



International Conference on Nanoscale
Catalysis and Energy Conversion

ABSTRACTS

Harnack House Berlin, Germany
November 15-16, 2023

WEDNESDAY, NOVEMBER 15 (REGISTRATION: 8:00 – 8:45)

08:45	Christopher Kley Florian Johann	Welcome and Introduction
09:00	Prof. Beatriz Roldán Cuenya Fritz Haber Institute (DE)	Life and Fate of Energy Conversion Electrocatalysts (Keynote)
09:30	Prof. Wolfgang Schuhmann Ruhr University Bochum (DE)	From single particle electrochemistry to electrocatalyst discovery (Invited)
09:50	Prof. Christine Kranz University of Ulm (DE)	In situ SPM studies of light-driven heterogenized molecular systems (Invited)
10:10	Prof. Georg Papastavrou University of Bayreuth (DE)	New AFM-cantilevers for Electrochemical in-situ Probing on the Local Scale (Contributed)
10:25 – 11:00	<i>Coffee break</i>	10:40 – 11:00 AFM hands-on Session
11:00	Prof. Fengtao Fan Dalian State Key Laboratory of Catalysis (CN)	Spatiotemporal imaging of charge transfer in photocatalyst particles (Invited)
11:20	Prof. Frieder Mugele University of Twente (NL)	In situ and operando characterization of photocatalytically active faceted semiconducting nanoparticles (Invited)
11:40	Prof. Bernhard Roling Philipps University of Marburg (DE)	AFM-based techniques for the electrochemical characterization of solid electrolytes and mixed ion-electron conductors (Invited)
12:00	Dr. Tom Miller University College London (UK)	Electrochemical atomic force microscopy of battery interfaces (Contributed)
12:15	Prof. Florian Hausen Forschungszentrum Jülich (DE)	Mechanical insights on the evolution of functional layers in batteries and Electrolyzers (Contributed)
12:30	<i>Lunch</i>	
13:30	Prof. Patrick Unwin University of Warwick (UK)	The new era of high throughput electrochemical multimicroscopy (Keynote)
14:00	Dr. Jan Balajka Technical University of Vienna (AT)	Atomic scale insights into oxide surfaces in aqueous environments (Invited)
14:20	Prof. Olaf Magnussen Christian Albrechts University Kiel (DE)	Scanning tunnelling microscopy studies of Cu surface restructuring during electrochemical CO ₂ reduction (Invited)
14:35	Prof. Tomasz Kosmala University of Wrocław (PL)	Uncovering active sites and enhancing catalytic activity in 2D materials for hydrogen evolution reaction (Contributed)
14:50 – 15:20	<i>Coffee break</i>	15:00 – 15:20 AFM hands-on Session
15:20	Dr. Wei Nie Helmholtz Center Berlin, Fritz Haber Institute (DE)	Nanoscale imaging of electrochemical interfaces by operando scanning probe microscopy (Invited)
15:40	Dr. Stacy Moore University of Bristol (UK)	Direct Observations of Electrochemical Processes Using Dynamic Scanning Probe Microscopy (Contributed)
16:00 – 18:00	Poster Session	
19:30	Conference Dinner	

THURSDAY, NOVEMBER 16

09:00	Prof. Takeshi Fukuma Kanazawa University (JP)	Visualizing EDL structures and chemical reactions by open-loop electric potential microscopy (Keynote)
09:30	Prof. Kislou Voitchovsky Durham University (UK)	Nanoscale probing of ions and water dynamics at interfaces (Invited)
09:50	Prof. Jaime Colchero University of Murcia (ES)	Non-Contact imaging of charges within the Debye Layer using Atomic Force Microscopy (Contributed)
10:05	Prof. Oleg Kolosov Lancaster University (UK)	3D nano-rheology microscopy: Operando nanomapping of 3D mechanical nanostructure of SEI in Na-ion batteries (Contributed)
10:20	Dr. Bizan Balzer University of Freiburg (DE)	Nanoscale programmable friction with ionic liquid mixtures (Contributed)
10:35 – 11:05	<i>Coffee break</i>	10:45 – 11:05 AFM hands-on Session
11:05	Prof. Núria López ICIQ Tarragona (ES)	Developments in CO ₂ electrochemical reduction: Insights from theory (Keynote)
11:35	Dr. Nicolas Hörmann Fritz Haber Institute (DE)	From Atomistic Interactions to Cyclic Voltammograms and Back Again (Invited)
11:55	Dr. Jun Huang Forschungszentrum Jülich (DE)	Overlapping electric double layers at the mesoscale (Contributed)
12:10	Prof. Stefan Weber University of Stuttgart	The nanoscale photovoltaics laboratory on a tip (Invited)
12:30	<i>Photo & Lunch</i>	
13:50	Dr. Roger Proksch Oxford Instruments Asylum Research (USA)	Accurate multifrequency electromechanics: Electrostatics, Null points and implications for functional nanoelectromechanics (Invited)
14:10	Prof. Tobias Cramer University of Bologna (IT)	Quantitative imaging of electroswelling in organic mixed ionic electronic conductors (Contributed)
14:25	Prof. Elad Gross Hebrew University (ISR)	Operando IR nanospectroscopy mapping of hydrogen dissociation and sorption on single Pd nanoparticles (Contributed)
14:40	Dr. Niklas Biere Oxford Instruments WITec (DE)	Correlative Raman Microscopy for Battery Research (Contributed)
14:55	Dr. Yujin Tong University of Duisburg-Essen (DE)	Characterization of Ultrafast Processes at Electrochemical Interfaces Using Femtosecond Lasers (Contributed)
15:10	Dr. Yu-Ping Ku Helmholtz-Institute Erlangen-Nürnberg (DE)	Degradation of Fe-N catalyst layers in alkaline media
15:25 – 16:00	<i>Coffee break</i>	15:40 – 16:00 AFM hands-on Session
16:00	Panel discussion	Fundamental research and technological innovation in catalysis and energy conversion Moderator: Dr. Davide Esposito, Editor-in-Chief Nature Catalysis
16:45	Poster Award & Closing	

Beyond Static Models: Dynamics in Electrocatalysis

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Climate change concerns have spurred a growing interest in developing environmentally friendly technologies for energy generation, as the production of green H₂ from water splitting. Moreover, the electrochemical reduction of CO₂ (CO₂RR) into value-added chemicals offers an additional possibility to store renewable energy into chemical bonds. Thus, efficient, selective and durable catalysts must be developed. Nonetheless, in order to tailor the chemical reactivity of nanocatalysts, fundamental understanding of their structure and surface composition under reaction conditions must be obtained. However, even morphologically and chemically well-defined pre-catalysts will be susceptible to drastic modifications during catalysis. Even more, such changes might be reversible when the applied external stimulus (e.g. electrical potential and/or chemical environment) is removed, resulting in misleading information on the nature of the active sites when in situ or operando characterization data are not available.

This talk will provide examples of the operando evolution of catalysts employed for the CO₂RR as well as the oxygen evolution reaction (OER) using model pre-catalysts ranging from nanoparticles (Cu₂O cubes, CoO_x NPs, NiO_x NPs) to thin films (Co_{1+δ}Fe_{2-δ}O₄). Based on a multi-technique microscopy and spectroscopy characterization approach I will discuss the active state formation and the correlation between the dynamically evolving structure and composition of the working catalysts and their catalytic performance. Our studies are expected to open up new routes for the reutilization of CO₂ through its direct conversion into industrially relevant chemicals and fuels and a more efficient green hydrogen production.

From single particle nanoelectrochemistry to electrocatalyst discovery

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High-entropy materials were discovered as a novel nearly unlimited source of compositional variation for the discovery of new electrocatalysts. I will report on high-throughput screening of electrocatalysts for energy for reactions for energy conversion and storage.^[1]

During the last decade tools for single-entity electrochemistry were instrumental to provide in-depth insight into electrocatalytic reactions at the nanoscale. This is mainly due to the possibility of determining intrinsic electrocatalytic properties of a given material avoiding any convolution with ensemble properties, and the influence of diffusional limitations or additives.

In this presentation, I will present a journey from the determination of the local pH value at the interface of an electrocatalyst-modified electrode or gas-diffusion electrode during high current density oxygen evolution, hydrogen evolution, or CO₂ reduction^[2] to identical location TEM/single-nanoparticle-at-the-nanoelectrode techniques.^[3,4]

Using high-resolution nanoelectrochemical tools in combination with high-throughput catalyst discovery opens the way for progress in electrochemical energy conversion and storage.

Acknowledgements: These projects would not have been possible without the contribution of many coworkers over the years including T. Löffler, J. R. C. Junqueira, S. Dieckhöfer, E. B. Tetteh, M. Kim, S. Varhade, G. Arruda de Oliveira, J. Zhang, C. Santana Santos, T. Quast, O. Krysiak, W. He, T. Tarnev, T. Erichsen as well as cooperation partners including C. Andronescu, P. Unwin, A. Ludwig, M. Koper. The work has received funding from European Research Council (ERC) under the European Union's Horizon 2020 research and innovation program (CasCat [833408]), the Deutsche Forschungsgemeinschaft (DFG) in the framework of the research unit FOR 2397e2 (276655237), the research unit FOR2982 (413163866), the CRC247 [388390466], and Germany's Excellence Strategy–EXC 2033-390677874-RESOLV. The TEM was funded by the „Center for Solvation Science ZEMOS“ supported by the German Federal Ministry of Education and Research BMBF and by the Ministry of Culture and Research of Nord Rhine-Westphalia.

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Light-driven molecular catalysis: in situ SPM measurements at heterogenized systems

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Light-driven catalysis has attracted broad interest to enable carbon-neutral energy conversion and storage. The development and design of artificial molecular devices (i.e., artificial photosynthesis systems) using visible light, requires the heterogenization of catalysts (CAT) and photosensitizers (PS) within functional materials like membranes. Reaction products of light-driven catalytic activity of heterogenized systems are predominantly determined via gas-phase head-space gas chromatography, or spectroscopic measurements [1]. However, such bulk measurements hardly provide insight into heterogeneities of such molecule-in-matrix systems such as active component distributions and local activity. Moreover, due to the complexity of realizing systems e.g., for hydrogen (H₂) and oxygen (O₂) evolution, it is important to understand the mechanisms that govern the light-driven processes and the stability of the photoactive systems [2].

In this contribution, we use scanning electrochemical probe microscopy (SEPM) techniques to gain insight into light driven catalysis, ranging from nanoscale surface modifications like deposition of earth-abundant CAT [3] and co-deposition of CAT/PS for activity screening experiments using scanning electrochemical cell microscopy (SECCM). SECM and atomic force microscopy (AFM)-SECM allow spatially resolved *in situ* / *operando* detection of light-driven reaction intermediates and products such as H₂, O₂ and hydrogen peroxide (H₂O₂) at polyoxometalates (POM)/PS modified nanoporous block polymers [4] or polymeric carbon nitride (PCN) films [5].

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New AFM-cantilevers for Electrochemical *in-situ* Probing on the Local Scale

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The development of *in-situ* and *in-operando* methods has been always closely related to the availability of new technical solutions. Scanning probe techniques have largely profited from high-speed electronics, new actuator designs, and fast signal processing. However, also the probe itself also plays an essential role in the performance of an atomic force microscope (AFM). Various approaches for cantilevers enabling SECM combined with AFM have been presented in recent years, enabling increasingly the application of AFM-SECM for *in-situ* and *in-operando* studies.[1] Recently, commercial probes that integrate the imaging probe and electrochemical electrode on the same tip apex have become widely available.[2] However, also the usage of such probes does raise the question how topographic and electrochemical resolution can be validated. We could recently demonstrate that a resolution in the order to two times the theoretical limit could be achieved in the electrochemical channel.[2] Various methods for the calibration of the lateral resolution in the electrochemical channel will be compared in this contribution. In particular, simple preparation techniques for suitable calibration samples will be presented. Improvements for AFM-SECM setups have not to be restricted to the probe itself. By incorporating all elements of a three-electrode cell to the cantilever substrate miniaturized electrochemical cell for AFM become feasible.[3]

For some applications, probes with highly-defined probe geometry and large radii are required, such as mechanical indentation measurements or the quantitative measurement of interaction forces. A new approach for the preparation of ‘electrochemical colloidal probes’ (eCPs) will be presented.[4] Attaching micrometer-sized, solid gold particles to otherwise electrically isolated cantilevers allow for defined electrode and interaction geometry. Such probes can be used for measuring the mechanical response of actuator materials, defined electrical contacts on soft materials or direct force measurements under potentiostatic control. Recently, this preparation approach for eCPs has been extended in the direction of electrochemical grippers suitable for the handling of colloidal particles.[5]

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Spatiotemporal imaging of charge transfer in photocatalyst particles

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Understanding the charge separation mechanism at the spatiotemporal scale is the core scientific problem in solar energy conversion, yet it is highly challenging. Focusing on this crucial point, we developed the surface photovoltage microscopic method with high spatial resolution. With this method, the charge distribution on the photocatalytic particle was quantitatively studied at the nm/ μ m scale. Moreover, the vector addition effect of the built-in electric field on efficient charge separation has been revealed. On the basis of the above understanding, electric field management through asymmetric tuning strategies was proposed to align the electric field to the catalytic reaction site precisely, resulting in improved photocatalytic performances. Furthermore, spatiotemporally resolved surface photovoltage (SPV) techniques were developed to map charge transfer processes holistically from the femtosecond to second time scale at the single-particle level. New processes of ultrafast hot electron transfer and anisotropic trapping regimes were found, challenging the classical model and contributing to efficient charge separation in photocatalysis. These findings pave the way for the rational design of photocatalysts with improved performance.

In Situ and Operando Characterization of Photocatalytically Active Faceted Semiconducting Nanoparticles

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Photo- and electrocatalytically active materials play an essential role in the transition towards sustainable processes for energy storage and chemical conversion. Performance and stability of the materials still need to be improved. Yet, the microscopic origin of their current limitations are often poorly understood, often due to a lack of suitable techniques for characterizing the structural and electrical properties of surfaces on the nanometer scale.

In this lecture, I will introduce the methods that we have established in recent years to characterize solid-liquid interfaces using AFM from high resolution atomic scale imaging to colloidal scale electrostatic interactions[1, 2]. Subsequently, I will report on our recent progress in establishing in situ and operando AFM spectroscopy for characterizing charge distribution and optical response of photocatalytically active faceted nanoparticles of SrTiO₃[3] and BiVO₄ in ambient electrolytes of variable composition. Our measurements demonstrate the existence and pH-dependence of differences in surface potential between adjacent crystal facets, which are believed to drive the separation of photo-generated electron-hole pairs in photocatalysis. For visible light-driven BiVO₄, we monitor the variations of the local surface charge upon illumination, from which we extract the local surface photovoltage and thus the accumulation of charge carriers at the interfaces. The measurements suggest a strong influence of surface defects such as steps and disordered regions between adjacent facets for the accumulation of photo-excited charge carriers.

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AFM-based Techniques for the Electrochemical Characterization of Solid Electrolytes and Mixed Ion-Electron Conductors

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Various AFM techniques are available for the electrochemical characterization of materials at the nanoscale. The application of a voltage bias to a conductive AFM tip can lead to various response signals, such as electric currents (conductive AFM), forces/force gradients (electrostatic force microscopy), compositional changes in a subsurface volume of the sample below the tip manifesting in a Vegard strain (electrochemical strain microscopy), and changes in the Volta potential of the material surface (Kelvin probe force microscopy). In many of these techniques, the quantification and interpretation of obtained signals is by no means straightforward.

Here, we show a number of examples for AFM-based electrochemical measurements on solid electrolytes and on mixed ion-electron conductors. In the case of solid electrolytes, the application of a voltage bias to the AFM tip leads to ion transport and double layer formation in a sub-surface volume of the sample. These processes can be probed in non-contact mode by electrostatic force spectroscopy [1] or in contact mode by electrochemical strain microscopy [2]. In the case of mixed ion-electron conductors, ambipolar diffusion of ions and electrons takes place, leading to compositional changes in the sub-surface volume. This can be probed by Kelvin probe force microscopy [3] or by electrochemical strain microscopy [2].

Electrochemical strain microscopy (ESM) can be used for the characterization of both types of materials, since ESM signals can originate from electrostatic interactions as well as from Vegard strains. We present a comprehensive model for the cantilever dynamics at the contact resonance frequency, which provides information on the origin of ESM signals for the material under study [4,5]. Furthermore, we demonstrate an advanced ESM technique for the quantification of Vegard strains in mixed ion-electron conductors [6,7].

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Electrochemical Atomic Force Microscopy of Battery Interfaces

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The successful deployment of materials for advanced batteries requires an in-depth understanding of the correlation between their electrochemical performance and structural and mechanical evolution across multiple length scales. We must also quantify the reaction kinetics of their interfacial processes. In situ and operando electrochemical atomic force microscopy (EC-AFM) is a powerful tool that can simultaneously reveal these relationships with nanoscale resolution.¹

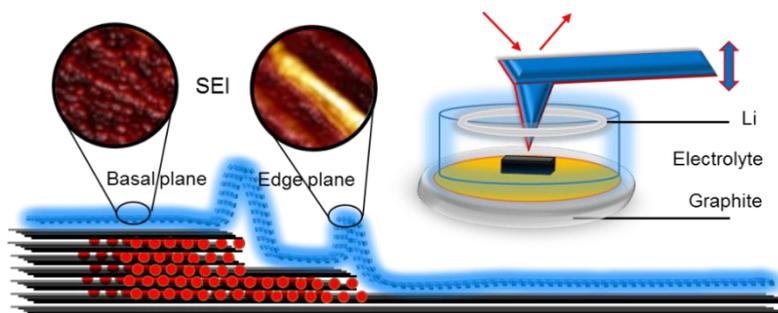


Figure 1: Electrochemical Atomic Force Microscopy (EC-AFM) at a graphite anode²

By studying the electrode-electrolyte interface of battery materials using EC-AFM we have been able to reveal unique changes in their morphological and nano-mechanical behavior as they cycle, develop and degrade. In lithium ion batteries (LIBs) we have utilized graphitic anode materials to reveal how solid electrolyte interface behavior (structure, stability) is highly dependent on the various electrolytes and commercially relevant additives used (Figure 1).² Whereas in zinc ion batteries (ZIBs) we have studied Zn deposition on metallic anodes, showing that the pre-cycling roughness of the Zn foil electrode defines the subsequent plating/stripping morphology and cycling behaviour.³⁻⁵ Finally, by studying two dimensional materials,⁶ which offer greatly enhanced properties when compared to their bulk counterparts, for application in sodium ion batteries (NIBs) we have visualized structural and phase change at materials that may be vital in the next-generation of batteries. Together, by discussing these studies, the versatility of EC-AFM for characterizing batteries will be demonstrated, in particular its ability to reveal phenomena that other commonly utilized tools are blind to. This will highlight the important role EC-AFM can play in facilitating the progress of future battery research.

