Materials Development for Automotive Propulsion

680. WE-Heraeus-Seminar

Oct 14th to Oct 17th, 2018
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm and Else Heraeus Foundation (Wilhelm und Else Heraeus-Stiftung) is a private foundation which supports research and education in science, especially in physics. A major activity is the organization of seminars. To German physicists the foundation is recognized as the most important private funding institution in their fields. Some activities of the foundation are carried out in cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft).

Scope of the 680. WE-Heraeus-Seminar:

During this meeting, scientists working in the broad fields of Batteries, Synthetic Fuels (SynFuels) and Fuel Cells will come together to discuss the latest trends in these fields in academia and industry. Due to a limited number of participants (around 60), an intimate format and ideal platform is achieved allowing ideal visibility, fruitful discussions and efficient networking opportunities.

Highlights of the meeting include:

- Invited Talks given by international experts in the field/s
- Contributing Talks by younger researchers
- 1-3 Poster Awards
- 1 Award for the most instructional lecture (Contributing Talk)

Scientific Organizers:

Prof. Dr. Ulrike Kramm	Technische Universität Darmstadt D-64287 Darmstadt, Germany E-mail kramm@ese.tu-darmstadt.de
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Prof. Dr. Bai-Xiang Xu	Technische Universität Darmstadt D-64287 Darmstadt, Germany E-mail Xu@mfm.tu-darmstadt.de

Program

Sunday, October 14, 2018

09:00 – 15:00	Registration	
12:30	*LUNCH*	
14:00 – 14:15	Ulrike Kramm	**Opening remarks**
	Chair: Ulrike Kramm	
14:15 – 15:15	**Jin Suntivich**	**Designer Catalysts: A Material-Centric Approach to the Energy Storage Challenge**
15:15 – 16:15	**Tanja Graf**	**Designing advanced energy materials for automotive applications**
16:15 – 16:45	*COFFEE BREAK*	
16:45 – 17:45	**Bettina Lotsch**	**"Soft photocatalysis": Carbon-based materials for solar fuel production**
17:45 – 18:45	**Anke Weidenkaff**	**Substitution and Recycling of Critical Elements in Energy Technologies**
19:00	*BUFFET SUPPER / Informal get together*	

Monday, October 15, 2018

07:30	*BREAKFAST*	
	Chair: Maria Escudero-Escribano	
08:30 – 09:20	**Elena Savinova**	**Hydrogen Oxidation on mono- and bimetallic Ni electrodes in alkaline media**
09:20 – 09:45	Elena S. Davydova	Challenges in the development of Ni-based electrocatalysts for hydrogen oxidation reaction
09:45 – 10:10	Guillaume Braesch	Comparison of noble and promising non-noble materials as electrocatalyst for the Borohydride Oxidation Reaction

Program

Monday, October 15, 2018

10:10 – 10:40	*COFFEE BREAK*	
	Chair : Christina Roth	
10:40 – 11:30	**Stefania Specchia**	**3D multi-physics, multi-phase, and non iso-thermal modeling of PEMFC and DMFC**
11:30 – 11:55	Jonathan Quinson	Systematic studies of supported electrocatalysts for the oxygen reduction reaction: from surfactant-free colloidal syntheses to method development
11:55 – 12:20	Natascha Weidler	Effect of Structure Forming Agents on the Porosity of the Carbon Structure of Fe-N-C catalysts for the Oxygen Reduction Reaction
12:20 – 12:30	**Conference Photo**	
12:30	*LUNCH*	
	Chair: Serena Corr	
14:00 – 14:50	**Nina Balke**	**In-situ characterization of energy storage materials on the nanoscale**
14:50 – 15:15	Samuel Booth	Microwave synthesised $H_2V_30_8$ nanowires: a study of lithium intercalation
15:15 – 15:45	*COFFEE BREAK*	

Program

Monday, October 15, 2018

Chair: Bai-Xiang Xu

15:45 – 16:35	**Nancy Sottos**	**Autonomous Intervention Strategies for Electro-Chemo-Mechanical Stability in Li-ion Batteries**
16:35 – 17:00	Peter Stein	Under stress: enhancing the low diffusivity in lithium-ion batteries through surface stresses and the elastic fields of material defects
17:00 – 17:25	Beth Johnston	Muon spin spectroscopy for studying local ionic diffusion in electrode materials for Li ion batteries
17:30 – 18:00	**Postersession even poster numbers**	
18:00 – 18:30	**Postersession odd poster numbers**	
18:45 – 19:00	Stefan Jorda	**About the Wilhelm and Else Heraeus Foundation**
19:00	*HERAEUS DINNER at the Physikzentrum* *(cold & warm buffet, free beverages)*	

Program

Tuesday, October 16, 2018

07:30	*BREAKFAST*	
	Chair: Fabio Dionigi	
08:30 – 09:20	**Jennifer Strunk**	**Photocatalytic CO_2 Reduction: An Alternative Source of Renewable Fuels?**
09:20 – 10:10	**Ivelina Zaharieva**	**Manganese oxides as water oxidation catalysts**
10:10 – 10:35	Anna Mechler	Impact of Fe-impurities on a Ni-Co-Oxide Catalyst for Oxygen Evolution
10:35 – 11:05	*COFFEE BREAK*	
	Chair : Jin Suntivich	
11:05 – 11:55	**Anna Fischer**	**Materials for ORR and OER - from platinum free electrocatalysts to advanced photoanodes**
11:55 – 12:20	Alexandr Oshchepkov	Tuning the Activity of Ni in the Hydrogen Electrode Reactions and Borohydride Oxidation Reaction by Varying its Surface State
12:20 – 12:45	Kathrin Ebner	A novel synthesis approach for Fe/N/C-type ORR-catalysts - insights on composition and activity
12:45	*LUNCH*	
	Chair: Ivelina Zaharieva	
14:15 – 15:05	**Christina Roth**	**In-operando characterization of novel fuel cell catalysts using XAS and DRIFTS**
15:05 – 15:30	Viktoriia Saveleva	Degrading of the Carbon Support in Fe/N/C Catalysts used for the Reduction of Oxygen in PEM Fuel Cells

Program

Tuesday, October 16, 2018

15:30 – 16:00	*COFFEE BREAK*	
	Chair : Christina Birkel	
16:00 – 16:50	**Kimberly See**	**The Behavior of Multivalent Cations in Next-Generation Battery Systems**
16:50 – 17:15	Elinor Josef	Replacing metals: free-standing carbon fibers derived from a poly(ionic liquid) as a current collector
17:15 – 17:40	Oliver Clemens	New Battery Technologies based on Fluoride Ions
17:40 – 19:00	**Discussion table**	
19:00	*DINNER*	

Program

Wednesday, October 17, 2018

07:30	*BREAKFAST*	
	Chair: Nina Balke	
08:30 – 09:20	**Serena Corr**	**A new series of active materials for safer energy storage**
09:20 – 09:45	Saneyuki Ohno	Development of the solid electrolytes and their applications for solid-state Li-S batteries
09:45 – 10:10	Molleigh Preefer	Crosslinked disulfide polymers for stable cycling in Lithium-Sulfur batteries
10:10 – 10:35	Filip Podjaski	Toward New Solar Batteries: Graphitic Carbon Nitrides Enabling Direct Solar Energy Storage
10:35 – 11:00	*COFFEE BREAK*	
	Chair : Anna Mechler	
11:00 – 11:50	**Maria Escudero-Escribano**	**Elucidating the Active Phase of Pt-Based Electrocatalysts for Oxygen Reduction**
11:50 – 12:15	Fabio Dionigi	Octahedral Fuel Cell Nano Catalysts
12:15 – 12:40	Anders Jensen	Nanoporous Pt-based network catalysts for oxygen reduction
12:40 – 13:05	Ulrike Kramm Christina Birkel Bai-Xiang Xu	**Poster awards and closing words**
13:05 – 14:30	*LUNCH*	

End of the seminar and Departure

Posters

Posters

BATTERY

01	Justin **Andrews**	**Topochemically-stabilized vanadium oxides: Expanding the palette of functional multivalent-ion cathode materials**
02	Lothar **Bischoff and** Jan **Siebert**	**Sol-Gel Assisted Synthesis of MAX phase Cr_2GaC**
03	Manuel **Donzelli**	**Garnets meet polymers: From synthesis to flexible SSBs with stable interfaces?**
04	Maren **Lepple**	**Experimental and computational thermochemistry of oxide-based material systems for energy conversion and storage applications**
05	Wei **Liu**	**The electro-chemo-mechanical modelling of lithium ion battery**
06	Mohammad Ali **Nowroozi**	**Intercalation-Based Cathode Materials for All Solid-State Fluoride Ion Batteries**
07	Christoph **Reimuth**	**Multi-scale-modeling of dislocations in lithium-ion-battery-electrodes**
08	David **Santos**	**Defining and Modulating Diffusion Pathways in Intercalation Cathode Materials: Some Lessons from V_2O_5 on Directing Cation Traffic**
09	Sebastian **Wissel**	**Chemo-mechanical analysis of inverse opal structures for application in lithium-ion battery electrodes**

Posters

FUEL CELLS

10	Lingmei **Ni**	**In-situ Cell Design for ^{57}Fe Mößbauer Spectroscopy on Fe-N-C Catalysts**
11	Deborah **Salmazo**	**Theoretical insights in NiCu catalysts for the HER**
12	Humera Khatoon **Siddiqui**	**From RDE towards Fuel Cell - Influence of temperature change and electrode structure on the ORR activity**
13	Pascal **Theis**	**Relation between preparation parameters and ORR activity and selectivity for a silica-templated synthesis of Fe-N-C catalysts**
14	Codrutta Aurelia **Vlaic**	**Electrochemical etching of Ti_2AlC MAX phase obtained by non-conventional solid-state synthesis**
15	Aamir **Waidha**	**Understanding water incorporation in barium cobaltates and their role for protonic ceramic fuel cells**
16	Daniel **Weber**	**Effect of various monovalent Cations on HOR/HER Activity in alkaline Environment**

SYN FUELS

17	Kim Alexander **Creutz**	**CoS_x/C catalysts for the hydrogen evolution reaction - Influence of the pyrolysis temperature**
18	Julia **Kröger**	**Toward enhanced photocatalytic hydrogen evolution by carbon nitrides with a true 2D topology**
19	Stephen **Paul**	**Influence of the metal species on the selectivity in $C0_2$ reduction on Me-N-C catalysts**
20	Minh Hai **Tran**	**Adding a new member to the MXene family: $V_4C_3\mathit{T}_x$**

Abstracts of Lectures

(in chronological order)

Designer Catalysts: A Material-Centric Approach to the Energy Storage Challenge

D.Y. Kuo,[a] J.N. Nelson,[b] H. Paik,[a] K.M. Shen[b], D.G. Schlom,[a] J. Suntivich[a]*

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Wind and solar are becoming economical, aided by rapidly declining cost and increasing efficiencies. As the renewables gain momentum, electrochemical processes that use renewable electricity to transform readily available resources (such as water and carbon dioxide) to energy-dense fuels and high-valued chemicals represents an opportunity ripe for development. Presently, these transformations are not cost-effective because of the slow kinetics of the electrochemical transformations. Past research efforts attribute these sluggish kinetics to the catalyst's inability to stabilize reaction intermediates; even precious-metal catalysts have limitations. I will describe our experimental assessment of this hypothesis. Advanced syntheses and deposition tools can now routinely grow single-orientation oxides and model surfaces with high structural perfections. We utilize these advances with surface science and spectroscopy tools to measure the intermediate stabilization energy. We use this information to experimentally establish the relationship between the intermediate stabilization and electrochemical kinetics. I will discuss the implications of these results, including new insights on the mechanisms of electrochemical transformations and how to design and explore phases not accessible via thermochemical means to realize higher-performing catalysts.

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   DOI: 10.1021/jacs.6b11932
3. R. Tang, Y. Nie, J. Kawasaki, D.Y. Kuo, G. Petretto, G. Hautier, G.M. Rignanese, K.M. Shen, D.G. Schlom, J. Suntivich, *J. Mater. Chem. A.* **4** (2016) pp 6831–6836.
   DOI: 10.1039/C5TA09530A

Designing advanced energy materials for automotive applications.

