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Book of Abstracts

Talk Abstracts

Searching the needle in the haystack: Which organics drive the phase transition of atmospheric aerosols?

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Aerosols are ubiquitous in the atmosphere and an essential part of the climate system. Especially aerosols formed by secondary processes, i.e., through the phase transition of gaseous precursors to liquid or solid ultrafine (<100 nm) particles, are the main source of cloud condensation nuclei and hence their abundance determines the properties of clouds.

Over the continents, organic substances are the main driver of secondary aerosol formation. There are typically around 10.000-100.000 different organic molecules present in continental ambient air. They range from volatile compounds which have been emitted by the bio- and anthroposphere to ultra-low volatility compounds, formed through atmospheric oxidation and capable to change back to the solid or liquid phase, i.e., being drivers of secondary aerosol formation. However, it remains a major challenge to simplify this variety, elucidate the oxidation pathways and model the phase transition of atmospheric organics to better describe aerosol formation in global climate models.

Here we present our recent progress in modeling aerosol growth processes through the usage of a 2D-volatility basis set (Stolzenburg et al., 2022, J. of Aerosol Sci.) and show how to find the needle in the haystack: Which molecules are the least volatiles (Dada, Stolzenburg et al., Sci. Adv., accepted), where do they originate from (Stolzenburg et al., Rev. Mod. Phys., accepted) and how do they drive the formation of new aerosol particles under various atmospheric conditions (Stolzenburg et al., 2018, Proc. Nat. Acad. Sci.)? Our work explores the physical chemistry of atmospheric phase transitions and our developed frameworks for the simplifications of complex mixtures could also provide valuable insights beyond the atmospheric community.

High-speed cryo-microscopy proves that ice-nucleating proteins of *Pseudomonas syringae* trigger freezing at hydrophobic interfaces

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Ice nucleating proteins (INpro) trigger freezing of supercooled water droplets of atmospheric, biological, and technological relevance. The high ice nucleation activity of INpro, isolated from the bacteria *Pseudomonas syringae*, has been suggested to occur by aggregation of proteins at hydrophobic interfaces, such as the bacterial membrane or the air-water interface (AWI) of droplets. However, direct imaging of ice-nucleation at hydrophobic interfaces has yet to be reported, thereby hindering experimental proof of the proposed mechanism. In this study, we monitored ice nucleation events at the AWI of a droplet, between two hydrophobic glass slides, with a high-speed camera on a cryo-microscope. By investigating INpro from *P. syringae* under different concentrations we found that nucleation sites were not randomly distributed in the bulk of the droplet, but enriched at the AWI, since 50 % of the nucleation events were detected in the outermost fifth of the droplet's volume. A comparison with docosanol and birch pollen extracts, as examples for AWI and bulk ice-nucleators, confirm the AWI affinity of the INpro samples. Furthermore, the nucleation frequency at the AWI increased after filtering the INpro sample (< 220 nm) from 50 % to 59 %, due to the removal of cellular fragments. Experiments with different hydrophobic interfaces indicate specific INpro-interface interactions. Finally, we showed that intact bacteria cells nucleate ice without the AWI. Overall, we've developed a high speed cryo-microscope setup and confirmed that INpro from *P. syringae* trigger freezing at hydrophobic interfaces, such as the AWI or the cellular membrane.

Detection of Nanoplastics using Interferometric Scattering Microscopy

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The growing accumulation of micro- and nanoplastics (MNP) in natural systems poses a significant threat to the global environment.¹ While most measurements of MNP pollution have focused on the ocean, recent studies have also detected MNP in the atmosphere,² drinking water,³ and even the human body.⁴ The pervasive distribution of MNP in our environment underscores the urgent need for straightforward and effective methods to quantify and characterize the less well-measured but surely more abundant fraction that is present as plastic nanoparticles. But, the sub-diffraction limit size of these particles presents a formidable detection challenge. They are invisible to conventional optical microscopy. Electron microscopy reveals them, but only at a considerable cost of sample preparation time and analysis dollars.

This study introduces a novel approach for the detection and characterization of nanoplastics (< 200 nm) using interferometric scattering microscopy (iSCAT). iSCAT detects and images a nanoparticle by measuring the detected contrast arising from the phase shift of light scattered from a nano-object compared with the reference beam back-reflected from the sample coverslip. The isolation of this signal by ratiometric detection typically requires electrostatic binding of the nanoparticle to the coverslip. Our work actively achieves this by means of a controlled potential applied to a coverslip surface coated with a transparent conducting thin film of indium-tin oxide (ITO). This potential of 1 V or less causes nanoplastic particles in the size range from 25 to 500 nm to bind to the surface, producing a distinct scattering signal that serves as a reliable indicator of the size of the nanoparticle. We demonstrate the effectiveness of iSCAT for aqueous suspensions of nanoplastics, rapidly detecting a wide range of particle sizes with minimal sample preparation.

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Biological Aerosol Particles in the Finnish Sub-Arctic:

Influences of Snow Coverage and Snow Melt

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Primary biological aerosol particles or short PBAPs are ubiquitous in the atmosphere. PBAPs include airborne bacteria, fungal spores, pollen, viruses and many more. The spatial and temporal abundance of PBAPs in the atmosphere is still not sufficiently investigated, despite the influence of these particles on e.g. human health and their ability to act as Ice Nucleating Particles (INPs).

This study investigates primary biological aerosol particles (PBAPs) at the Pallas supersite, a pristine site in Finnish Lapland 170 km north of the Arctic circle. We use a Wideband Integrating Bioaerosol Sensor (WIBS 5/NEO – Droplet Measurement Technologies, Longmont, USA) to measure the concentration and size distribution of fluorescent aerosol particles (FAPs). The WIBS detects and sizes particles from 0.5 to 30 μm and measures the autofluorescence of single particles using two excitation wavelengths (280 nm and 370 nm) and two emission bands (310 – 400 nm and 420 – 650 nm), resulting in three fluorescence channels which can further be combined to define 7 types of fluorescent particles.

During the campaign (Mid-September to Mid-December), the average total FAP (Fluorescent Aerosol Particles) concentration is about 0.05 cm^{-3} , a contribution of 11 % to the total aerosol concentration measured with the WIBS. The fraction of FAPs increases with particles size and in the coarse fraction approximately 50 % of all particles fluoresce. From October 24th the surrounding land is covered in snow. Snow coverage has a strong influence on FAPs: The average concentration during snow coverage of is reduced from 10 to more than 80 %, depending on the fluorescent particle type and the size distribution of FAPs shifts to smaller particles. Comparison with backward trajectories of airmasses suggests that most FAPs are emitted from local vegetation. A special observation was that just the slight melting of the thick snow layer leads to a significant re-emission of biological particles – an effect that has not been described in literature so far.

Realising scalable synthesis and integration of two-dimensional materials

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Having unique combinations of many exceptional and useful properties, two-dimensional (2D) materials are essentially “transferrable surfaces” with a widespread application profile. Key to realisation of real-world applications of 2D materials is development of scalable synthesis, integration and operation protocols. Such process development however requires understanding of atomistic mechanisms of the physical and chemical processes happening during 2D materials growth, interfacing with other materials and environmental interactions under operation. Using advanced in-situ and high-resolution materials characterisation techniques, we develop rational synthesis and integration protocols for various 2D materials incl. graphene, hexagonal Boron-Nitride, transition metal dichalcogenides and pnictogens as well as their hybrids with metals, metal-oxides, organics, down to the controlled single-atom level. Our key techniques for 2D materials synthesis are hereby chemical vapour deposition (CVD) and, since recently, also liquid-phase-exfoliation (LPE). For materials characterisation we in particular employ a unique combination of spectroscopic and diffractive in-situ techniques during realistic synthesis and processing conditions (in-situ x-ray photoelectron spectroscopy (XPS) and x-ray diffractometry (XRD)) coupled with high-resolution (scanning) transmission electron microscopy ((S)TEM). I will introduce in this contribution a short overview of our recent and ongoing research activities.