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Mechanical Insights on the Evolution of Functional Layers in Batteries and Electrolyzers

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In-situ and *operando* atomic force microscopy is a powerful tool to investigate the formation of functional layers in batteries and materials for energy conversion, such as fuel cells or electrolyzers. The solid electrolyte interface (SEI) formation as well as Li intercalation and deposition on silicon and metallic Lithium anode materials for lithium-ion batteries in conventional and ionic liquids have been elucidated by electrochemical atomic force microscopy (EC-AFM).[1,2,3] Various degrees of heterogeneity are found depending on the exact system under investigation. The valuable mechanical information obtained in addition to the morphology is critically discussed, as well as influences of the substrate and electrolyte.

Especially, it is demonstrated that the tip could interact significantly with the material in contact, even under conditions where this is less expected, and the obtained results depend critically on the tip material.

Furthermore, electrochemical friction force microscopy is employed to investigate the initial dynamic degradation in epitaxially grown perovskite catalysts for the oxygen evolution reaction (OER). Friction is sensitive to chemical differences and thus, reflects subtle chemical transformations as a function of applied potential.[4] Fundamentals of the technique and first results with respect to dynamic electrocatalysis processes are reported.

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The New Era of High Throughput Electrochemical Multimicroscopy

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Scientists have sought to visualise processes at electrochemical interfaces *in operando* for more than two centuries! This aspiration has never been more important than today, particularly with the need to understand and improve electrocatalysis and energy storage. In this contribution, I will describe scanning electrochemical cell microscopy (SECCM), which employs an electrochemical (half-)cell nanopipette probe that makes meniscus contact with an (electrode) surface of interest to visualise nanoscale activity quantitatively in the form of maps and movies. Alongside topographical data of the surface, recorded synchronously, these electrochemical datasets are further mapped onto data from complementary co-located high-resolution microscopy and spectroscopy techniques. The resulting structure-activity correlations from this electrochemical multimicroscopy strategy can be analysed and modelled to provide detailed microscopic pictures of electrochemical processes and reactivity, and to predict and test the behaviour of electrodes on larger length scales.

I will show how electrochemical multimicroscopy can be used to answer important questions in electrochemical and interfacial science, spanning applications connected to energy storage materials, electrocatalysts and membranes. In essence, complex interfaces are studied with SECCM as a set of “single entities”, *inter alia*, individual steps, terraces, defects, crystal facets, grain boundaries, and single particles. Furthermore, SECCM facilitates high throughput combinatorial experiments, because parameters can be varied from spot to spot. This aspect of SECCM is further enhanced with *in-situ* (or *operando*) optical microscopy techniques to enable smart scanning and visualisation of the SECCM meniscus in real time.

With sincere gratitude to members of the *Warwick Electrochemistry & Interfaces Group* and collaborators who have contributed to our work in this area.

Atomic scale insights into oxide surfaces in aqueous environments

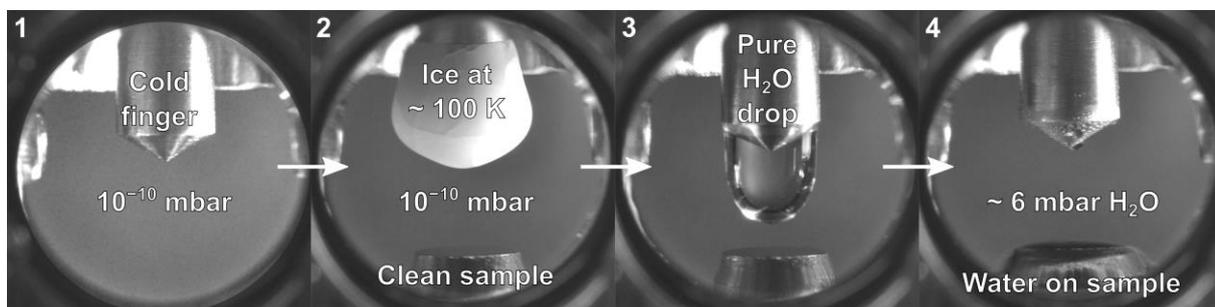
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Water-insoluble materials are thought to remain intact upon water exposure. At the atomic level, the reality is often more complex. The structure of many oxide surfaces has been established with atomic precision owing to the tremendous advance in surface science methods. Most analyses, however, have been conducted under the idealized conditions of ultrahigh vacuum while in natural and industrial environments, surfaces are often exposed to air or immersed in aqueous solutions.

Using atomically resolved imaging and surface-sensitive spectroscopic methods in combination with a custom-designed apparatus for dosing ultrapure liquid water [1,2] our experiments demonstrate a variety of responses of selected binary oxide surfaces to an aqueous environment. Specifically, the differences between stable (110) [1] and (011) [3] faces of rutile TiO_2 , the environmental stability of reconstructed anatase $\text{TiO}_2(001)$, the formation of an oxyhydroxide phase at magnetite $\text{Fe}_3\text{O}_4(001)$ [4], and the exchange of oxygen atoms at the aqueous interface of hematite $\text{Fe}_2\text{O}_3(1-102)$ [5] will be reviewed. I will show the experimental challenges of working with liquid water in ultrahigh vacuum and our recent efforts to determine surface tension of pure water under strictly controlled conditions. As a next step from idealized conditions towards the complex situation in ambient, the effects of pH and electrochemical potential on $\text{TiO}_2(110)$ and $\text{Fe}_3\text{O}_4(001)$ surfaces [6,7] will be discussed.

The experiments unveil the atomic structure and properties of oxide surfaces under realistic conditions and provide fundamental insights into important processes occurring in nature and technology.



Dosing ultrapure liquid water under UHV-compatible conditions

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Scanning tunnelling microscopy studies of Cu surface restructuring during electrochemical CO₂ reduction

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The electrochemical reduction of carbon dioxide holds great promise for sustainable production of base chemicals and synthetic fuels. Copper catalysts are of particular interest, as they enable formation of multi-carbon compounds. The formation of multi-carbon products can be further promoted by a secondary metal species, such as silver. Here, we present *in situ* scanning tunnelling microscopy studies of well-defined Cu and AgCu electrodes in CO₂-saturated 0.1 M KHCO₃, which is one of the most common electrolyte for CO₂ electroreduction (CO₂RR).

For Cu(100) in the double layer potential range, coexistence of two ordered (bi)carbonate adlayer phases was observed.[1] These adlayer phases have a highly complex structure, exhibit dynamic fluctuations, and undergo a potential dependent order-disorder transition at about 0 V vs. the reversible hydrogen electrode. Detailed density functional calculations reveal that the observed layer is composed of carbonate and water that coadsorb on the electrode surface, underlining the key role of water in the stabilization of the (bi)carbonate adlayers.

Upon decreasing the potential to the onset of CO₂RR, the formation of Cu nanoclusters is observed on the Cu(100) surfaces by *in situ* STM. This surface restructuring can be assigned to the influence of CO intermediates formed in the CO₂RR. Upon subsequent increase of the potential back into the double layer range, the clusters disperse, resulting in a highly disordered interface structure that contains Cu adatoms, (bi)carbonates, and further molecular adsorbates. This irreversible change of the molecular-scale electrode surface is supported by spectroscopic results.

In addition, AgCu bimetallic model catalyst were prepared by electrodeposition of submono-layer coverages of Ag on Cu(100) in 0.1 M H₂SO₄. After exchanging the electrolyte under potential control to 0.1 M KHCO₃ in the double layer potential range, distinct restructuring of the Ag islands, the appearance of new islands, and a reduced surface mobility are observed. Furthermore, high-resolution STM images show a disordered molecular adlayer.

Our results demonstrate the pronounced role of adsorbed (bi)carbonate at the catalyst/electrolyte interface and its impact on the surface morphology and dynamics already at potentials in the double layer regime. These adsorbate-induced structural changes need to be considered for a fundamental understanding and rational design of electrocatalysts for CO₂RR.

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Uncovering active sites and enhancing catalytic activity in 2D materials for hydrogen evolution reaction

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Developing and researching new materials for energy storage and conversion is a top priority in modern scientific research and a crucial challenge in the context of sustainable energy development based on alternative and renewable sources. The efficient conversion of chemical energy into electrical energy and vice versa necessitates the development of innovative electrocatalysts for use in fuel cells, batteries, or electrolyzers. However, current optimization methods primarily rely on the empirical "trial and error" approach, significantly impeding their development.

During this talk, I will showcase some of our recent work on the use of 2D materials in electrochemistry. I will present model systems that have been investigated using innovative in operando and in situ technique (Electrochemical Scanning Tunneling Microscope - EC-STM), allowing for the identification of catalytically active sites with atomic precision, along with changes in chemical and electronic states [1-3]. The presentation will also discuss various strategies for increasing electrocatalytic activity and optimizing catalysts using a knowledge-based approach. I will demonstrate the use of intrinsic defects such as metallic twin boundaries in chalcogenides [3,4], the electron hybridization effect in the Fe/graphene system, and catalysis on single atoms [1] during the presentation.

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Nanoscale imaging of electrochemical interfaces by operando scanning probe microscopy

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Recent advances in correlative electrochemical atomic force microscopy will be presented, aiming to elucidate the nanoscale electrochemical properties of electrocatalysts under liquid phase CO₂ electroreduction reaction (CO₂RR) and oxygen evolution reaction (OER) conditions. Key results include unveiling (i) the *in situ* atomic-level structural evolution of Co-based plates and thin film during OER, (ii) the surface structures of Cu electrodes during CO₂RR, (iii) the local electrical conductivity, chemical-frictional, and morphological properties of bimetallic electrocatalysts, and (iv) intermediates and products as well as hydration layer ordering effects during CO₂RR by complementary spectroscopy. A perspective of the potential of scanning probe microscopy for nanoscale catalysis and rational innovation of energy conversion materials will be given.

Direct Observations of Electrochemical Processes Using Dynamic Scanning Probe Microscopy

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Dynamic scanning probe microscopy (DSPM) is a type of contact-mode SPM capable of in-situ and real-time measurements of nanoscale structures and processes. A DSPM produces maps of a sample surface by monitoring the response of a sharp tip at the end of a cantilever as it is scanned across an area. The tip is in constant contact with the sample surface, enabling measurements of surface properties such as electrical or thermal conductivity, in addition to high-resolution (nanometre-scale) mapping of surface topography. Topographic maps can be collected in ambient, liquid, or gaseous environments enabling a wide range of experimental possibilities.

DSPM has been used to study a number of electrochemical phenomena. The sub-second temporal resolution has enabled in-situ observations of localised corrosion processes such as pitting corrosion [1] and stress corrosion cracking [2], as well as electrochemical processes such as electrodeposition [3]. In the presented work, results demonstrating simultaneous DSPM analysis and potentiostatic control will be presented. This work includes a series of experiments performed to probe metastable pitting behaviour in 300 series stainless steels. Various experimental set-ups are explored, including a microelectrode set-up implemented to reduce the frequency of pitting events with the aim of deconvoluting global electrochemistry. These electrodes were produced using 25 µm diameter Type 316 wire. The reduced area in which pitting events may occur also allowed for the whole electrode to be imaged by DSPM in approximately 2.5 minutes.

By achieving direct, in-situ measurements of electrochemical phenomena, such as pitting corrosion, a better understanding of the nanoscale mechanisms, and the order by which they occur, is achieved. In future work, the unique combination of capabilities of DSPM may be applied to new applications such as in-operando measurements of batteries [4-6].

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Visualizing EDL structures and chemical reactions by open-loop electric potential microscopy

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There have been strong needs for in-liquid potential measurement techniques with nanoscale resolution. To understand the reaction mechanisms of metal corrosion, catalysis, battery, and biosensors, local potential distribution during these reactions should be valuable information. To understand the molecular ordering inside the interfacial devices such as electric double layer (EDL) transistors and liquid crystal devices, it is potential distribution inside the EDL should give important insights. However, direct visualization of nanoscale potential distribution in electrolytes has been a great challenge.

Kelvin probe force microscopy (KPFM) has been the most widely used nanoscale potential measurement technique in air and vacuum. However, this method cannot be used in electrolytes. This is because applying a DC bias voltage between the tip and the sample is essential in this method, which results in uncontrolled electrochemical reactions and redistribution of water and ions. To overcome this problem, we developed open-loop electric potential microscopy (OL-EPM) [1]. In this method, only a high-frequency AC bias voltage is applied at the tip-sample junction and induced 1st and 2nd harmonic oscillation of a cantilever is detected and used for the calculation of local surface potential. As we do not need to apply a DC or low-frequency AC bias voltage, we can avoid the aforementioned problems in KPFM.

So far, we have used this technique to investigate the corrosion mechanisms of various metals such as stainless steels, Cu fine wires, and Al alloys [2-4]. In these studies, direct observation of local corrosion cells (i.e., a pair of anode and cathode) greatly helped us to understand the corrosion mechanisms. In addition, by combining this method with the electrochemical control system [5], we recently succeeded in the direct visualization of subnanometer-scale potential distribution inside EDL capacitance using ionic liquids. Combined with molecular dynamics simulation, we were able to explain the correlation between the interfacial structures and the device functions. These results highlight the effectiveness of the method for the studies on electrochemical reactions and interfacial devices.

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Nanoscale probing of ions and water dynamics at interfaces

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The local dynamics of ions and water molecules at electrochemical interfaces underpins many energy-related processes in science and technology. Atomic Force Microscopy (AFM) can routinely image the equilibrium arrangement of single adsorbed ions or molecules on immersed solids [1-3], but capturing their dynamics remains a considerable challenge. Using the AFM tip as a nano-antenna, it is possible to apply highly localized AC electric field over frequencies analogous to dielectric spectroscopy. The resulting force experienced by the AFM probe is modulated by the dielectric properties of sample [4-5] and depends on the dynamics of charges and molecular dipoles in the solution. While well-established [5-6], the technique has poorer spatial resolution than standard AFM and interpreting local forces variations in terms of molecular dynamics remains difficult.

Here we present a multifrequency strategy to combine electrical AC measurements with high-resolution AFM at interfaces immersed in ionic solutions. The approach can decouple nanoscale topography from local dielectric variations, with both information acquired simultaneously. It also offers a direct measurement of the force dependence on the AC frequency. Molecular dynamics (MD) computer simulations of the system provide novel insights into the measurements, indicating a complex and geometry-dependent interplay between the water and ions' response to the applied AC electric field.

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Non-Contact imaging of charges within the Debye Layer using Atomic Force Microscopy

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Biomolecules in physiological medium have a surface charge which fundamentally determines their function. These charges can be measured on a mesoscopic scale by different techniques. Measuring these charges on a nanoscale is much more challenging. Atomic Force Microscopy (AFM), with its high spatial and force resolution is a powerful tool and has proven its potential in this field. Determination of surface charge has been mainly achieved by acquiring and processing force spectroscopy curves [1-3].

In the present work we will discuss how the simultaneous measurement of amplitude, force and frequency shift (or phase) allows accessing the electrostatic force induced by the Electrical Double Layer -and thus the surface charge- without spectroscopy approaches. We will show that using careful adjustment of the excitation of the cantilever (small amplitude and correct phase) it is possible to acquire images at very low interaction forces (of the order of 10-25 pN) in the non-contact regime where essentially only electrostatic forces act. We show that for “heterogeneous-charge” samples correct imaging and measuring of electrostatic measurements cannot be performed in force mode or frequency modulation dynamic AFM (FM-DAFM) in the non-contact regime; instead low oscillation amplitude modulation (AM-DAFM) has to be used for stable SFM-imaging [4]. We present experimental data acquired in liquid environment on DNA and a mixed lipid bi-layer (1,2-dioleoyl-3-trimethylammonium-propane, DOTAP, and 1,2-dipalmitoyl-sn-glycero-3-phosphocholine, DPPC) on mica that supports our hypothesis.

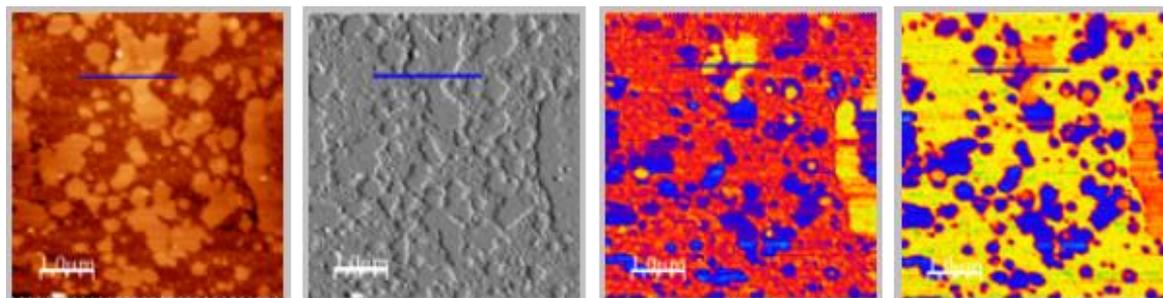


Figure: Bi-lipid membrane imaged in liquid environment at (relatively) low oscillation amplitude (1nm) in the non-contact regime using AM-DSFM. Images correspond (from left to right) to topography (total scale of gold colors: 8 nm), oscillation amplitude (grey, error signal), phase and normal force. The phase and the normal force images show the variation of tip-sample interaction due to local charge differences.