T. Graf,[a]

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The automotive industry is facing major challenges. Sustainable mobility will strongly rely on the successful design and implementation of advanced energy materials. Furthermore, future mobility concepts, such as automated driving, car-to-car communication and digitalization will require the use of high-performance, energy efficient and reliable materials. Therefore, making smart materials choices will be essential to meet these challenges.

Modern computational methods combined with experimental analytics can accelerate materials development by reducing trial-and-error and allow for the design of materials with targeted properties for a specific application. Here, a fundamental understanding of the potential and the limitations of existing materials as well as the possibility to design new materials will be the keys to accelerate material innovation and guarantee competitiveness of future products.

Specific examples of how modern materials design is employed in the field of cathode materials for Li ion batteries will be discussed. Furthermore, the development of a high performance fuel cell catalyst material based on computational materials research combined with advanced manufacturing methods will be described.

"Soft photocatalysis": Carbon-based materials for solar fuel production

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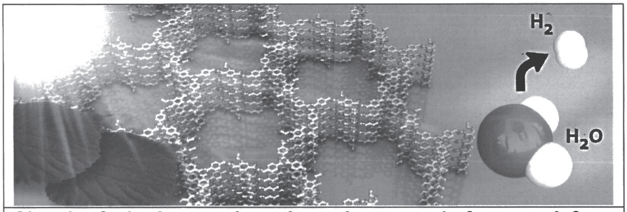
[b]Department Chemie, Ludwig-Maximilians-Universität München, Germany

The conversion of sunlight into storable chemical fuels through photocatalysis has been identified as a viable strategy to alleviate future energy shortage. Although a number of potent semiconductors for solar water splitting are at hand, key features such as earth-abundance, stability and low toxicity still need to be addressed, thus calling for new and flexible material solutions for sustainable photocatalysis. We have recently shown that covalent organic frameworks (COFs) and related 2D carbon nitrides hold promise as a new generation of molecularly tunable, earth-abundant photocatalysts that combine the stability of heterogeneous systems with the single-site definition of homogeneous catalysts.

In this talk, general principles of photo(electro)catalytic water splitting will be revisited and evaluated for the design of carbon-based, "soft" photocatalysts. We will discuss possible catalyst optimization strategies and highlight the challenges lying ahead in this emerging field of "soft photocatalysis".



Sketch of a hydrazone-based covalent organic framework for hydrogen evolution. ©NIM

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Substitution and Recycling of Critical Elements in Energy Technologies

Anke Weidenkaff[a], **Wenjie Xie, Songhak Yoon, Marc Widenmeyer**

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Modern energy technologies like electric cars, wind turbines, solar cells or fuel cells are based on electroceramics and other materials containing critical elements (1,2). The prerequisite for a durable active material is the constant regeneration of the structure under electrical current, thermochemical and heating cooling cycles.

Complex oxide ceramics as well as their nanocomposites can be tuned to enable for multifunctional energy converters to reduce the use of scarce or toxic materials. Their good performance relies on their flexible crystal structure being able to accommodate defects during electrical, thermal and chemical redox processes. The design of sustainable materials is based on theoretical predictions and a deep knowledge on composition-structure-property relationship to enable the substitution of critical elements. The perovskite- or the Half Heusler structure allow diverse substitution reactions to tune the band structure, charge carrier density and mobility as well as thermal and ionic transport.

The electronic mobility can become high while the ionic and thermal conductivity can remain low. Strongly correlated electronic systems are employed as additional design elements for a materials design (3).

Tailored soft chemistry synthesis methods result in nanostructured regenerative oxide materials as well as intermetallics, nitride and chalcogenite phases. These materials are characterized and tested in-situ for e.g. high temperature thermoelectric and catalytic applications to improve the efficiency and energy density of energy conversion devices.

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Hydrogen Oxidation on mono- and bimetallic Ni electrodes in alkaline media

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Research into anion exchange membrane fuel cells (AEMFCs) has recently become a hot topic. Since hydrogen oxidation reaction (HOR) is significantly slower in alkaline compared to acid media, the future of AEMFCs largely depends on the availability of materials capable of catalyzing the HOR at low overpotentials and containing little or no noble metals. Numerous groups are working on the understanding of the mechanism of the HOR in alkaline media, on factors determining electrocatalytic activity, and on the development of active and stable materials for the AEMFC anode.

In this presentation we will discuss the HOR on monometallic and bimetallic NiM electrodes (M=Cu or Mo). By combining experimental electrochemistry with kinetic modeling, density functional theory (DFT), and Monte Carlo calculations we will try to understand why the activity of metallic Ni in the HOR is low, why it increases following partial surface oxidation [1], how and why the activity depends on the electrolyte pH, why addition of Cu [2] and Mo [3] increases the electrocatalytic activity and whether the alleged bifunctional mechanism [4] is operating on Ni and NiM anodes.

Acknowledgement
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Challenges in the development of Ni-based electrocatalysts for hydrogen oxidation reaction

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The last ten years, alkaline anion exchange membrane fuel cells (AEMFCs) undergo rapid progress [1]. This progress is the result of the development of more conductive and stable anion exchange membranes (AEMs), and the growth in understanding of the AEMFC water management [2]. To the lower extent, the progress is driven by the advancement in oxygen reduction and hydrogen oxidation electrocatalysts [3]. Till now, mainly platinum group metals (Pt, PtRu, Pd) are used at relatively high loading levels, up to 0.6 mg_{cat} cm^{-2}, on the both electrodes of AEMFCs. In order to benefit from the main advantage of AEMFCs, alkalinity, and, as a consequence, potentially low cost due to the use of abundant electrode materials, reliable platinum group metals-free electrocatalysts must be developed. This would allow keeping pace with the progress in the AEM development and meeting the future demands of AEMFCs.

This work is devoted to the comprehensive analysis of the main challenges in the development of Ni-based electrocatalysts for hydrogen oxidation reaction (HOR) in alkaline media as the anode material for AEMFCs. The analysis is mainly based on our experimental and theoretical data [], as well as thorough literature analysis [3].

Within the scope of the work are 1) synthetic procedures used to develop Ni-based HOR electrocatalysts, with pros and cons (chemical, hydrothermal, thermal reduction); 2) negative and/or positive effects of chemical and electrochemical oxidation of Ni surface (CV, RDE, XPS, EDS, in operando EXAFS, TPR, H_2-TPD); 3) chemical and electrochemical stability of Ni nanoparticles at elevated temperature in aqueous alkaline electrolytes (in situ ICP-MS, RDE); 4) slow kinetics of HOR on Ni and transition-metal doped nickel (RDE); 5) theoretical predictions (DFT) vs. experimental results (HOR kinetic parameters).

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Comparison of noble and promising non-noble materials as electrocatalyst for the Borohydride Oxidation Reaction

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Proton Exchange Membrane Fuel Cells (PEMFC) currently dominate the fuel cell market. However, it is not the best suited technology for all applications, such as portable and mobile devices. Indeed the difficulties regarding the production, purification, compression, transportation, and storage of gaseous hydrogen lead to safety and technological concerns [1]. In order to avoid these concerns, Direct Liquid Fuel Cells (DLFCs) such as the Direct Borohydride Fuel Cell (DBFC) represent an interesting alternative. Borohydride fuel displays unique properties, e.g. very low theoretical standard potential (-1.24 V vs NHE, pH = 14) and 8 electrons produced for the total oxidation of one BH_4^- anion, resulting in high theoretical energy density.

Nevertheless, these properties are often not fully harnessed when noble materials like platinum or palladium are used as Borohydride Oxidation Reaction (BOR) electrocatalysts: they are very active for the hydrogen evolution reaction (HER), which prevents any oxidation currents below 0 V vs RHE and results in unavoidable escape of H_2 gas [2], thus limiting the benefits of DBFC compared to PEMFC. Since DBFCs are working in alkaline conditions, it is possible to use platinum-group metal-free (PGM-free) electrocatalysts for the BOR, which offers the advantage of being cheap and widely available. Among non-noble metals, Ni-based electrocatalysts have been investigated as possible candidates for the BOR [3], but the performances reached were modest. Being admitted that the state of surface of nickel has a critical influence on its catalytic performances [4,5] and that alloying Ni with another metal is a classical strategy to tune its electrocatalytic properties, the activity of Ni-based electrodes for the BOR was revisited in the present study.

In this presentation, the performances of metallic nickel and various bimetallic NiM alloys (M= Co, Mo, Ag, Pd) for the BOR catalysis are presented. It is shown that the non-PGM surfaces must not be scanned to “high” potentials, to prevent detrimental surface oxidation, that results in deactivation for the BOR. When compared with noble metals (Pt, Pd, Au) surfaces, Ni-based electrocatalysts hold significant advantages over their noble counterparts: the BOR onset potential reached can be significantly shifted negative on the Ni-based surfaces, provided their degree of oxidation is well-controlled, leaving hope to fully exploit the potential of BH_4^- in Ni-catalyzed DBFCs. At this low potentials, the Ni-based catalysts also show minor poisoning by adsorbate species compared to noble metals where this issue is detrimental [6].

Acknowledgments

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3D multi-physics, multi-phase, and non iso-thermal modeling of PEMFC and DMFC

S. Specchia*

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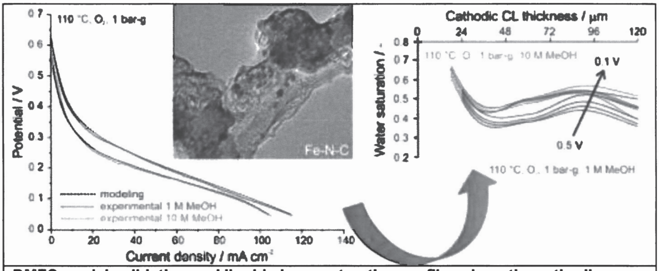
A series of 3D multi-physics, multi-component and not isothermal models of PEMFC and DMFC have been computed to analyze the effects of catalyst structures (Pt-based or Pr-free, uniform or gradual distribution), type of membranes, type of flow-field, flooding effects, on the performance, with specific attention to the oxygen reduction reaction [1–3].

All models include Stokes–Brinkman, Maxwell–Stefan, extended two-phase Darcy Law, modified Butler–Volmer and Tafel equations for simulating the performance of either PEMFC or DMFC, and evaluating the electrochemical, fluid-dynamics, and thermal phenomena. The models have been computed with Comsol® Multiphysics v4.4 platform, with a finite element analysis solver and simulation software.

All models have been validated against sets of experimental data, showing congruent and convergent data (commercial 25 cm^2 MEAs and lab-made 5 cm^2 MEAs), varying the type of catalysts, catalyst distribution, membranes, flow-fields, operative conditions (temperature, pressure and reactants concentrations). The use of 3D models considering porous equation such as Stokes-Brinkman is helpful for understanding, describing the motions and hydrodynamic forces of interacting particles in Stokes flow, which is more realistic regarding catalyst description and validation. Moreover, the models can be used for evaluating intrinsic parameters of novel electrocatalysts (Pt-free ones, based on Fe-N-C), mass transport and diffusivity parameters of the electrocatalyst, identifying the controlling variable in the process.



DMFC model validation and liquid phase saturation profiles along the cathodic catalytic layer thickness (Fe-N-C catalyst, 2.5 mg cm^{-2} loading) at various voltages.

This lecture will show how 3D multiphysic models can be used as a predicting and optimization tools for further improvement of catalyst synthesis, suggesting which properties can be tuned to improve the overall performance in the catalyst design phase.

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Systematic studies of supported electrocatalysts for the oxygen reduction reaction: from surfactant-free colloidal syntheses to method development

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Developing efficient catalysts for energy applications like polymer electrolyte membrane fuel cells (PEMFCs), require the **screening, understanding and optimisation of supported electrocatalysts**. For example Pt nanoparticles supported on carbon (Pt/C) are key catalysts for the oxygen reduction reaction (ORR) in these devices. Different properties of supported nanoparticles like composition, size, loading on a support material, nature of the support material, etc. strongly influence the efficiency of the catalyst (activity, stability, etc.). Several other parameters in the preparation of the catalyst influence the final performances: e.g. amount of ionomer, solvent, pH used in the 'ink' preparation. Finally, the variety of electrochemical tests and set up used can also influence the performances reported for a given catalyst.