Weak effects on electron transfer reactions

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The photo-induced electron transfer (PET) plays an important role in many areas of chemistry. With individual changes in the environment, such as an external magnetic field or solvent parameters, one can systematically study the nature of the PET reaction. Since they proved to be helpful for the clarification of chemical reaction mechanisms, studies of magnetic field effects on chemical reactions are of great interest. The measurements focus on the experimental investigation of magnetic field effects in exciplex forming organic fluorophore-quencher pairs. In these systems quenching occurs via bimolecular PET (or direct exciplex formation) and the recombination fluorescence is magnetosensitive. The magnetic field effect relies on the coherent interconversion between the singlet and the three triplet states as described by the radical pair mechanism.

The physical properties of the solvent influence the rate constant of PET reactions in many ways. Dielectric constant ϵ and refractive index n influence the solvent dipole reorientations and contribute to the activation energy of the electron transfer reactions [1]. That is why solvent-dependent measurements of ET reactions started quite early. But, electron-transfer kinetics is also influenced by diffusion and, therefore, by the solvent viscosity η . The results of polar and unipolar solvents are compared with high- and low-viscous ones. We will give an overview of possible individual changes in the reaction environment [2] for thermal ET as well as PET reaction. Pure organic solvents and ionic liquids are applicable for these changes depending on the demands of the reaction partners.

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Materials research on solid oxide cells for sustainable and efficient energy conversion and storage

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Energy conversion systems based on solid oxide fuel cells (SOFCs) and solid oxide electrolysis cells (SOECs) are among the most promising future technologies for sustainable clean energy supply and storage. SOFCs convert the chemical energy of a fuel into electrical energy with high efficiency, low noise and without NO_x-emissions. They can be operated with a wide range of fuels ranging from pure hydrogen and ammonia to syngas, methane and reformates of liquid energy carriers such as methanol, ethanol, diesel etc., which is a unique selling point of this technology. SOECs, on the other hand, provide an efficient and sustainable path for storage of electrical energy in form of chemical energy carriers. In the case of an SOEC, the working principle of the SOFC is reversed and water is decomposed into O₂ and H₂, applying electricity from renewable sources (wind, solar). SOECs are also capable of co-electrolysis, where a mixture of H₂O and CO₂ is converted into synthesis gas (H₂/CO) for further production of methane, methanol, ammonia, etc. in a catalytic reactor (power-to-gas, e-fuels). Using CO₂ from industrial sources such as cement mills, refineries or iron and steel plants can thus contribute to a reduction of greenhouse gases.

In our research, we develop materials for solid oxide cells (i.e. SOFCs and SOECs) and investigate their fundamental properties such as crystal structure, thermal and chemical expansion, mass- and charge transport etc. Promising compositions are processed into porous electrodes, where the focus is put on the relationships between material properties, morphology and electrochemistry of the air electrode and the air electrode-electrolyte interface. Together with our project partners, competences in the field of material development, electrode and cell preparation as well as electrochemical characterization are combined with detailed microstructural, chemical and defect chemical analyses. The goal is to develop a knowledge-based design approach for the next generation of solid oxide cells for sustainable and efficient energy conversion and storage.

Rechargeable oxygen ion batteries based on mixed conducting oxides

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Mixed ionic electronic conducting (MIEC) oxides are frequently studied as electrode materials for solid oxide fuel or electrolysis cells. However, their ability to change stoichiometry depending on the oxygen chemical potential also enables charge storage typical for battery electrodes: By applying a current, formally neutral oxygen in the form of oxide ions and electron holes can be incorporated or released, thereby annihilating oxygen vacancies and creating electron holes or vice versa. This reversible electrochemical oxidation or reduction of the MIEC oxide can be exploited for energy storage, similar to lithium intercalation in lithium ion batteries. Thin film model electrodes were grown by pulsed laser deposition on yttria stabilized zirconia single crystal electrolytes and covered with dense zirconia to inhibit oxygen exchange with the atmosphere. The charge–voltage characteristics of difference MIEC oxide electrodes — $\text{La}_{0.6}\text{Sr}_{0.4}\text{FeO}_{3-\delta}$ (LSF), $\text{La}_{0.6}\text{Sr}_{0.4}\text{CoO}_{3-\delta}$ (LSC), $\text{La}_{0.9}\text{Sr}_{0.1}\text{CrO}_{3-\delta}$ (LSCr), $\text{La}_{0.5}\text{Sr}_{0.5}\text{Cr}_{0.2}\text{Mn}_{0.8}\text{O}_{3-\delta}$ (LSCrMn) and $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) — were studied by galvanostatic DC measurements at 350 to 500 °C, revealing specific electrode capacities up to 1250 C/cm³ (350 mAh/cm³) at half-cell potentials between +0.1 and - 0.85 V vs. 1 bar O₂ and excellent coulomb efficiency and cycle stability. Operando electrochemical impedance spectroscopy and in-situ synchrotron X-ray absorption spectroscopy were employed to investigate the defect chemical processes during charging and discharging of the electrodes, revealing the close relationship between the MIEC oxide defect chemistry (Brouwer diagram) and the charge–voltage characteristics of the corresponding electrode: Specifically, a MIEC oxide's reducibility determines the electrode half-cell potential and its dopant concentration governs the electrode capacity. Electrodes with different reducibility of the oxide thus allow operation of an oxide ion battery. Full cell oxygen ion batteries with LSF cathodes and LSCrMn anodes were fabricated and operated at 350 to 400 °C with electrode related energy densities up to 250 J/cm³ (70 mWh/cm³), coulomb efficiencies >99 % and good cycling performance.

On the nanoscale structural evolution of solid discharge products in Li-S batteries using X-ray, neutron and electron techniques

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Lithium-sulfur (Li-S) batteries could be game-changers in many respects: a theoretical specific capacity amongst the highest of all batteries paired with low cost and sustainability of sulfur. However, a lack of understanding of the mechanism that converts sulfur into lithium sulfide (Li₂S) via soluble polysulfides hinders the development of high-performance Li-S cells. The conventional explanation for Li₂S formation involves the direct electroreduction of a PS to Li₂S; however, this does not align with the size and shape of the observed insulating Li₂S deposits. Here, we present operando small and wide angle X-ray scattering (SAXS/WAXS) and operando small angle neutron scattering (SANS) to track the growth and dissolution of solid deposits from atomic to sub-micron scales during charge and discharge [C. Prehal et al. *Nature Communications* **13**, 2022, 6326]. Stochastic modelling based on the SANS data and convolutional neural networks allows quantifying the chemical phase evolution during discharge and charge. Combined with complementary data from electron microscopy and Raman spectroscopy, we show that the deposit is comprised of the expected nanocrystalline Li₂S and smaller solid Li₂S_x nanoparticles. Our data are consistent with solid Li₂S₂ precipitating from solution and then being partially converted in the solid state to Li₂S, likely via direct electroreduction and chemical diffusion through the Li₂S₂ particle network. The found mechanism also explains why not all S is converted to Li₂S; a certain amount of Li₂S₂ remains as a second solid discharge product.

The example on Li-S batteries highlights the importance of real-time structural information on nanoscopic length scales to understand complex phase transformations and electrochemical mechanisms in beyond-intercalation-type battery cathodes. At the end of the talk, we will briefly outline how we plan to tackle the challenges of electrochemical sulfur conversion in Metal-sulfur batteries in our future research.

pH induced poly (methacrylic acid) / poly (ethylene glycol) restructuring on a molecular level

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Emulsions play a crucial role in industries like cosmetics, food, and oil recovery¹. Responsive emulsions that can adapt to external stimuli have gained interest due to, for example, their potential to release large payloads². To optimize the properties of these emulsions, it is essential to comprehend the underlying molecular behavior that triggers their switching mechanism.

In this work, we focus on a pH-responsive polymeric emulsifier composed of a poly (methacrylic acid) (PMAA) backbone and poly (ethylene glycol) methyl ether methacrylate (PEGMA) grafts. These two components exhibit a strong pH-dependent interaction, being present at acidic pH and absent at alkaline conditions³. To investigate the molecular mechanism that triggers the switching, we employ sum frequency generation spectroscopy (SFG).