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3D nano-rheology microscopy: *operando* nanomapping of 3D mechanical nanostructure of SEI in Na-ion batteries

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The Solid Electrolyte Interphase (SEI) is a nanoscale thickness passivation layer that is formed as the product of electrolyte decomposition through a combination of chemical and electrochemical reactions in the cell and defines the fundamental battery properties - its capacity, cycle stability and safety. While local mechanical properties of SEI hold a clue to its performance, their *operando* characterisation is difficult as one has to probe nanoscale surface features in electrochemical environment that are also dynamically changing. Here, we report novel 3D nano-rheology microscopy (3D-NRM) that uses a tiny (sub-nm to few nm) lateral dithering of the sharp SPM tip at kHz

frequencies to probe the minute sample reaction forces. By mapping the increments of the real and imaginary components of these forces, while the tip penetrates the soft interfacial layers, we obtain the true 3D nanoscale structure of sub- μm thick layers [1]. 3D-NRM allows to elucidate the key role of solvents in SEI formation and predict the conditions for building SEI for robust, safe and efficient Li-ion and Na-ion batteries.

Here, we discuss the extension of these studies on smooth HOPG and inhomogeneous and rough copper anodes as sodium ion battery electrodes. Essentially, the new approach allows nanoscale characterisation of SEI with a few nm precision on the electrodes with 1000 nm roughness, and quantitatively evaluate the real and imaginary parts of the elastic moduli over the whole thickness of SEI layer.

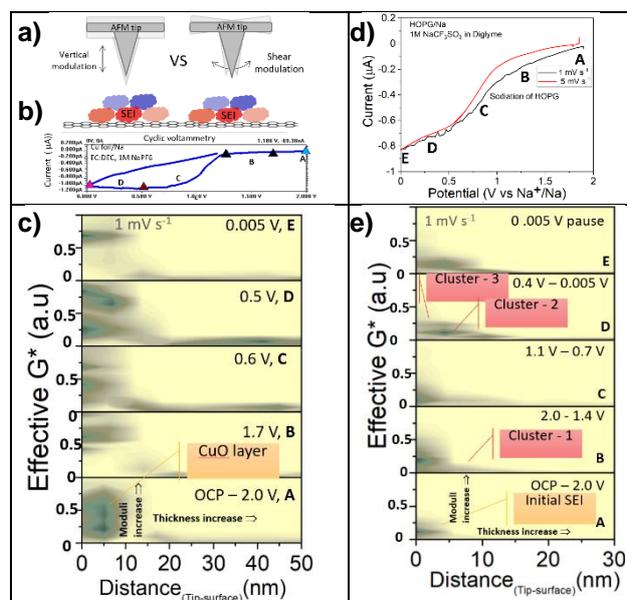


Fig.1 a) Principle of 3D-nanorheology, b) cyclic voltammetry (CV) of Na/Cu anode system, c) average SEI layer mechanical moduli G^* vs thickness, d) at different stages of charge-discharge cycle, e) CV of Na/HOPG anode cycle, f) G^* vs distance for Na/HOPG at different CV points.

The observation of the change in moduli and the tip-surface distance helps to evaluate the growth of SEI as a function of the electrolyte, additives, electrode material and charge-discharge rate. We believe that such evaluation of key interfacial nanomechanical properties of SEI will allow us to develop the electrochemically and mechanically robust SEI surface passivation layer and the development of efficient and safe rechargeable batteries.

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Nanoscale Programmable Friction with Ionic Liquid Mixtures

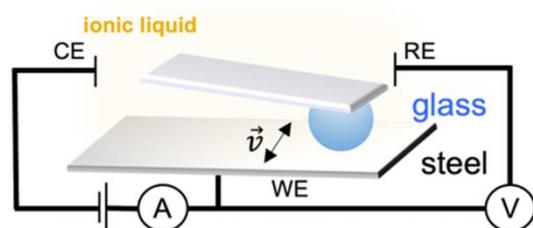
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Global challenges for environmental protection and energy efficiency require novel concepts in the field of tribology, such as sustainable lubrication. The different properties of the lubricants make ideal friction behavior at all operating conditions impossible. However, potential controlled friction can solve that problem by changing the friction via an electric stimulus [1]. Programmable friction is the targeted control of friction in a tribological system. It can be obtained through additional integrated condition monitoring systems and computer-controlled coefficient of friction (COF) adjustment, wherein the lubrication properties are continuously and automatically adapted [2].



Here, friction force microscopy (FFM) is performed in an electrochemical cell to monitor the effect of electrical potential application on the COF of an ionic liquid mixture (ILM) on steel [3]. FFM experiments are compared to macroscale experiments with a specially designed tribo-setup cell. At the molecular level, the ILM molecules undergo orientation, adsorption, and

electromigration upon an applied electrical potential. The application of different electrical potentials leads to an increase in the concentration of either the anion or the cation in the friction gap, which affects the COF. This correlation between the structure of surface-bound ionic liquid layers and the friction behavior can be used to control friction and thus obtain programmable friction.

These results provide an important contribution to understand the mechanisms of switchable and programmable friction with ILMs leading to increased energy efficiency and service life for tribological systems.

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Developments in CO₂ electrochemical reduction: insights from theory

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In my talk I will describe the last advances in the field of electrochemical CO₂ reduction from a computational standpoint. I will present the most advanced integrated modeling able to account for the multiscale problem and how transport can influence the properties investigated adding value. On the more chemical part I will center in the use of electrolytes and how they interfere with the reactivity of the electrochemical system.

From Atomistic Interactions to Cyclic Voltammograms and Back Again

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Recent theoretical advances, in particular the coupling of ab-initio density functional theory codes to continuum implicit solvent models, have allowed to simulate electrified interfaces at constant electrode potential conditions [1]. Such simulations enable to determine the grand canonical (GC) ensemble energetics, as a result of which one can directly assess e.g. the adsorption energetics at constant potential conditions [2].

As I elaborate, the GC energetics directly yields electrochemical potentials of adsorbed species whose electrode-potential-dependence is given by a single, well-defined quantity: the electrosorption valency l . It is determined by the adsorbate's influence on the potential of zero charge U^{PZC} and a second order response parameter C^{PZC} , which is closely connected to the interfacial capacitance [3]. As a result, the adsorbate energetics at applied potential can be condensed into three quantities only – the adsorption energy E^{ads} and U^{PZC} and C^{PZC} – which we previously termed the CHE+DL approximation. The accuracy of the CHE+DL energetics is confirmed by comparing to a variety of explicit GC calculations for a variety of adsorbates.

Finally, by combining CHE+DL energetics with Mean Field and GC Monte Carlo sampling I demonstrate the accuracy of the method to simulate theoretically Cyclic Voltammograms (CVs) [4]. While our approach thus helps to understand some experimental observations, we believe that a more detailed comparison between theoretical and experimental CVs will help in the future to pinpoint better the various sources of errors in current theoretical models.

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Overlapping Electric Double Layers at the Mesoscale

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Supported nanoparticle catalysts (SNPC) are ubiquitous in electrochemical energy conversion technologies. The electric double layer (EDL) in SNPC, where the crucial electrochemical reactions occur, is characteristically different from EDLs at extended planar electrodes; at SNPCs, individual EDLs of the catalytic material and the support material overlap. The overlapping EDL at the mesoscale (1-100 nm) is much less understood than individual EDLs at extended planar electrodes, hindering rational improvements of SNPC performance via regulating the mesoscopic EDL effects.

From a theoretical perspective, the key challenge, shared across disciplines, lies in modelling realistic nanostructures under operating conditions.[1] In the context of electrochemistry, the most important parameter of operating conditions is the electrode potential. A method that can capture both the quantum nature of electrons and almost classical nature of electrolyte species at the mesoscale under constant potential conditions is much needed.

In this talk, I will present our initial results about the overlapping EDL at carbon-supported Pt nanoparticles for oxygen reduction. Specifically, the overlapping EDL is modelled using a semiclassical, constant-potential functional approach.[2] This approach allows to describe electronic equilibration between Pt nanoparticles and carbon support as a functional of the electrode potential, and the three-dimensional distributions of ions and electrostatic potential within the EDL. The potential of zero charge (PZC) and differential double-layer capacitance (C_{dl}) of this system are calculated as a function of size and coverage of Pt nanoparticles.

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The nanoscale photovoltaics laboratory on a tip

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University of Stuttgart

Solar cells based on metal halide perovskite (MHP) materials will enable cheaper and more energy-efficient photovoltaic and optoelectronic devices compared to current silicon-based technologies. To advance MHP technology further, however, will require a better understanding of the fundamental processes leading to energy losses, unstable operation conditions and premature aging. The macroscopically observed properties of optoelectronic MHP materials and devices are the result of the complicated interplay between nanoscale structure and function. Thus, the key to understanding MHP materials is the micro- and nanoscale characterization of the many nano- and microscale structures; from sub-granular twin domains, over grain boundaries and interfaces to lateral variations in crystal grains orientations and facets. For such nanoscale photovoltaic measurements, scanning force microscopy methods are ideal, as they allow correlated measurements of structure and function.

In this presentation, I will present some of our recent activities in the development of specialized scanning probe microscopy methods to study hybrid perovskite materials. Based on static and time-resolved Kelvin probe force microscopy (KPFM), we have developed unique techniques for mapping the surface potential and photovoltage. Using cross sectional measurements, we map and record the potential distribution across different layers of solar cell devices under operating conditions [1–4]. Here, the key to a reliable cross-sectional KPFM measurement is the connection of a high-resolution quantitative KPFM operation mode [5] and the preparation of a smooth surface through the solar cell. We use a combination of mechanical fracturing of the cells with a complex polishing process using ion beams. Using a pointwise spectroscopy technique, we can record and map the surface photovoltage (SPV) dynamics with 10-20 nm lateral resolution. With this Nano-SPV technique, we revealed local SPV overshoots in the vicinity of grain boundaries following an illumination pulse. The overall aim of our research is to address some of the key challenges of MHP research, such as phase segregation, degradation and interface heterogeneity, to enable a deeper understanding of the different loss mechanisms and intrinsic instabilities that currently limit the application of MHP solar cells.

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Accurate multifrequency electromechanics: Electrostatics, Null points and implications for functional nanoelectromechanics

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Last year marked the 30th anniversary since piezoresponse force microscopy (PFM) was demonstrated on ferroelectric polymers by Guthner and Dransfield. Since then, it has emerged as the preeminent nanoscale approach to characterizing electromechanical response and is commonly used as a verification for ferroelectricity on the nanoscale. The recent advent of weaker, beyond Moore's law materials has accelerated the reporting of "strange ferroelectrics" – synonymous with materials that are mistakenly interpreted as ferroelectric. Motivated in many cases by the need for ever smaller dimensions in micro- and nano-electronics, there has been a rapid expansion of research on thin film ferroelectric materials. Ideally, materials that go into these beyond Moore's law devices should be compatible with currently used CMOS technologies, leading, for example to Hafnia based materials and layered van der Waals ferroelectrics. These materials commonly have inverse piezo coefficients that are small, often less than 1pm/volt. They also often have small switching voltages, required for low power device performance but that also limits the range of the excitation potential. In this talk, I will discuss some recent results that demonstrate quantitative PFM measurements at noise floors as low as 100fm/Volt. I will also report on a large series of systematic studies exploring null positions where the measured amplitude and phase are independent of electrostatic crosstalk. These exhaustive measurements were simultaneously made with both a standard optical beam (beam bounce) detector and a quantitative interferometric detector. The results are in good agreement with Euler-Bernoulli beam theory and allow a quantitative comparison of various strategies for quantifying electromechanical response and for eliminating crosstalk. These results have broad implications for AFM-based nanomechanical measurements in general.

Quantitative imaging of electroswelling in organic mixed ionic electronic conductors

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Ionic transport and accumulation into active layers of electrodes is of crucial relevance for energy storage and conversion processes. Organic mixed ionic electronic conductors (OMIECs) are a well characterized model system that exhibits a 3D electrified interface. As a result, unconventional properties emerge such as volumetric capacitance or strong electroswelling.[1] Electroswelling allows to achieve volume changes and mechanical actuation controlled by small electrical potentials. The electroswelling effect is exploited in electrochemical actuators with low-voltage drive, nanoscale precision and miniaturization, with applications in soft robotics, soft micromechanical devices or actuated biomedical devices. However, electroswelling can also trigger delamination in OMIECs thin film devices used for sensors or electrochemical energy storage and puts their long-term stability at risk.

To investigate ionic transport and accumulation at the microscale we introduce a novel type of modulated electrochemically controlled AFM experiment (mEC-AFM) that combines local surface strain measurements with electrochemical impedance spectroscopy. We test the experiment on OMIEC covered microelectrodes and obtain multidimensional spectroscopic data that explains the relevant processes and their timescales in electroswelling. Combining the technique with the PinPoint imaging mode, we record high resolution maps that report the local amplitude and the phase of electroswelling on soft polymer thin films. The data demonstrates that electroswelling in PEDOT:PSS used as OMIEC material is driven by the volume of hydrated ions entering the thin film and does not depend on slower diffusive processes.[2] In more complex materials such as PPY-DBS ionic transport is more hindered and the multidimensional spectroscopic data allows for in-depth profiling of ionic transport and swelling properties.

Operando IR nanospectroscopy mapping of hydrogen dissociation and sorption on single Pd nanoparticles

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Heterogeneities in the size, structure, and composition of solid (electro)catalysts make it essential to gain nanoscale chemical information for understanding how surface properties direct their reactivity [1]. We have recently demonstrated that IR nanospectroscopy measurements can uncover reactivity variations on single nanoparticles [2], identify the interconnection between neighboring surface sites [3], and probe the influence of various atomic facets on the reactivity of catalytic nanocrystals [4].

Herein, it is shown that *operando* AFM-IR nanospectroscopy measurements under reaction conditions provide a mechanistic understanding of hydrogen dissociation and sorption on single Pd nanoparticles and uncover the impact of poisoning on the reactivity pattern (Figure 1). Pd nanoparticles have been utilized as sensors for hydrogen leak detection [5], but their reactivity deteriorates once exposed to harsh environmental conditions. AFM-IR nanospectroscopy measurements under flow conditions, along with KPFM measurements, revealed that on crystalline nanoparticles both H₂ dissociation and hydrogen sorption are facilitated at the nanoparticle-substrate interface.

The influence of sulfur poisoning on hydrogen sorption was probed by mapping the vibrational signals under reaction conditions. Sulfur was preferably adsorbed on sites that were characterized by a high density of surface defects. Following sulfur adsorption, the hydrogen dissociation and sorption affinity were dramatically reduced, demonstrating the crucial impact of poisons on hydrogen sorption affinity. Exposure to hydrogen under elevated temperature revealed a novel nanoscale self-cleaning mechanism that led to sulfur diffusion and re-generation of the hydrogen sorption affinity of Pd nanoparticles.

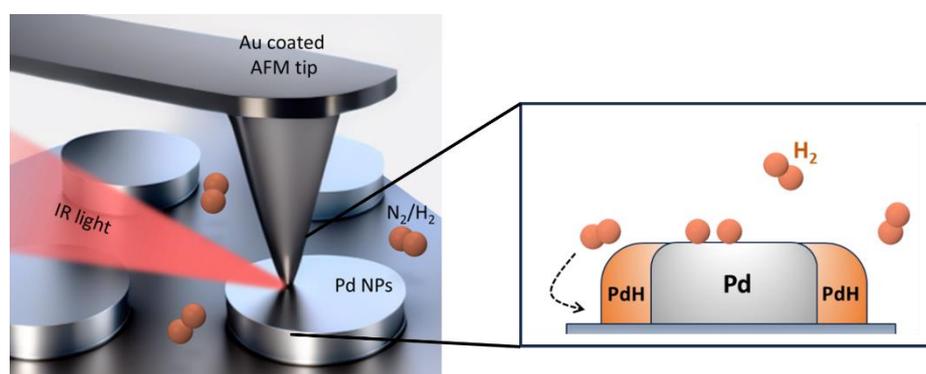


Figure 1: Operando AFM-IR nanospectroscopy measurements identified the role of structural heterogeneities and sulfur poisoning on H₂ dissociation and sorption on Pd nanoparticles.

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Correlative Raman Microscopy for Battery Research

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To gain more insight into the processes occurring in battery cells (i.e., microstructurally arranged composites), it is crucial to understand property-structure relationships between materials, manufacturing steps and electrochemical properties. Therefore, robust visualization tools that use correlative microscopy offer great advantages for evaluating micro-structural fabric, chemical composition, crystallographic properties, and phase transitions. This presentation will describe how high-resolution microscopy methods such as AFM and SEM can be combined with material-sensitive techniques such as Raman and EDS to provide a more comprehensive understanding of processes taking place within Li-ion battery components.

Characterization of Ultrafast Processes at Electrochemical Interfaces Using Femtosecond Lasers

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Electrochemistry relies on charge transfer, which can occur on time scales from femtoseconds to seconds or longer. Traditional electrochemical detection methods are limited in their ability to study ultrafast processes such as solvent reorganization and electron tunneling (Fig. 1). To address this problem, nonlinear spectroelectrochemical methods using ultrashort lasers are being used to study these dynamics at electrochemical interfaces. This talk will discuss our recent efforts in this area [1-3].

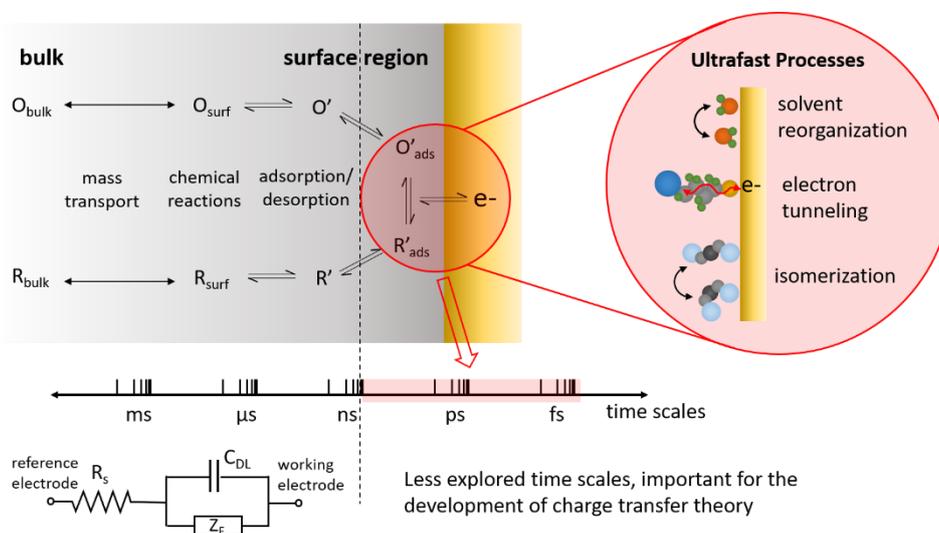


Figure 1: Elementary processes that may be involved in charge transfer at electrochemical interfaces. Adapted from Ref [1].