It is therefore a general challenge to compare catalysts prepared by different routes, tested under different conditions, following different protocols. To provide deeper inside into the influence of a given set of physical properties, the related properties, e.g. size and loading on the support, must be tuned independently of other properties, in a systematic way. Such **systematic studies** are challenging to perform but are extremely rewarding to study, understand and finally optimise precious metal catalysts.

The talk will introduce a 'toolbox' approach for systematics studies of Pt/C for PEMFCs **[1]**. The philosophy of this approach will be detailed and recent achievements will be highlighted. First, a **controlled surfactant-free synthesis** of colloidal Pt nanoparticles used as model catalysts will be discussed **[2]**. Second, the importance of controlling the **'ink' properties** for thin film rotating disk electrode electrochemical tests will be demonstrated **[3]**. The talk will then show how to combine the previous achievements to investigate and discriminate '**size and proximity effects**' and their influence for the ORR. To take a step further, the needs for the development of **new electrochemical set-up and tests** to better assess the activity and stability of Pt/C catalysts will be stressed **[4]**. Finally the talk will illustrate how this strategy and the knowledge gained can be transferred to an **industry-relevant new surfactant-free synthesis** of precious metal nanoparticles **[5]** well suited to develop catalysts for the ORR but also the oxygen evolution reaction (OER), key reactions for a future hydrogen economy.

Overall, the talk will highlight the challenges in systematic studies of supported metal catalysts but also the long run benefits of this rewarding approach in terms of knowledge gained: from the synthesis, to catalyst preparation, all the way down to catalyst testing to optimise PEMFCs.

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Effect of Structure Forming Agents on the Porosity of the Carbon Structure of Fe-N-C Catalyst for the Oxygen Reduction Reaction

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In view of the transfer from fossil fuels to renewable energies, electrochemical reactions offer the chance of a fast and environmentally friendly production of chemicals or the transfer of chemical energy into electric energy (e.g. via fuel cells). Metal-nitrogen-carbon (Me-N-C) materials are intensively investigated as promising alternative for Pt/C catalysts on the cathode in PEM (Polymer-electrolyte membrane) fuel cell applications [1]. One of the main challenges developing Me-N-C catalysts represents the engineering of the carbon structure and morphology especially with respect to porosity. The use of template materials like MOFs, SiO_2 or metal oxalates are commonly used as successful strategies to engineer the carbon morphology [2-5].

In this work, we focus on the preparation using one distinct SFA. It is investigated to what extend variations such as template/polymer ratio or particle size of the template have on the ORR activity. Especially the template/polymer ratio turned out to have a significant effect on the resulting ORR activity. The final Fe-N-C catalyst was evaluated by the particle size distribution, N_2-sorption measurements, Raman spectroscopy and Photoelectron-Spectroscopy. Rotating ring disk (RRDE) studies were performed to investigate the ORR activity and selectivity of the Fe-N-C catalysts.

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In-situ characterization of energy storage materials on the nanoscale

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Energy storage in form of electrochemical batteries and capacitors are an important part of today's energy management plans. Depending on the application, the demands on the energy storage systems can be very different and often require pushing the limits of energy density and power. This requires a comprehensive understanding of energy storage processes on many different length scales. While macroscopic length scales are more easily accessible, electrochemical processes on the length scales of individual grains and below, i.e. 10's of nm length scales, are little understood. Atomic force microscopy (AFM) gives insight into local materials functionality on nanometer length scales but is rarely used in the field of electrochemistry and mostly limited to topographic measurements. This is because traditional electrochemical characterization techniques are based on current which is not obtainable through a SPM tip on a local scale due to the liquid environment and the small contact area which reduces the current to below the detection limit. Currently, there is no technique available which allows to study local electrochemical reactions in-situ in a liquid environment on nanometer length scales which can be directly compared with traditional characterization techniques. This means there is a huge untapped potential in AFM development and possibility of gaining new scientific insights into electrochemical reactions. This can help answer questions such as: What controls local electrochemical reactions? Do electrochemical reactions vary across the electrode? Are different grain facets more or less electrochemically active? This ultimately will allow to identify and modify limiting electrochemical reactions and their rates for improved electrochemical performance.

In this talk, recent examples of using AFM to study electrochemical reactions in-situ will be discussed. The process of ionic transport into the electrode can be tracked and imaged with AFM through the electro-chemo-mechanical coupling resulting in changes in mechanical properties (volume or Young's modulus). We will demonstrate how this approach can be used to track ion insertion dynamics into porous electrodes and to identify high diffusion pathways in layered electrodes as well as measure local redox potentials. Using SPM can help us to answer some core questions about fundamental processes in ECs to achieve a more complete understanding of charge storage mechanisms hence improving future ECs. In the end, current challenges and suitability for other forms of electrochemical charge storage are discussed.

Microwave synthesized $H_2V_3O_8$ nanowires: a study of lithium intercalation

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In the search for replacement materials to act as electrode materials in the next generation of batteries, vanadium is promising due to the number of readily accessible oxidation states leading to a high theoretical capacity. $H_2V_3O_8$ has been reported on as a suitable material as the initial mixed V^{4+} and V^{5+} oxidation states can be reduced to V^{3+}.[1] The material does, however, suffer from poor capacity retention on repeated cycling.[1]

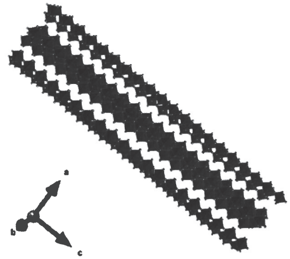

Figure 1. $H_2V_3O_8$ nanowire crystal structure.

In this study we present a simple and rapid microwave synthesis procedure to form $H_2V_3O_8$ nanowires from V_2O_5. The nanowire morphology contributes to rapid lithium intercalation. In our own studies we have measured an initial capacity of 206 mA h g^{-1} between 2 and 3.75 V with a retention of 95% capacity after 100 cycles at a rate of 100 mA g^{-1}. Analysis of the material by muon spin relaxation and under in operando conditions by X-ray absorption spectroscopy has allowed us to measure the rate of lithium diffusion within the material and to follow the modification in the local coordination environment around the vanadium centres. We observe rapid lithium diffusion within the material and a partially reversible breathing mode of the $H_2V_3O_8$ structure.[2] These measurements have enabled us to characterize the behavior in the early stages of $H_2V_3O_8$ battery cycling and to provide further information on the possible degradation processes from the first cycle. The reported data provides an indication of the possible use of $H_2V_3O_8$ or doped structures as cathode materials alongside broader statements on the intercalation mechanism and the influence on the host structure, which will have a more wide-ranging application for further battery materials under development.

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Autonomous Intervention Strategies for Electro-Chemo-Mechanical Stability in Li-ion Batteries

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The high-rate exchange of lithium ions required for more power and faster charging of Li-ion batteries generates significant stresses and strains in the electrodes that ultimately lead to performance degradation. Use of high energy density materials, overcharging, physical damage, and aging can trigger a variety of complex degradation mechanisms, resulting in loss of function or potentially thermal runaway. We are investigating the mechanisms for stress and strain development in electrodes and the surprising effects of interfacial coatings. These measurements provide new insights into the electrochemical-induced volumetric changes in electrodes with progressing cycling and provide guidance for both passive and dynamic materials-based strategies to reduce strain, minimize capacity fade, and stabilize electrode interfaces. Inspired by biological systems that routinely accomplish self-healing, thermal regulation, and other autonomous responses, we are developing functional materials that enable self-protection, self-healing, and complete shutdown in Li-ion batteries. Both microcapsule and intrinsic, reversible bonding schemes are employed to achieve autonomous function. Encapsulation of the desired core materials, integration of capsules and dynamic polymers into the battery environment, and experimental protocols for in situ characterization of electromechanical response, conductivity restoration and shut down performance will be discussed.

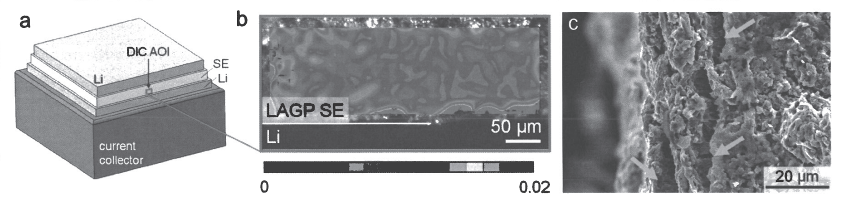

Fig. 1. (a) Schematic view of solid-state battery showing DIC area of interest, (b) equivalent strain developed near the SE/electrode interface in a Li/LAGP/Li cell, (c) SEM image of interfacial damage.

Under stress: enhancing the low diffusivity in lithium-ion batteries through surface stresses and the elastic fields of material defects

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The increasing demand for higher storage capacity and power density of lithium-ion batteries calls for the optimization of electrode microstructures, in particular at the micro- and nanoscale. Key factors are thereby short diffusion paths and large surface areas exposed to the electrolyte in order to achieve faster intercalation and solid-state transport in the electrode materials. Candidate structures for these design goals can be found in nanoporous materials, fractal(like) morphologies, and metamaterials such as inverse opals. At these length scales, surface stresses gain an appreciable impact on the behavior of these materials. They induce a (non-uniform) pressure field in the material that promotes mechanical stability, but that also affects the electrochemical behavior of the particle, modifying, among other things, surface reaction rates and ionic mobility. Alternatively, one can turn towards exploitation of material defects such as dislocation that have been known for a long time to constitute paths of higher diffusivity in various metals and ceramics.

In this contribution, we give an overview of our current research in the field of stress-enhanced diffusion for lithium-ion batteries. The talk will focus on the impact of surface stresses on the thermodynamics of point defects in and on the electrochemical behavior of nanostructured battery electrode particles. We will further give an outlook towards modeling diffusion in the near-field of dislocation systems.

Muon spin spectroscopy for studying local ionic diffusion in electrode materials for Li ion batteries

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Lithium ion batteries are ubiquitous in today's technology: they power our phones, laptops and are finding greater use for larger scale applications such as electric vehicles. Developments in sodium ion batteries are also of great current interest for use in stationary energy storage technologies such as grid storage for renewable energy sources. The movement of Li^+ or Na^+ ions through the active electrode material in a battery is crucial for its electrochemical performance, yet quantifying this behaviour can be very technique dependant. For example, macroscopic ionic diffusion measurements can indicate greater activation energies for ion diffusion due to the extra impedance imparted by macroscopic grain boundaries. Here, we demonstrate the use of muon spin relaxation spectroscopy (μ^+-SR) as a valuable local tool to probe the Li^+ and Na^+ diffusion dynamics in battery electrode materials. The μ^+-SR method allows one to probe the local diffusion of ions via the muon spin perturbation caused by these diffusing ions.[1] Developing a clearer understanding of these diffusion processes at a local scale can provide us insights into electrochemical behaviour and the opportunity to optimise and tailor performance.[2]

We present the investigation of local ion diffusion in the polyanionic positive insertion electrode materials $LiFeSO_4F$ and Na_2FePO_4F using μ^+-SR for the first time. It is predicted that these structures possess multi-dimensional ionic diffusion pathways, suggesting facile ion diffusion.[3] In addition to enhanced ionic diffusion, these compounds display high energy densities driven by the inductive effect. The results obtained from these μ^+-SR studies indicate lower activation energies and larger diffusion coefficients at room temperature compared to values obtained by computational and bulk characterisation means. This indicates intrinsically favourable diffusion dynamics which could be accessed by improvements in, for example, engineering of materials to reduce impedance effects from grain boundaries.

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Photocatalytic CO_2 Reduction: An Alternative Source of Renewable Fuels?

