mV s^{-1} (a). Tafel plots of Pt and Pt-PG electrodes (b). Required overpotential to reach a current density of 10, 50 and 100 mA cm^{-2} for Pt and Pt-PG electrodes (c).

The electrode with 250 µg cm^{-2} Pt loading revealed the best electrocatalytic activity, at both low and high current densities, needing only an ultralow overpotential of 43 mV to reach a current density of 10 mA cm^{-2}. This work has been published: Materials 2022, 15, 73. https://doi.org/10.3390/ma15010073

A robust electrode arrangement with a glassy carbon working electrode for sulfite detection

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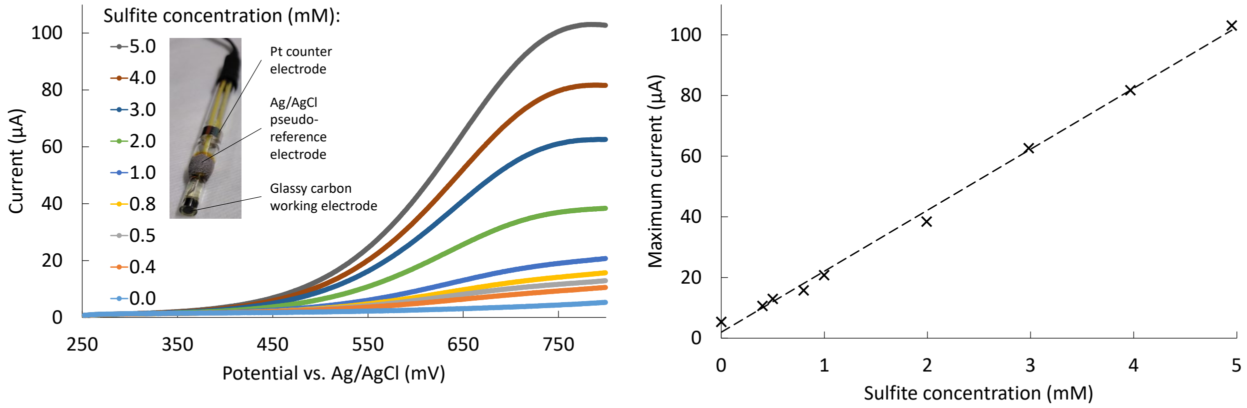
Sulfur dioxide is a gas which is formed in many industrial processes when coal or oil are used as fuel [1]. It is readily soluble in water and forms sulfite ions (SO_3^{2-}). Furthermore, sulfite is a common preservative for foods and beverages. Thus, it is an analyte of interest to be monitored with respect to human health [2].
In this work, linear sweep voltammetry is used for the detection of sulfite (SO_3^{2-}) in seawater. To this aim, a robust electrode arrangement was developed in glass with a glassy carbon electrode as working electrode, an Ag/AgCl pseudo reference electrode and a platinum ring as a counter electrode (Figure inset, left). The advantage of this arrangement is the robust geometry of the electrode in one glass body being suitable for application in chemically harsh environment like extreme pH values and high salt concentrations. The presented electrode arrangement, without any internals liquids for the reference electrode, was applied to detect sulfite in seawater by means of linear sweep voltammetry. Therefore, a stock solution of 500 mM Na_2SO_3 was repeatedly added to a sample from the Norwegian Sea. The current was recorded during the potential sweep of 1 V/s from 250 mV to 800 mV (Figure, left). A linear relation of the maximum current as a function of the sulfite concentration up to 5 mM could be determined (Figure, right).



Linear sweep voltammetry in a sample from the Norwegian Sea with repeated additions of Na_2SO_3 (left) using the electrode arrangement in glass (left, inset). Maximum currents in the linear sweep voltammetry curves as a function of the sulfite concentration.

Additionally, the identical electrode arrangement can be used to determine the conductivity of the sample by measuring the electrical impedance. Both the working and the counter electrodes are robust enough for numerous mechanical, chemical and electrochemical cleaning processes. This allows for electrochemically reproducible starting conditions, especially for voltammetrical measurements. Finally, the developed electrode arrangement is supposed to be applicable for long-time electrochemical monitoring in industrial and environmental water samples.

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Yeast pheromone-based amplification system for diclofenac detection