SFG measures vibrational spectra at interfaces and can detect changes in the polymer structure. Since the intensity of the vibrational bands in an SFG spectrum relates to the number of molecules and their orientation, this technique becomes an optimal tool to recognize changes in the polymer structure occurring at the interface. As model system of the oil in water emulsion, we study the water-air interfaces treating the air phase as hydrophobic. By comparing SFG spectra of the PMAA/PEGMA polymer at the aqueous air interface under acidic (pH 3) and basic (pH 11) conditions in the O-H/C-H stretch region, we observe clear differences. At alkaline pH, we detect the presence of negatively charged PMAA at the interface, concluding that PMAA negative shell surrounds the emulsion droplets, preventing interactions from occurring. However, at pH 3, this shell is absent, and the obtained spectra in the C=O region point to a hydrogen bonding interaction between PMAA and PEG chains.

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Modified $\text{H}_2\text{V}_3\text{O}_8$ as promising cathode material for Mg^{2+} insertion

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To meet the energy demand of humanity in the future it is inescapable to store renewable energy sources more efficiently in energy storage devices such as batteries.[1] Lithium-ion batteries are already well established in our society due to their high theoretical specific capacity and the low redox potential vs. SHE. However, the reserve of lithium sources and the accessibility are limited. Therefore, alternatives, such as magnesium, which can be used as counter electrode in batteries are of great importance.

Magnesium is more abundant than lithium, has a similar small ionic radius, and low redox potential vs. SHE as lithium. [2] However, suitable cathode materials, which allow the reversible intercalation of the doubly charged Mg^{2+} in their structure, are limited due to the strong polarization effects induced by the divalent charge compared to the single charged Li^+ . Therefore, the improvement of the cathode material is a major challenge in current magnesium-ion battery research. One promising cathode material, which allows a reversible intercalation of Mg^{2+} , is hydrated vanadium oxide $\text{H}_2\text{V}_3\text{O}_8$. [3]

In this context, we show structural and electrochemical properties of $\text{H}_2\text{V}_3\text{O}_8$ as cathode material with respect to Mg^{2+} insertion. We present structural and morphological properties of $\text{H}_2\text{V}_3\text{O}_8$ synthesized under hydrothermal conditions with modifications or additives such as substitution of V-sites by Mo or the composite formation with reduced Graphene Oxide (rGO). Furthermore, we investigate how the different modifications of $\text{H}_2\text{V}_3\text{O}_8$ influence the electrochemical properties, in terms of specific capacity and stability, compared to unmodified $\text{H}_2\text{V}_3\text{O}_8$.

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Surface Functionalization of Nanoporous Gold by Self-Assembled Monolayers:

A Case Study of Electrochemical Fluoride Detection in Water

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The application of self-assembled monolayers (SAMs), formed by self-organization of organic molecules with an anchoring group at the one end and a functional group at the other end, is a popular strategy for surface functionalization of electrodes. SAMs on planar surfaces are intensively studied in literature, but this knowledge cannot trivially be transferred to curved, defect-rich or even porous materials, providing high surface areas, which are beneficial e.g. for sensing applications.

In this contribution we give an overview of our group's systematic work on the SAM-functionalization of nanoporous gold (np-Au), obtained by the selective etching process of electrochemical dealloying. Via in-situ resistometry, three distinct stages can be identified in the SAM formation process on the np metal. After rapid binding on external surfaces, diffusion and ordering inside the porous structure can take hours or up to days [1]. Using the example of 16-mercaptohexadecanoic acid (MHDA), we demonstrate that the SAM's surface charge can be effectively controlled by electrochemical charging, where in comparison to planar gold the surface imperfection of np-Au even leads to a superior controllability of the SAM [2].

As a specific application, we demonstrate the selective detection of fluoride ions in water using np-Au electrodes, modified with a SAM of 4-mercaptophenylboronic acid (MPBA) [3]. Fluoride binding alters the charge state of the boronic acid functional groups, causing sensitive and fast changes of the electrode's surface potential in well-defined steps upon stepwise F^- addition with a detection limit of 0.2 mM. Deeper insight into the reaction of fluoride binding on the MPBA modified surface is provided by electrochemical impedance spectroscopy (EIS). Regarding future applications, we can show that after fluoride contact, used electrodes can be regenerated in alkaline media, which is an important aspect from an economic as well as environmental viewpoint.

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Electrochemical Performance of Structural Batteries based on Polymer Gel Electrolytes

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Structural batteries provide a promising solution regarding the electrification of the transport sector as they combine energy storage with load bearing capabilities resulting in multifunctional components. Replacing interior and/or exterior elements with structural batteries is especially interesting for the aeronautic industry which demands energy-dense and lightweight technologies [1]. However, there are still many open questions regarding the active and passive materials to be used in order to optimize the energy density as well as the structural capabilities.

Several paths for the realization of structural batteries are currently in development. In this contribution we show an approach based on state-of-the-art lithium ion battery (LIB) components which were modified to yield mechanical strength. Thermoplastic polyvinylidene fluoride (PVdF) based materials were used as reinforcing matrix of all three components of the battery including the graphite anode and $\text{LiNi}_{0.8}\text{Mn}_{0.1}\text{Co}_{0.1}\text{O}_2$ (NMC811) cathode as well as for the non-flammable ionic liquid electrolyte (ILE).

Electrochemical impedance spectroscopy and tensile testing showed that the reinforcing matrix indeed increases the mechanical stability, however it reduces the electrochemical performance by decreasing the mobility of Li^+ ions. Nevertheless, specific charge values of 100-120 mAh/g_{NMC811} could be achieved for coin (1-2 cm²) and pouch cells (70 cm²) and the electrolyte showed high ionic conductivities in the order of 1 mS cm⁻¹ at room temperature.

For increasing the mechanical and electrochemical performance of structural batteries, the interaction of the different components with the reinforcing matrix needs to be further investigated and understood. This is required to utilize the full potential of this technology.

Electrochemical near ambient pressure X-ray photoelectron spectroscopy for probing the electrified interface *in-situ*

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Abstract: Profound understanding of the solid liquid interface is central in electrochemistry and electrocatalysis, as the interfacial properties determine the electro-reactivity of any system. In particular, in the realm of electrochemical energy conversion, the interface chemistry determines the selectivity, efficiency and activity of the electrocatalyst, and its fundamental understanding is pivotal to further advance energy conversion technologies. Despite the availability of various methods to analyze surface structure under *operando* conditions, the surface chemistry, including knowledge of its oxidation states, is still often evaluated by *ex situ* X-ray photoelectron spectroscopy (XPS). Nevertheless, the surface and interface properties can undergo substantial changes under operating conditions ^[1,2]. Consequently, it would be vital to perform XPS experiments *in-situ* to further improve the fundamental understanding of electrocatalytic processes, in general.

In our study, we show the capabilities of near ambient pressure (NAP)-XPS as a laboratory technique to monitor the surface states of an electrode under electrochemical reaction conditions. Additionally, we investigate the potential drop at the electrified interface by analyzing the potential-dependent O 1s spectra. Through our approach, we shed light on the new possibilities that arise from using laboratory-based NAP-XPS to investigate (electro)chemical properties of the solid-liquid interface, which were previously hardly accessible.

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Nanoporous copper electrodes produced via electrochemical dealloying

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Nanoporous metals have received increasing interest in the last decades, mainly due to their high surface-to-volume ratio which allows them to be used in a variety of applications, ranging from sensing to energy storage, functional materials or (bio-)catalysis [1], which is our field of interest. We aim to develop suitable nanoporous metal structures that can act as enzyme carriers for future biocatalysis applications. Electrochemical dealloying enables the production of free-standing sponge-like structures by selectively removing the less noble component of a master alloy. The end result is a self-similar structure of interconnected pores and network branches called ‘ligaments’, with only the more noble element exposed on the surface. The best known of these structures is nanoporous gold (np-Au) made from Ag-Au alloys.