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Ever since the first reports on photocatalytic CO_2 reduction[1,2] research in this direction has been performed for almost 40 years. The reaction allows not only to recycle CO_2, but also to provide a source of renewable hydrocarbons (Figure 1). Yet, no industrial process has so far been realized, which is predominantly due to the extremely low yields and selectivities achieved so far. A thorough literature search furthermore revealed that many studies fail to prove that hydrocarbon formation truly originated from CO_2.[3] The potential of the photocatalyst may be overestimated, if impurities contribute to product formation.

To evaluate the potential of photocatalytic CO_2 reduction, we conducted a thorough study on TiO_2 as model photocatalyst. Under conditions of highest purity it is demonstrated that continuous production of CH_4 from CO_2 as carbon source is truly possible.[4] Reaction conditions are optimized with respect to light intensity and reactant concentration,[4,5] and potential intermediates of the reaction are identified under batch conditions.[6] It is also verified that the reaction is indeed light-induced, but that it contains classical catalytic steps that are accelerated by higher temperature.[5] Surface modification with noble metals and structural design is shown to alter the product distribution.[7]

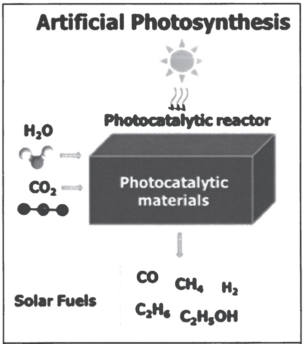

Figure 1. Schematic representation of photocatalytic CO_2 reduction.

However, yields remain low, and product formation ceases after some time. Apparent quantum yields, determined with TiO_2 thin films, are almost negligible. The catalytic cycle is most likely not closed, since oxygen formation in the gas phase does not occur. If oxygen is added to the reaction mixture, product formation completely ceases.[4] It is thus concluded that commercial TiO_2 can never be a viable option to realize an industrially feasible process. Instead, directions for future material and process development are suggested and discussed that bear the promise to realize such a process in the future.

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Manganese oxides as water oxidation catalysts

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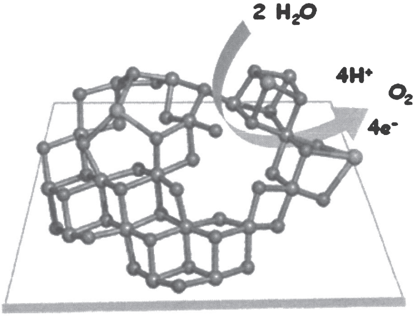
Water oxidation (splitting of water molecules into gaseous O_2, protons and electrons) is pivotal for the sustainable production of non-fossil fuels as water is the optimal source of electrons to reduce protons or CO_2 and convert them into storable fuels (H_2 or carbohydrates). One of the main requirements for the successful practical use of this process is the development of efficient noble-metal-free catalysts that can facilitate this highly energy demanding reaction. Biological water oxidation, responsible for the production of oxygen in the atmosphere, is catalyzed by a Mn_4CaO_5 center where the metal ions are connected by bridging oxygens and form a small oxide-like cluster.[1] This renders inorganic Mn oxides very attractive water oxidation catalysts for utilization in renewable fuel synthesis.

Efficient and stable electrochemical water oxidation catalyzed by Mn oxides is still a challenge but during the last five years, the number of the studies in this field increased tremendously and provided insights in the requirements for catalytic activity in synthetic manganese oxides. Going beyond characterization of the catalyst resting state, recent results from X-ray absorption spectroscopy and electrochemistry imply that Mn oxides are non-classical heterogeneous catalysts.[2,3] Their activity is not restricted to the surface and is determined by the dynamic interactions of several Mn ions. The structure allows for reversible transition between Mn(III) and Mn(IV) as well as bridging-type changes during the catalytic cycle. Based on recent results, possible strategies for development of catalysts with optimized activity and stability will be discussed.



Amorphous Mn oxides are promising catalysts for anodic water oxidation.

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Impact of Fe-impurities on a Ni-Co-Oxide Catalyst for Oxygen Evolution

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For the sustainable production of hydrogen from fluctuating, renewable energies water electrolysis is a promising technique. As for fuel cells, the oxygen reaction is however a limiting factor. The most active catalysts for the oxygen evolution reaction (OER) are based on expensive and rare Iridium or Ruthenium. In alkaline electrolyzers alternative materials like transition metal oxides can be used.[1]

Recent research implies that Fe-impurities from the electrolyte can affect the catalyst performance of Ni-based oxide catalysts.[2] In this work we demonstrate the detrimental effect of Fe contaminations in commercial KOH solution not only on the activity but also on the corrosion behavior of a Ni-Co-based OER catalyst. An electrochemical flow cell (EFC) is combined with an Inductively Coupled Plasma – Optical Emission Spectrometer (ICP-OES) (Figure 1).[3-4] With this setup we can quantify in-situ the incorporation of Fe from the electrolyte onto or into the catalyst. At the same time we follow the degradation behavior of the Ni-Co-Oxide catalyst during our standardized benchmarking protocol.[3] This reveals that not only the Fe-incorporation leads to an activation of the catalyst, but it also actively prevents the dissolution of Ni and Co-species from the catalyst.

For analytical measurements of potential OER catalysts this secondary effect of activation and stabilization by Fe impurities should be avoided or at least minimized. The till now presented method for KOH purification involves expensive chemicals and only allows small quantities of purified KOH.[2] We therefore also present a simple, cheap, and fast method to purify large batches of KOH for the general use of purified KOH in electrochemical measurements.

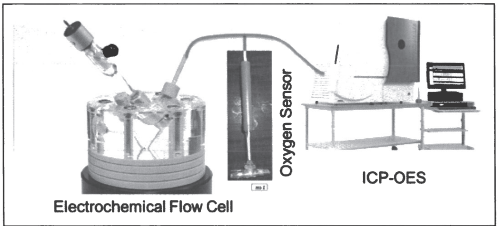

Figure 1. Flow cell design and combination with ICP-OES for performance and corrosion evaluation of OER catalysts

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Materials for ORR and OER - from platinum free electrocatalysts to advanced photoanodes

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The oxygen reduction reaction (ORR) and the oxygen evolution reaction (OER) are two important catalytic reactions in the field of energy conversion. Both suffer from sluggish kinetics and require the utilization of expensive electrocatalysts usually based on platinum group metals (PGM) to drive the reactions at acceptable rates. While the ORR represents a serious bottleneck for fuel cell development, the OER seriously limits advances in the field of water splitting and hence emission free hydrogen production.

In the present contribution, materials strategies for PGM-free ORR and OER electrocatalysts, respectively photoanodes, will be presented.

In terms of ORR, novel electrocatalysts derived from cheap N-containing polymers and simple Fe-precursors with high activities and stabilities in both acidic and basic media will be presented. [1]

Regarding OER, optimized $BiVO_4$ thin film photoanodes (cation/anion doping, heterojunction design and interface engineering) will be presented, yielding unprecedented performance for light induced oxygen evolution under visible light. [2,3]

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Tuning the Activity of Ni in the Hydrogen Electrode Reactions and Borohydride Oxidation Reaction by Varying its Surface State

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Recent advances in the development of alkaline membrane fuel cells and further progress in alkaline water electrolysis strongly stimulates the interest in platinum-group metal (PGM) free catalysts for various electrocatalytic processes. Among them Ni is considered as one of the most promising candidates due to its low cost and high corrosion stability in alkaline media. However, the activity values reported in the literature, for example, in the hydrogen oxidation and evolution reactions (HOR/HER) on Ni are rather contradictory and may differ by nearly two orders of magnitude.

In this presentation the reasons for the diversity of reported activity values will be discussed by analyzing Ni electrodes with varied surface states. An importance of the latter will be shown for two cases, namely, the hydrogen electrode reactions and the borohydride oxidation reaction (BOR). In particular the specific exchange current density of Ni electrodes in the HOR/HER varies from few $\mu A\ cm^{-2}$ on metallic Ni to several tens of $\mu A\ cm^{-2}$ in the presence of Ni surface oxide species [1-3]. On the contrary, oxidation of the Ni surface leads to a decrease of its activity in the BOR, while metallic Ni shows very high current density even below 0 V vs RHE. The reasons for the influence of the surface state of Ni electrode on its electrocatalytic activity will be discussed with the help of microkinetic modelling, which supports a change in the adsorption energy of H_{ad} species on Ni surface after its partial oxidation. Finally, it will be shown that the conclusions obtained for polycrystalline Ni electrodes remain valid for carbon supported Ni/C electrocatalysts with small (ca.10 nm) Ni nanoparticles.

Acknowledgments:
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A novel synthesis approach for Fe/N/C-type ORR-catalysts - insights on composition and activity

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Polymer electrolyte fuel cells (PEFCs) play a vital role in a future carbon-neutral transportation scenario based on hydrogen as the energy carrier. Since up to now seizing a significant market share has been hindered by the high price of these devices,[1] efforts are being made to reduce the excessive cathode catalysts' cost by replacing Pt-based materials with non-noble metal alternatives. The best performing materials of this class have been shown to be a viable option for catalyzing the oxygen reduction reaction (ORR) in PEFCs.[2,3] Pursuing higher catalytic activities, however, research is directed towards employing metal organic frameworks (MOFs) and reactive NH_3-based atmospheres in the synthesis thereby driving up the cost of the cathode system contradicting the initial aim of decreasing its contribution to the PEFC price.

Taking this into consideration, our work follows an alternative approach based on polyacrylonitrile as the C- and N-precursor, sodium carbonate as the pore inducing agent and Fe-phenanthroline as the metal precursor.[4] To elucidate the influence of different synthesis parameters on the composition and performance of the resulting catalysts, we employ electrochemical activity measurements (rotating disc electrode and PEFC tests) as well as surface and bulk characterization techniques (X-ray photoelectron, absorption and Mössbauer spectroscopies). By optimizing the heat treatment temperature, the precursors' ratio and the Fe-content of these materials, activities amongst the highest in their class (i.e. for catalysts synthesized without NH_3 or MOFs) as well as a satisfactory control over the Fe-speciation could be achieved.

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In-operando characterization of novel fuel cell catalysts using XAS and DRIFTS

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Critical issues for the broad commercialization of fuel cell catalysts, in particular for automotive applications, concern their cost and stability. With respect to cost, current research focusses on either replacing part of the expensive noble metal platinum in binary alloys, e.g. Pt-Co, or on using so-called non-PGM catalysts, such as Fe-N-C mimicking the active sites for respiration in vertebrates. With respect to stability, the corrosion-prone carbon support can be substituted by more stable materials, such as (doped) oxides or even electron-conducting polymers.

In-operando characterization is a necessary step towards active and stable fuel cell catalysts, as it allows monitoring their performance during operation. In this background, X-ray absorption spectroscopy (XAS) is a suitable tool, since it does neither require long-range order in the sample, nor UHV conditions during measurement. Analysis of the extended edge region (EXAFS) provides information on number, kind and distance of nearest neighbors and can be translated into particle size, alloying and oxidation. The near edge region (XANES) can be either compared to reference samples and fingerprinted or correlated with theoretical spectra, where it will give an indication of adsorbed species present at the catalyst surface during operation.

In previous work of our group, XAS was used to study carbon-supported Pt nanoparticles as catalysts in direct methanol fuel cells (DMFC), direct ethanol fuel cells (DEFC), and high-temperature polymer electrolyte fuel cells with phosphoric-acid imbibed PBI membranes (HT-PEMFC). Various questions were addressed by this approach, e.g. the effect of fuel starvation on catalyst degradation in DMFC and the poisoning of active catalyst sites by phosphoric acid in HT-PEMFC. When the carbon support was replaced by stable doped Sn oxide, CO can be used as a probe molecule to study the particle-support interaction.