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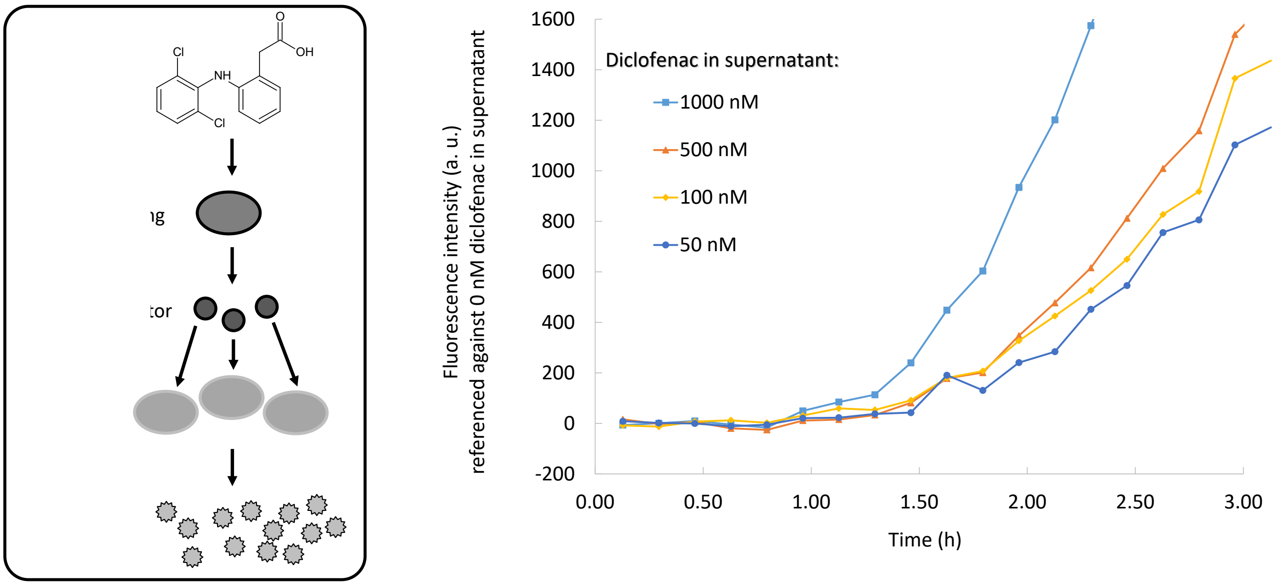
Pharmaceuticals and their metabolites in the environment are a worldwide problem, as these substances can be potentially harmful to health [1]. The aim of the presented work is the development of a sensor principle based on genetically modified yeast cells [2]. These yeasts are supposed to detect diclofenac in environmental samples [3, 4]. The used sensor principle (Figure, left) is based on the formation of the yeast pheromone (α-factor) by a genetically modified sensor yeast strain producing the α-factor in the presence of diclofenac. Subsequently, the α-factor leads to activation of a promoter in a reporter strain, resulting in the formation of a fluorescent protein [5].

Practically, suspensions of sensor yeast with different diclofenac concentrations are prepared. After 4 h incubation time, the α-factor is formed and is present in the supernatant of the centrifuged sensor cell suspensions. The addition of these supernatants to suspensions of the reporter yeast leads to the formation of the fluorescence protein (Figure, right). The described method can detect diclofenac concentrations of less than 50 nM within 6 h starting from the incubation of the sensor cells until a significant increase of the fluorescence signal in a reporter cell suspension is observed.



Scheme of the pheromone-based amplification system (left). Kinetics of referenced fluorescence intensity as a function of diclofenac concentration in the supernatant of the sensor yeast suspensions (right).

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Assessment of hollow-wire-corrosion by electrochemical methods

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Hollow-wire-corrosion (HWC) is a phenomenon particularly related to stainless steel (SS) wires of cables exposed to marine environment [1]. As the name implies, it is characterized by anodic dissolution of the metal in the inner of the wire, progressing axially, leaving behind a long, hollow, tube-like and fragile structure, see Figure 1a in cross section.

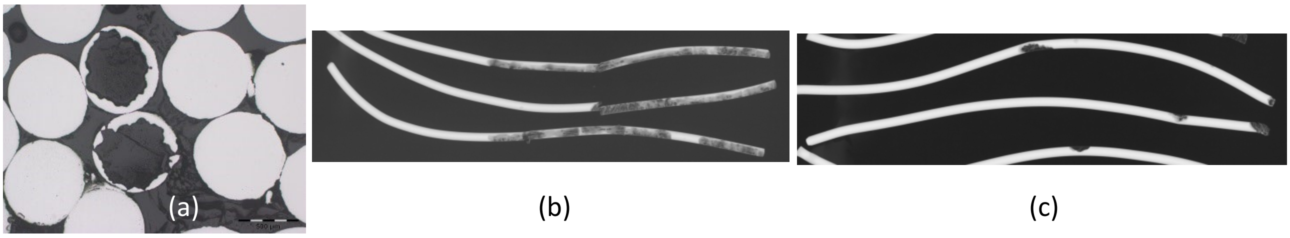
This research was triggered by unexpected HWC at cables used in mooring systems for floating platforms in shallow tropical waters. These cables were made from austenitic SS type X5CrNiMo17-12-2 (1.4401, AISI 316) and different production lots showed gradually different degrees of damage. Wires of 600 µm diameter from three such cables (#A1, #A2, #A3) and, for comparison, from an unused cable made by another producer (#C) with identical product specification, were included in this study. Their chemical composition was verified to comply with the nominal alloy composition.

It was the aim of this work to develop an electrochemical test method which replicates the characteristics of HWC, considering the practical environment (seawater) under realistic redox conditions (oxygen, biofilm), and which allows discriminating wires of gradually different susceptibilities to this phenomenon. Artificial seawater (DIN 50905-4) was used as electrolyte and experiments were carried out with wires, or with wires embedded in resin and cross sectioned, as working electrodes.

Potentiodynamic measurements indicated the pitting potential (E_{pit}) at ca. +590 $mV_{Ag/AgCl}$ for all types of samples, and did not replicate HWC. Potentiostatic tests at potentials above E_{pit} did neither replicate the axially oriented progress of HWC, just regular pitting corrosion was observed with all samples. Consequently, a potentiostatic switching procedure was established, using ca. 40 mm long wires immersed vertically ca. 10 mm deep in the electrolyte:

First, pitting corrosion is initialized by harsh polarization to +750 $mV_{Ag/AgCl}$ for 3 hours with a current limitation to 1.2 mA. Then, the potential is switched to +400 $mV_{Ag/AgCl}$, which is safely above what can be expected from marine biofilms, and the potential is held for 24 hours while the current, limited to 1.2 mA, is recorded. Based on the current-time-record, either the time to repassivation, or the total anodic charge may be used as quantitative measures for HWC susceptibility of a wire.

By using an 8-channel-potentiostat [2], parallel testing is facilitated, which allows applying statistics for discriminating reliably the susceptibility of wire products to HWC in the marine environment. X-ray photographs of tested specimens verified the HWC-characteristic attack achieved by this method, and demonstrates different susceptibility of wires from different producers, see Figure 1b, c.