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Degradation of Fe-N-C Catalyst Layers in Alkaline Media

^{1,2*}Ku, Y.-P., ^{1,2}Ehelebe, K., ¹Kumar, K., ¹Hutzler, A., ^{1,2}Götz, C., ^{1,2}Bierling, M., ³Bibent, N., ⁴Vorokhta, M., ⁵Zitolo, A., ¹Lloret, V., ⁴Khalakhan, I., ^{1,2}Thiele, S., ^{1,2}Mayrhofer, K.J.J., ¹Böhm, T., ³Jaouen, F., & ¹Cherevko, S.

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Iron-nitrogen-carbon (Fe-N-C) catalysts are promising for replacing platinum group metal catalysts for oxygen reduction reaction (ORR) in fuel cells (FCs) while they still endure considerable degradation during FCs' operation mode and start-stop events. The stability studies using scanning flow cell (SFC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) have provided information on the effects of various factors, such as potential and pH, on Fe leaching from Fe-N-C catalysts. ^[1-2] Yet, the degradation in relevant current density regions is difficult to track in such systems in operando. Thus, the loss of Fe active sites in the Fe-N-C cathodes of FCs can only be obtained by post-mortem analyses, such as Mössbauer spectroscopy. ^[3] To bridge this gap, a novel gas diffusion electrode half-cell (GDE) coupled with ICP-MS has been developed in our previous work ^[4] and can reveal the online Fe dissolution rate at ORR current densities up to $-200 \text{ mA}\cdot\text{cm}^{-2}$. ^[5]

Using this GDE-ICP-MS technique, this work shows the online Fe leaching rates in Fe-N-C catalyst layers in a broad potential window in alkaline media, simulating the operation mode ($E < 1.0 \text{ V}_{\text{RHE}}$) and start-stop events ($E > 1.0 \text{ V}_{\text{RHE}}$) in anion-exchange membrane FCs (AEMFCs). In the potential range between 0.57 and 0.87 V_{REH} , the amount of dissolved Fe species is intensified during ORR and is highly correlated to the oxygen reduction charge. ^[5] While in the potential range between 1.0 and 1.5 V_{RHE} , where the electrochemical oxidation of the N-C matrix may take place, the Fe dissolution rate is barely influenced by the presence of oxygen yet significantly enhanced by increased temperature. Based on *in situ* and post-mortem analyses, novel insights into the degradation mechanisms of alkaline Fe-N-C catalyst layers are revealed and can inspire rational designs of more durable Fe-N-C catalysts.

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POSTER OVERVIEW

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In-situ probing of adhesion forces at the electrochemical solid-liquid interface

Poster #03: Zohreh Asadi, FU Berlin
In-situ and operando studies on the evolution of ZnO:Al in reducing thermal treatment

Poster #04: Dr. Andrea Auer, Institute of Physical Chemistry, University of Innsbruck
Visualizing solvent structures at the electrified solid-liquid interface by electrochemical atomic force microscopy

Poster #05: Lithin Madayan Banatheth, University Duisburg-Essen
Investigation of phase dependent bifunctional activity of Ni₃B/Ni₂B catalysts for water splitting using Scanning Electrochemical Cell Microscopy

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Poster #16: Jun Huang, Forschungszentrum Jülich GmbH
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- Poster #22: Dr. Martin Munz, HZB & FHI Berlin
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- Poster #23: Dr. Kerstin Neuhaus, FZ Jülich
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- Poster #24: Dr. Inhee Park, FZ Jülich
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- Poster #25: Yujie Peng, HZB & FHI Berlin
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- Poster #27: Ali Rafsanjani Abbasi, TU Vienna
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Investigating proton reduction and hydrogen absorption on palladium via scanning electrochemical microscopy
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Multi-principal element alloy nanoparticle (MPEA-NP) electrocatalysts prepared by pulsed laser ablation for electroreduction of CO₂
- Poster #38: Dr. Dorothee Silbernagl, BAM Berlin
But it is already correlative microscopy
- Poster #39: Dr. Igor Siretanu, University Twente
On the relation between colloidal electrostatic and hydration forces on mineral surfaces in ambient electrolytes of variable composition: An Atomic Force Microscopy Study
- Poster #40: Dr. Igor Siretanu, University Twente
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- Poster #41: Dimitrios Valavanis, University of Warwick
Operando Optical Monitoring of Crystallisation in Confinement
- Poster #42: Xiangdong Xu, University of Warwick
Electrochemical Imaging of Thermochemical Catalysis

Characterization and Dealloying of Single Micelle-Nucleated AgAu Nanoparticles by Scanning Electrochemical Cell Microscopy

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Bimetallic nanoparticles (NPs) are highly interesting electrocatalyst materials due to synergistic effects generated by their additional active sites [1], and the ability for tuning their activity by (electro-)chemical dealloying-treatments [2]. Synthesis routes using 0D confinement in micelles give enhanced control over composition and morphology of these bimetallic NPs [3]. However, an unavoidable distribution of catalytic performances and abilities for dealloying remains among the NPs. This calls for electrochemical tools that offer activity measurements at the single-entity level. Scanning electrochemical cell microscopy (SECCM) is such a tool, probing electrocatalytic current locally in a nanodroplet cell, and collecting many data points on one sample that can be post-characterized by e. g., scanning electron microscopy (SEM). Furthermore, SECCM can be combined with in situ optical microscopy [4]. This allows a direct correlation between NP activity and morphology/composition. The great potential of SECCM to probe single entities has already been demonstrated in correlative multi-microscopy studies [5] and the technique is being continuously developed further.

In this work, precursor-loaded reverse block co-polymer micelles are electrodeposited on a conductive substrate forming Ag_xAu_y alloy NPs. Electrochemical dealloying of these bimetallic NPs is then used to tune their electrocatalytic activity for the hydrogen evolution reaction. This is done locally with SECCM using a big probe to create areas of NPs in different states of dealloying on a single sample. In a second SECCM experiment, the NPs in the different areas are then characterized as to their specific activity and Ag: Au ratio, followed by co-located SEM. Additionally, hybrid scanning electrochemical cell microscopy-interference reflection microscopy (SECCM-IRM) is used to study the optical features of the NPs and the droplet *operando* during the local dealloying. This is linked with identical-location TEM (transmission electron microscopy) and EDX (energy-dispersive x-ray spectroscopy) at different dealloying states. Thus, the correlation of morphology and composition with the specific activity of dealloyed bimetallic nanocatalysts is enabled at a single-catalyst level, by statistical analysis, paving the way towards a knowledge-based design of electrocatalysts.

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In-situ probing of adhesion forces at the electrochemical solid-liquid interface

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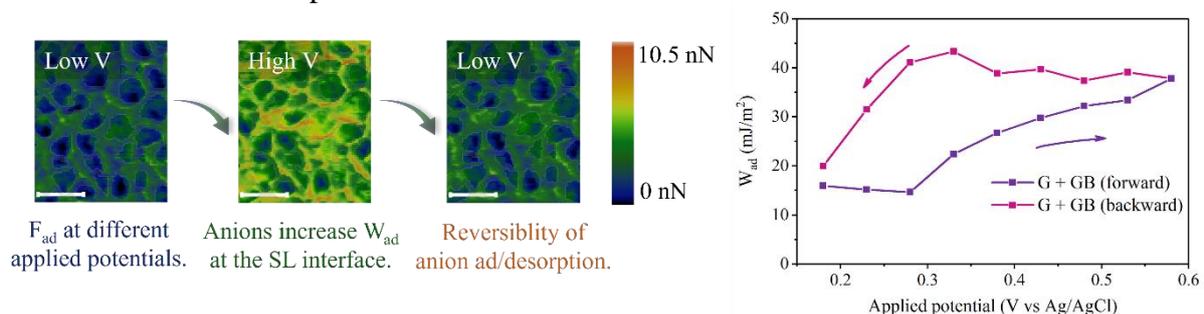
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The interface of an electrified catalyst and its electrolyte (solid-liquid interface) is complex, dynamic, and potential-dependent. Studying this interface and the local arrangement of all involved elements (solvent molecules, dissolved ions) is important as this few-nm layer interface dictates all electrochemical processes. To gain realistic insights on electrode processes, it is essential to monitor the solid-liquid interface in-situ under applied bias.

In this presentation, I will outline the use of Electrochemical-AFM (EC-AFM) to probe the interfacial surface energy of this interface in-situ under working conditions. In addition, to the regular morphology characterisation of the sample, EC-AFM can also be exploited to provide force-curves during the approach/retract from the sample surface. By analysing the force-curves and extracting the adhesion or pull-off forces on the retract part, we can understand the molecular arrangement of the solid-liquid interfaces. The observed adhesion forces are extremely sensitive to local changes at the solid-liquid interfacial changes. As a model system, we map the interfacial structure changes due to sulphate anion adsorption on polycrystalline gold electrodes under applied potential with high spatial resolution (<4 nm). As such, we visualize nanoscale inhomogeneities on the solid-liquid interface changes under applied bias.

We investigate a solid polycrystalline gold electrode in a neutral sodium sulphate electrolyte using a silicon nitride tip (scan area: 500 nm). Interestingly our map reveals, adhesion force inhomogeneities across the whole scan area. In addition, we observe a substantial increase in the interfacial adhesion forces during the presence of chemisorbed sulphates at the solid-liquid interface. We also notice reversibility in the measured adhesion forces as the adsorbed sulphate desorbs from the electrode as we cycle back. Upon closer investigation, we also identify a negative correlation between the gold grain curvature and the mean grain adhesion forces. Grains with small grain curvature tend to also show an increased interfacial adhesion force response under all applied potentials.

Our work shows the use of EC-AFM is a useful multi-modal technique to characterize and understand the solid/liquid interface in-situ under applied bias and the trend of the force of adhesion can be used to probe electrochemical features at the nanoscale.



***In-situ* and *operando* studies on the evolution of ZnO:Al in reducing thermal treatment**

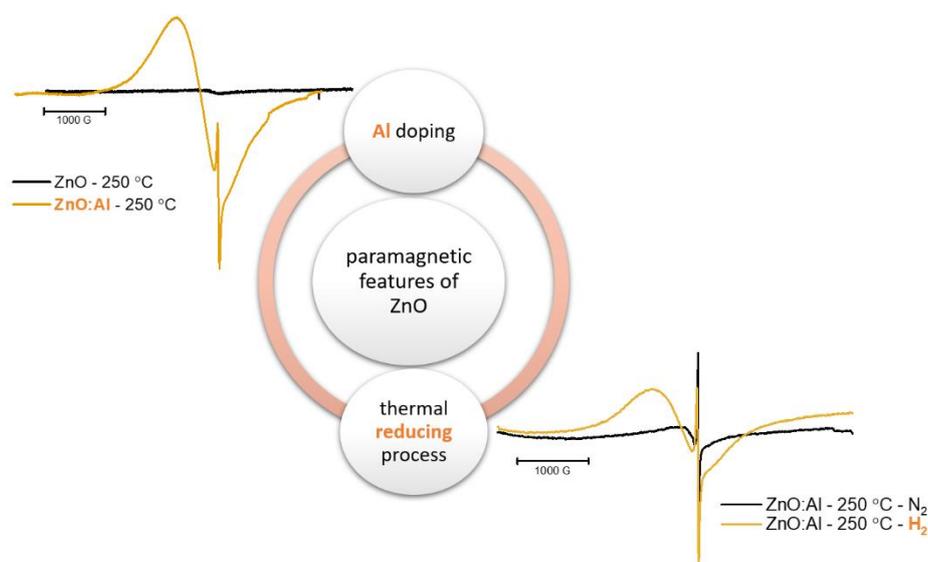
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Extensive studies have been dedicated to Al doped ZnO as a main support of Cu catalysts for the crucial methanol production from syngas or CO₂. Nevertheless, the synergic effect of Cu and ZnO:Al remains a subject of ongoing debate. It has been suggested that the activation process which proceeds the catalytic reaction is one of the deterministic parameters in metal-support interaction and active sites in Cu/ZnO:Al catalyst [1]. This contribution seeks to provide insight into the development of ZnO:Al, particularly during the thermal reduction process analogous to activation process of Cu/ZnO:Al, employing *in-situ* X-band continuous wave electron paramagnetic (EPR) spectroscopy, *in-situ* microwave cavity perturbation technique (MCPT) and *operando* thermal gravimetric mass spectrometry (TGMS).

During the thermal reduction process of 10 mass% Al doped ZnO synthesized via coprecipitation method, a broad paramagnetic signal at g_{eff} equal to 2.146 becomes evident. Investigation of nominally pure commercial and hydrothermally synthesized ZnO indicates a correlation between Al doping and genesis of this broad paramagnetic feature of ZnO:Al. Moreover, the thermal process in N₂ gas stream is solely not able to create a comparable EPR signal as the result of a thermal reducing process. Besides, for understanding the nature of the broad observed EPR signal, *in-situ* MCPT, TGMS and Q-band EPR measurement have been applied. Finally, the development of ZnO:Al upon the activation process has been compared with Cu/ZnO:Al catalyst.



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Visualizing solvent structures at the electrified solid-liquid interface by electrochemical atomic force microscopy

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To design efficient electrochemical interfaces for sustainable energy conversion, it is crucial to resolve the molecular structures of the electric double layer, where inevitably all electrocatalytic reactions take place. While most current electrochemical scanning probe microscopy approaches are successfully employed to study the structural evolution of an electrode surface, even under reaction conditions (see e.g., [1]), they are largely insensitive to the solvent structure formed at the electrolyte side. In contrast, high-resolution atomic force microscopy (AFM) has been shown to be able to visualize the vertical arrangement of solvent molecules in the direction normal to the surface (z-direction) with high accuracy (see e.g., [2]). However, only few reports exist with potential control in an operating electrochemical cell.

Here, we employ electrochemical AFM with stiff qPlus sensors[3,4], which allows us to not only probe the lateral structure of the electrode surface, but also the potential-dependent, vertical solvent layering at well-defined electrified solid-liquid interfaces. Investigations of a Au(111) electrode in various aqueous electrolytes reveal a distinct potential-dependent, oscillatory frequency shift modulation in z-direction, which based on the observed wavelength can be attributed to either water or an ionic layering close to the electrode. We find these different solvent structures to be highly dependent on the charge of the electrode with respect to the potential of zero charge, the electrolyte concentration and the type of ions.

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Investigation of phase dependent bifunctional activity of Ni₃B/Ni₂B catalysts for water splitting using Scanning Electrochemical Cell Microscopy

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Scaling up water electrolysis requires cheap, abundant, and active electrocatalysts. While up-to-date Ni is the state-of-the-art electrode material used in alkaline water electrolysis, more active electrocatalysts can be obtained by tuning the electronic structure of Ni via other elements. Particularly, nickel borides hold great potential as bifunctional catalysts for alkaline electrolysis with activity depending on their crystal structure and composition, as reported previously in macroscale studies [1][2]. While these studies provide an overview of the catalyst activity, the obtained electrochemical response often sums up the intrinsic electrocatalytic activity with other factors, such as mass transfer or conductivity of the catalyst layer.

In the present study, we aim to investigate the intrinsic electrocatalytic activity of nickel borides using model electrodes containing a mixture of micrometer-sized Ni₂B and Ni₃B phases. Scanning electrochemical cell microscopy (SECCM) was used to perform electrochemical studies at the nanoscale. In SECCM, a hanging droplet is approached to the catalyst surface, allowing nm-sized areas to be probed only, in a high-throughput screening approach, allowing activity-structure correlations to be derived [3]. While no significant difference could be observed between the Ni₂B and Ni₃B phases with respect to their electrocatalytic activity towards oxygen evolution reaction (OER), different shapes of the linear sweep voltammograms (LSVs) were recorded during hydrogen evolution reaction (HER). The different LSV shapes indicate different HER mechanisms on the Ni₂B and Ni₃B phases, previously not reported in the macroscale experiments. Understanding of the factors that may contribute to the observed features in LSV is attempted via controlled oxidation of the Ni borides and Auger spectroscopy.

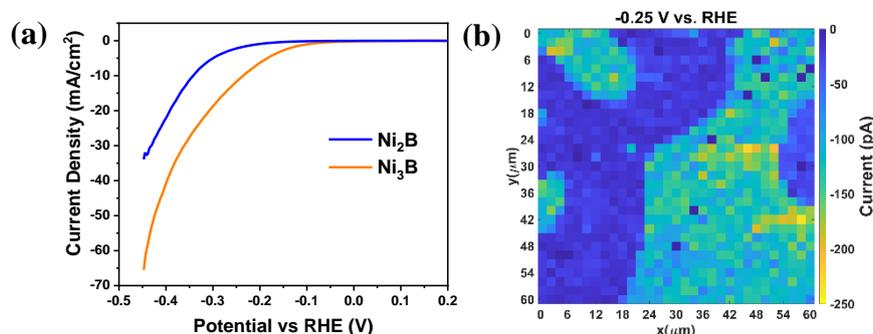


Fig: (a) HER polarization curves of Ni₂B and Ni₃B. (b) The electrochemical current map at -0.25 V vs RHE revealing the different electrocatalytic activity between the Ni₂B and Ni₃B

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Thermodynamic Cyclic Voltammograms from first Principles

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Cyclic voltammograms (CVs) are a central experimental tool for assessing the structure and activity of electrochemical interfaces. Computationally, a predictive-quality modeling of CVs is challenging due to the entangled need to accurately account for the interactions and reactive chemistry at the liquid electrolyte/solid electrode interface as well as for the electrostatic interactions of the diffuse double layer at applied potential conditions [1]. For sufficiently small scan rates, thermodynamic approaches help to meet these challenges.