A novel in-situ cell was developed to allow for the combination of X-ray absorption spectroscopy (XAS) and diffuse infrared Fourier transform reflectance spectroscopy (DRIFTS) at the same time and with high quality [1]. The cell is based on a design of Drochner et al. [2], in which a reference and the sample material are tested under identical conditions. XAS and DRIFTS were recorded simultaneously and analyzed with respect to kind of surface adsorbates, binding sites, coverage as well as nanoparticle structure. We benefit from the DRIFTS being able to distinguish between different CO binding sites (atop, bridge, analyzed also by DFT calculations) and XAS being able to probe adsorption (XANES) and nanoparticle structure (EXAFS) [3]. Further results and preliminary measurements will be highlighted in the talk.

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Degradation of the Carbon Support in Fe/N/C Catalysts used for the Reduction of Oxygen in PEM Fuel Cells

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One of the main obstacles to the commercialization of low temperature proton exchange membrane fuel cells (PEMFCs) is related to the expensive state-of-the-art platinum catalyst used for the oxygen reduction reaction (ORR). Among a vast variety of non-noble metal catalysts, Fe/N/C materials are demonstrating the most promising performance. While the nature of the active sites of these catalysts has been commonly accepted as FeN_4-moieties [1], the degradation mechanism(s) are not established yet. The following paths have been proposed in the literature in order to explain the poor stability of Fe/N/C materials: leaching of Fe [2, 3]; carbon and/or site oxidation by H_2O_2, a by-product of the ORR [4]; protonation of the active sites [5]. The aim of this work was to follow the changes in the state of the carbon support in Fe/N/C catalysts within their deactivation in a PEMFC.

The Fe/N/C catalyst was synthesized using the following precursors: polyacrylonitrile as C- and N- source, Fe^{II}-phenanthroline as Fe source, and Na_2CO_3 as a pore-inducing agent [6]. The synthesized catalyst has been integrated into a Nafion-based membrane electrode assembly and studied in the fuel cell by measuring the polarization curves before and after galvanostatic stability tests. The chemical composition of the pristine and post-mortem catalyst and particularly of its carbon support was controlled by X-ray photoelectron and Raman spectroscopies, and offer insight on the changes undergone at this crucial component upon PEMFC operation.

Acknowledgements

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The Behavior of Multivalent Cations in Next-Generation Battery Systems

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Rechargeable Li-ion batteries revolutionized energy storage but the fundamental limitations imposed by intercalation chemistry and the cost associated with common components in Li-ion cells, such as Co, drives the need for new, less expensive batteries. The search for these so called "beyond Li-ion" technologies include systems based on sulfur cathodes, multi-electron intercalation cathodes, and new working ions, to name a few. Here, we focus on chemistries based in divalent working ions as promising alternatives to lithium-based chemistry as they open the door to the use of metal anodes, as opposed to intercalation anodes, while using abundant and inexpensive resources.

We will explore the behavior of divalent Mg^{2+} in Mg metal batteries. Mg electrodeposition and stripping, the process occurring at the anode of a Mg metal battery, is dependent on the coordination chemistry of Mg^{2+} in the electrolyte solution. This talk will discuss the speciation of Mg^{2+} in Cl-containing electrolytes that support reversible Mg electrodeposition and stripping.[1,2] Hypotheses regarding processes at the interface will be put forth as possible mechanistic pathways. An underexplored area of Mg-S batteries using these electrolytes will also be discussed including the effect of desolvation of Mg^{2+} at the cathode-electrolyte interface.

In the second part of the talk, we will explore the ability of divalent cations to conduct in solid-state electrolytes. Solid-state electrolytes bypass many of the downfalls of organic solvent-based electrolytes including issues with flammability and desolvation at the electrolyte-electrode interface. Divalent cations show lower conductivity in solid-state lattices compared to monovalent Li^+ due to their high charge density. Despite these challenges, we have developed an electronically insulating divalent ion conductor. Possible ion diffusion pathways in this material and future strategies towards higher conductivity materials will be discussed.

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Replacing metals: carbon fibers derived from a poly(ionic liquid) as a current collector

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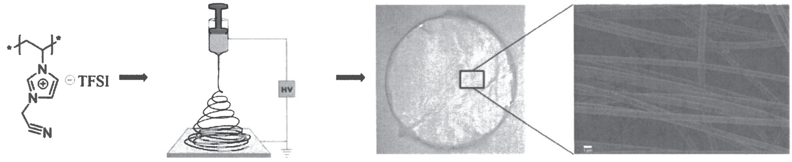
The demands of modern electric vehicles necessitates that all the components be optimized, effective and cheap. Out of all the components in batteries, current collectors have received less attention. In lithium ion batteries, typically aluminum and copper foils are used as the current collector for the cathode and anode respectively. The copper foil is expensive and heavy, and the aluminum foil, although cheap, reacts with lithium. In supercapacitors, the demanding requirements for a current collector are even higher, since its faster rate capability means that a high conductivity is critical. Thus, supercapacitors can be considered a benchmark for performance of current collectors in batteries. The golden standard is platinum, albeit its high cost and weight hinders the wide-spread application of supercapacitors.

In this context we developed a new current collector, by electrospinning poly(ionic liquid)s (PILs), crosslinking and carbonizing. PILs are an emerging class of polymers that feature an ionic liquid species in each monomer repeating unit, combining the advantages of polymers and ionic liquids. Electrospinning is a technique to produce continuous fibers with diameters of a few micrometers down to tenths of nanometers. Electrospun fibers have the advantages of being stand-alone, and having a high surface area, continuity of the material, and low percolation threshold. The spun fibers were crosslinked to maintain their structure and carbonized to 950°C to increase their conductivity. Up to now, the conductivity of amorphous carbons was too low to replace the current collector in supercapacitors. However, these PILs fibers show performance that matches that of platinum, and works in both aqueous (1M Na_2SO_4 in water) and organic (1M $TEABF_4$ in Acetonitrile) electrolytes. Their high macroporosity makes them lightweight, at least two order of magnitude lower than a typical platinum collector. Both the precursor material and the fibrous form are essential, as PILs as a film or carbon fibers made from polyacrylonitrile as a precursor don't resemble platinum performance.



Poly(ionic liquid) synthesis

Electrospinning
PIL solution

Collected sheet

SEM of fibers

Figure 1: process scheme

New Battery Technologies based on Fluoride Ions

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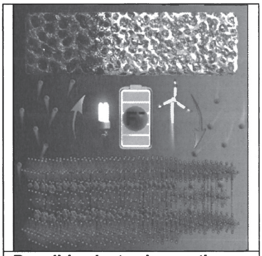
All-Solid-State Batteries are currently investigated for their increased intrinsic safety. Apart from the field of lithium ion systems, such batteries can also be based on a shuttling of fluoride ions [1] in a fluoride ion battery (FIB). The active electrode materials can be based on two different types of reactions. Conversion based materials, i. e., for which a metal fluoride is transformed to the corresponding metal and vice versa, can give high capacities and energy densities. However, conversion reactions usually go with high volume changes, which is highly problematic in an all solid state battery to maintain electrochemically active interfaces. Consequently, FIBs based on conversion electrodes suffer from strong capacity fading, and intercalation based systems could help to obtain systems with increased cycling stability. In this field our aim is to find systems with high cell voltages and high capacities.



Possible electrode reactions for fluoride ion batteries.

In this talk results will be presented on the examination of different potential cathode materials, anion-deficient perovskites [2], Ruddlesden-Popper [3], and schafarzikite type materials [4]. It will be shown that the structure type is of high importance to obtain good reversibility, and that the detailed kind of transition metal plays a vital role to obtain systems with high cycling stability. We will further show that the establishing of anode systems could also be facilitated within the Ruddlesden-Popper structure type and its flexibility to accommodate ions in unusual low-valent oxidation states, e. g., Ni^+ and low-valent Ti [5].

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A new series of active materials for safer energy storage

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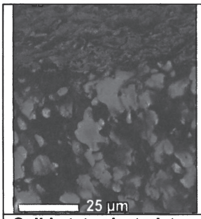
All solid-state batteries present highly promising opportunities for safer energy storage. High ionic conducting solid electrolytes may overcome some of the limitations of organic polymer electrolytes, where safety concerns limit the electrochemical stability window, to provide a way to increase energy densities in a safe manner. However, resistance to ion mobility across the solid-solid electrode-electrolyte interface remains a bottle-neck to be overcome in realising this technology. The synthetic approach employed can potentially influence conductivities (and hence battery performance) exhibited by solid electrolytes and this talk will detail our efforts to maximise these properties through developments in our synthetic approaches. I will present some of our latest results on systems such as the NASICONs and perovskites where we apply electrodes and electrolytes with similar crystal structures, as well as Li-S systems where we apply nanostructuring at the electrode/electrolyte interface, in our attempts to encourage ion mobility at the interface. I will present our study of these materials including the use of X-ray and neutron diffraction, total scattering, X-ray absorption analysis, impedance spectroscopy, muon spin relaxation measurements and electrochemical evaluation. I will show that careful synthetic design can enable performance and a comprehensive analysis provides greater insight into materials properties.



Solid state electrolyte LZP and electrode LTP

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Development of the solid electrolytes and their applications for solid-state Li-S batteries

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A deeper understanding of the underlying chemistry behind the ion conduction in solids is key to the further development of solid electrolytes and, consequently, solid-state batteries.[1] Recently, the correlation between lattice dynamics and observed ionic conductivities attracts significant attention.[2–4] The speed of sound measurements, Raman spectroscopy, and inelastic neutron scattering are conducted to experimentally probe the changes of phonons in various frequency ranges and compared with computationally obtained phonon density of states. The differences of those potential descriptors for investigating the influence of lattice dynamics on the ionic transport will be discussed. The influence of the varied polarizability of anion frameworks residing along the ion-conduction pathways, which we call an inductive effect, is another point of view to explain the observed trend in the ion transport. The stronger Coulombic interactions between anionic frames and moving ions seemingly give a detrimental influence on the ionic conductivities. This highlights the importance of the better understandings of the structure-property relationships.

In addition to the fundamental studies of solid electrolytes, we also construct batteries with them to better understand the physicochemical phenomena in the solid-state batteries. One important aspect is the influence of volume changes. Although the conventional liquid electrolytes can freely move to keep the contacts among components intact in conventional Li-ion batteries, the "breathing" of the active materials surrounded by solid electrolytes can lead to the crucial contact losses due to their rigid mechanical properties, which results in a loss of the capacity.[5] Employing sulfur as an active cathode material, we demonstrated the chemo-mechanical failure in solid-state Li-S batteries, which significantly deteriorate the battery performance. This work emphasizes the importance of the processing methods of cathode composites, not only for the intimate contact to achieve a high capacity (1000 mAh g_{sulfur}^{-1}), but also to minimize the loss due to the chemo-mechanical failure.

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New Sulfur-containing polymers for stable cycling in Lithium–Sulfur batteries

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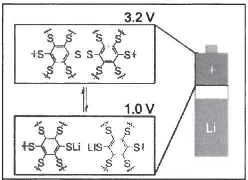

Schematic of representative crosslinked disulfide polymer as a cathode in Li–S batteries.

The main advantages of Lithium-Sulfur batteries are the high theoretical capacity of elemental sulfur and the sustainability of sulfur-based materials over toxic, expensive heavy metals such as cobalt. Sulfur can theoretically achieve 1675 mAh g^{-1}, but due to the parasitic polysulfide shuttle problem, the capacity rapidly fades. We demonstrate new crosslinked disulfides as promising cathode materials for Li–S cells that are designed to have only a single point of S–S scission, preventing the formation of polysulfides. The first model crosslinked disulfide system we synthesized (shown in schematic format here) was designed to maximize the ratio of S–S to the electrochemically inactive framework. The material contains a 1:1 ratio of S:C with a theoretical gravimetric capacity of 609 mAh g^{-1}. Cells made with this crosslinked disulfide cathode material gain capacity through 100 cycles and have 98 % capacity retention thereafter through 200 cycles, demonstrating promise for stable, long-term cycling. Raman spectroscopy confirms the proposed mechanism of disulfide bonds breaking to form a S–Li thiolate species upon discharge and reformation upon charge. Coulombic efficiencies near 100% for every cycle, suggesting the suppression of polysulfide shuttle through molecular design. Further iterations of this crosslinked disulfide design aim to increase ionic and electronic conductivities to achieve higher gravimetric capacities that will lead these stable sulfur-based batteries closer to a commercially viable technology.