(a) (b) (c)

Figure 1: Cross section of a HWC damaged cable (a). X-ray photos after testing of wires #A1 being highly susceptible to HWC (b), compared to wires #C not prone to HWC under identical test conditions (c). Wire diameter ca. 600 µm.

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Paper-based electrodes for immuno sensing

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The analytical demands in many areas including every-day life situations have increased the need for easy and quick bioanalytical detection devices with a high accuracy and low costs [1,2]. Electrochemical biosensors provide a great promise for the utilization in point-of-care diagnostics since they are simple, cheap in operation and portable. Here paper-based sensors have become more and more in the focus of research and industry. The implementation of electrochemical methods in paper-based systems holds some interesting features, making them attractive as analytical tool. Paper materials are commercially available in various compositions and thicknesses, are biodegradable and environmentally friendly, and thus, well-suited for disposable systems. Due to the hydrophilicity and the high porosity, paper is nicely suited for the fabrication of microfluidic channels, which can be operated without external fluid control. Moreover, the paper surface can be modified by different techniques such as printing and coating of chemicals or biomolecules.

This study will demonstrate some basic electrochemical characterization of paper-based electrodes needed for the elaboration of an analytical test system. Therefore, a carbon working electrode and a combined silver counter/reference electrode has been printed onto paper strips using a screen-printing procedure. Fluidic channels are defined by a wax printing process. This 2-electrode arrangement has been applied for an amperometric detection scheme and has resulted in a defined faradaic response, when a redox mediator is added to the paper. In order to investigate the possible application in antibody-based analysis, a model test system has been tested on the paper-based electrodes. Therefore, a capture antibody has been immobilized on the paper fibers and subsequently the binding of a signalling antibody modified with an enzyme has been monitored electrochemically. Initial experiments suggest that the paper-based electrodes can clearly discriminate between the analyte and control samples. Thus, application for detection of bacteria species can be envisaged.

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Phenol removal from wastewater by electro-Fenton process

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In addition to electrooxidation, electro-Fenton is one of the most popular and most efficient electrochemical advanced oxidation processes in wastewater treatment. This research is based on the oxidation of phenol and the examination of various process parameters by using electro-Fenton processes. The study was performed in a batch electrochemical reactor capacity of 400 mL and with the possibility of constant stirring. Model wastewater contained 50 mg/L of phenol, and sulfuric acid was used as supporting electrolyte (electrical conductivity ≈3 mS/cm, pH≈2.5). The influence of different anode materials was examined: boron doped diamond (BDD), mixed metal oxides (MMO) anodes - Ru mixed oxide on a titanium substrate (Ru-MMO) and Ir-Ru mixed oxide on a titanium substrate (Ir-Ru MMO). The useful area of BDD and MMO anodes was approximately 52 cm^2. Also, the influence of different current density (2.5 - 10 mA/cm^2), cathode material and catalyst concentration (c_{Fe2+} = 0.05 - 0.5 mM) on the phenol removal efficiency was investigated. After 180 minutes of treatment 93.8% of phenol and 75% of total organic carbon (TOC) was removed by applying a BDD anode at a current density of 2.5 mA/cm^2 and at catalyst concentration of 0.1 mM. Under these experimental conditions energy consumption was 3.49 kWh/m^3 of treated water.

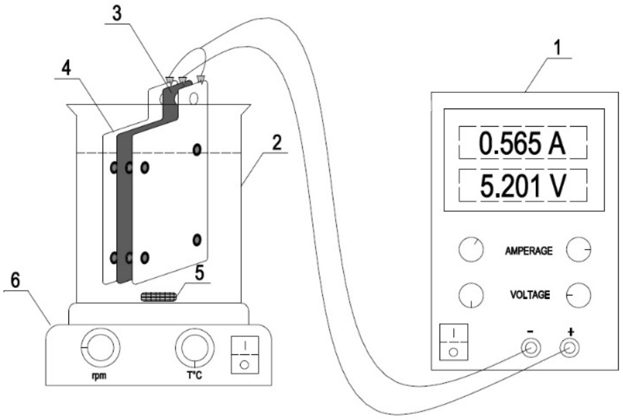

Figure 1. Scheme of a laboratory batch reactor: 1 – source of electric power; 2 – electrochemical cell; 3 – anode; 4 – cathodes; 5 – magnetic stir bar; 6 – magnetic stirrer/heater.

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Comparative study of bi-functional catalysts for GDE with application in Zn-Air batteries

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Rechargeable Zn-air batteries have received a lot of attention in the last few years as a promising technology for electrical storage and regeneration of renewable energy systems because of their high specific energy, great availability and low-level pollution. The poor zinc electrode reversibility and unstable bifunctional air electrode are the issues which have to be eliminate before the fully commercialization of the system. Current efforts to avoided the problems associated with gas diffusion electrode (GDE) involved optimization in terms of materials, ratio between them, microstructure and technology for the electrode preparation and configuration. The both layers the porous gas-diffusion layer GDL, which serves for oxygen transport, and the catalytic (active) layer (CL), which ensures the electrochemical reaction (reduction of oxygen during charge and oxidation, i.e. releasing oxygen during charge), also reviewed the major developments leading to improvements of each of the components, but the most attention being paid to the type of catalysts. In this paper we examine and compare the behavior of two potential candidates for GDL fabrication, namely perovskite type catalysts (Lanthanum Strontium Manganite, LSM and Lanthanum Strontium Cobalt Ferrite, LSCF) and spinel transition-metal oxides (Ni/Co_3O_4 and $NiCo_2O_4$) in respect to their stability and catalytic activity. Using typically carbon-based material carbon black (Vulkan XC-72) and the most commonly applied hydrophobic bonding material, polytetrafluoroethylene (PTFE) as gas-diffusion layer, the GDEs are fabricated by hot pressing with the abovementioned catalysts and PTFE binder on a porous stainless steel. Volt-ampere characteristics, charge/discharge tests and impedance measurements were performed at room temperature in a 6M KOH electrolyte in a half cell configuration with RHE reference electrode and stainless steel counter electrode. The results were compared with state-of-the-art carbon based GDE (Teflonized carbon blacks, Ag/Co_3O_4 catalyst, PTFE) and it was confirmed that the two types of investigated catalysts can successfully replace the classic catalysts containing precious metal. The combination of volt/ampere characteristics and impedance measurements/analysis determines very precisely oxygen transport limitations through the gas-diffusion electrodes, which are one of the main reasons for the air electrode failure. A future optimization direction is resulting.