As an alternative to np-Au, we present nanoporous copper (np-Cu) electrodes, which have the advantage of being more sustainable and more economically viable. We investigate np-Cu produced by dealloying Al-Cu and Mn-Cu master alloys. In addition to conventional electrochemical characterization by cyclic voltammetry, in-situ resistometry allows an in-depth analysis of the dealloying process [2], which is strongly influenced by the formation of oxides, which in turn can be functionalized. So-called ‘coarsening’ can also be used to increase the pore size of the samples during or after dealloying. Both electrochemical and thermal coarsening are investigated as possible methods for pore size control of np-Cu.

As an outlook, the potential advantages of multi-hierarchical porosity over the conventional single-hierarchy nanoporous structures will be discussed.

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Oxygen exchange and transport properties of the first-order Ruddlesden-Popper phase



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Solid oxide cells (SOCs) represent a key technology for future energy systems. However, a fundamental challenge of materials research for SOCs is the development of air electrodes with high electronic and ionic conductivities and fast oxygen exchange kinetics. Strontium-free Ruddlesden-Popper type solid oxides $\text{Ln}_{n+1}\text{B}_n\text{O}_{3n+1}$, such as rare earth nickelates, are promising candidates to achieve these goals.

In this work, a comprehensive characterization of the first-order Ruddlesden-Popper cobalt-substituted lanthanum nickelate $\text{La}_2\text{Ni}_{0.9}\text{Co}_{0.1}\text{O}_{4+\delta}$ (LNCO) was performed. The material was synthesized via the citric acid/EDTA sol-gel method. X-ray powder diffraction confirmed that the material crystallizes in the K_2NiF_4 -type structure, which consists of alternating rock-salt AO- and perovskite ABO_3 -layers, representing the first member of the $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ Ruddlesden-Popper series. Rietveld refinement provided information about phase purity, lattice constants and atomic positions. The thermal expansion coefficient of LNCO between 600 °C and 850 °C and $0.001 \leq p\text{O}_2 / \text{bar} \leq 0.1$ agrees well with those of common solid electrolytes such as gadolinium-doped ceria (GDC) and yttria-stabilized zirconia (YSZ). The chemical oxygen surface exchange coefficient (k_{chem}) and the chemical diffusion coefficient of oxygen (D_{chem}) were determined using the in-situ dc-conductivity relaxation method. It was found that k_{chem} of LNCO is significantly higher than for the undoped nickelate $\text{La}_2\text{NiO}_{4+\delta}$ (LNO) and has half the activation energy, showing that cobalt substitution has a very positive effect on the oxygen surface exchange rates. The electronic conductivity was measured on a bar-shaped sample in linear four-point geometry and lies in the range of 45 - 70 S cm^{-1} between 600 °C and 850 °C and $0.001 \leq p\text{O}_2 / \text{bar} \leq 0.1$. Especially with regard to the significant improvement of the oxygen surface exchange kinetics, the cobalt substitution of lanthanum nickelate on the B-site has its justification and the results illustrate that LNCO offers great potential for application as air electrode in SOCs.

GÖCH-Symposium 2023

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**Metal/YSZ Model Electrodes with optimized Triple Phase Boundary Geometry for
fundamental *Operando* Spectroscopic Studies**

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Abstract: *Operando* identification of thermo-electrochemical surface processes on metal-based yttria-stabilized-zirconia (YSZ) cermet electrodes using solid oxide fuel/electrolyzer cells as function of temperature, gas-phase and polarization is fundamental for the understanding of advanced electrocatalytic materials and their knowledge-based improvement. As the electrochemically active area of cermet electrodes is restricted to the interface of the ceramic solid electrolyte, the respective metallic component and the gas phase, the design of sophisticated 2D structured model systems exhibiting their active sites on a spectroscopically accessible quasi-2D interface is of ultimate importance. An approach to fabricate electron metal/electrolyte interfaces suitable for XPS with optimized triple phase boundary dimensions is presented. Utilizing a combined lab-based NAP-XPS, QMS and EIS setup, proof-of-principle *operando* experiments revealing the redox processes as well as the electrode surface chemistry under cathodic water electrolysis conditions over metal- and alloy- based (i.e., Ni and NiCu) YSZ cermet electrodes were carried out.

CANCELLED

Modified Pechini synthesis of a perovskite-type rWGS catalyst

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Perovskite-type oxides are promising catalysts in CO₂ utilization pathways, for example the **reverse Water-Gas Shift** reaction (rWGS). Due to their ability to exsolve metallic nanoparticles under reducing conditions, catalytic activity can be further increased [1]. Synthesis of perovskite-type oxides is often carried out using a modified Pechini synthesis, for which a wide range of additives and complexing agents can be used [2]. But their influence on surface area, morphology and catalytic activity is not fully understood.

In this work various modified Pechini syntheses at different pH values and with varying amounts of ethylene glycol in the precursor solution were used to produce Nd_{0.6}Ca_{0.4}Fe_{0.9}Co_{0.1}O_{3-δ}. A phase pure catalyst was confirmed using **powder X-ray diffraction (PXRD)**. Additionally, surface areas, using **Brunnauer-Emmet-Teller (BET)** method, and morphologies, using **scanning electron microscopy (SEM)**, were investigated. **Temperature programmed reduction (TPR)** and catalytic testing were carried out to further examine the exsolution behaviour of the catalysts and the effect of the changed morphology on the catalytic performance. A basic pH value of 8 combined with ethylene glycol addition is beneficial for the formation of a higher surface area which is in turn leading to higher conversion rates at temperatures up to 600 °C compared to a synthesis with acidic pH values.

Acknowledgements:

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Pseudocapacitive Materials: Substantial Na-Ion Storage at High Current Rates through Sodium Surface Film Formation on Planar Metal Oxide Electrodes

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Abstract: Storage of intermittent, renewable energy is considered key for mitigating the issues related to man-made global warming. Batteries and supercapacitors, both found to be an indispensable storage technology for electrical energy, are governed by electrochemical processes, but operate by different electrochemical mechanisms. Battery materials store large amounts of energy by ion intercalation. Electrical double-layer capacitors store charge through surface-controlled ion adsorption which leads to high power and rapid charging, but much smaller amounts of energy stored. Pseudocapacitive materials offer the promise to combine these properties by storing charge through surface-controlled, battery-like redox reactions but at high rates approaching those of electrochemical double-layer capacitors. In this presentation we report on excellent, self-improving sodiation rate capabilities in combination with a high capacity retention upon galvanostatic charge/discharge cycling that has been found for oxygen deficient, carburized and self-organized titanium dioxide (TiO_{2-x}) nanotubes (NTs). By comparing TiO_{2-x} NTs to flat TiO_{2-x} surface films, having distinctively different oxide mass and surface area ratios, it is shown that NaO_2 and Na_2O_2 formation, which constitutes the active surface film material, is governed by the metal oxide bulk. Our results corroborate that oxygen diffusion from the lattice oxide is key to NaO_2 and Na_2O_2 formation. These studies allow to envisaged a "self-improving" Na-ion storage mechanism that enhances the performance of the electrodes during long-term galvanostatic cycling measurements in both, the specific gravimetric Na-ion storage capacity as well as their sodiation/desodiation rate capability. Furthermore, by comparing different metal oxide electrodes, our findings point to a universal Na-ion storage mechanism, that may proof relevant to transition metal oxides, in general.

Observing catalytic reactions by in situ surface microscopy

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The chemical identity of surface species and atomic surface configurations substantially influence heterogeneously catalyzed reactions. Therefore, detection of the structure sensitivity of a particular catalytic reaction is a key aspect in understanding the atomistic mechanism of the reaction process. This can be extended to compartmentalized systems, where chemical reactions may proceed in different ways even in adjacent compartments. Spatial interaction of adsorbed species between compartments enables complex catalytic reaction behavior whose spatio-temporal modes are difficult to resolve experimentally, especially at the nanoscale (1). Employing a Rh nanotip for mimicking a single Rh nanoparticle and field electron microscopy (FEM) for in situ monitoring of H₂ oxidation in the pressure range of 10⁻⁶ mbar, different reaction modes were observed, including multifrequential oscillations (2, 3) and a transition to spatio-temporal chaos (4). The oscillatory mode of the catalytic reaction provides a tool for studying the intraparticle communication between specific types of local surface atomic configurations (reaction pacemakers) that initiate kinetic transitions. By means of customized video analysis (5) and the development of micro-kinetic models based on a network of coupled oscillators (3), the versatile interaction modes of such catalytic functionalities were revealed. This elucidated novel reaction mechanisms and origins of the different reaction modes caused e.g. by variations of the hydrogen pressure, that modifies the strength of diffusive coupling between individual nanofacets. Since diffusive coupling is characteristic for many compartmentalized systems, the current findings may be relevant for a wide class of reaction systems, revealing the true potential of in situ surface microscopy.