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Toward New Solar Batteries: Graphitic Carbon Nitrides Enabling Direct Solar Energy Storage

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Graphitic carbon nitrides are earth-abundant polymeric materials that are used for various photo- and electro-catalytic applications. Herein, we report a 2D cyanamide-functionalized polyheptazine imide (NCN-PHI), which enables the synergistic coupling of two key functions of energy conversion within one single material for the first time: visible light harvesting and electrochemical energy storage. We reveal the underlying mechanism of this "solar battery" material, showing that the charge storage in NCN-PHI is based on the photoreduction of the carbon nitride backbone while charge compensation is realized by the adsorption of alkali metal ions within the NCN-PHI layers and at the solution interface. The photoreduced carbon nitride can thus be described as a battery anode operating as a pseudocapacitor, which can store light-induced charge in the form of long-lived, "trapped" electrons for hours. Importantly, the potential window of this process is not limited by the water reduction reaction. Owing to these properties, the complexity of solar batteries is significantly reduced and higher cell voltages for aqueous batteries are possibly enabled. Thus, the feasibility of light-induced electrical energy storage and release on demand by a one-component light-charged battery anode is demonstrated. This approach provides a sustainable, earth abundant solution to overcome the intermittency of solar irradiation and other renewable electrical energy sources at a time.

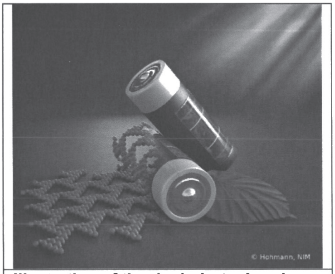

Illustration of the dual photoabsorber-battery-functionality enabled by the carbon nitride NCN-PHI.

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Elucidating the Active Phase of Pt-Based Electrocatalysts for Oxygen Reduction

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The slow kinetics of the oxygen reduction reaction (ORR) limits the performance of sustainable energy conversion devices such as low-temperature fuel cells and metal-air batteries. Pt-alloys are the most active and stable ORR catalysts in both acidic and alkaline electrolyte. Elucidating the factors governing the ORR electrocatalysis and the structure-activity-stability relationships is essential to design more efficient catalysts [1].

The effect of subsurface alloying on the ORR can be studying by using model electrode surfaces such as Cu/Pt(111) near-surface alloys (NSAs) [2,3]. The ORR activity as a function of the OH adsorption follows a Sabatier volcano relation. This volcano-type relation exists both in acidic and alkaline media, suggesting that the ORR shares the same reaction intermediates in both electrolytes. The results on Cu/Pt(111) NSAs provide the key design principle for the ORR in both acidic and alkaline electrolytes [3].

On the other hand, we have systematically studied the ORR activity and stability trends by controlling strain effects on Pt-lanthanide alloys [4]. These materials present up to a 6-fold activity enhancement over Pt. The activity versus the bulk Pt-Pt distance follows a volcano relation, the maximum activity corresponding to the optimum level of strain [4]. The active phase consists of a Pt overlayer formed by acid leaching [4-6]. We used *in situ* grazing-incidence X-ray diffraction to study the formation and stability of the compressed Pt overlayer on Gd/Pt(111) [6]. The overlayer forms upon exposure to the acidic electrolyte under open circuit conditions. The compressive strain relaxes slightly upon repeated electrochemical cycling between 0.6 and 1.0 V vs. the reversible hydrogen electrode (RHE) [6].

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Octahedral Fuel Cell Nano Catalysts

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The development of cheap, active and stable catalysts for the cathodes of proton exchange membrane fuel cells is challenging due to the harsh environment and the sluggish kinetics of the oxygen reduction reaction (ORR). Shape-controlled bi- or tri-metallic Pt alloy nanoparticles are considered a highly promising family of catalysts due to the very high Pt-mass based activity which they show in rotating disk electrode (RDE) experiments.[1] In particular octahedral PtNi nanoparticles have been highly investigated. The octahedral shape maximizes the (111) surface facet, which has been observed to possess extraordinary high specific activity for single crystal with Pt_3Ni composition.[2] Despite the high mass activity, during prolonged electrochemical testing, Ni loss and other degradation processes often results in shape changes into more "rounded" or concave structures with loss of the (111) facet and lower activity (figure 1).[3]

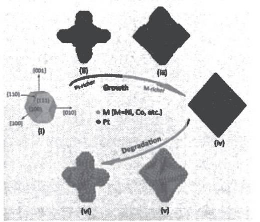

Figure 1. Life cycle of an octahedral PtNi nanoparticle[3]

In this contribution we will show our recent efforts in improving the activity and especially the durability and morphological stability of PtNi based octahedral nanoparticle catalysts. The catalysts are produced by solvothermal methods and investigated by a combination of in situ wide angle X-ray scattering (WAXS), elemental mapping and X-ray fluorescence spectroscopy. Activity and stability are evaluated from RDE measurements following a protocol developed inside the INSPIRE project.[4]

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Acknowledgement: This project has received funding from the Fuel Cells and Hydrogen 2 Joint Undertaking under grant agreement No 700127 INSPIRE. This Joint Undertaking receives support from the European Union's Horizon 2020 research and innovation programme.

Nanoporous Pt-based network catalysts for oxygen reduction

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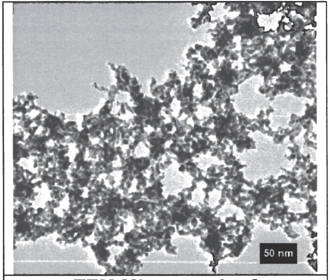
Fuel-cell catalysts have traditionally consisted of Pt-based nanoparticles (NPs) supported on high surface area carbon (Pt/C). In recent years, several concepts have presented activities far exceeding Pt/C [1]; however, many of these concepts achieve their high mass activities at 0.9 V_{RHE} by increasing their intrinsic activities at a cost of lower electrochemically active surface area (ECSA), a critical parameter a fuel cell operating voltage ~0.6–0.7 V_{RHE} [1].



TEM Micrograph of Nanoporous Pt network

Herein, we present a novel catalyst concept consisting of a supportless nanoporous Pt-based network. The synthesis was performed using alternated sputtering of Pt and Co in a dual magnetron physical vapor deposition (PVD) chamber follow by a dealloyed process [2]. The residual core-shell Pt-Co network was characterized both structurally and electrochemically. Revealing a specific activity for oxygen reduction equal to polycrystalline Pt_3Co combined with ECSA values exceeding Pt/C, overall resulting in an extraordinary high mass activity.
To further enhance the catalytic properties, we currently explore alloys of Pt-lanthanides, as these present up to a 6-fold activity enhancement over Pt [3]. Until now, the high oxygen affinity of rare earth metals has hindered synthesis using convention methods. Exploiting the high vacuum in the PVD chamber we synthesized PtGd-based networks with intrinsic activities comparable to their bulk counter parts.
Finally, nanoporous Pt-network and Pt/C were measured in a gas diffusion electrode half-cell [4] enabling benchmarking at fuel cell relevant condition, allowing for direct comparison to MEA measurements [4].

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Abstracts of Posters

(in alphabetical order
BATTERY; FUEL CELLS; SYN FUELS)

Topochemically-stabilized V_2O_5 polymorphs: Expanding the palette of functional multivalent-ion cathode materials

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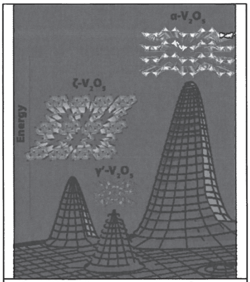
The discovery of solid-state electrode materials that demonstrate reversible intercalation of large and highly polarizing ions has progressed slowly, effectively stymieing the development of Mg-, Ca-, and Al-ion battery technologies. The current dearth of available multivalent-ion cathode materials, relative to their Li-ion counterparts, can be attributed in part to a very narrow sampling of phase space. Indeed, the majority of evaluated multivalent-ion cathode materials have fallen within the sphere of thermodynamically-stable phase space, rendering metastable phases-space under-explored. We have recently detailed a systematic approach using ternary vanadium pentoxide bronzes as templates for realizing novel bonding and functionality in metastable, binary vanadium oxides. We report on the successful stabilization of two metastable polymorphs and discuss their subsequent utilization as cathode materials in Li-, Mg-, and Ca-ion batteries. The first example, ζ-V_2O_5, is far superior to its thermodynamically stable counterpart, α-V_2O_5, in its ability to avoid detrimental, irreversible phase transitions and furthermore mitigate polaronic confinement effects to allow the fully-reversible insertion of up to 3 Li^+, 0.33 Mg^{2+}, and 0.33 Ca^{2+} per V_2O_5 at moderately high operating voltages. In a second example, the metastable γ'-V_2O_5 polymorph shows promising results as a cathode material in nonaqueous Mg- and aqueous Ca-ion batteries. In both instances, the consequences of the metastability of these materials is central to explaining their improved performance at the atomic and mesoscales. Not only is such a systematic exploration of phase space fruitful for the discovery of novel multivalent-ion cathode materials, but it also facilitates the direct comparison of the role of bonding motifs and structure-function relationships in facilitating multivalent ion diffusion across varied structures.



The relative stability of Metastable V_2O_5 phases

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Sol-Gel Assisted Synthesis of MAX Phase Cr_2GaC

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Ternary carbides that belong to the family of MAX phases are typically prepared by high-temperature solid state methods, such as hot isostatic pressing, spark plasma sintering, arc melting of metals or binary precursors and carbothermal reduction of oxides.[1,2] Here, we report a sol-gel assisted approach for the synthesis of Cr_2GaC. In brief, an aqueous, amorphous gel consisting of metal nitrates and citric acid is heated at 900 °C under Ar for a few hours resulting in the formation of a highly crystalline MAX phase. X-ray powder diffraction data show the presence of side phases (Cr_3C_2, Cr_2O_3, <10wt%) that can be influenced/prevented by the addition of small molecules, e.g. tetraethylen glycol. Ex-situ powder diffraction after gel-treatment at different temperatures along with initial thermal analysis data indicate the reaction to progress through the carbothermal reduction of chromium oxide and subsequent reaction with carbon to form the final product.

The versatility of this wet chemical approach offers a plethora of ways to tune this reaction, especially the chemical composition and morphology of the obtained MAX phase.

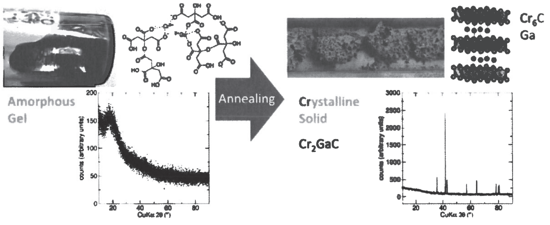

Figure 1. Reaction scheme showing the transformation of an amorphous gel into crystalline Cr_2GaC.

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Garnets meet polymers: From synthesis to flexible SSBs with stable interfaces?

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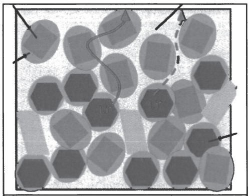
In order to enhance the performance of lithium ion batteries many efforts were made on solid state electrolytes. The aim of this project is to combine the advantages of two different solid electrolytes by mixing them. A garnet type solid electrolyte (e. g., $Li_{7-3x-y}Al_xLa_3Zr_{2-y}Ta_yO_{12}$, Al-doped LL(Z,T)O) and a polymeric MEEP based electrolyte.

For the investigation of the behavior of LLZO at interfaces with other materials, our lab has established an LASER assisted CVD process (LA-CVD), which can provide high quality thin film garnet based electrolytes[1]. By a combination with various coating and deposition techniques, a broad variety of interfaces can then be studied[2].

In this work, we report on the deposition of doped LL(Z,T)O via LA-CVD on different substrates. We will show initial results on the *in situ* preparation and characterization of 2D interfaces of LL(Z,T)O with a model polymer. Further, we extended this study to the preparation of mixtures of polymers and LLZO particles in order to obtain flexible electrolyte membranes and electrode composites, and characterize their overall temperature dependent conductivity.