Acknowledgements

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Hybrid nanoparticles for exploitation of surface plasmon effects in photoelectrochemical sensing

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Semiconductor nanostructures are valuable tools in developing light-triggred electrodes. Areas of application of such systems can be seen in sensing and biosensing, but also in bioenergetics. By illumination charge carriers are generated inside the semiconductor material which allow reactions to occur at the surface and electron transfer to the underlying electrode [1]. One of the distinct advantages of such photoelectrochemical detection schemes can be seen in the improved potential behaviour since the energetic state of the charge carriers is changed upon interaction with light.

On this basis we have already developed a number of light-sensitive electrodes [2-5]. In this study we combine properties of CeO_2 nanoparticles related to the catalytic conversion of hydrogen peroxide with the transduction ability of these semiconductor particles for photoelectrochemical sensing. The excitatation of CeO_2 is however limited to the UV range of the spectrum. In order to extend the excitation range we have used hybrid particles with an Au part (Au/CeO_2 core shell nanoparticles). These particles have been immobilized on modified gold electrodes resulting in the generation of photocurrents upon illumination. The direction of current flow can be controlled by the applied dc potential. We can clearly observe a higher photocurrent for the hybrid particles compared to pure CeO_2 particles immobilised on the gold electrode. Wavelength dependent measurements demonstrate that the excitation of surface plasmon states inside the gold nanoparticles can be exploited for photocurrent generation in the visible range of the spectrum although the gold particles alone do not result in photocurrent generation and CeO_2 can not be excited at these wavelengths [6]. We can also demonstrate that such improved usage of light can also be achieved with other types of semiconductor/metal hybrid nanoparticles.

We have applied these Au/CeO_2 hybrid particles - modified electrodes for hydrogen peroxide detection. Thus, we can show the usefulness of this construction principle with this model analyte. When comparing pure CeO_2 and hybrid Au/CeO_2 particles similar electrochemical activity with respect to hydrogen peroxide reduction has been detected (in the absence of light). However, the photoelectrochemical cathodic response with a white light source is significantly enhanced with the hybrid particles. By means of the layer-by-layer technique the amount of immobilised nanoparticles can be enhanced and consequently the response can be increased with higher layer numbers in a defined way. For example, with a 5-layer electrode (Au/CeO_2) H_2O_2 detection down to 3 µM with a linear range up to 2000 µM is feasible.

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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/energy dispersive X-ray spectroscopy. It turned out to be essential analyzing 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/energy dispersive X-ray spectroscopy, secondary neutral mass spectrometry, and X-ray photoelectron spectroscopy. The consistent results provide the basis for a reliable interpretation of electrochemical impedance data recorded during soaking.

Acknowledgements

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Cu sub-monolayer decorated Pd/C and Pt/C as electrocatalyst for ethanol oxidation in alkaline solution

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Easy storage and handling, high energy density, wide availability, and low toxicity are features that make ethanol attractive fuel cell liquid combustibles and the most promising among alternative power sources [1,2]. Unfortunately, the slow and incomplete ethanol oxidation reaction (EOR) occurs at the anode even on the best available catalysts known to date. Pure Pt and Pd are not capable of catalyzing the oxidation of ethanol through the total oxidation pathway [2]. However, Pt and Pd are necessary catalyst constituents to provide efficient adsorption of ethanol, which is the first reaction step in ethanol oxidation. The activity of Pd and Pt for alcohol oxidation can be enhanced by adding a co-catalytic element, mainly oxophilic metal (either d- or p-metals), or compounds such as oxides [3]. Therefore, in the present work, the influence of Cu sub-monolayers decoration of carbon-supported Pd and Pt nanoparticles was investigated for ethanol oxidation reaction (EOR) in the alkaline solution.

Commercial Pt/C (E-TEK®) and Pd/C catalyst synthesized by borohydride reduction method [4] were electrochemically characterized by cyclic voltammetry and CO_{ads} stripping in acid and alkaline solutions. The onset potential and the peak potential of CO_{ads} oxidation on Pd/C were more positive than those for Pt/C in both solutions, indicating lower oxophilicity and/or stronger bonding with CO_{ads} in the case of Pd than Pt. Catalysts were decorated by underpotential deposition of Cu atoms (Cu_{upd}) in acid solution with various surface coverages (up to 0.5). Electrochemically active surface area (ECSA) of undecorated catalysts was calculated from the charge of desorption of CO and Cu_{upd} in acid solution, while ECSA of Cu_{upd} decorated catalyst was calculated from the charge of CO desorption in alkaline solution. Cyclic voltammetry showed that on the Cu_{upd} decorated surfaces the onset of CO desorption was negatively shifted. This indicates that Cu_{upd} atoms provide oxygen-containing species at adjacent Pt or Pd sites at a lower potential than that achieved on pure metals.