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Electrocatalytic CO₂ reduction using Metal Organic Chalcogenolate Assemblies

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Electrocatalytic CO₂ reduction is a promising method for reducing the greenhouse gas CO₂ and thus provides a potential solution to global warming and deceleration of climate change. However, electrolysis of CO₂ in aqueous media at room temperature always competes with hydrogen evolution reaction. Finding suitable, cheap, selective and stable electrocatalysts which are up to the task, is still a huge challenge in the field of electrocatalytic CO₂RR. Metal Organic Chalcogenolate Assemblies (MOCHAs) are a type of crystalline coordination polymers, exhibiting a 1D or 2D structure. Their diverse synthesis routes, structural and optoelectronic properties have been studied over the past five years extensively^{1–3}. Our microwave-assisted synthesis, allowed large scale synthesis of MOCHAs and consequently facilitated application testing of these materials⁴. Our research showed that the silver-containing MOCHAs [AgSePh]_∞ and [AgSPh]_∞ are catalysts for electrocatalytic syngas formation at ambient conditions⁴. Based on these findings, the performance of [AgSePh]_∞ as a CO₂ reduction catalyst was further improved and studied. The effect of atmosphere on the counter side, choice of counter electrode and influence of pH on the CO₂ reduction performance was investigated. Extensive stability tests have been performed for 9h and 15h on the [AgSePh]_∞/CP electrode. The influence of CO₂ depletion on its CO₂ reduction performance was shown during these long-term stability tests. XPS and TXRF studies enabled a suggestion for a mechanism and gave detailed insights into the stability of MOCHAs upon electrolysis.

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Mn-promoted MoS₂ as a catalyst for CO₂ hydrogenation to methanol: Investigating the interaction between MoS₂ and Mn oxides

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Introduction. With the ongoing scenario of anthropogenic climate change, the capture and utilization of CO₂ has been increasingly considered as an alternative starting point for the production of a variety of value-added products, such as alcohols and hydrocarbons. In this context, the direct hydrogenation of CO₂ into methanol has been most effectively performed using Cu/ZnO/Al₂O₃ catalysts, but the applicability of this material at industrial scales is still limited by its low selectivity to methanol, instability of the active phase and surface poisoning in the presence of sulfur-containing gasses. [1]

Because of these constraints, non-metallic catalysts such as MoS₂ might offer a promising alternative due to their high stability and tolerance to sulfur. Pure MoS₂ is typically selective towards CO₂ hydrogenation to methane, although some promoters have been shown to induce CO production instead. [2] In this work, we demonstrate that Mn-promoted MoS₂ can work as a selective catalyst for methanol production from CO₂ hydrogenation as a result of the interaction between MoS₂ with Mn oxides.

Experimental/methodology. Mn-promoted MoS₂ was produced by a hydrothermal method. Material characterization was carried out via X-ray diffraction (XRD), in-situ Near-Ambient Pressure X-ray Photoelectron Spectroscopy (NAP-XPS), Extended X-ray absorption fine structure (EXAFS) and Scanning Electron Microscopy (SEM). Catalytic testing took place with 1g of catalyst in a fixed bed reactor at 21 bar under flow of 1 mL/min CO₂, 3 mL/min H₂ and 1 mL/min He. Prior to each reaction, catalysts were activated at 400 °C under pure H₂. Reaction products were evaluated by gas chromatography.

Results and discussion. Mn-promoted MoS₂ produced by a hydrothermal method was shown to present favorable properties as a catalyst for CO₂ hydrogenation to methanol. Although MoS₂ is typically selective towards methane in the presence of H₂ and CO₂ above 180 °C, the addition of Mn precursors to the hydrothermal synthesis of MoS₂ switches catalyst selectivity towards methanol. Interestingly, the highest methanol yield is achieved at temperatures below 200 °C. This enhanced activity under mild conditions may offer promising possibilities for industrial application, given the economical advantage of utilizing lower temperatures.

Material characterization by XRD, EXAFS and in-situ XPS shows that the manganese promoter is initially present as MnCO₃, which is converted to bulk MnO with a combination of surface Mn(II) and Mn(III) species after H₂ pretreatment. This composition is maintained at low temperature reaction conditions (< 200 °C), as higher reaction temperatures promote the carbonation of MnO into MnCO₃, compromising catalytic activity. Therefore, the results indicate that the synergy between MoS₂ and manganese oxides may be a key factor for the high methanol selectivity during CO₂ hydrogenation.

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7. GÖCh-Symposium

Physikalische Chemie und Elektrochemie in Österreich

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28.09. und 29.09.2023

Book of Abstracts

Poster Abstracts

Printing novel 2D sulfides as catalysts for electrochemical water splitting

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Two-dimensional (2D) sulfides such as MoS₂ are promising non-noble catalysts for sustainable hydrogen production by electrochemical water splitting. Here we compare different printing strategies for novel 2D sulfide electrocatalysts on carbon and 2D graphene electrodes. Our study investigates variations in printing conditions (planar towards 3D-printing) as well as variations in 2D sulfide composition (simple 2D MoS₂ towards multi-elemental 2D sulfides) and their respective impact on the electrochemical water splitting performance of the resulting catalyst electrodes.

Molecular structure of polymer photocatalyst-water interfaces

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Due to climate change and the need for renewable energy the application of hydrogen as an energy source is discussed heavily. However, the major part of hydrogen is produced by non-environmentally friendly techniques like steam reforming. To produce clean hydrogen, photocatalytic water splitting is a promising alternative.

Several materials are known to be able to catalyse the reaction, such as mineral oxides or polymers. Here, three different polymers that show different efficiencies in the water splitting reaction are studied. We study a thin film of these polymers spincoated on CaF₂ in contact with aqueous solutions of different pH and ionic strength. The molecular structures at the photocatalyst-water interface are investigated in order to understand the mechanism behind the water splitting reaction and guide further advances in material engineering. As we are interested in the molecules at the interface only, we use homodyne- and heterodyne detected sum frequency generation spectroscopy, which is sensitive to the net orientation of the probed molecules. We conclude that the polymer at the aqueous interfaces are charged at high pH values, and that the polymer sidechains show different net orientation at the interface for the different polymers.

Synthesis and Characterisation of Composite Air Electrodes for Highly Efficient Co-Electrolysis of H₂O/CO₂

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Co-electrolysis of CO₂ and H₂O in high-temperature solid oxide cells (SOCs) is a promising future technology, as it enables the storage of volatile renewable energy and the simultaneous reduction of CO₂ emissions. Material development for SOCs is currently aimed at pushing the limits of cell efficiency and lifetime. In this context, La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) / Ce_{0.8}Gd_{0.2}O_{2-δ} (GDC) composite electrodes are a promising way to improve the electrochemical performance, microstructure, and stability of the air electrode.

For electrode preparation a terpeneol-based ink containing 50 wt% LSCF and 50 wt% GDC powder is screen printed onto a substrate. The substrate consists of the fuel electrode and the electrolyte with a GDC diffusion barrier. The cell is sintered at 1060°C for 2 h.

The cell is electrochemically characterized at a temperature of 800°C, using a gas with 20% O₂ (rest Ar) at the air electrode, and either 50% H₂O or 70% H₂O (rest H₂), at the fuel electrode. In co-electrolysis mode, gases at the fuel electrode are switched between two modes 25% H₂, 25% CO₂, 50% H₂O, and 10% H₂, 45% CO₂, 45% H₂O, respectively. Current-voltage curves show current densities of - 1.37 A/cm² for H₂O electrolysis and - 2.37 A/cm² for H₂O/CO₂ co-electrolysis at 1.2 V. We compared the discussed cell configurations with a cell with single-phase LSCF- air electrode. The latter shows a much lower current density of -0.84 A/cm² at 1.2 V for H₂O electrolysis.