Here, we compare different options to derive thermodynamic CVs consistently and at low computational cost. Using the well-studied model system of Ag(100) in a Br-containing electrolyte as a test case, we present our generalized ansatz to derive continuous expressions within a mean-field (MF) model. We shine light on the inherent accuracy limitations of MF theory, by comparing it to CVs from grand-canonical lattice Monte Carlo simulations. Finally, we show how augmenting traditional zero-field calculations (computational hydrogen electrode, CHE) with capacitive double layer energetics (CHE+DL) [1] within an implicit solvent model influences the theoretical results.

We further show how our methodology can bridge the gap between experiment and theory, by examining the as-of-yet unknown system of a Cu(100) electrode in alkaline I-containing electrolytes.

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Revealing in-situ activation of TaS₂ towards hydrogen evolution reaction

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Recently, a solution to environmental challenges has emerged in the form of energy storage via molecular hydrogen, obtained with utilization of water-splitting^[1]. To make this process efficient catalysts are required which have to be abundant, stable and with high redox-activity. Platinum currently stands as one of the most effective materials for catalysing the hydrogen evolution reaction (HER); however, its scarcity cannot meet the demands of industry.

Transition metal dichalcogenides (TMDCs) have emerged as potential efficient catalysts for HER, with activity comparable to platinum^[2]. The TMDCs can exhibit high efficiency per unit mass due to their two-dimensional structure, which results in a substantial surface area exposed to the environment for HER. Among these materials, TaS₂ was supposed to be one of the most efficient^[3,4]. Nonetheless, the redox-active sites in the structure of TaS₂, responsible for HER catalytic activity remain a topic of debate^[5]. One can suppose that chalcogenide vacancies on the basal plane are responsible for catalytic activity of TaS₂, while the other suggests that the edge sites of the 2D flakes play this role.

Experimental investigation has revealed, that so called activation of TMDCs can be performed to enhance their catalytic activity. Activation can be achieved by variety of treatment methods, such as plasma treatment^[6], mechanical deformation or self-activation during HER^[3,4]. In spite of multiple observation of activity enhancement, such treatments, however, do not reveal the real active sites, as the amount of both types (i.e. edges sites and vacancy-related sites) is usually increased. Thus, understanding of the activation mechanism is of great importance for the TMDC engineering. In addition, during electrochemical activation the possible dissolution of Pt, commonly used as the counter electrode, can occur, which might cause redeposition on the working electrode in sufficient amount to show enhanced activity.

In this study, we have investigated the phenomenon of self-activation in TaS₂ during the hydrogen evolution process. Various counter electrodes, including carbon and platinum, were employed to examine their influence on this activation. An electrochemical cell designed for grazing incidence X-ray spectroscopy was fabricated in our laboratory to perform in-operando observation of TaS₂ flakes activation.

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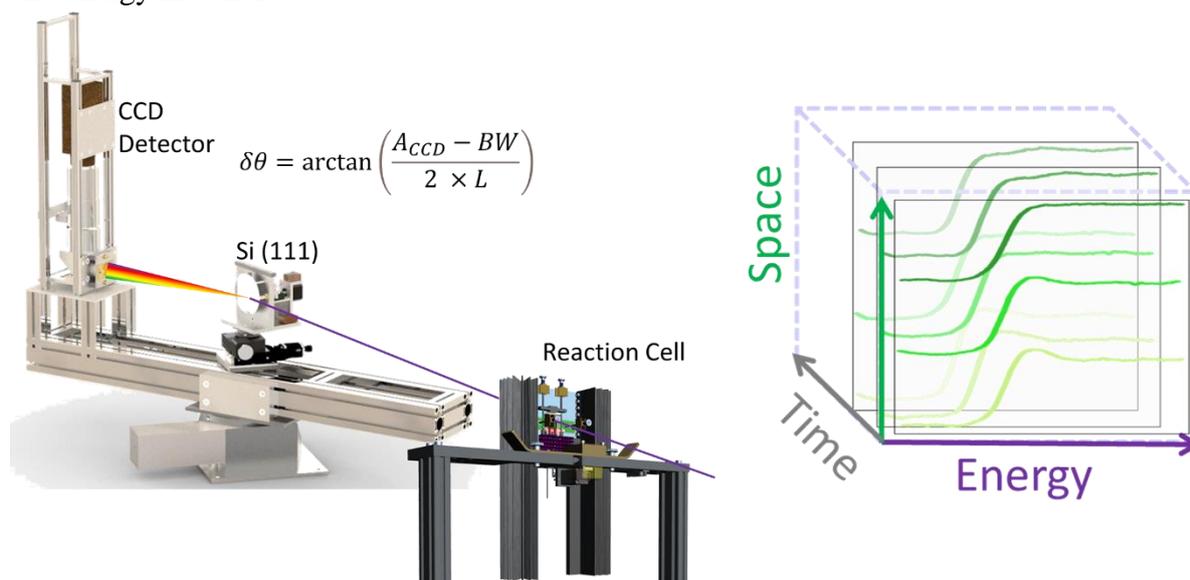
Time-, space- and energy-resolved X-ray absorption spectroscopy for *in situ* characterization of catalysts

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We demonstrate the application of a custom-designed dispersive X-ray absorption spectroscopy (XAS) setup to characterize catalyst materials *in situ* [1]. Highlights of this setup are the use of a wide X-ray beam (2 to 10 mm wide) allowing both spatial and temporal resolved *in situ* studies, while keeping a constant energy bandwidth that covers the whole XAS spectrum in one shot. With this 3-Dimensional analysis method (energy, time and space) we extended the analytical toolbox to characterize catalyst materials at work, where e.g. gradient reduction or oxidation processes occur in heterogeneous catalysts. The dehydroaromatization of methane (MDA) is one way to address the future aromatics gap [2], but there are still many unanswered questions about catalyst behavior during the reaction that are addressed with our research. Through investigation of Mo/HZSM-5 catalyst during the MDA we observed a reduction/carburization gradient along the packed bed, which will lead us to novel catalyst and reactor concepts to ensure more homogeneous active site generation. By presenting these capabilities we hope to trigger fruitful discussions and its applicability in the field of catalytic and energy materials.



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Antimicrobial properties of polydopamine films and the role of surface charge *via* atomic force spectroscopy

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Biofilms are microbial communities that can attach to both biotic and abiotic surfaces. In comparison with planktonic cell cultures, biofilms exhibit an increased tolerance against antimicrobial and antibiotic treatments due to the presence of extracellular polymeric substances (EPS), which provide bacteria physical protection against external stressors [1].

The crucial step in biofilm formation is the cell-surface interaction that leads to the attachment and subsequent proliferation of bacteria and with that to biofilm formation [1]. Bacterial attachment is highly influenced by several surface properties, including hydrophobicity, surface charge density, surface roughness and the potential presence of antimicrobials. Thus, functionalization and surface modification are one of the most effective strategies to inhibit the formation of biofilms, by preventing the first cell attachments.

In the last decades, novel coatings frequently in combination with nanoparticles have been developed to prevent the formation of biofilms. Among antimicrobial polymers (AMP), poly- ϵ -lysine and polydopamine (PDA) have been investigated, due to their versatility in terms of chemical modification and antimicrobial properties [2]. PDA is a unique nature-inspired functional polymer, which mechanical, chemical and electrical properties are strongly dependent on the deposition method as well on the experimental conditions, in which the polymer is studied. For instance, the adhesion properties and the antimicrobial properties of PDA [3] are strongly influenced by pH and the oxidation state of the polymer [4,5].

In this contribution, in situ surface charge density measurements at PDA films have been locally investigated as a function of the pH using AFM force spectroscopy and the point of zero charge of the polymer has been determined. Further, we present scanning electrochemical cell microscopy (SECCM) as a suitable tool to locally deposit Ag-NPs on PDA, allowing the screening and optimization of the parameters such as silver(I) concentration and thickness of the polymer. The antimicrobial effects of PDA and AgNPs-PDA have been studied in-situ against *E. coli* as a function of the surface charge density of the polymer, by controlling the pH of the culture media and the presence of AgNPs.

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Nanoscale Low-Frequency Dielectric Spectroscopy on Photovoltaic Perovskites

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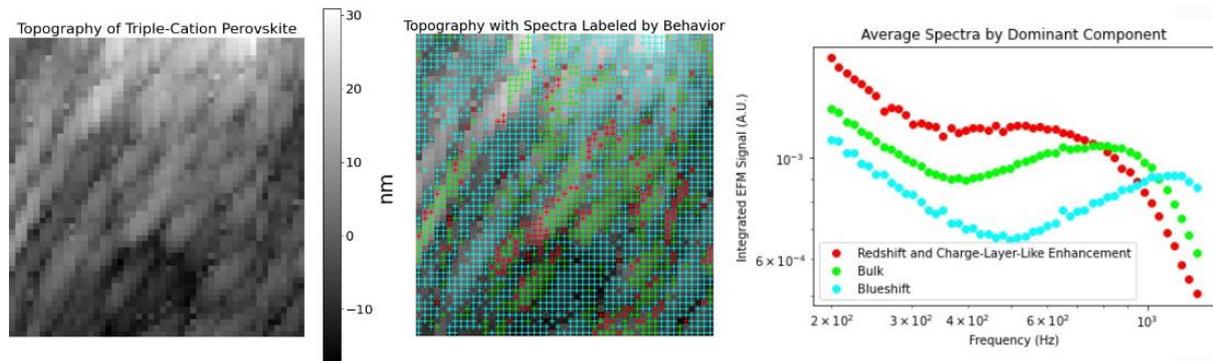
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Relatively slow (kHz-range) ionic processes play a major but poorly-understood role in perovskite solar cell function and degradation. In this study, we implement a novel atomic force microscopy (AFM) configuration whereby we can probe the local capacitive and dielectric response in the 10 Hz to 10 kHz regime with nm resolution. In particular, an oscillating tip is further excited electrically as in a typical electric force microscopy (EFM) measurement, but the excitation frequency is swept to obtain the characteristic frequency-dependence of the local dielectric constant. By spatially resolving the distribution of dielectric spectrum features, we can map e.g. variations in defect and charge-carrier density and mobility, segregation of ion species, and more. Since the measurements are taking place in an AFM, a full range of experimental parameters is available, including illumination, sample bias voltage, heating (and cooling), etc.

The method is demonstrated on triple-cation perovskite ($\text{FA}_{0.78}\text{MA}_{0.16}\text{Cs}_{0.06}\text{Pb}(\text{I}_{0.84}\text{Br}_{0.16})_3$) grain boundaries and MAPbI_3 single crystal twin domains.



Dynamic Knoevenagel Condensation for Conjugated 2D-Covalent Organic Framework Formation: From Multilayer to Monolayer

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Covalent organic frameworks (COFs) are layered crystalline porous organic materials that enable the integration of organic building blocks with molecular precision. As of today, a wide class of connections are developed leading to the formation of covalent bonds (i.e. from boroxine, to imine) with tunable properties making these materials optimal candidates for applications ranging from catalysis to gas separation and (opto)electronics. The latter is realized by establishing p-conjugation via C=C connections between linkers and knots. Herein we show a new approach for the synthesis of such organic materials by combination of a Knoevenagel polycondensation and a Michael addition-elimination reactions followed via an in-situ NMR study and characterized by the formation of crystalline vinylene-linked COFs[1].

Yet until now – differently from the inorganic counterpart “2D-materials” such as graphite (multilayer) and graphene (monolayer) – no monolayer formation or isolation of this interesting class of materials has been described in literature due to the high synthetic challenge. Our very recent work demonstrates that correct design and on-surface deposition of monomers lead to the fast formation of 2D-covalent nanostructures under solvothermal conditions characterized by Scanning Tunneling Microscopy (STM) at the solid-liquid interface. Surprisingly, self-assembly of the monomers and slow evaporation of the solvent reveals the slow formation of the same extended covalent networks at room temperature without the use of any additional reagent or catalyst[2].

The described approaches grant the possibility to access multilayered vinylene-linked COFs as well more challenging monolayered covalent nanostructures under both solvothermal and room temperature conditions. Understanding of their formation paves the way for the study of their fundamental properties as well for the formation of hybrid inorganic-organic devices.

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Investigation of local photocurrent and photopotential distributions on ALD-synthesized TiO₂ photoelectrode coatings

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Photoelectrochemical cells (PECs) are an environmentally friendly technology for the conversion of sunlight into valuable chemicals. However, the semiconductor components of PEC photoelectrodes are susceptible to corrosion under photoelectrochemical conditions.

Thin films of Titanium dioxide (TiO₂) synthesized by atomic layer deposition (ALD) are often used to protect the surface of photoelectrodes. In addition to their protecting function, the physicochemical properties of these coatings contribute to the overall performance of the device. The local nano-scale optoelectronic characteristics on the surface of these thin films, which significantly influence their macroscopic properties, have not been exhaustively reported in the literature.

SPM methods are a powerful tool for the study photo-induced charge separation, charge transport and recombination on photoelectrode surfaces with nanometer resolution.

We have employed Tunneling Conductive AFM (TUNA) and Kelvin Probe Force Microscopy (KPFM), both without and with sample illumination, in order to investigate ALD-grown TiO₂ thin films. Variations in morphology, achieved by controlling the synthesis conditions, have a strong impact on the local optoelectronic properties. On TUNA measurements, higher photogenerated currents are observed along grain and facet boundaries. On KPFM experiments, quantitative measurements can be obtained of the more efficient photo-induced charge separation on the crystalline TiO₂ inclusions, which generate a surface photovoltage of ~450 mV upon UV-illumination. Through classification of different regions of interest on topography maps based on morphological and other property-based criteria, the evolution of surface potential over time can be analyzed, and localized time constants can be obtained for carrier dynamic processes on the films. This spatially resolved information at the nano scale can be a helpful guide to the development of thin protecting films for macroscopically stable and efficient photoelectrodes.

Quantitative X-ray photon beam damage investigations of solid-state electrolytes.

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The Li/S battery concept (mostly based on liquid electrolytes) is characterised by a high theoretical gravimetric energy density of 2500 Wh/kg as well as environmentally friendly and ubiquitous cathode materials (sulphur, carbon) [1]. Solid electrolytes (SE) are a promising class of materials that can further enhance the safety of Li/S battery cells and have the potential to further improve energy density [2].

To improve the material parameters of the SE, traceable quantitative analysis is required to fully understand the transport and conversion processes. Reference-free X-ray Fluorescence (XRF) [3] is a highly sensitive technique that provides access to absolute elemental mass depositions and chemical speciation of elements of interest. It enables the operando characterization of depth profiles and interphases [4].

Since battery materials are sensitive electrochemical systems, it is necessary to evaluate the experimental results with respect to X-ray exposure. For this purpose, within the BMBF “Batterie 2020 Transfer” project “FestPoLiS”, systematic and quantitative radiation damage studies of two representative SE material classes (solid polymer electrolyte and hybrid electrolyte) are being performed. Using the energy-tunability of synchrotron radiation, Near Edge X-ray Absorption Fine Structure (NEXAFS) is applied to monitor dose dependent X-ray radiation induced changes of the speciation of sulphur carbon and oxygen. Applying absolute radiometrically calibrated instrumentation, the material and photon energy dependent associated radiation damage thresholds are determined.

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Application of Tip-Enhanced Raman Spectroscopy for characterizing adsorbates at sub(monolayer) coverages

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Current(electro)chemical technologies for green energy conversion/storage are not ready for mass commercialization, and demand for a deep and fundamental research, especially with regard to slow kinetics of primary reactions. Thus, improving (electro)catalysts' performance and stability is critical for future applications. Here, selective molecular patterning of noble metals with foreign adsorbates is a common strategy applied to modify reactivity and selectivity of a given material. However, getting insights into the chemical environment of surfaces at nanoscopic level, such as identification of adsorbates at (sub)monolayer coverages, identification of adsorption sites and molecular orientation, crucial information for a rational design of catalytic materials, are among the most challenging issues in heterogeneous catalysis.

Tip-enhanced Raman spectroscopy (TERS), a combination of Scanning Probe Microscope, and enhanced Raman scattering, is a promising tool to get molecular-scale insights into catalytic surface reactions [1-3]. In this work, the capabilities of TERS for identifying different types of adsorbates on planar surfaces will be discussed. In addition, since adsorbates may exhibit different interactions depending on the substrate, giving rise to (small) changes in vibrational frequencies and relative intensities, TERS can be used on multicomponent systems as a diagnostic tool for identifying to which surface the observed vibrational response belongs [3]. This knowledge can be latter extended to study more complex, practical catalytical systems, relevant for energy conversion/storage reactions to get insights into molecular details of processes under realistic working conditions.

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Towards combined operando electrochemical impedance and X-ray absorption spectroscopy of batteries

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In the framework of the EPM-OpMetBatt project [1], we work on the establishment and characterization of a measurement protocols for operando X-ray absorption and impedance measurements of cycling battery cells. X-ray absorption spectroscopy (XAS) is a widely applied experimental technique to gain insights into the chemical species present within the sample and can also be applied for operando battery characterizations [2,3]. Electrochemical Impedance Spectroscopy (EIS) is a widely applied technique in energy storage research [4]. Since most standard potentiostat systems support this method, EIS has a high availability in the research community, both in academia and industry, and represents a powerful route to gaining valuable insights into electrochemical processes. EIS measurements are typically performed under equilibrium and open circuit conditions, which provide little information on the properties of the materials and components during operation. To address this issue a novel measurement protocol and data analysis platform for operando EIS is being developed and experimentally validated. Both, the measurement protocol and the data analysis platform will eventually be used to perform measurements under charging/discharging conditions, enabling thus the coupling of operando EIS with simultaneous high resolution X-ray spectrometry measurements using calibrated instrumentation to reveal structure performance relationships with unprecedented detail and in a traceable manner.

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Are there nontrivial couplings between cathode and anode electric double layers in an electrochemical cell?

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Any working electrochemical cell has an electric double layer (EDL) at the cathode and anode, respectively, yet the two EDLs are often studied separately with the aid of reliable reference electrodes. In practical applications, a reference electrode is seldom used, yet the two EDLs are assumed to be decoupled, or trivially coupled, since they are disparate remote compared to their own nanometric thicknesses. In this presentation, I maintain that nontrivial couplings exist between cathode and anode EDLs; by nontrivial couplings we refer to new phenomena that are absent in separate studies of each EDL.^[1,2] This calls for fundamental understandings of nontrivial inter-EDL couplings in a vastly broad landscape of different electrodes, operation conditions, and behaviors, and exploitation of the obtained understanding to advance electrochemical technologies via leveraging the inter-EDL couplings.