The influence of Cu_{upd} decoration of the Pt/C and Pd/C catalysts on activity for EOR in 0.1 M KOH was investigated under potentiodynamic conditions. Although the onset potential was the same, Pd/C was more active for EOR than Pt/C with the 1.5-fold enhancement of maximum current. Pd/C with Cu_{upd} coverage of 0.30 exhibited lower onset potential and up to 2.5-fold increase in EOR activity with respect to Pd/C (calculated per Pd ECSA). However, with further increase in coverage the positive effect of Cu_{upd} disappeared and activity even decreased. In the case of Pt/C the promotion effect of Cu_{upd} was negligible, because only the catalyst with coverage of 0.11 showed lower onset potential and slightly higher current at low potentials. The higher EOR activity of Pd/C compared to Pt/C can be attributed to the optimum oxophilicity of Pd which provides ample space for adsorption of ethanol and still provides oxygen containing species for its oxidation. Decoration of Pd/C by 0.3 monolayer of Cu_{upd} increases the amount of oxygen containing species that intensify ethanol oxidation rate on Pd.

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Polyaniline coated carbon in PEMFC

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Hydrogen based technologies such as fuel cells, are a prominent energy-based approach for achieving the 2030 climate target plan. In the automobile and heavy-duty transportation sector, polymer electrolyte membrane (PEM) fuel cell has shown high potential to replace the combustion engine. However considerable lifetime enhancements of the components must be achieved to satisfy the demand for low cost and durability.

One of the major degradation mechanisms is the corrosion of the carbon used as catalyst support and in the gas diffusion layers. The catalyst is present in the cathode and anode catalyst layer of the MEA and is a crucial link in facilitating the reaction of hydrogen and oxygen. In this master thesis, the aim is to optimize the catalyst to increase the lifetime and the activity of the catalyst towards proposed technical targets. For this reason, polyaniline coating of the carbon was studied as a promising way of increasing corrosion resistance without using potentially problematic transition metals.

The catalyst is prepared by varying the composition of the aqueous synthesis solution, aniline to carbon ratio and the type of used carbon. The effect on the corrosion resistance and activity of the catalyst was studied. The activity for oxygen reduction reaction and the ECSA (electrochemically active surface area) is determined by the RDE-CV measurements and an accelerated stress test protocol is specifically designed for the task of comparing the corrosion resistance.

Flexibility and Rigidity of Molecular Rods Induced by Electron Transfer

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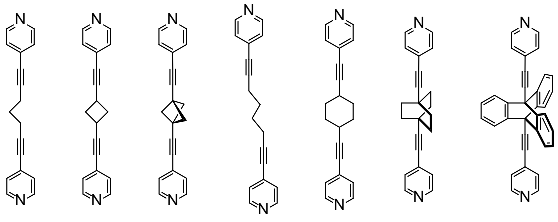
Long new molecular rods have two terminal 4-ethynylpyridine groups (Figure 1). Their alkyl conection determines a different structural rigidity or conformational flexibility. Bridges have single, double or triple connectors in parallel: propyl, 1,3-cyclobutyl, 1,3-bicyclo[1.1.1.]pentyl, 1,4-butyl, 1,4-cyclohexyl, and 1,4-bicyclo[2.2.2]octyl. Compound **7** has a triptycene bridge. Terminal groups are electro-chemically active and yield simple irreversible voltammetry, like 4-ethynylpyridine itself. Voltammetric current maxima are at -2.1 V. A detailed inspection by voltammetry, impedance, spectroscopic and EPR techniques revealed important effects of the structure of molecular bridges connecting two ethynylpyridine terminal groups. Compounds **1** and **4** with a single —CH_2— or —CH_2CH_2— bridge are reduced only by two electrons, like 4-ethynylpyridine. Two or three such loops in a bridge lead to a four-electron transfer in a total electron uptake. This is a striking difference. Compounds **1** and **4** have several stereoisomers, some of which are substantially folded (Figure 2). The folding leads to a two-electron reduction, appearence of an intensive absorption at 600 nm and an EPR signal. Such features are not observed for other compounds, which are evidently rigid. Absorption in the range 500 to 700 nm and the EPR signal in the EPR spectra decrease for more rigid compounds having multi-loop bridges. Figures 3 show a typical example of spectroscopic differences caused by single or double bridges in compounds **4** and **5**. These features are valid for the whole series of compounds. Experimental results are supported by extensive theoretical calculations by DFT methods. Only flexible rods yield intramolecular charge transfer interactions responsible for observed spectral features. This study will help in the future interpretation of single molecule conductivities.



1 2 3 4 5 6 7

Figure 1 Structure of molecular "rods".

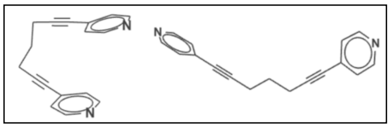


Figure 2 Example of folded and linear isomers

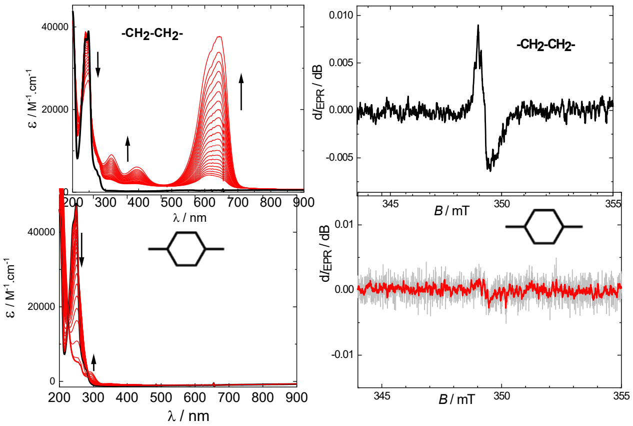


Figure 3 Dependence of UVvis spectra during the voltage scan (left column) and EPR spectra (right column) on the bridge type.