The microstructure and elemental distribution of the composite air electrode are studied by field emission scanning electron microscopy (FESEM) with high resolution energy dispersive X-ray spectroscopy (EDX).

Due to the promising electrochemical performance and efficient microstructure of the 50:50 wt% LSCF-GDC electrode, we plan in the next step to vary phase ratios of the LSCF and GDC, as well as to fabricate full cells with an optimized fuel electrode, electrolyte and diffusion barrier. This shall enable us to obtain electrolyser cells with higher performance and improved long-term stability.

Analysis of the Lithium-Ion Storage Characteristics in Silicon Carbide

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Lithium-Ion Batteries (LIBs) are currently the power source of choice for most electronic devices, ranging from smartphones to electric cars. This is because they offer high energy density, long cycle life, and fast charging capabilities. Despite their success, there is a need to develop even better batteries by novel, alternative anode materials with higher theoretical capacities. One such material is silicon carbide (SiC), which is considered to be a promising candidate as a potential anode material due to its high theoretical capacities, expected to exceed 1000 mA h/g in future experiments. [1]

To gain insight into the electrochemical Li-Ion storage characteristics of SiC with Li-Ion, several SiC samples were synthesized with various doping levels and used to prepare electrodes for battery half-cells. Electrochemical Impedance Spectroscopy (EIS), Cyclic Voltammetry (CV) and Galvanostatic charge-discharge Cycling with Potential Limitation (GCPL) were employed to investigate the battery characteristics.

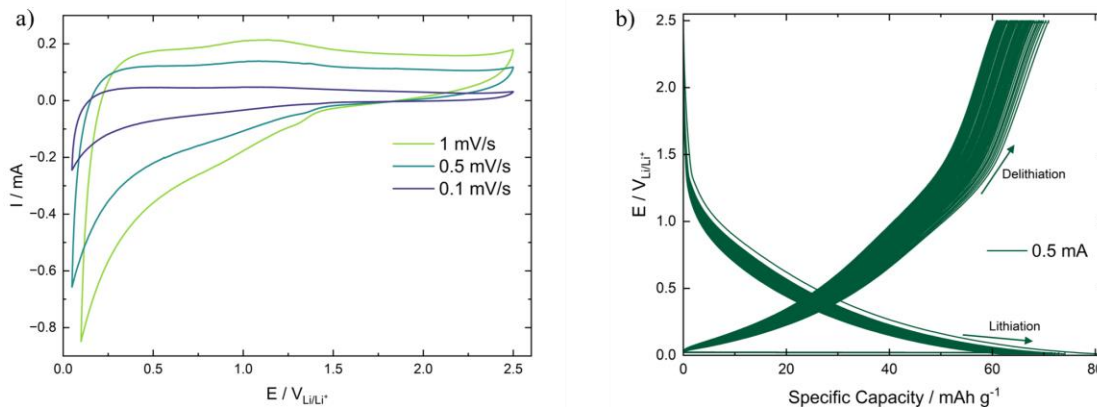


Figure 1: a) CV measurements of doped SiC at different scan rates from 1 mV/s to 0.1 mV/s, b) Galvanostatic cycling of doped SiC with a constant current of 0.5 mA (C/20).

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Nerve component analysis by means of Raman spectroscopy

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The detection of nerves and differentiation from surrounding tissue, as well as the diagnostic examination of nerve injuries, is a major challenge in medicine. Current methods to evaluate the health status of nerves are physical examination, electrodiagnostics, and imaging of nerve tissue. These techniques are often very dependent on surgeon, high cost, and have poor contrast resolution. When it comes to analyzing nerve components quantitatively and determining the level of myelination, the options are currently limited to destructive methodologies such as histology. Therefore, current in vivo diagnostic methods provide only general information about the nerves, making personalized treatment impossible.

We apply Raman spectroscopy to effectively detect nerves and distinguish them from surrounding tissue. Nerves themselves are composed of different types of tissues and their respective proportions provide information about the status of health. By decomposing the spectral information of nerves into individual spectral contribution and assigning them to the respective tissue, a quantification of the different tissue components inside the nerve is to be achieved. Since histology is an established method that provides quantitative information about tissue, this method serves as a comparative method.

Ion dynamics in porous carbon electrode of supercapacitor via simultaneous EIS of anode and cathode

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Ion transport within the carbon pores underpins charging/discharging rate, which afterward governs the energy storage in supercapacitors. When the cell is assembled (before charging), the carbon pores are saturated with countless electrolyte ions, so charge storage is not as simple as counter-ion adsorption. Studies based on various spectroscopic [1], electrochemical [2,3] and theoretical [4] methods have recently attempted to unravel the complex charging nature of porous carbon electrodes of supercapacitors. Among them, electrochemical impedance spectroscopy (EIS) is one of the most readily available approaches for elucidating the ion diffusivity in carbon pores [2,4]. However, the electrochemical approaches including EIS, have not shown a good agreement with the diffusivity values obtained by PFG NMR [5,6]. All EIS-based studies used the full cell impedance spectrum to estimate both cation and anion diffusivity which could be one of the possible reasons for the mismatched diffusivity values with NMR. Although Zoran Mandić *et al.* recently reported the simultaneous EIS of both electrodes of a carbon supercapacitor [7]. However, they reported an unexpected inductive loop i.e. an artefact in the high-frequency region of the working electrode, which is ambiguous [7]. In this context, we utilized a high-frequency shunt with a double-reference electrode assembly for the successful acquisition of simultaneous EIS of anode and cathode from the carbon EDL supercapacitor assembled with aqueous NaNO_3 electrolyte. To obtain the in-pore ion diffusivity, we considered the porosity and tortuosity of the carbon sheet and the ion diffusivity values of the bulk electrolyte [4]. For different concentrations of NaNO_3 , the in-pore carbon ion diffusivity values ($\bar{x} \cdot 10^{-7} \text{ cm}^2 \cdot \text{s}^{-1}$) were found to be two orders of magnitude smaller than those of the bulk electrolyte ($\bar{y} \cdot 10^{-5} \text{ cm}^2 \cdot \text{s}^{-1}$), thus maintaining a good agreement with the NMR studies. Finally, the in-pore ion diffusivity values were correlated with the cell power density and time constant to realise the overall rate performance of the device.

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Hybridizing liquid phase exfoliated 2D-sulfides with metal-organic frameworks for photocatalytic applications

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Our work presents a comprehensive investigation of the use of a hybrid material composed of twodimensional (2D) MoS₂ nanosheets and Ti-MIL-125 metal-organic-frameworks (MOFs) in photocatalytic hydrogen evolution reactions (HER) for sustainable hydrogen production from water splitting under UV-light. Ti-MIL-125 is a promising MOF for photocatalytic water splitting [1] and the MoS₂ is here investigated as a non-noble HER co-catalyst, replacing the expensive benchmark Pt HER co-catalyst. MoS₂ nanosheets and MIL-125 were synthesized by liquid phase exfoliation and solvothermal synthesis, respectively, then two simple methods were used to hybridize them. The resulting hybrid material was characterized using various techniques such as transmission electron microscopy, scanning electron microscopy, X-ray diffraction and UV-visible spectroscopy. The photocatalytic performance of the hybrid material was then evaluated. The results showed that hybridization resulted in remarkable HER performance, which was close to the performance values for benchmark Ti-MIL-125 with conventional Pt-co catalyst.