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Understanding electrochemically driven CaCO_3 nucleation and growth

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Coupling carbon capture and electrochemical conversion in a “reactive capture” scheme is a promising approach for integrating carbon capture and conversion processes with renewable electrons.[1] However, reactive capture systems are difficult to characterize because the reactions of interest only occur under applied potential near the electrode surface, where conditions (i.e. pH, reactant concentrations, water activity, electric field) differ significantly from the bulk electrolyte.[2] *Operando* surface sensitive techniques are needed to understand how the microenvironment local to the electrode dictates reactive-capture performance.

This poster presents the use of electrochemical atomic force microscopy (EC-AFM) for observing electrochemically induced carbon mineralization from calcium containing bicarbonate electrolytes. CO_2 electroreduction at a Ag electrode shifts the local pH more alkaline and induces the precipitation of CaCO_3 . Operando EC-AFM measurements allow observation of this electrochemically driven growth as a function of applied potential and time. Complementary continuum modelling will elucidate experimentally inaccessible information about the carbonate/electrode microenvironment and predict solid carbonate formation for hard-to-precipitate species. Overall, we demonstrate that EC-AFM as a powerful technique for the study of electrochemical reactive capture systems and show how these transformations of CO_2 depend on and dictate the properties of the near-electrode microenvironment.

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Tracking fuel cells catalyst aging with EC-AFM

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One of the most promising candidates to lead the transition from energy production based on fossil fuels to zero-emission technologies is Proton Exchange Membrane Fuel Cells (PEMFC). However, large-scale deployment of PEMFCs is still constrained due to several shortcomings, among which the high cost of the cathode catalyst and its stability are the most prominent.

While recent technological advancements have begun to meet cost-efficiency targets by replacing conventional platinum catalysts with platinum alloys with cheaper transition metals, the challenge of durability persists. Even though platinum is a noble metal, it is not entirely resistant to degradation under a hostile electrochemical environment of the cathode. Relatively high potentials in combination with an acidic environment cause Pt dissolution and carbon support corrosion, which further trigger secondary degradation processes, such as detachment of Pt nanoparticles from the support, particle coalescence, and the so-called electrochemical Ostwald ripening [1]. This leads to a detrimental effect on fuel cell performance owing to continuous reduction of the available catalyst active sites. Moreover, in the case of binary systems, faster dissolution of the less noble metal further affects the above degradation pathways. It is thus essential to describe the entire chain of interconnected degradation mechanisms to formulate a comprehensive model of catalyst degradation and to develop a corresponding mitigation strategy leading toward a more robust catalyst.

Reaching the above goal becomes possible with the availability of multiple *in situ/operando* techniques, among which EC-AFM stands out among the most promising [2]. It allows for the simultaneous utilization of cyclic voltammetry to simulate the working conditions of the PEMFC catalyst and AFM imaging at the electrode/electrolyte interface, enabling tracking catalyst morphological changes during its operation.

Herein, the findings of our investigations into the degradation of monometallic Pt and PtNi catalysts using EC-AFM are presented [3,4]. The emphasis is given to potential-dependent degradation, which simulates various operational conditions in PEMFCs.

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Observing light induced charge propagation through organic epitaxial nanoneedle networks on hexagonal boron nitride

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The main route towards future scalable mass production of two-dimensional (2D) materials is highly likely to be chemical vapor deposition (CVD). Nevertheless, typically exfoliated, wrinkle free materials are considered to set the benchmarks for what is possible with CVD materials. Therefore, gathering data on the performance of exfoliated 2D materials is highly necessary in order to establish a reference for comparison with the CVD materials.

An example for broadening the field of applications for 2D materials is their integration into heterostructures with organic semiconductors. Under proper conditions, organic molecules can self-organize into crystalline nanoneedles on 2D materials with well defined interfaces. The comparably weak interaction between 2D material and the organics tends to widely preserve the intrinsic properties of both constituents. This has been confirmed in a number of studies for both, CVD grown and exfoliated 2D materials. [1,2]

Here, the light-assisted propagation of charges through organic semiconductor networks was investigated. The network was formed by quasi-one-dimensional crystallites, which epitaxially grew on exfoliated hexagonal boron nitride. By means of electrostatic force microscopy, an increase in conductivity by two orders of magnitude upon light exposure could be demonstrated. Further, we took advantage of the highly anisotropic optical properties of the organic nanoneedles to guide charge propagation along specific needle directions by matching them with the polarization direction of the incident light. This way, a kind of “light-gate” was realized to controllably alter the conductivity of organic nanostructures and even to steer the charges along desired directions within the crystallite networks. [3]

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Degradation of Fe-N-C Catalyst Layers in Alkaline Media

^{1,2*}Ku, Y.-P., ^{1,2}Ehelebe, K., ¹Kumar, K., ¹Hutzler, A., ^{1,2}Götz, C., ^{1,2}Bierling, M., ³Bibent, N., ⁴Vorokhta, M., ⁵Zitolo, A., ¹Lloret, V., ⁴Khalakhan, I., ^{1,2}Thiele, S., ^{1,2}Mayrhofer, K.J.J., ¹Böhm, T., ³Jaouen, F., & ¹Cherevko, S.

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Iron-nitrogen-carbon (Fe-N-C) catalysts are promising for replacing platinum group metal catalysts for oxygen reduction reaction (ORR) in fuel cells (FCs) while they still endure considerable degradation during FCs' operation mode and start-stop events. The stability studies using scanning flow cell (SFC) coupled with inductively coupled plasma mass spectrometry (ICP-MS) have provided information on the effects of various factors, such as potential and pH, on Fe leaching from Fe-N-C catalysts.^[1-2] Yet, the degradation in relevant current density regions is difficult to track in such systems in operando. Thus, the loss of Fe active sites in the Fe-N-C cathodes of FCs can only be obtained by post-mortem analyses, such as Mössbauer spectroscopy.^[3] To bridge this gap, a novel gas diffusion electrode half-cell (GDE) coupled with ICP-MS has been developed in our previous work^[4] and can reveal the online Fe dissolution rate at ORR current densities up to $-200 \text{ mA}\cdot\text{cm}^{-2}$.^[5]

Using this GDE-ICP-MS technique, this work shows the online Fe leaching rates in Fe-N-C catalyst layers in a broad potential window in alkaline media, simulating the operation mode ($E < 1.0 \text{ V}_{\text{RHE}}$) and start-stop events ($E > 1.0 \text{ V}_{\text{RHE}}$) in anion-exchange membrane FCs (AEMFCs). In the potential range between 0.57 and 0.87 V_{REH} , the amount of dissolved Fe species is intensified during ORR and is highly correlated to the oxygen reduction charge.^[5] While in the potential range between 1.0 and 1.5 V_{RHE} , where the electrochemical oxidation of the N-C matrix may take place, the Fe dissolution rate is barely influenced by the presence of oxygen yet significantly enhanced by increased temperature. Based on *in situ* and post-mortem analyses, novel insights into the degradation mechanisms of alkaline Fe-N-C catalyst layers are revealed and can inspire rational designs of more durable Fe-N-C catalysts.

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Exploring Fe-modified ceria-based model catalysts through the integration of in-situ near-ambient pressure XPS and STM

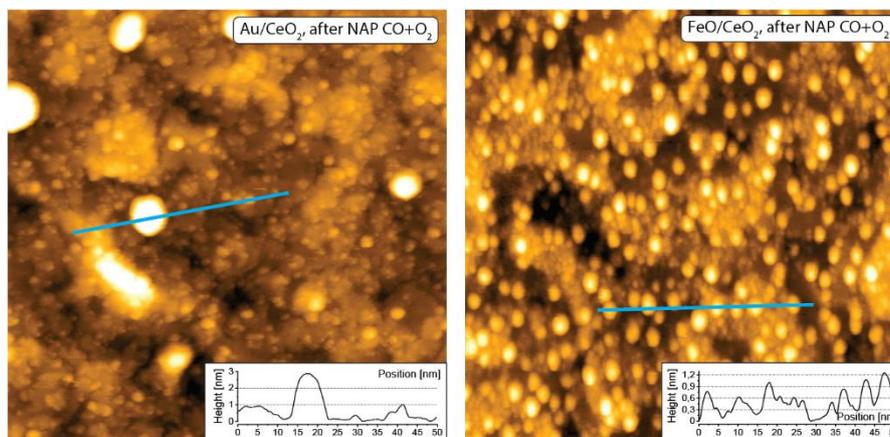
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The study of catalytic reactions has long been a topic of interest in the fields of chemistry and materials science. In recent years, advancements in analytical techniques have allowed for more in-depth studies of catalysts at the atomic level under operando conditions. In this presentation, we will highlight the benefits of combining in-situ near-ambient pressure X-ray photoelectron spectroscopy (NAP-XPS) and near-ambient pressure scanning tunneling microscopy (NAP-STM). The integration of XPS and STM provides a unique combination of analytical techniques that can be used to probe both the electronic and geometric structures of model surfaces while being catalytically active under pressures up to the millibar range.

We showcase the use of the combined ultra-high vacuum NAP-STM/XPS system in the study of the room-temperature CO oxidation on the Au clusters supported by Fe-modified epitaxial CeO₂(111) layers. Clean CeO₂ layers, CeO₂ layers modified by sub-monolayer 2D iron oxide films and mixed Ce-Fe oxide layers were prepared in UHV and were subsequently exposed to 0.5 mbar of CO, 1 mbar of CO+O₂ mixture and 0.5 mbar of O₂. Our results show that the Au/CeO₂ system exhibits significant chemical and morphological changes upon exposure to the mixture of CO and O₂ at room temperature (1 mbar). At the same conditions, active Au clusters on epitaxial and intermixed Ce-Fe oxide layers are significantly more stable. This increased stability likely contributes to the enhanced catalytic activity of Au clusters supported by the Ce-Fe oxides compared to single-component Ce oxide.



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Hydration layer ordering effects at gold–electrolyte interfaces probed by *in situ* correlative atomic force microscopy and vibrational spectroscopy

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The solid-electrolyte interfaces of electrocatalysts are highly dynamic entities with their morphology, structure, oxidation state and composition changing during the electrochemical CO₂ reduction reaction (CO₂RR). While mechanistic models have been proposed [1]-[3], a comprehensive analysis of interfacial processes is needed to gain fundamental insights and optimize catalyst-electrolyte interfaces. We introduce a correlative microscopy approach, combining *in situ* conductive atomic force microscopy (c-AFM) with simultaneous friction force and morphology imaging, thus enabling nanoscale physical-chemical interrogation of the catalyst–electrode interface. For the class of bimetallic electrocatalysts, the electric conductivity variations across nanopatterned CuO_x islands on Au electrodes can be resolved in air, water and bicarbonate aqueous electrolytes [4]. In line with current contrasts between catalyst surface areas of different composition and oxidation state, *in situ* measured *I-V* curves show highly resistive CuO_x islands. Simultaneously measured friction force images suggest a qualitative contrast variation upon transitioning from water to bicarbonate electrolyte, indicating that friction forces are subject to hydration layer ordering effects. Complementary *in situ* friction force measurements reveal a decrease in the friction coefficient with increasing ionic concentration, consistent with a mild chaotropic effect expected for K⁺ ions. To gain further molecular-level insight, we paired up this spatially resolved analysis of interfacial physical-chemical properties with *operando* spectroscopy. Time-resolved attenuated total reflection-surface enhanced infrared adsorption spectroscopy (ATR-SEIRAS) and on-line differential electrochemical mass spectroscopy (DEMS) investigations were performed to clarify that H₂O primarily serves as proton donor for CO₂RR and HER, while HCO₃⁻ is only involved in the Heyrovsky step. *Operando* IR spectra indicate that hydrated CO₃²⁻ plays a key role in promoting hydration layer ordering and the formation of a network of short H-bonds, facilitating the rapid delivery of electrons and protons to the Au surface. This, in turn, suppresses the CO₂RR due to promoted H^{*} formation through the increased connectivity of the CO₃²⁻ induced interfacial water network in the high current density region. Overall, pairing-up *in situ* nanoscale probing of catalyst–electrolyte physical characteristics with *operando* vibrational analysis of molecular interactions paves the way for in-depth analysis of electrochemical reactions.

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Determining chemical diffusion coefficients via polarization-relaxation measurements using KPFM

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Kelvin Probe Force Microscopy (KPFM) is an AFM-based technique to measure the local surface potential of a sample. The surface potential is - under ideal conditions - a measure for local changes of the surface-near defect chemistry of a semi-conductor, as it is directly related to the local Fermi level. Time dependent measurements of the surface potential can thus be used to analyze local relaxation processes after a previous polarization event, which introduces a local defect gradient at the point of contact. If there is ionic conductivity, a typical exponential dependence of the surface potential difference on time occurs, which can be used to calculate the chemical diffusion coefficient. [1].

For the experiments, a ceramic pellet is connected with a large back contact and the AFM tip is used as working electrode to polarize the sample with a given voltage for a given time. Since the tip is very small compared to the back contact, a large proportion of the voltage drop and most of the associated reactions take place in the immediate vicinity of the contact point. Directly after the end of the polarization, the AFM is switched to KPFM mapping with a high imaging rate (typically one image per minute) to analyze the relaxation of the introduced surface potential gradient over time.

The advantage of this method is that one can not only measure the temporal course of the relaxation as with conventional polarization-relaxation setups, but also observe the spatial expansion. It is typically in the range of 100 nm to several μm and depends on the applied voltage and charge carrier concentration. This allows additional information to be gained, e.g. about the effect of grain boundaries or of flaws on the surface on the charge transport. Another advantage is that, for example, ion-conducting components of a ceramic composite material can be specifically targeted. The method works particularly well for materials with comparatively slow ion transport, where the relaxation processes can last between 10 minutes and several hours.

As examples, measurements on ceria-based oxygen permeation membranes [1,2] as well as on the mixed electron- and zinc-ion-conducting material $\text{ZnFe}_{2-x}\text{Ti}_x\text{O}_4$ will be presented.

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***In-Situ* electrochemical mapping of local activity on Zn and Zn-Al alloys using scanning electrochemical microscopy (SECM)**

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Metal-air batteries have gained tremendous attention in the past years as promising technologies due to their theoretically high specific energy and environmentally friendly use of oxygen ¹. Considering the cost-effectiveness and natural abundance, Zn and Al are good candidates for metal-air batteries. However, in Zn-air systems, stable cyclability is an issue due to the passivation layer on Zn electrodes in neutral electrolyte. Guerrero *et al.* reported recently that ethylenediaminetetraacetic acid (EDTA) as an electrolyte additive activates the surface of Zn electrode to maintain metallic property, thereby improving the performance of Zn-air batteries in near-neutral chloride-based electrolyte ².

In this study, we investigate the local activity on Zn and Zn-10Al alloy electrodes in 2 M NaCl (pH 10) containing EDTA by using scanning electrochemical microscopy (SECM). We observed that the surfaces of Zn and Zn-10Al alloy electrodes are passivated at open circuit potential (OCP) and these passivation layers disappear at OCP by adding EDTA in the electrolyte. As the potential is applied to slightly positive of OCP, the formation of the passivation layer is more dominant than the activation by EDTA, resulting from the limited amount of dissociated EDTA in near-neutral electrolyte. It is noteworthy that a clear topographic change is observed by means of AFM-SECM after the electrode contacts with EDTA, which demonstrates the effect of EDTA.

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Resolving the morphology and surface structure of CO₂RR and OER catalysts by in situ AFM

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While copper (Cu) and cobalt (Co)-based materials are remarkable for catalyzing CO₂ electroreduction (CO₂RR) at the cathode and oxygen evolution reaction (OER) at the anode, respectively, the rational design of selective, active, and robust electrocatalysts is hindered by lacking nano- and atomic-scale structure information derived in relevant electrolytes under operating conditions^[1-2]. Using electrochemical atomic force microscopy (EC-AFM), we reveal the real-space surface structure and morphology of single crystalline Cu and well-defined Co-based thin film/platelet electrocatalysts *in situ*. The surface morphology of Cu (100) is found to exhibit a pronounced dependence on applied potentials and electrolyte composition. Reversible and irreversible transformations between round and straight step edges are observed for Cu (100) in KOH and bicarbonate electrolytes, respectively. CO as critical intermediate in CO₂RR could inhibit this structural transition at step edges and also induce complex reconstructions on the terraces. Copper aggregates can also be found evolving on the terraces after mild surface oxidation/reduction. For OER, we provide first *in situ* insights into the facet-dependent morphology evolution and transformation of ordered atomic structure to an (adsorbate-induced) amorphous layer on ultra-high vacuum (UHV)-prepared Co₃O₄ thin films. In addition, hexagonal Co(OH)₂ and Co₃O₄ platelets are found to have significantly varied morphology at OER potentials. Potentiodynamic OER current transients of both Co-based platelets exhibit a similar pseudocapacitive charging kinetics with Co(OH)₂ featuring a higher capacity for storing oxidation equivalents. The presented findings demonstrate the potential of EC-AFM to advance fundamental understanding of transition metal-based electrocatalysts under working conditions, which will help developing new design principle for energy conversion materials.

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Determination of the local potential of zero charge on noble metal-based electrocatalysts using SECCM

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Scanning electrochemical cell microscopy (SECCM) is a powerful technique to assess the local electrochemical activity of different surfaces with nanoscale resolution and to investigate correlations between the electrochemical properties and the surface structure/composition, which is crucial for developing improved catalysts.^[1,2] Recently, this technique was used to measure the potential of zero charge (PZC) at the nanoscale. The feasibility of the measurements was confirmed for polycrystalline Pt and noble-metal-based high entropy alloys (HEA) using a nanopipette with a diameter $\sim 1 \mu\text{m}$.^[3,4] While it was found that the PZC correlates positively with the catalytic activity for the hydrogen evolution reaction (HER) in acidic media, the reported values range between 0.7 and 0.8 V vs. SHE,^[3] which is considerably higher than the value of 0.3 V vs. SHE found using macroscale electrochemical measurements and optical methods.^[5-7] This discrepancy could be related to specific adsorption processes that can hinder the analysis by means of electrochemical methods only.^[5] For Pt(111), cyclic voltammetry or chronoamperometry can be used to determine the PZC, due to its well-defined double-layer potential window.^[6]

Herein, we aim to measure the local PZC with increased lateral resolution on Pt-based electrocatalysts. To achieve this, smaller nano-pipettes were used ($\sim 300 \text{ nm}$ compared to the previously used $1 \mu\text{m}$ ^[3,4]), and a measuring protocol was adapted to circumvent cases in which the transient currents in the non-Faradaic region have low signal-to-noise ratio (potentials around PZC). The feasibility of the measurement was demonstrated on (111) surfaces of a polycrystalline Pt film with grains oriented in [111] direction, where PZC values of 0.3 V vs. SHE with high statistical reliability were derived, in line with previous reports at the macroscale.^[5-7] A zooming-in approach was performed on Pt-based high entropy alloys and phosphorus-implanted Pt films measuring the electrocatalytic activity and PZC on different areas. The results showed that the PZC can be correlated with the HER activity at the nanoscale.