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Development of an electrochemical simulation model for PEM electrolysis stacks

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The project Recycalyse aims to disrupt the energy storage market through novel and recyclable catalytic materials to be used in proton exchange membrane electrolysers (PEMEC). To overcome the main barriers that remain for PEMEC, namely high capital cost and use of critical raw materials (CRM), two main objectives have been defined. Firstly, highly active sustainable oxygen evolution catalysts that will reduce the use of CRMs will be developed and manufactured, thus decreasing CO_2 emissions, and reducing cost. Secondly, a recycling scheme for PEMEC catalysts, electrodes and overall system will be developed, thus reducing or avoiding the dependence on materials imports in Europe and reaching a full circular economy.

The viability of the innovative single cells is proven by implementing the newly developed or recovered catalyst materials into a fully functional PEMEC system. To run this stack in the most efficient way, the operation strategies and software for control have to be analysed and optimised using a control strategy model. The electrolyser model presented here, is the most important component of this control strategy model and has to represent the true behaviour of the stack as accurately as possible.

In contrast to the already quite sophisticated model approaches for PEM fuel cell system optimisation, simulation of PEM electrolyser systems is still early in its development. While simulation models exist, they are less comprehensive and mature than comparable models for fuel cells. An early work that focused on modelling of the overvoltages and the mass transport in contrast to only using fits of experimental data, was developed by Sartory et. al. at HyCentA and forms the basis of the model presented here.[1]

The electrolyser stack model consists of four submodels that represent different physical behaviours but interact with each other as seen in Figure 1. All models are 0-dimensional and quasi stationary apart from the thermal model, which uses a single thermal mass to simulate the time-dependent change in average temperature of the stack.

The whole model can not only be used as part of the control strategy but also by itself, as the calculated results make it possible to determine permissible operating conditions and identify optimisation potentials concerning electric losses. This supports electrolyser stack development and facilitates testing procedures. The developed model also contributes to a deeper understanding of the processes happening in an electrolyser stack and give the possibility to perform sensitivity analyses concerning stack specific input parameters. The combination of the stack model and the control model helps to anticipate the effects of different operation strategies on the performance of the newly developed PEM stack in Recycalyse.

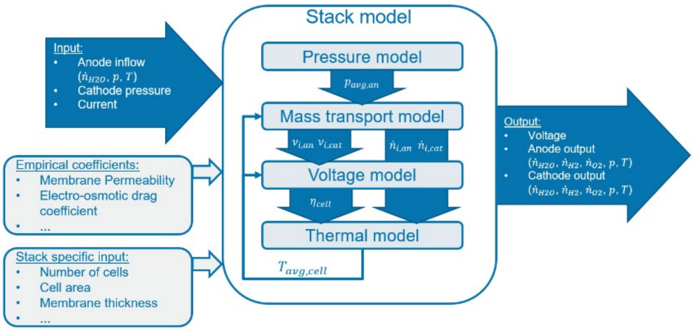

Figure 1: Overview of the stack model and its submodels

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Studies on the Hybrid Sulfur Cycle for Hydrogen Production

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In a world confronted with the environmental impact of human activities, the need for carbon-free energy is growing. Hydrogen is one of the main candidates for this socio-environmental transition, as it can be used for both energy production and energy storage. Due to this prominent role, the demand for hydrogen is expected to dramatically increase in the next decades. Currently, though numerous production ways are being studied using renewable energies such as solar energy, more than 99% of the hydrogen supply comes from fossil resources[1]. To progressively replace gasification and steam reforming, efforts must be made in the development of economically viable and more environment-friendly technical solutions. Among the proposed alternatives, thermochemical cycles seem to have particularly attracted researchers' attention with an annual number of publications on the subject growing from less than a dozen to more than 150 in the last twenty years[2]. Reasons for this include their scalability, their ability to be used in synergy with already existing processes that imply thermal energy[3], their low carbon footprint[2], and their high hydrogen purity[4]. After screening hundreds of thermochemical cycles[5] in terms of global efficiency, improvement potential and economic viability and other criteria, only a few remained, and the sulfur-based water splitting cycles, including the sulfur-iodine (S-I), sulfur bromine or sulfur ammonia cycle, emerged as relevant. However, the most studied and thought to be the most promising is the hybrid sulfur (HyS) cycle. Invented in the seventies by the Westinghouse Electric Corporation[6] to be used in tandem with new generation nuclear plants or solar heaters as electricity and heat sources, this cycle comprises the use of electrochemistry and thermochemistry for indirect water splitting as follows.

In the electrochemical part, sulfur dioxide is introduced in the anode to react with water to form sulfuric acid, protons and electrons. The protons and electrons are transferred to the cathodic part of the electrolyser through a proton exchange membrane (PEM) and current collectors, respectively, to undergo HER, producing hydrogen. The produced sulfuric acid is then further concentrated in the thermochemical part to form back and re-inject sulfur dioxide and water into the system, while obtaining oxygen as a co-product. With a reversible potential at best seven times lower than that of classical electrochemical water splitting[7] - hence the name "Sulfur Depolarised Electrolysis" (SDE) – and a really low carbon footprint[2], this technology has the theoretical potential to assist society in its transition towards carbon-free energy.