Project aim: Mixture of electrode particles with solid electrolyte in a polymer matrix

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Experimental and computational thermochemistry of oxide-based material systems for energy conversion and storage applications

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New and highly efficient methods for energy conversion and storage are mandatory to decelerate global warming and to stint the consumption of finite fossil fuel. The technological innovations are often accompanied with new demands on materials properties. Hereby, the CALPHAD method (Computer Coupling of Phase Diagrams and Thermochemistry) is an invaluable tool to support the search for high performance materials by combining key experiments with thermodynamic modeling for a deeper understanding of the entire material system. In this work, experimental and computational thermochemistry were applied to the research of new potential anode materials for lithium ion batteries and of high temperature stable materials for next generation thermal barrier coatings applied in advanced stationary and aircraft turbines.

Copper and iron oxides exhibit the conversion mechanism and were investigated as model materials. The aim was to develop thermodynamic descriptions of the Li-Cu-O and Li-Fe-O systems based on key experimental data [1-4]. Using the thermodynamic descriptions of the multi-component systems, open circuit voltages and plateau capacities can be predicted.

Compositions in the tetragonal phase field of the ZrO_2-Y_2O_3-Ta_2O_5 system are promising for thermal barrier coating applications [5]. The development of thermodynamic models of the complex multi-component phases within the material system allows identification of operating temperature limits, phase equilibria as well as calculation of the driving forces for equilibrium and non-equilibrium phase formation. Thermochemical experiments, such as calorimetry to obtain enthalpies of formation and heat capacities in dependence of composition build a solid base for consistent thermodynamic modelling.

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The electro-chemo-mechanical modelling of lithium ion battery

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The performance of lithium ion battery shows a strong dependence on the active materials, which brings the importance of modelling the electro-chemo-mechanical physics inside a particle for the cell. the multiphysics coupled single particle model has been presented to predict the cell performance under galvanostatic discharge [1,2], where the influence of phase separation and mechanics on the diffusion behavior of lithium inside the particle has been considered. In this study, In order to incorporate the particle level into the cell level, an extended Pseudo-Two-Dimensional (P2D) [3] model of $LiPF_6|LiMn_2O_4$ is developed, where the intercalation of Li ions into particle from electrolyte is described via a BV equation. Results show that the existed stress can enhance the bulk diffusion, and with a limited increase of the stiffness of the particle, the attainable capacity can be improved, besides that, the phase separation behavior of the active material brings a higher capacity. Other than this, the different shapes and sizes of the particle show a not negligible impact on the battery cell performance, the oblate shape particle with smaller size brings a much better battery cell performance. We extend the model to consider the defects of the particle, where the cohesive zone model is applied for the particle, the fracture and debonding of active particle influence is predicted in great details.

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Intercalation-Based Cathode Materials for All Solid-State Fluoride Ion Batteries

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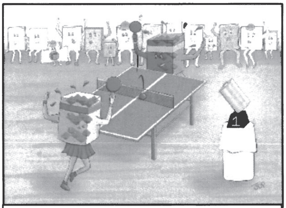
Fluoride ion batteries (FIBs) represent an alternative energy storage technology to lithium ion batteries (LIBs), which can provide a large electrochemical potential window[1] due to the high stability of the fluoride ion. Previously, such batteries were developed based on the use of conversion type electrodes, which can result in a strong capacity fading due to the complexity of stabilizing systems with large volume changes in all solid state batteries. A way to overcome this could lie in the use of intercalation based electrode materials. In our recent work, we have demonstrated that K_2NiF_4 type compounds such as $LaSrMnO_4$[2], and La_2CoO_4[3] can work as high voltage intercalation type cathode materials with theoretical capacities similar than found for intercalation type electrodes in LIBs, giving an enhancement in cyclability. The results indicate that carbon based conductive additives can be a limiting factor for the development of high voltage cathodes due to carbon side reaction. Further, we will show that Ni based compounds can give excellent cycling stability with capacity retention of > 99 % per cycle for at least 70 cycles, which is high considering the use of an all solid state system.



La_2CoO_4 as a cathode material for fluoride ion batteries.

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Multi-scale-modeling of dislocations in lithium-ion-battery-electrodes

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Dislocations are known as paths of high diffusivity for a broad range of materials, for example electrochemical active materials used in lithium ion battery electrodes. The underlying mechanisms for Diffusion in and along dislocations are not fully recorded, especially as dislocations show a negative effect on diffusion in some materials. Mechanical strains around dislocations influencing the energy barriers for diffusion offer a possible Explanation for an enhanced diffusion. Correlations between a dislocation-rich microstructure and the electro-chemical behavior of a battery cell can be analyzed using continuum-models and multi-scale-simulations. Current approaches for modeling the correlation between dislocation and diffusion are limited on the segregation of impurities along the dislocation line, while the effect of the stress is addressed only in a simplified manner, if not neglected. Until now dislocations in lithium ion battery models have been viewed only as an additional source for stresses excluding the influence on the diffusion. The effect of a defect rich microstructure on the battery cell performance is completely unknown. In this work these relationships will be analyzed by utilization of continuum models and finite-element-simulation on three length scales. On the microscale, dislocation structures can be explained in a phase-field-model including stress-driven diffusion effects. Simulations of the transport within dislocation networks give information on the effective diffusivity of a micro-scaled sample depending on the dislocation density. The effective diffusivity can be implemented to simulate the charging of meso-scaled free standing electrode particles. Finally these models can be integrated into a macro-scale battery-cell-model to link the effect of the cell performance to the influence of the defect-rich microstructure.

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Defining and Modulating Diffusion Pathways in Intercalation Cathode Materials: Some Lessons from V_2O_5 on Directing Cation Traffic

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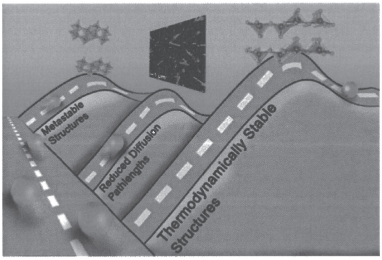

Limitations to the power and energy densities of Li-ion batteries constitute a major impediment to our energy future, particularly with regards to electric vehicles and grid-level storage. Current battery technologies suffer from a number of challenges e.g., capacity loss, limited ion diffusion kinetics, and failure upon prolonged cycling. The development of novel battery architectures and altogether new battery chemistries is imperative to address these challenges. In recent work, we have used V_2O_5 as a model system to seek atomistic understanding of diffusion pathways upon scaling to nanometer-sized dimensions. Scanning transmission X-ray microscopy (STXM) studies in conjunction with density functional theory suggest that polaron localization plays a key role in limiting cation mobility at low levels of intercalation,[1] giving rise to heterogeneous lithiation across individual cathode particles. Distinctive compositional striping is evidenced within 1D nanowires resulting in large strain gradients[2]. Conventionally, these mechanical strains are regarded as adverse by-products of the battery electrochemistry; however, the pre-existing strains and defects can potentially be used to program and define diffusion pathways with reduced migration barriers. Here, we will discuss the influence of local phenomena e.g., pre-existing and emergent strains, constrictions in ionic conduction pathways as a result of extended defects such as dislocations, and the stabilization and self-trapping of polarons with regards to their implications for introducing multiscale compositional and phase heterogeneities. Moreover, we will address mesoscale structuring as a means of directing intercalated cations such as by reducing diffusion pathlengths and through the design of metastable frameworks that yield frustrated coordination and provide decreased barriers for migration of polarons[3].

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Chemo-mechanical analysis of inverse opal structures for application in lithium-ion battery electrodes

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The increasing demand for higher storage capacity and power density of lithium-ion batteries calls for the optimization of electrode microstructures, in particular at the micro- and nanoscale. Key factors are thereby short diffusion paths and large surface areas exposed to the electrolyte in order to achieve faster intercalation and solid-state transport in the electrode materials. Candidate structures for these design goals can be found in nanoporous materials, fractal(like) morphologies, and metamaterials such as inverse opals. Thereby the surface effect can have impact.

In this contribution, we present finite element simulation results on microstructured inverse opal structures and reveal diffusion-induced stresses along with the influence of surface stress. We describe the characteristic distribution of mechanical stresses and lithium concentration within the material and highlight problems and opportunities for optimization that can arise from these features.

In-situ Cell Design for ^{57}Fe Mößbauer Spectroscopy on Fe-N-C Catalysts

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With the increasing of world-wide energy demand, new energy sources are required, especially for the transportation sector. Electrochemical energy conversion as conducted in proton exchange fuel cells (PEFCs) and batteries are very promising in this respect [1,2]. However, due to the common use of platinum in PEFCs the technology is commercially not competitive. For the oxygen reduction reaction (ORR), Fe–N-C catalysts are cheap and in terms of activity the most promising substituents for the replacement of platinum. Besides, Mößbauer spectroscopy is quite useful for identification of iron species [3,4]. In-situ Mößbauer spectroscopy could give detailed information of iron sites, as well as changes in the coordination environment and electronic states during electrochemical polarization. However, so far no data are available for Fe-N-C catalysts and only a rare number of publications on FeN_4 centers is available for carbon supported macrocycles for the ORR [5-7]. The major problem is related to the different requirements for electrocatalysis and Mößbauer spectroscopy in combination with the low iron loadings typically found in Fe-N-C catalysts [8]. The former needs only the surface accessible part, thus above a specific loading the ORR activity will not increase anymore. The later gives as better spectra as more of the Mößbauer active Fe-57 isotope is present, which is a paradox.

In this work, we will present our results on the new in-situ cell design and related results obtained by in-situ Mößbauer measurements will be discussed.

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Theoretical insights in NiCu catalysts for the HER

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The attention towards anion-exchange membrane fuel cells has been increasing in the last few decades due to their ability to function without expensive Pt-group metals. Anodes of this fuel cell are usually Ni-based, but Ni adsorbs hydrogen too strongly resulting in a much lower hydrogen oxidation activity when compared with Pt. Development of NiM bimetallic materials is a promising strategy. The idea behind is to develop electrodes that approach or exceed the activity of the Pt metal. Cu is one of the most promising metals to combine with Ni because it adsorbs hydrogen weaker than Ni. Bimetallic NiCu materials have been studied both theoretically[1] and experimentally.[2]

In this work, we computed the energies of H and OH adsorption separately as well as activation energies for their recombination reaction on mixed NiCu surfaces with different Cu content in the top layer: 25%, 50%, 75% and 100%. The corresponding values for Ni(111) and Cu (111) were also used for comparison and are listed in the Table. 50% and 75% Cu appear as the most promising surfaces for the water formation through Had + OHad surface recombination.

Surface	Initial state	H_{ads}	OH_{ads}	E_{act}	G_{ini}	E_{tot}
Ni (111)	fcc	-0.49	-3.29	0.84	-0.90	0.74
25% Cu	H: 3 Ni OH: 3Ni	-0.57	-3.37	0.78	-1.11	0.54
	H: 3 Ni OH: 1Cu	-0.57	-3.18	0.75	-0.99	0.16
	H: 1 Cu OH: 1Cu	-0.24	-3.18	0.26	-0.57	-0.26
50% Cu	H: 2 Cu OH: 2Cu	-0.26	-2.99	0.34	-0.67	0.05
	H: 1Cu OH: 2Cu	-	-	0.20	-0.40	-0.23
75% Cu	H: 2Cu OH: 2Cu	-0.21	-2.82	0.50	-0.54	-0.31
	H: 2Cu OH: 3Cu	-0.21	-2.86	0.22	-0.08	0.50
	H: 3Cu OH: 3Cu	-0.09	-2.86	0.82	-0.83	0.01
100% Cu	fcc	-0.18	-2.98	0.45	-0.16	-0.28
Cu (111)	fcc	-0.19	-2.88	0.58	-0.13	-0.48

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From RDE towards Fuel Cell – Influence of temperature change and electrode structure on the ORR activity

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Considering a CO_2 neutral energy supply in the future, especially solutions are also required for the transportation sector. Proton exchange fuel cells (PEFCs) play an important role. However, so far high costs hinder a commercial breakthrough. To a significant extend this is cause by the high costs of platinum based catalysts that are used, today. Fe-N-C catalysts are a very promising alternative to commercial Pt/C as they reach almost similar activity.