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Fabrication and Surface Characterization of Fe₂O₃ and Fe₃O₄ on Calcium Fluoride Substrates

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Abstract

Iron oxide materials like Fe₂O₃ and Fe₃O₄ (spinel ferrites) are widely studied for their applicability in various domains such as optoelectronics, catalysis, energy conversions, purification systems, and sensing due to their distinct magnetic properties. [1-4] Out of these, utilization of spinel ferrites for photocatalytic processes is of great interest owing to its environmental significance and recycling ability. [2,3] The aim of this work is to explore the structural properties and morphology of spinel ferrites fabricated on a CaF₂ substrate for their potential implication towards photocatalytic water splitting process. The fabrication procedure will involve sputtering of the iron oxide targets on the CaF₂ substrate. The sputter-coated CaF₂ substrates will be characterized for their electronic and surface properties by UV-visible absorption spectroscopy, ellipsometry, scanning electron microscopy, and atomic force microscopy. These substrates will then be examined for their interfacial behavior in presence and absence of water by employing an interface-sensitive tool i.e., sum frequency generation vibrational spectroscopy. [5] Through the interfacial investigations, we intend to provide a mechanistic insight towards the impact of spinel oxide coatings on the interfacial water structure and its dynamics in their immediate vicinity. Through our preliminary studies, we aim to contribute towards the fundamental understanding of water splitting at the molecular scale.

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Exploring Cross-Linking Pathways and Reaction Parameters for Nanocoating Applications: Synthesis and Characterization of One-Phase 2D-IPN at the Air-Water Interface

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Thin films of polymers and cross-linked polymers have extensive applications in protective coatings, and surface restoration. Polymer blends offer improved properties compared to pure polymers, but they often undergo phase separation in three-dimensional (3D) blends. To address this challenge, the concept of interpenetrating polymer networks has been introduced, where polymers are cross-linked using two different pathways to prevent phase separation. Our aim is to comprehensively understand the impact of physical and chemical parameters and cross-linking reactions on phase separation in two-dimensional IPN films. The ultimate goal is to regulate the morphology and synthesize well-defined and satisfactory nanocoatings.

The Langmuir film technique at the air-water interface will be employed to prepare 2D IPN films, enabling the creation of nanometer-thick films with precise and ordered architectures. Sum-frequency generation spectroscopy will be used to provide molecular-level insights into their organizational patterns. Additionally, two cross-linking pathways, acetalization and free-radical cross-linking, will be explored. Sum-frequency spectroscopy will monitor the progression of the reactions and investigate the influence of cross-linking density and relative kinetics of network formation.

This poster will showcase our preliminary findings, accompanied by a comprehensive theoretical examination of the aforementioned methodologies.

Imaging Au(111) under (CO) Oxidation Conditions in Alkaline Media with Electrochemical STM

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The electrochemical oxidation of Au(111) is a widely studied topic due to its relevance in catalysis, but the understanding of the oxidation process remains incomplete. Although several studies have investigated the surface during and after oxidation using electrochemical scanning tunneling microscopy (EC-STM) in acidic media^{1,2}, there has been a lack of investigation in alkaline media. This is surprising considering that carbon monoxide (CO) oxidation on Au is strongly enhanced under alkaline conditions and has been extensively studied^{3,4} due to its significance in low-temperature fuel cells, where CO is considered a key intermediate. In this EC-STM study, we show the Herringbone reconstruction (Fig. 1A), the oxidation (Fig. 1B), and the subsequent reduction (Fig. 1C) in oxygen-free 0.1 M NaOH. Similar observations were made as in acidic media², where it was shown that the surface morphology is dependent on whether the reduction occurs during a potential sweep or a potential step. The surface smoothens after the reduction of the surface oxide, while (vacancy) islands remain. However, far fewer islands are observed after potential jumps when compared to acidic electrolyte, and most islands disappear with time.

To ultimately investigate possible CO oxidation pathways^{3,4}, the surface morphology and structure were imaged during CO oxidation.

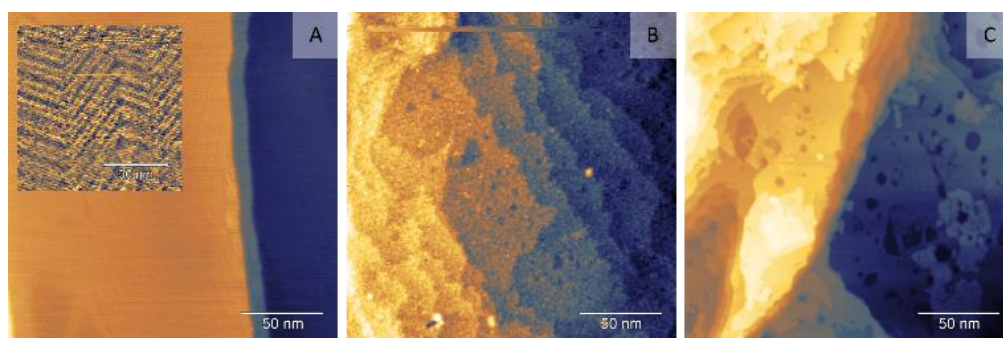


Figure 1: *In situ* electrochemical STM images of the Au(111) oxidation in de-aerated 0.1M NaOH. A) Au⁰(111) at 0.45 V_{RHE} (inset: Herringbone Reconstruction), B) oxidized surface at 1.55 V_{RHE}, C) Au(111) surface at 0 V_{RHE} after oxidation.

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The relevance of the interfacial water structure for CO reduction on Cu(*hkl*)

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The electrochemical reduction of CO₂ is crucial for converting waste gas into valuable fuels and chemicals. Understanding intermediate steps, like CO electro-reduction, is vital for its success¹. Copper (Cu) surfaces play a key role in CO reduction (CORR) involving water as hydrogen donor in alkaline or neutral electrolytes. We investigate how water interaction with Cu(100) and Cu(111) surfaces influences the CORR in alkaline media.

In situ EC-STM reveals that on Cu(100), the CORR leads to the formation of small Cu ad-islands in the potential range for ethylene production when the OH surface concentration is high. In contrast, structural changes on Cu(111) are minor due to faster transport of hydroxide species away from the surface, indicating a less rigid interfacial water structure. As a result, Cu(111) exhibits faster hydrogen adsorption kinetics and the highest CO reduction activity. Our findings reveal that this interaction significantly affects the product distribution by influencing the interface chemistry and structure of Cu under reaction conditions².

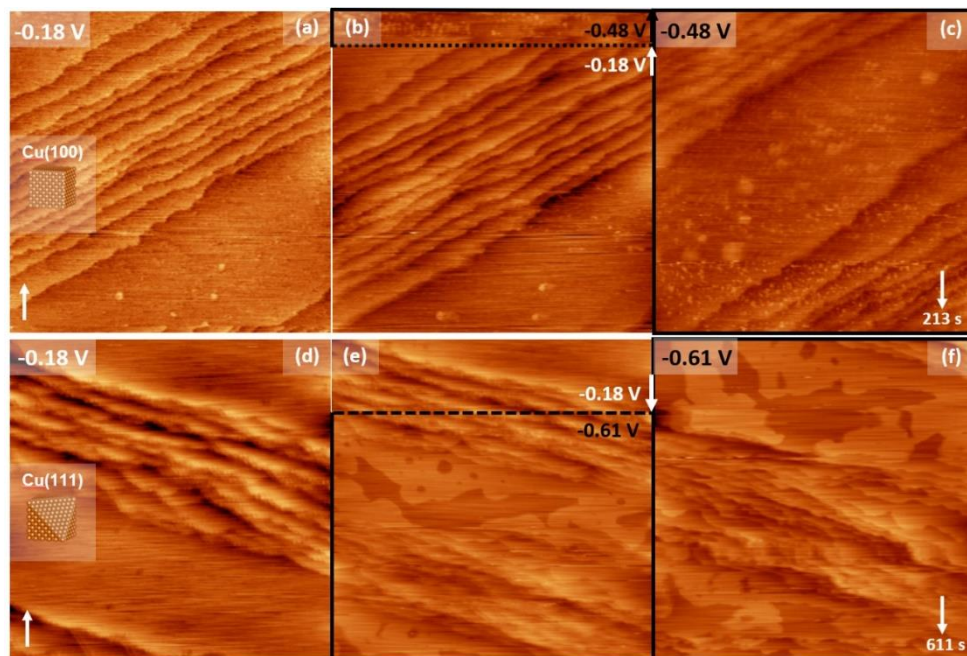


Figure 1. EC-STM images of Cu(100) ((a)-(c)) and Cu(111) ((d)-(f)) during CORR.