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Dissolution and electrolysis of lunar regolith in ionic liquids

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Oxygen extraction from lunar regolith is one of the key in-situ resource utilization (ISRU) objectives. Several different extraction processes based on reactive gases, pyrolysis and electrolysis are described in literature [1]. This study investigated a promising process based on the dissolution of regolith in an acidic ionic liquid and subsequent electrolysis [2]. The method works with rather innocuous chemicals and at moderate temperatures of only 100°C. It was found that up to 30 wt.% of the regolith simulant EAC-1 can be solubilized in the acidic ionic liquid. An inductively coupled plasma optical emission spectroscopy analysis revealed that phosphorous oxide is the best dissolving oxide, followed by MgO, Na2O, K2O, Al2O3, iron oxides, TiO2 and CaO in decreasing order. Water, which is formed during the dissolution of regolith, is electrolysed within the ionic liquid yielding oxygen and hydrogen as an intermediate product. Finally, the ionic liquid is regenerated by the cathodic electrodeposition of dissolved metal ions and the anodic oxidation of hydrogen. The electrochemical potential window of the neat ionic liquid was determined with cyclic voltammetry experiments and the cathodic hydrogen evolution reaction was identified as the primary cause for ionic liquid decomposition. During potential controlled electrolysis experiments at strongly negative potentials, no current, which could be attributed to metal deposition and thus ionic liquid regeneration, was recorded. Further inspection of the electrode surfaces with electron microscopy and energy-dispersive X-ray spectroscopy confirmed that no metal deposition occurred. Hence, more work is required to enable this method by either limiting the hydrogen evolution reaction or by facilitating metal deposition. This might be achieved by choosing a different ionic liquid as the primary electrolyte.

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Analytical applications of glassy carbon modified electrode based on new copper(II) complex for cysteine analysis

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Copper complexes play an important role in catalyzing enzymatic activity, and consequently, some copper(II) carboxylates are used as pharmaceuticals. Apart from the importance of copper as a metal center in many biochemical processes, pyridinecarboxylic acids and their derivatives also play important roles in the metabolism of all living cells. Insufficient nicotinic acid cause diseases like anemia, headache, tiredness, nausea and skin infection. Cu(II) complexes with nicotinic acid also showed antimicrobial activity against Bacillus subtilis and super oxidedismutase (SOD) mimetic activity.

In order to further understand the coordination chemistry of rigid carboxylate with N-donor ligands, we synthesized, by layering and characterized the copper(II) coordination compound with 2-hydroxynicotinic acid (2-OHnic). The structure characterizations were based on elemental analysis, electrospray ionization mass spectrometry (ESI-MS), matrix-assisted laser desorption/ionization-time-of-flight mass spectrometry (MALDI-TOFMS) and single crystal X-ray diffraction analyses (SCXRD). The electrochemical properties of the compound were carefully investigated by cyclic voltammetry and a prepared coordination compound has been used to obtain modified electrodes with potential applications in cysteine analysis. Based on cyclic voltammetry measurement, the mechanisms for the Cys-SH oxidation have been discussed. Square wave voltammetry obtained a linear response between 0.2 and 20 μM with an estimated detection limit of 0.09 μM.

Application of electrochemical impedance spectroscopy for hydrogen detection with metal oxide gas sensors

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Highly sensitive and selective H_2 sensors with a lower detection limit of $\varphi(H_2)$ = 100 ppbv are of great importance nowadays. They are especially in demand in the developing H_2 economy, which poses risks with explosive H_2/O_2 gas mixtures in a wide concentration range [1]. Metal oxide gas (MO_X) sensors may be suitable for such H_2 monitoring in plant buildings or fuel cell vehicles [2].

In MO_X gas sensors, the resistance (*R*) of a sensitive layer changes when redox gases are in the surrounding atmosphere. Electrochemical impedance spectroscopy (EIS) is a promising measuring method [3] for measuring this resistance. However, this method is much less commonly used with MO_X gas sensors because of its higher complexity and possible misinterpretations in comparison to measurements with DC.

In this work, EIS experiments were performed on MO_X sensors at H_2 concentrations from 3 to 30 vol-ppm. The MO_X sensor elements used, described in more detail in [4], consist of a supporting substrate (Al_2O_3) with a pair of Pt electrodes on one side and a heater on the other. The Pt electrodes are coated with a gas-sensitive layer consisting of SnO_2 nanoparticles mixed with Pd particles. The laboratory setup for these measurements allows a constant flow of synthetic air with precisely controlled humidity and H_2 concentration.

EIS measurements (Fig. 1) have shown that the maximum measured Z_{real} value decreases significantly with increasing H_2 concentration. Even at very low H_2 concentration of 3 vol.-ppm, a detectable change of the value of the complex impedance has been observed. The low-frequency part of the spectrum contains information about the contact area between the Pt electrodes and the sensor layer.

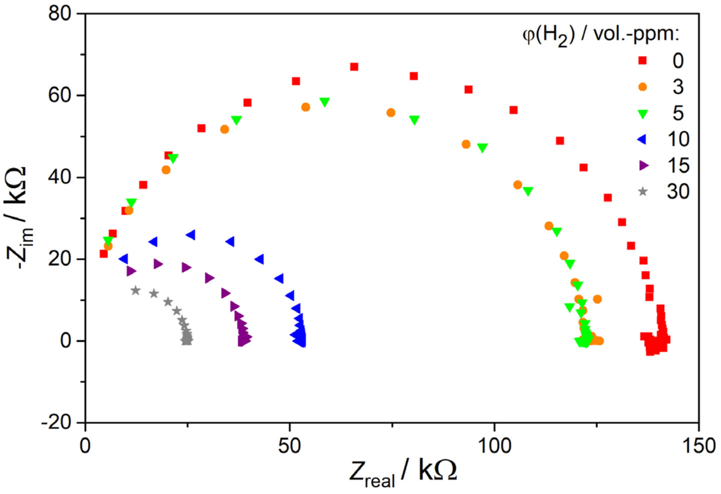

Figure 1: Impedance plots at different hydrogen concentrations in synthetic air at 30% relative humidity, sensor temperature = 400 °C.