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A Comparative Study of Adsorption Sites and Thermal Stability of Platinum and Iridium Adatoms on $\text{Fe}_2\text{O}_3(1\bar{1}02)$

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Precious metals supported on oxides exhibit exceptional effectiveness in numerous significant chemical reactions, such as hydrogen evolution, water gas shift, photocatalytic processes, and CO-oxidation reactions due to their elevated activity and/or selectivity. Downsizing catalyst clusters to single atoms is an effective way to reach maximum efficiency, and so-called “single-atom catalysis” is now an important and fast-emerging field of research [1]. However, significant challenges persist in achieving the stabilization of single atoms of late-transition metals on oxide supports without compromising their catalytic activity, as well as identifying the specific adsorption sites where these adatoms remain stabilized. In this study, we employ surface science techniques to examine the specific binding environment of thermally evaporated platinum and iridium adatoms on $\alpha\text{-Fe}_2\text{O}_3(1\bar{1}02)-(1\times 1)$, all conducted under ultrahigh vacuum (UHV) conditions. Through comprehensive scanning tunneling microscopy (STM) and x-ray photoelectron spectroscopy (XPS) analyses of various surface coverages of Pt and Ir on $\alpha\text{-Fe}_2\text{O}_3(1\bar{1}02)-(1\times 1)$, it was discovered that both metals have highly stable single atoms at room temperature adsorbing at different sites with different apparent heights. Furthermore, by conducting a thorough analysis of STM data, the relative contributions arising from different types of adsorption sites and the impact of O_2 on these contributions for both Pt and Ir were determined, relying on the apparent height. Additionally, the sintering of single atoms at elevated temperatures was tracked using XPS and STM.

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Implementation of an in situ atomic force microscopy (AFM) setup to study the dynamics of (electro)catalytic interfaces

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Solid/liquid interfaces play a fundamental role in heterogeneous and electrocatalysis and are highly dynamic under operation conditions.[1] One example is the so-called “Solid Catalyst with Ionic Liquid Layer” (SCILL), which is the one of the research foci of the Collaborative Research Center 1452 “Catalysis at Liquid Interfaces”. [2] In SCILL systems, a thin layer of ionic liquid (IL) improves the selectivity of supported, catalytically active metal nanoparticles.[3-5] Some SCILL systems outperform conventional catalysts, e.g., in selective hydrogenation reactions, and are even applied in large-scale industrial processes.[6] To further improve the performance of SCILL systems in a knowledge-driven way, we need to understand the dynamic interaction of the IL with the (electro)catalytic surface and the morphological changes of the (electro)catalyst at the molecular/atomistic level.

High-resolution atomic force microscopy (AFM) can provide the required information. We implemented a new in situ AFM setup (Cypher AFM, Oxford Instruments), which permits studies under reaction conditions at gas/solid, liquid/solid, and electrochemical interfaces. In particular, the in-situ cells allow us to precisely control the experimental parameters such as temperature, pressure, the composition and flow rates of gases and liquids, and the applied potential. Thus, we can study (electro)catalytically active interfaces under (or close to) reaction conditions by in situ AFM. In a first step, we investigated the influence of ILs on the stability of electrode materials, such as Au(111).

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Nanoscale analysis of the electric double layer formed between platinum and the protic ionic liquid [Dema][TfO]

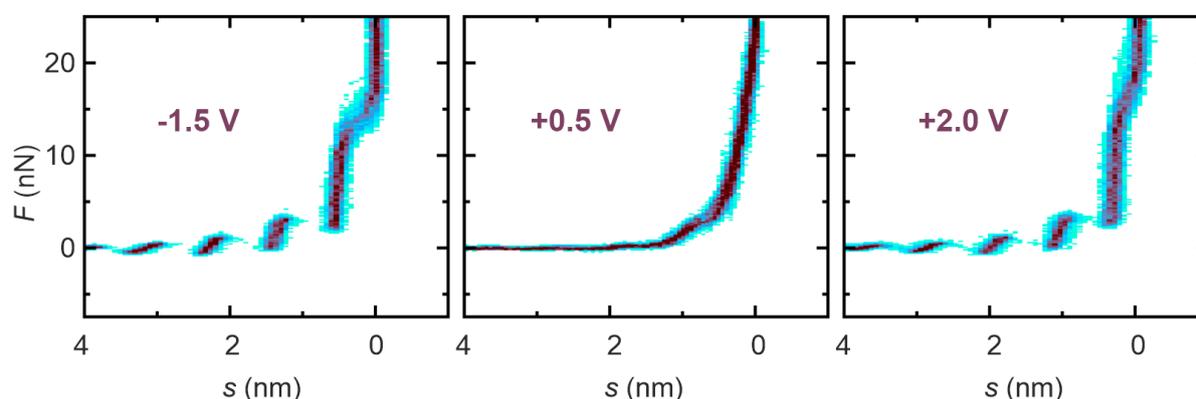
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Polymer electrolyte membrane fuel cells (PEMFCs) are essential for building up a hydrogen-based energy system. A promising concept to increase their efficiency is increasing the operation temperature from typically 80 °C used nowadays to temperatures above 120 °C. Such high-temperature PEMFCs would offer a variety of advantages such as an easier heat and water management resulting in a compact system design and higher CO tolerance. Since standard fuel cell electrolytes are not applicable at higher temperatures anymore, we investigate ionic liquids as promising alternative [1].

In ionic liquids, complex intermolecular interactions are present, which determine the structure of the electrode-electrolyte interface. We present investigations of the model ionic liquid diethylmethylammonium trifluoromethanesulfonate [Dema][TfO] at different water contents and under electrical polarization of the Pt electrode by atomic force microscopy [2] in combination with atomistic simulations [3].

Force spectroscopy recorded during approaching and retracting the tip to the solid/liquid interface shows that a compact nanostructure consisting of alternate cation and anion layers is present as soon as a potential is applied to the electrode. This finding is supported by molecular dynamics simulations, which reveal that a dense and ordered layer is formed, expanding several nanometers into the bulk of the liquid. Upon the addition of water, the layering is distorted and water molecules are found to accumulate in the interface region [4].



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Nanoscale Surface Photovoltage Spectroscopy

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Understanding electron and ion dynamics is an important task for improving modern energy materials, such as photovoltaic perovskites. These materials usually have a delicate nano- and micro structure that influences the device parameters. To resolve detailed structure-function relationships on the relevant micro- and nanometer length scales, the current macroscopic and microscopic measurement techniques are often not sufficient.

Here, we introduce nanoscale surface photovoltage spectroscopy (Nano-SPV) and nanoscale ideality factor mapping (Nano-IFM) via time-resolved Kelvin probe force microscopy (tr-KPFM). These methods can map nanoscale variations in charge carrier recombination, ion migration, and defects. To show the potential of Nano-SPV and Nano-IFM, these methods are applied on perovskite samples with different morphologies. A scheme is shown in Figure 1.

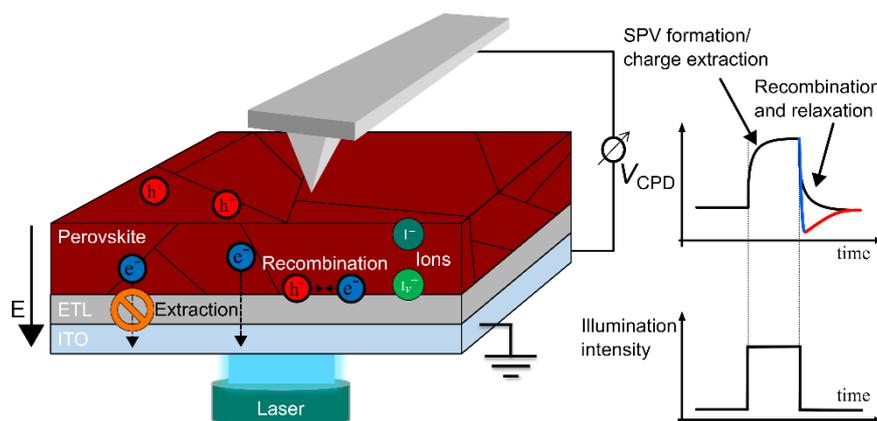


Figure 1: Schematic overview of the tr-KPFM setup. The laser intensity is either modulated in a pulse shape or a slow intensity increase with the tip engaged to the surface while the local CPD signal is recorded. The CPD traces contain information about local charge carrier extraction processes, which result in the formation of an electric field E (arrow on the left). After the light pulse, the CPD trace reveals information about recombination processes and the presence of defect states such as GBs and interfaces, which hinder the extraction of charges (blocking symbol).

The results clearly show an improved uniformity of the SPV and SPV decay distribution within the perovskite films upon passivation and increasing the grain size. Nevertheless, Nano-SPV and Nano-IFM could still detect local variations in the defect density on these optimized samples, guiding the way for further optimization.

Study of the Ionomer Distribution in Catalyst Layers by Atomic Force Microscopy

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The optimal distribution of the ionomer in fuel cell and electrolyser catalyst layers (CL) is crucial for the efficient utilization of the catalyst and therefore on the performance and stability during operation. Inside the CL, the conductance of ions and electrons as well as mass transport of educts and products at the catalytic centers need to be ensured. The ionomer allows the ion conductance of cations (H⁺ in proton exchange technologies) and anions (OH⁻ in anion exchange membrane technologies). Both are expected to be ideal, when the ionomer is homogeneously distributed around the catalytic centers. Furthermore, too thin and too thick ionomer coverages can lead to ion conductance and mass transport resistances, respectively [1, 2]. Insights into the ionomer distribution complements the electrochemical characterization and allows optimization of the CL preparation.

The visualization of the ionomer in CL is challenging, because high resolution techniques like TEM usually not allow measuring conditions close to fuel cell operations and are destructive towards the ionomer. Recently, the feasibility of atomic force microscopy (AFM) from ambient to operando conditions was proven by analyzing the ionomer distribution in fuel cells and electrolyzers [3, 4]. Thus, the nano-mechanical properties of the different materials in the CL, namely the catalyst and the ionomer, lead to a material contrast (c.f. figure). Within our contribution we utilize and give an overview on the AFM technique used to image fuel cell and electrolyser CLs. Thereby the average ionomer layer thickness is analyzed for different ionomer loadings. Furthermore, results on elevated temperatures and defined relative humidities are presented, which allowed *in situ* observation of ionomer swelling in the CL.

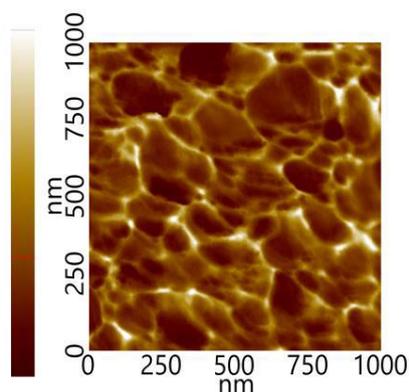


Figure of the adhesion force of a catalyst layer with Nafion[®] as ionomer by AFM. Lighter areas are showing the ionomer (strong adhesive) and darker areas the Pt/C catalyst (weak adhesive).

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Scanning Photo-Electrochemical Microscopy of Hot Carrier Photochemistry on Monocrystalline Plasmonic Nanostructures

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High-definition monocrystalline nanostructures with well-controlled optical absorption characteristics can be used to obtain fundamental understanding of the role of hot-carriers in plasmonic photocatalysis [1,2]. However, despite many studies on the optical properties of high-definition monocrystalline gold (Au) nano-antennas, photocatalytic performance of these array structures has not been studied so far due to the challenges associated with fabricating cm-scale array structures and the incapability of the conventional photoelectrochemical systems in detecting signals from tiny reactions on um-scale array structures. In this work, we report on light-assisted scanning electrochemical microscopy (SECM) studies of a series of μm -scale Au nano-antenna arrays fabricated by electron beam lithography on high-aspect ratio Au microflakes on a TiO_2 -coated glass substrate (Figure 1a) [3]. SECM experiments were performed at different excitation wavelengths and intensities in an aqueous solution containing ferri- and ferrocyanide redox molecules for the test photocatalytic reaction on Au nano-antennas having different thicknesses. We observed that the external quantum efficiency tracks the surface plasmon resonance of the Au nano-antennas while the internal quantum efficiency maximizes at a wavelength in the inter-band threshold of Au and not at the resonance wavelength for all the thicknesses (Figure 1b,c). The results provide important insight into the quantum efficiencies of plasmonic photocatalytic devices, as well as the generation, transport, and collection of hot carriers.

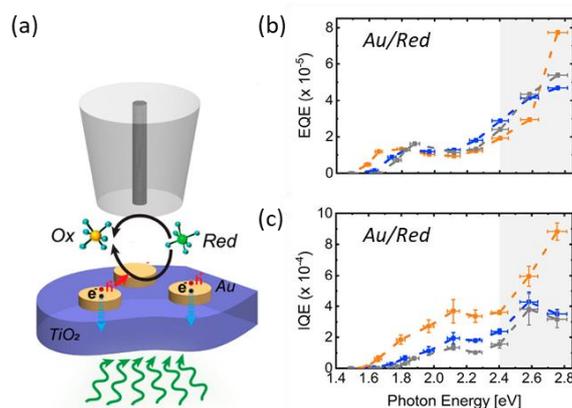


Figure 1. Schematic of wavelength-dependent scanning photo-electrochemical microscopy and interfacial hot-carrier collection on Au nanodiscs/ TiO_2 photoanode in contact with a reductant (Red) molecule. (b) Experimentally determined external quantum efficiency (EQE) and (c) internal quantum efficiency (IQE) spectra for the Au/ TiO_2 heterostructures having different Au nanodisc thicknesses of 16 (orange), 25 (blue), and 33 nm (gray) exhibiting resonance peaks at 1.57, 1.66, and 1.75 eV, respectively [3].

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Local contact potential of Biofabricated Gold Nanotriangles

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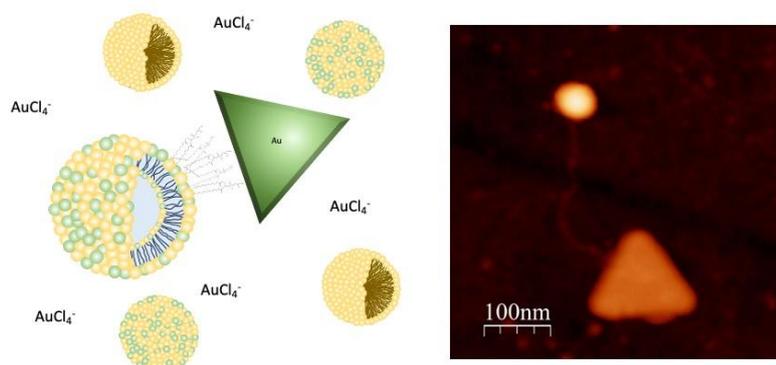
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Anisotropic gold nanoparticles have very important and unique applications in a wide range of fields, including optical sensing, biomedicine, and chemical catalysis, among others. A synthetic pathway to gold nanotriangles (GNTs) used negatively charged liposomes accomplished both functions as a reducing and stabilizing agent in the synthesis. Liposomes are based on a mixture of phospholipids, and they were used as a template phase to perform the GNTs. Isotropic and anisotropic gold nanoparticles are formed simultaneously during the synthesis. Therefore, by combining centrifugation and depletion flocculation strategies, the sample was concentrated in terms of GNTs from 15% crude to 80% by using sodium dodecyl sulfate (SDS). As a result, a green colored dispersion was obtained containing highly purified, well-defined, negatively charged GNTs, where the edge length of most particles is centered in the range of 60–80 nm with an average thickness of 7.8 ± 0.1 nm. The characterization of the nanotriangles was carried out with DLS, TEM, UV-vis, AFM, KPFM and Raman spectroscopy techniques.



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Oxide formation and oxide/metal interaction in Ni(111)

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Metal-oxide interactions are of great importance when studying catalytic materials. In particular, ceria/metal model systems have been studied in many combinations, showing to be excellent systems for studying fundamental properties measured by surface science techniques [1]. The variation of the oxygen chemical potential on the surface of metallic substrates such as Cu(111)[2], Ru(0001)[3] and Au(111)[4] has been shown to significantly affect ceria structures in terms of facet promotion and oxidation states. In the case of Ni, its strong catalytic behavior results in Ni(111) oxidation upon oxygen exposure under the CeO_x deposition conditions; thus, increasing the complexity of the system as multiple interfaces (oxide/metal, oxide/oxide) might be present.

As a preliminary step of the study of the CeO_x on nickel(111) system, we show the structural and spectroscopic effects of exposing the substrate at different oxygen partial pressures and temperatures. We present LEED, XPS and UPS measurements taken in a UHV surface science cluster. At room temperature, the oxygen gets absorbed forming ordered structures, until the formation of NiO(111) layers[5]. For higher temperatures, the formation of NiO(001) islands has been observed[5], although more recent LEEM/PEEM measurements show that the NiO(111) facet can be formed for temperatures up to 750K [6], in accordance with our measurements. By studying the oxygen energy range in XPS, we can differentiate the absorbed oxygen giving rise to the LEED pattern from the more superficial and disordered components.