Within catalyst optimization, usually the first step are structure activity correlations in RDE conditions (room temperature, low loading, oxygen saturated H_2SO_4) while the conditions are slightly different in PEFCs (80 °C, oxygen gas, high loading, proton conducting membrane, importance of transport properties).

Not in all cases the results from RDE are directly transferrable to PEFCs. Moreover, the quotient between RDE and PEFCs depends on the preparation route etc.

In this work, we try to gain a better understanding on the changes in performance as a function of operation conditions in order to bridge between RDE and PEFC.

Relation between preparation parameters and ORR activity and selectivity for a silica-templated synthesis of Fe-N-C catalysts

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Fuel Cells (FCs) are considered as a key technology for future automotive propulsion, since they provide a sustainable and efficient way to convert chemical into electrical energy. One important downside lies within the high production costs of FCs, which derive mostly by the use of platinum based materials to catalyse the cathodic oxygen reduction reaction (ORR). Therefore, it is of great importance to develop cost-efficient alternatives such as Fe-N-C catalysts. It is known, that the morphology and porosity of these catalysts has a great influence on their activity and selectivity towards ORR. These important parameters not only define the mass transport inside the catalyst layer, but also directly affect the accessability of the active sites.[1-3]

The aim of this work is to investigate the ORR activity and selectivity of iron porphyrin based catalysts, obtained by a template synthesis approach with silica nanoparticles as a support. The variation of the surface coverage degree of iron porphyrin and the size of the silica nanoparticles allows for a precise control of the catalysts morphology and porosity during synthesis. The obtained catalysts are characterized by N_2-sorption, TEM, XPS and Mößbauer spectroscopy.

The results show that both, the degree of coverage of the template and the template size, both have a crucial impact on the ORR activity as well as selectivity of the investigated catalysts.

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Electrochemical etching of Ti_2AlC MAX phase obtained by non-conventional solid-state synthesis

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MXenes first synthesized in 2011 are a novel family of two-dimensional (2D) early transition metal carbides or nitrides obtained from their corresponding three dimensional (3D) MAX phases. MXenes offer a unique combination of metallic conductivity and hydrophilicity and can potentially be prepared from the large family of over 70 members of known MAX phases. These appealing properties and a large number of DFT studies predict that MXenes will play a major role in key research fields such as energy storage, photo-, electro- and chemical catalysis, electromagnetic interference shielding, electrochemical biosensors, environmental remediation and other fields that remain still to be identified [1].

Alternative synthetic methods for new MAX phases as well as HF-free etching procedures for obtaining the MXenes from the corresponding MAX Phases are important research directions in order to fill the gaps in the current knowledge [1]. Among the alternative methods non-conventional solid-state synthesis techniques (microwave heating and spark plasma sintering) have been successfully used to prepare bulk MAX phases [2]

In this work an electrochemical approach was investigated for the etching of the MAX phase Ti_2AlC obtained by a non-conventional solid-state technique. The present work is a feasibility study if electrochemical etching could be an alternative to the etching procedures with hazardous HF or LiF/HCl solutions that are currently used to prepare MXenes from their corresponding MAX phases.

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Understanding water incorporation in barium cobaltates and the role for protonic ceramic fuel cells

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Perovskite based cobaltates and ferrates ($ACo_{1-x}Fe_xO_{3-y}$) have attracted a lot of attention due to their interesting catalytic properties for the oxygen reduction reaction in solid oxide fuel and electrolysis cells (SOFC, SOEC). The perovskite structure can exist in cubic (only ccp stacking of AX_{3-y} layers) and hexagonal modifications (partly to full hcp stacking of AX_{3-y} layers), and especially the cubic modifications are reported for their high catalytic activity. Further, water incorporation on anion vacancies y can result in proton conduction, making the materials interesting for protonic ceramic fuel and electrolysis cells (PCFC, PCEC), and a high symmetry then allows for higher ionic conducitivity in polycrystalline samples [1].

In the system $BaCoO_{3-y}$, a wide range of different modifications are known, which were summarized by Raveau et al [2]. as well as in a recent article by Mentré et al. [3] a variety of hexagonal perovskite type modifications for oxygen richer systems (2H, 12H, 5H, 5H'), the most oxygen deficient cubic perovskite phase $BaCoO_{2.23}$ as well as $BaCoO_2$. For the latter two, the structure is derived from a ccp stacking of BaO_{3-y} layers. In our recent efforts to prepare oxygen deficient perovskites phases using different synthesis routes, we re-investigated the system $BaCoO_{3-y}$ and found at least three new modifications with different value of y, but also two water rich compound with composition $BaCoO_{1.80}(OH)_{0.86}$ [4] and $BaCoO_{1.60}(OH)$ [5].

In this talk, an overview will be given about the new phases of such barium cobaltates, reporting a detailed characterization of their crystal structure, the role of water incorporation on proton ordering and conductivity, as well as the importance to understand such ordering behaviour of protonic charge carriers in Ba-rich compounds in order to further improve their catalytic activity and applicability.

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Effects of Cation Ions on the Reactivity of Pt/C during the Hydrogen Oxidation

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Improvements in the development of anion-exchange membranes and non-noble-metal catalysts for electro-reduction of oxygen, have attracted large attention in the application of alkaline membrane fuel cells (AMFCs). However, high Pt loadings are still required to accelerate the sluggish kinetics of the hydrogen oxidation reaction (HOR) in alkaline environment and therefore a breakthrough of AMFCs is further hindered [1,2].

In this work, the catalytic activity of HOR/HER on polycrystalline platinum (poly-Pt) and high surface area carbon-supported platinum nanoparticles (HSAC-Pt) in various alkaline 0.1 M electrolyte solutions (MOH, M=Li^+, K^+ and Na^+) were studied using rotating disc electrode (RDE) technique. In addition, the polarization curves of the HOR were analysed by using the Butler-Volmer equation to determine the exchange current density and symmetry factor. Based on our results of the micro-kinetics, we show that the catalytic properties of platinum are strongly influenced by the non-covalent interactions and arrangement of different mono- and bivalent cation ions in the outer Helmholtz plane. We suggest that due to the water arrangement controlled by the monovalent cations effects the energetics of the adsorbed hydrogen and promote the HOR activity on Pt in 0.1 M LiOH. Our work provides a deeper understanding about the effect of cations on the kinetics of the HOR/HER and show that the energetics of adsorbed hydrogen on the metal can be used as a critical descriptor to improve the HER/HOR kinetics in alkaline media.

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CoS_x/C catalysts for the hydrogen evolution reaction - Influence of the pyrolysis temperature

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According to the German Federal Environmental Agency in 2016 traffic made up 29.5 % of the final energy consumption in Germany, while renewable energies stagnated at 5.2 % to 6.0 % within this sector between 2008 and 2017. In order to reach the climate protection goals and reduce the CO_2 emissions, it is therefore essential to move on from fossil fuels to a CO_2 neutral energy supply. Fuel cells and hydrogen as fuel are considered promising candidates. One way to produce hydrogen is the electrolysis of water (electrochemical water splitting) using excess electrical energy from renewable sources. In this context, transition metal sulfides like CoS_x and MoS_x have gained attention as hydrogen evolution reaction (HER) catalyst, in recent years. [1,2]

In this work, we stepwise investigated the transition from molecular CoS_4 complexes to sulfide nanoparticles and study its impact on the HER activity. A CoS_4 molecular complex was synthesized according to literature and impregnated on carbon black [3,4]. The HER activity was investigated as function of pyrolysis temperature and acid-leaching.

We will show to what extend the HER activity changes upon pyrolysis temperature and to what extend these changes can be explained by changes in the structural composition.

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Towards enhanced photocatalytic hydrogen evolution by carbon nitrides with a true 2D topology

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Solar energy harvesting and storage of high energy chemical fuels are an important research topic nowadays, which is addressed directly and efficiently by photocatalytic water splitting. One of the most famous metal-free photocatalysts for aqueous hydrogen evolution is Melon, a 1D polymer also known as graphitic carbon nitride (g-C_3N_4).[1,2] Its advantages over other photocatalysts are chemical and thermal stability up to 600°C, synthesis from inexpensive precursors as well as suitable energy levels to straddle the water redox potentials under visible light illumination. To further improve the activity of this and other carbon nitrides, it is important to understand the photocatalytic mechanism and to gain insights into the structure – property – activity relationship in these multifunctional materials.

A new generation of extended carbon nitride solids can be obtained by transformation and functionalization of Melon by a salt melt synthesis that converts the primary amine groups to cyanamide.[3,4] The backbone of the resulting polymer is a poly(heptazine imide) (PHI) that has a true 2D layered structure. To study the relationship of structure and photocatalytic activity, light-driven hydrogen evolution was measured. PHI that is functionalized with cyanamide groups outperforms non-functionalized Melon by more than an order of magnitude in the solar hydrogen production rate and in the apparent quantum efficiency at 400 nm.[4,5] Moreover, this carbon nitride mimics artificial photosynthesis by storing solar energy for time delayed hydrogen evolution in the dark. As such, it enables "dark photocatalysis". [6]

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Influence of the metal species on the selectivity in CO_2 reduction on Me-N-C catalysts

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CO_2 reduction will play a crucial role within a future environmentally friendly economy. There are several possible products that can be formed, CH_4, formic acid or CO are among them. Some chemicals might be used directly, some others might be used as precursors in follow-up reactions. Regardless, a high selectivity for one distinct product is anticipated to avoid time and cost intensive separation steps. It is well known for metals, and MeN_4 macrocycles, that the type of metal center strongly determines its selectivity [1]. Me-N-C catalysts are the heat-treated analogs of the macrocycles. There is one distinct difference: their affinity towards CO binding is significantly less, CO adsorption is not even possible at RT [2,3]. As a consequence, the product distribution will also change. In recent studies the role of metal center was investigated for catalysts prepared at 900 °C [4,5]. However, at such high temperature it is likely that catalysts also contain inorganic metal species. Thus, it remains unclear to what extent MeN_4 sites contribute to the activity and selectivity.

In this work, we therefore focused on Me-N-C catalysts prepared from Me porphyrins (where Me = Fe, Co, Cu, Sn, Zn) supported on carbon. Thus, the N_4 coordination is already present in the precursor and catalysts were prepared at a low pyrolysis temperature to avoid the presence of inorganic metal species from side reactions [6].

Catalysts were characterized by several spectroscopic techniques. The reaction products of the gaseous phases have been analyzed by mass spectroscopy to determine faradaic efficiencies.

The results will be discussed in comparison to MeN_4 macrocycles and other Me-N-C catalysts.

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Adding a new member to the MXene family: $V_4C_3T_x$

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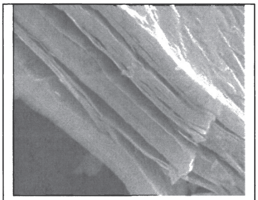
Since the discovery of MXenes as a new class of two-dimensional materials, more than 20 different MXene have successfully been synthesized and many more have been predicted theoretically.[1] They are very promising materials for various applications due to their unique physical and chemical properties. Consequentially, they are discussed in the context of a variety of applications, such as battery materials, heterogeneous electrocatalysts, sensors, and many more. Herein, we can add a new “43”-type carbide MXene to the family. The synthesis of $V_4C_3T_x$ was realized through selective etching of V_4AlC_3 using hydrofluoric acid. The required precursor MAX phase V_4AlC_3 was initially synthesized via a non-conventional solid-state method, microwave heating.[2] The characterization of both structures were carried out by X-ray powder diffraction and electron microscopy techniques. Furthermore, we present the catalytic performance towards the hydrogen evolution reaction of the new $V_4C_3T_x$ MXene.



SEM image of the new $V_4C_3T_x$ MXene

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