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Highly biocompatible antibiotic-loaded hydroxyapatite-based coatings electrodeposited on titanium

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The successful combinations of biocompatible components with embedded antimicrobial agents are commonly used in orthopedic and trauma surgery nowadays. The high potential is recognized for composite materials loaded with antibiotics, thus enabling local administration of high antibiotic concentration at the infection site, complementing systemic drug therapy. Very versatile electrophoretic deposition (EPD) is very often the technique of choice for composite bioactive coatings preparation. A single step deposition of bioactive composite coating of hydroxyapatite (HAP), polymers polyvinyl alcohol (PVA) and chitosan (CS), and antibiotic gentamicin (Gent) was successfully achieved. Cathodic EPD was carried out on titanium (Ti) substrate from four-component aqueous suspension. Detailed physico-chemical and biological characterizations of antibiotic-free (HAP/PVA/CS) as well as antibiotic loaded (HAP/PVA/CS/Gent) composite coatings were performed [1,2]. Successful deposition of HAP/PVA/CS and HAP/PVA/CS/Gent composite coatings was confirmed by Fourier transform infrared spectroscopy (FTIR) through the detection of characteristics bands, revealing intermolecular and intramolecular interaction between components. According to the X-ray diffraction (XRD) results, presence of carbonate substituted HAP was found in both composite coatings, making these materials potentially good candidates for biomedical applications. Strong interfacial interaction between HAP, PVA and CS was verified through the formation of porous, homogeneous, fracture-free coating surface, according to the field emission scanning electron microscopy (FE-SEM) results. Strong antibacterial activity against two bacteria strains, *Staphylococcus aureus* and *Escherichia coli, was confirmed by agar diffusion test of HAP/PVA/CS/Gent coating and quantified by trends of* antibacterial activity kinetics. Biocompatibility assays (MTT and DET tests) were also carried out, showing *low cytotoxicity against* MRC-5 and L929 cell lines for both composite coatings, with and without antibiotic.

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Towards developing Accelerated Stress Tests for Room-Temperature Metal Hydride Storage Tanks

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Metal hydride (MH) hydrogen storage is a highly promising method, especially under room temperature conditions. Compared to other hydrogen storage methods no significant energy input for heating, cooling, or achieving high pressure is needed [1]. The process of hydrogen sorption in the MH is an exothermic reaction, which involves heat release, and the desorption process occurs with a heat energy consumption i.e., this process is endothermic. Therefore, the reaction rate of these processes depends on the temperature conditions in which the charging- and discharging cycles are carried out. The cyclic stability is one of the most important properties for the evaluation and characterisation of metal hydride storage tanks. It is the ability to absorb and release hydrogen over a large number of charge- and discharge cycles without a loss in capacity.

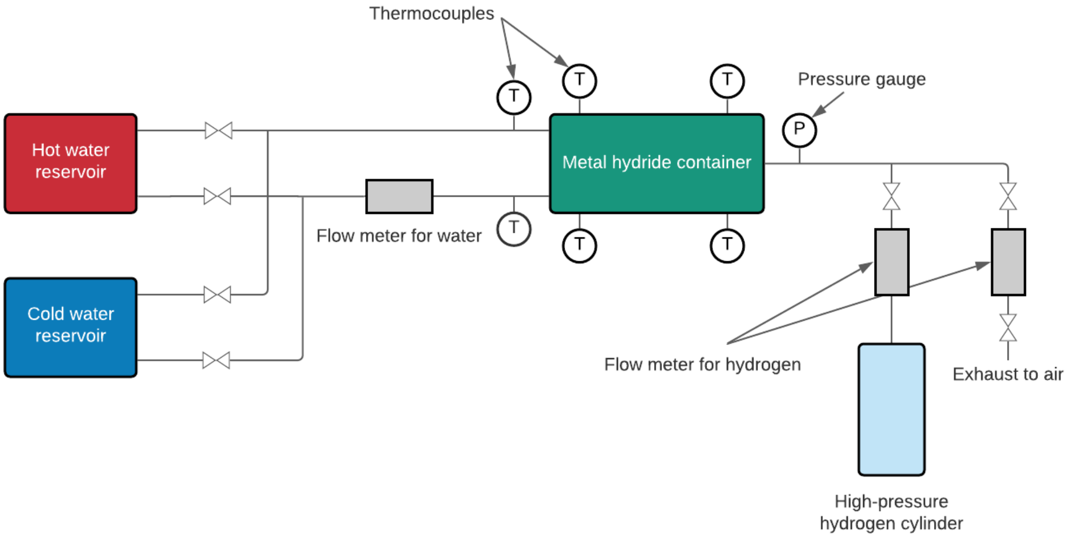

Figure 14. P&ID of the Metal Hydride Storage Test Rig.

In this work a method for accelerated cyclic stress testing is developed by controlling the charge- and discharge temperature of MH storage. The object of the study is a 20 nL TiFe metal hydride storage tank. Thermal parameters of the charging and discharging process are measured by a thermocouple and a thermal imaging camera. The charge- and discharge rate, volumetric values as well as the flow rate (mL/min) are determined by a mass flow meter. The desired temperature range is achieved by the use of a water circulator. In the process of experiments, it was found that by controlling and maintaining the targeted temperature (in the range of 50 to −40 °C) of sorption- and desorption, both the charging and discharging cycles are significantly accelerated. The increase in the flow rate in the first 15-20 minutes of the cycle allows the development of a set of accelerated stress test protocols.

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