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SECM as tool for investigating charge-transfer processes at interfaces of energy storage devices: from Li batteries to beyond-Li batteries

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We have employed scanning electrochemical microscopy (SECM) to elucidate the electrochemical activity of interfaces in lithium-ion batteries (LIBs)[1,2] and beyond-Li batteries, specifically Mg-ion batteries (MIBs)[3]. During the first charge/discharge cycles, a solid-electrolyte interphase (SEI) is deposited on the negative electrode of the metal-ion batteries due to reductive electrolyte decomposition. The stability and integrity of the SEI have been identified as the main limitation on the progress in development of long cycle-life metal-ion batteries. The reason that the SEI plays a key role in the battery performance is due to its ability to prevent the continuous degradation of the electrolyte at the negative electrode, thus providing a protective property of the SEI. Importantly, the SEI needs to block electronic conductivity to prevent further electrolyte deposition while it should concomitantly allow metal ions to pass with a nearly undisturbed ion conductivity (Figure 1).

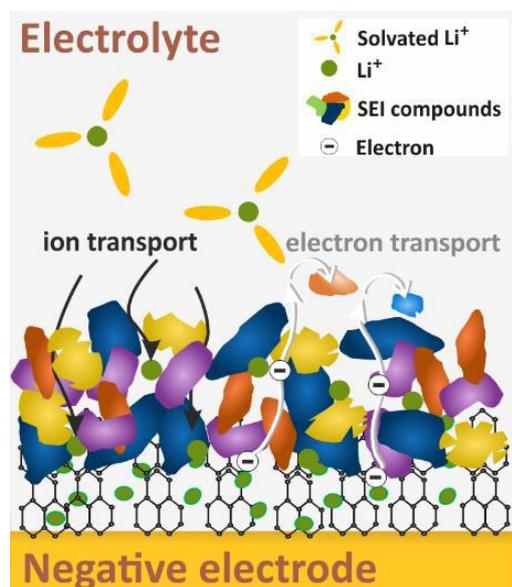


Figure 1. Schematic of the ion and electron transport through the SEI at the negative electrode.

We propose SECM as a powerful technique to elucidating the electrolyte roles in the formation of the protective film in LIBs[1] and MIBs[3]. Moreover, SECM was used as a tool for the accelerated evaluation of the integrity of the SEI in next-generation anodes, which experience large volume changes leading to an unstable SEI.[2]

We have performed systematic feedback-mode SECM analysis of anodes prepared in standard electrolytes and the in-situ SECM results correlate with macroscopic electrochemical impedance (EIS) measurements and post-mortem analysis such as e.g. XPS (X-ray photoelectron spectroscopy) measurements.

Acknowledgements: This project has received funding from the European Union's Horizon Europe research and innovation programme – European Innovation Council (EIC) under grant agreement No 101046742 (MeBattery).

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Investigating proton reduction and hydrogen absorption on palladium via scanning electrochemical microscopy

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This study aims to explore the electrochemical behavior of Palladium (Pd) systems in hydrogen reactions, namely, hydrogen evolution reaction (HER) and hydrogen oxidation reaction (HOR), using scanning electrochemical microscopy (SECM). For the HER, we utilized a Pd monolayer (ML) electrodeposited onto a polycrystalline (pc) gold (Au) substrate. The edge between the Pd and Au area was studied by monitoring the HOR current in 0.1 M HClO₄ at the microelectrode using a sample generation-tip collection (SG-TC) [1] mode. The results reveal a pronounced increase in the HOR current on the Pd ML compared to the Au region, emphasizing the enhanced HER activity of Pd in contrast to Au. For the HOR and H-absorption, we employed Pd nanoparticles (NPs) immobilized on Au(pc), fabricated via Atomic Layer Deposition (ALD). Recently, ALD has proven to be a viable technique to create noble metal NPs of different sizes [2] on different substrates. Their electrochemical performance was analyzed by recording the HOR current at the microelectrode during a redox competition (RC)-SECM [3] experiment. Following this, we developed an evaluation method combining surface integration and H₂ molecule normalization to critically examine effects like the influence of different alkali metal (AM) cations, such as Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, in 0.1 M AM(OH) electrolytes towards the HOR/H-absorption activity. The resulting (current*area)/(number of H₂ molecules) ratio emerges as a parameter to assess the HOR/H-absorption activity. A higher ratio corresponds to a smaller and a lower ratio to a larger HOR/H-absorption activity. Using this procedure, our results reveal a direct correlation between HOR/H-absorption activity and cation size/hydration energy, with the HOR/H-absorption activity increasing from Li⁺ to Cs⁺ for the Pd NPs.

This work has received funding from the European Union's Horizon 2020 research and innovation programme under grant agreement HERMES No 952184.

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Multi-principal element alloy nanoparticle (MPEA-NP) electrocatalysts prepared by pulsed laser ablation for electroreduction of CO₂

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Multi-principal element alloy (MPEA) nanoparticle electrocatalysts have the potential to provide a cost-effective and efficient alternative to noble metal electrocatalysts. The chemically complex nature and the high configurational entropy of MPEAs offer advantages in tailoring catalytic activity, product selectivity, and improved stability under harsh reaction conditions. Cu-containing bimetallic catalyst systems have already been demonstrated to lead to a significant increase in catalytic efficiency compared to monometallic systems. Thus, this project aims at the design of Cu-containing MPEAs and nanoparticle electrocatalysts for carbon dioxide reduction reaction.

In this project, base alloys were prepared by means of arc melting with subsequent homogenization treatments and processed by pulsed laser ablation in water and organic solvents into high-purity nanoparticles. The nanoparticles were characterized by means of transmission electron microscopy (TEM) and energy-dispersive X-ray spectroscopy (EDX). Electrochemical testing was performed both on bulk alloy samples and nanoparticle film coated glassy carbon electrodes by means of cyclic voltammetry (CV), linear sweep voltammetry (LSV) and electrochemical impedance spectroscopy (EIS). Nanoparticle coated electrodes have been investigated by means of atomic force microscopy (AFM) and scanning kelvin probe force microscopy (SKPFM) to assure a homogeneous distribution on the electrode surface. The presentation will summarize our initial results on the electrocatalytic activity of Cu-MPEA system for carbon dioxide reduction.

But it is already correlative microscopy

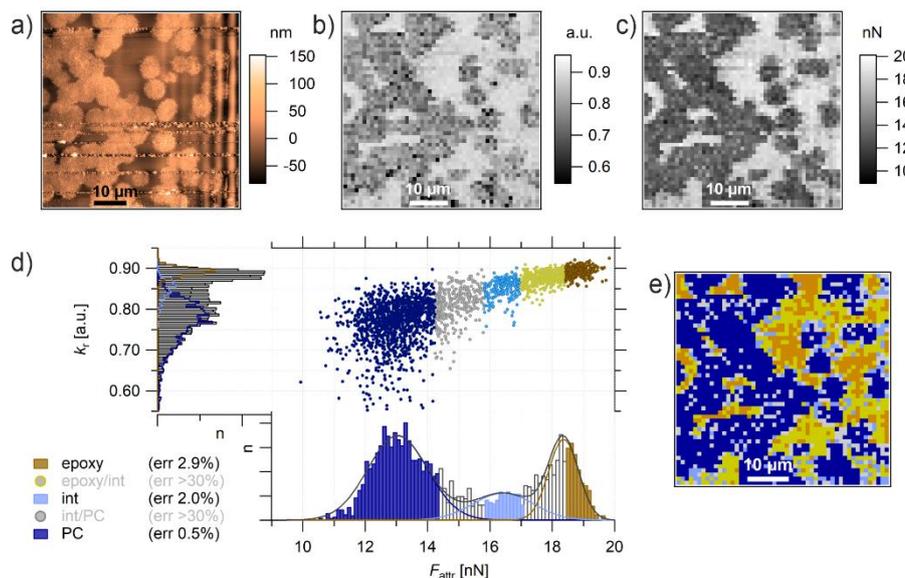
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Key application of atomic force microscopy (AFM) is the measurement of physical properties at sub-micrometer resolution. For a complete structure–property correlation, these physical measurements are considered to lack the ability to identify the chemical structure of heterogeneous materials. A promising trend to overcome this disadvantage is the combination of different microscopy methods with AFM. In the case of separate measurements, such EDX or XPS one has to find again the same region of interest on the sample and lateral coordinates have to be synchronized with those of the AFM measurements. Complementary AFM measurements are easier to implement, since no additional sample preparation is necessary. For example, AFM-based infrared spectroscopy (AFM-IR) and Kelvin probe force microscopy (KPFM) are uniquely suitable to identify local chemical and structural properties of a samples. However, we propose a third option, which is to use different information inherent to AFM force spectroscopy to assess both, structure and physical properties of a given sample in one measurement. Here different channels, such as stiffness k_{eff} , attractive forces F_{attr} , adhesive forces F_{adh} and dissipative energy E_{dis} are taken and correlated. Since these channels are independent, their correlation gives already a holistic view on the structure property correlation. Here, we show examples of nanoscopic composite materials (inorganic and organic), which were studied with combinational microscopy, complementary microscopy, and inherent correlative microscopy and discuss the different approaches.[1]



(a) AFM tapping-mode topography of PC in epoxy (b) k_r and (c) F_{attr} of AFM FDC maps (d) property domain with PCA (e) results of PCA in the spatial domain.

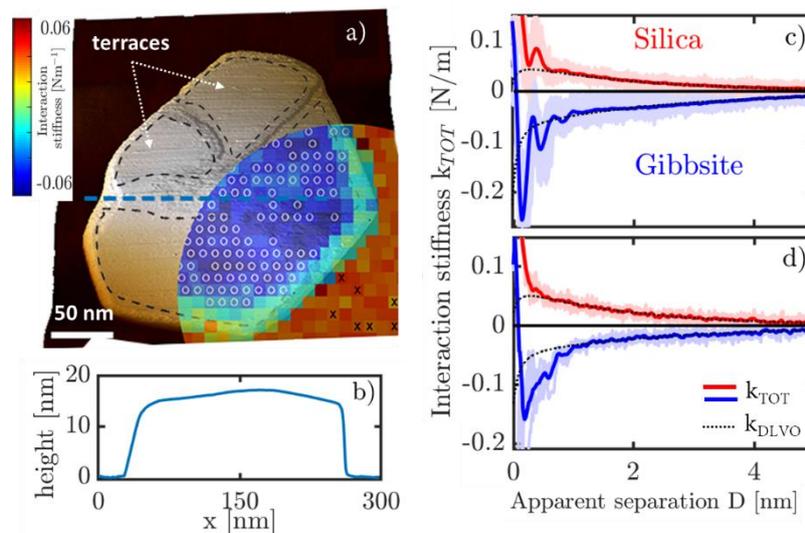
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On the relation between colloidal electrostatic and hydration forces on mineral surfaces in ambient electrolytes of variable composition: An Atomic Force Microscopy Study

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The balance between hydration and Derjaguin–Landau–Verwey–Overbeek (DLVO) forces at the solid-liquid interface controls many processes, such as colloidal stability, wetting, biomolecular self-assembly, ion adsorption and electro-/photocatalysis. However, our current understanding of what governs the molecular scale hydration forces and their correlation with continuum electrostatics is still limited, especially at the level of single nanoparticles. Here, using atomic force microscopy and tip size of 9nm, we simultaneously map the DLVO and hydration forces on heterogeneous surfaces of gibbsite nanoparticles deposited on silica substrate in ambient NaCl, LiCl, CsCl solutions of variable concentration and pH with nanoscale precision. We show that the hydration force with a decay length ($\approx 0,25\text{nm}$) is composed of an oscillatory force superimposed onto a monotonically decaying background force. The hydration layers on crystalline gibbsite surface are more organized than the ones observed on an amorphous silica. Moreover, strength and decay length of the oscillatory hydration force are found to be rather independent with respect to variations of surface charge density that varies with pH and salt concentrations as expected from DLVO theory. This indicates that the behavior of the hydration force is not caused by continuum electrostatics, but by surface microscopic structure and distribution of hydroxyl groups [1,2].



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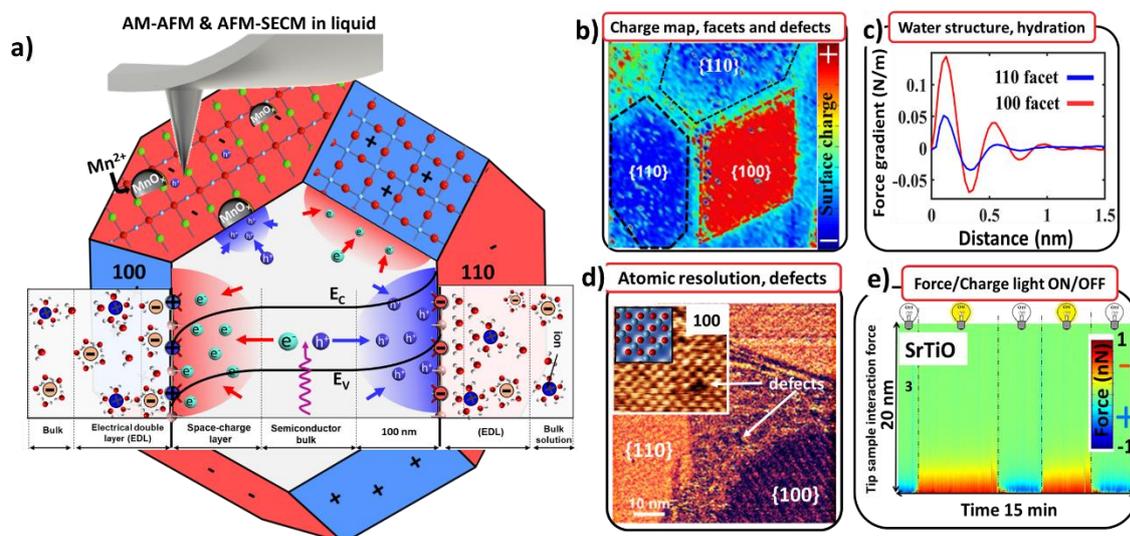
Towards high efficiency photocatalyst materials: *In situ* characterization of faceted SrTiO₃ nano-particle-electrolyte interfaces by Atomic Force Microscopy

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Anisotropy of shape and surface properties determine the functionality of faceted nanoparticles in various contexts including facet selective colloidal self-assembly, crystal growth, biosensing, improved photo/electrocatalytic activity and enhanced selective cellular and ions uptake. The characteristic anisotropy, surface proprieties and function of solid-liquid interfaces of crystalline faceted nanoparticles are believed to be essential for their performance but remains poorly understood and difficult to characterize and quantify. We use dual scale Atomic Force Microscopy to measure electrostatic and hydration forces of faceted SrTiO₃ nanoparticles in aqueous electrolyte at variable pH. We demonstrate (i) the ability to quantify strongly facet-dependent surface charges yielding isoelectric points of the dominant {100} and {110} facets that differ by as much as 2 pH units, ii) fluids composition controlled facet-dependent accumulation of oppositely charged (SiO₂) particles, and iii) that atomic scale defects can be resolved but are in fact rare for the samples investigated [1]. Atomically resolved images and facet-dependent hydration structure suggest a microscopic hydration and charge generation mechanism [1].



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Operando Optical Monitoring of Crystallisation in Confinement

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Scanning electrochemical cell microscopy (SECCM) [1] is an SPM technique that utilises a mobile pipette probe and a hanging electrolyte droplet at its tip, that is brought in contact with the sample surface. A large area of a sample can be interrogated in a scanning array fashion, and – at each contact spot – the wetted area is well-defined and serves as the working electrode of the miniature electrochemical cell. Imaging the contact spots, post-experiment, by microscopy, enables a comprehensive description of the locally probed area and the establishment of property-function relationships. Additionally, in the direction of quantifying these relationships, the simple geometry of the pipette-droplet-substrate system is open to finite element method simulation.

SECCM has more recently been coupled with *in situ* optical microscopy, [2-3] allowing a direct and *operando* view of the boundaries of the droplet electrochemical cell and any phase changes that take place within. By utilising optically suitable and conductive substrates, the interference effect that develops in the reflected light configuration (interference reflection microscopy – IRM), highlights changes in the local refractive index that occur very close to the electrode-electrolyte interface. The SECCM platform can then be used to repeatedly land the miniature cell, at fresh spots on the substrate, performing an electrochemical experiment each time, under the same or varied conditions. This leads to the acquisition of statistically relevant datasets, in short time, while boasting high spatial and temporal resolution. [3]

In this work, we present the use of the hybrid SECCM-IRM method in studying crystallisation in confinement. A double-channel pipette variant is preferred, with each of the two compartments filled with a different reagent and a separate counter electrode. Specific ions from each channel can be pushed towards the droplet to be mixed, or pulled back into separation, depending on the bias applied between the two counter electrodes. The working electrode potential can be individually controlled, to investigate its effect on crystallisation and growth processes. The model systems of sodium chloride and calcium carbonate are herein shown to form crystals on a variety of substrates (indium tin oxide, gold, graphite), while the effects of mixing conditions and surface charge are demonstrated. The chemical environment within the droplet cell is simulated for those conditions, in an effort to rationalise the optical and electrical recordings. This combined approach, of on demand manufacturing *via* SPM and *operando* optical monitoring, is showcased as an exemplary method for simultaneous screening and characterisation of fabrication in the micro- and nano-scale.

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Electrochemical Imaging of Thermochemical Catalysis

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Thermochemical redox catalysis is critical to a wide array of key chemical transformations and is known to be sensitive to catalyst surface structure. Yet there exist limited operando tools for quantitatively imaging heterogeneities in catalytic rate across a surface. Since many thermochemical redox reactions can proceed via the coupling of electrochemical half-reactions, electrochemical microscopies can, in principle, be used to image heterogeneities in thermochemical redox catalysis. Herein, we develop a general methodology for imaging variations in the rate of thermochemical redox catalysis using electrochemical microscopy. Using Pt-catalyzed aerobic oxidation of formic acid oxidation as a test reaction, scanning electrochemical cell microscopy (SECCM) imaging reveals grain-dependent variations in catalytic rate for the underlying oxygen reduction and formic acid oxidation half-reactions. These spatial heterogeneities lead to a distribution of mixed potentials across the surface during the overall reaction, implying that microscopic lateral current flows across the surface galvanically couple disparate sites during thermochemical catalysis. Tafel analysis of current-potential profiles in the presence of both reactants reveals the nature of cross-talk between the two half-reactions and provides quantitative spatially-resolved images of catalytic rates for the net thermochemical reaction. These studies establish a general methodology for using electrochemical microscopy to image thermochemical redox catalysis.