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Sum Frequency Generation (SFG) Laser Spectroscopy: CO Adsorption and its Orientation on Single Crystal Surfaces

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Surface science has to a large extent been driven by heterogeneous catalysis, which mostly occurs at solid-gas interfaces. Much of the fundamental understanding of elementary steps originates from studies of well-defined model catalysts such as single crystals [1-3]. The “drosophila” molecule CO has not only been frequently used as a probe to “titrate” the number and nature of exposed metal atom/sites of a catalyst, but is also involved in many processes of environmental and energy catalysis (e.g., exhaust cleaning, reforming, water gas shift, Boudouard, methanation, Fischer-Tropsch) [3-4]. Sum frequency generation (SFG) spectroscopy is a versatile surface/interface-specific technique, which has been successfully employed to study a variety of solid-gas, solid-liquid and air-liquid interfaces [3-5]. In this contribution, SFG was the main technique used to determine the adsorption sites, orientation, and dissociation of CO molecules on single crystals at different CO pressures and substrate temperatures [6-8]. Low energy electron diffraction (LEED), Auger electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), and density functional theory (DFT) calculations were used as complementary techniques in the characterization of catalyst surface cleanliness, ordering, composition and CO dissociation.

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Displaced Sagnac Interferometer for Passive Phase-Stabilization in 2D IR Spectroscopy

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Two-dimensional infrared (2D IR) spectra measured in the time domain provide ultimate time and frequency resolution, which are limited only by the bandwidth of laser pulses and the maximum time delay between the two pump pulses, respectively. Such measurements require producing a pair of pump pulses with highly stable, yet tunable time delay. [1,2] Instability of the time delay results in significant distortions of the line shape of the obtained spectra. [2] However, creating such pulse pairs is technologically challenging. In pump-probe geometry, it is typically achieved by either using active phase stabilization (or phase correction) [3] or pulse shaping [4]. Here, we simplify a 2D IR setup by using passive phase stabilization. To this end, we utilize a displaced Sagnac, or ring, interferometer. [5] In this type of interferometer, an incoming beam is split into two pump beams of same power by a broadband beam splitter (1250-5000 cm^{-1}). One beam travels clockwise (c), and the other counterclockwise (cc) through the interferometer reflected by the same mirrors. Upon returning to the beam splitter, the two beams combine and exit the interferometer. Because the beams reflect from the same optics, the time delay between the two pathways is highly stable. To control this time delay, we install a pair of zinc selenide wedged windows in each path. [6] One of the wedges in the cc path is mounted on a translation stage. The movement of this wedge along the wedge axis changes the thickness of the medium, and thus the time delay, in the cc pathway. This design allows cost-effective and simple implementation of 2D IR spectroscopy in a broad, 1250-5000 cm^{-1} , frequency range.

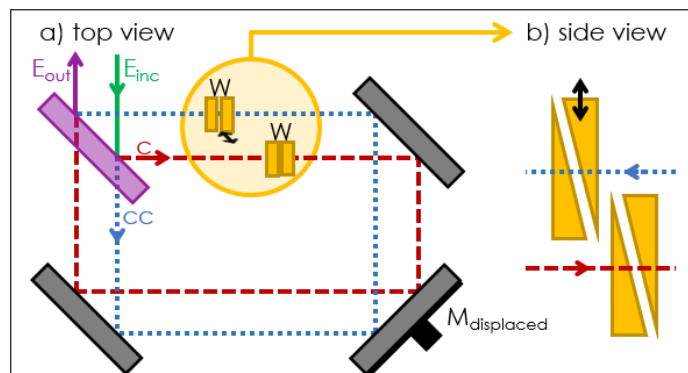


Figure: a) Displaced Sagnac interferometer top view. An incoming beam (E_{inc}) is split on a beam splitter into two paths, which travel the same distance clockwise (c) or counterclockwise (cc) through the interferometer, are transmitted through a pair of ZnSe wedges (W), recombine at the beam splitter and leave the interferometer (E_{out}). b) Side view of the wedges.

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Engineering of the copper-perovskite interface for promotional steering of the catalytic NO reduction by CO

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Abstract

As the major air pollutants emitted from industrial and transportation sectors, nitric oxides (NO_x) not only lead to serious environmental problems, but also have many negative effects on human health. Perovskite-based materials with their unique structural and chemical properties, have attracted attention as suitable alternatives for noble metal-based catalysts in deNO_x applications. Especially, an oxygen-deficient metal-perovskite interface can have a bifunctional synergism in terms of NO reactivity and N₂ selectivity. For this purpose, a series of LaCu_xMn_{1-x}O₃ (x = 0, 0.3, 0.5, 0.7, 0.9 and 1) perovskite structures was synthesized following a sol-gel method to study the effects of Cu doping (as the active metal of this reaction) on perovskite stability and catalytic reactivity. The results show, that, although the increase in calcination temperature increases the amount of copper within the perovskite structure (up to x=0.5) without Cu exsolution and also the catalyst stability, it causes a decrease in catalytic activity due to sintering of the perovskite. For catalysts calcined at 700 °C, although increasing the amount of copper further to x=0.7 and 0.9, causes activity enhancement at elevated temperatures, it also leads to a delay in the reaction onset temperature compared to x=0.3 and 0.5. We address this to self-poisoning effects of strongly adsorbed NO species on the copper particles exsolved from the perovskite structure, which is the result of initial over-doping during synthesis starting at x=0.7. With increasing reaction temperature and the start of desorption of NO from the catalyst surface, vacant sites necessary for its dissociation and also adsorption of CO are available. Therefore, the catalyst with a higher amount of copper (x=0.7 and 0.9 calcined at 700 °C) shows better activity at high temperatures.

Solid-State-Chemistries for Batteries at AIT

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Research and development efforts in industry and academia are highly focused on the progress of solid-state batteries (SSBs), to increase safety and performance of currently established lithium-ion batteries (LIBs). Solid electrolytes (SEs) have suffered from low ionic conductivity (0.1 mS cm^{-1}) compared to liquid electrolytes (1 mS cm^{-1}). Therefore, great efforts have been made to address this issue resulting in novel materials that even outperform liquid electrolytes. However, ionic conductivity is only one of several parameters that need to be addressed to enable SSBs. This includes electrochemical and chemical stability, processability, and costs. Some materials such as polymers, gels and ceramics used as solid electrolytes cover some of these parameters, however, none fulfill all of them at once. At Austrian Institute of Technology (AIT) different materials are evaluated for their applicability in SSBs:

- Polymer electrolytes (PEs), they excel in processability, however they show low room temperature ion conductivity. AIT directs efforts to improve PE formulations and anode and cathode films [1].
- Gel electrolytes (GEs), they show high ionic conductivity and good processability, AIT focuses on the improvement of the electrode-electrolyte interfaces [2].
- Ceramic electrolytes (CEs), they have the highest ionic conductivities, nevertheless, their processability is challenging, to address this issue AIT works on developing oxides-, sulfides- and halides-based electrolytes [3].

A compromise on key parameters is essential for obtaining SSBs suitable for complying with the safety, sustainability, and energy storage demands of today and tomorrow.

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High-yield liquid phase exfoliation of graphene utilizing low boiling co-solvent solutions and ammonia

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Graphene is a two-dimensional carbon material with unique chemical, electrical and mechanical properties that has a wide range of potential applications in various fields. One of the most effective methods of producing graphene is liquid phase exfoliation (LPE), in which bulk graphite is broken down into its individual layers while suspended in a suitable suspension medium ('solvent'). However, this exfoliation process can be challenging due to the complex effects of the solvent system on exfoliation, dispersibility and yield.

To overcome these challenges, and extending previous findings by Arao et al.[1], we have developed a highly efficient method for exfoliation of graphite to graphene using a cosolvent system of low boiling point organic solvents in combination with water and ammonia (NH₃) as surfactant/additive. Our method results in high yields of graphene and, importantly, all suspension components including the ammonia surfactant/additive are also readily removable. Our work thus demonstrates a facile route to improved graphene LPE yields by introducing a very easily removable surfactant/additive (NH₃) in a wide range of solvent mixtures (including low boiling point and benign mixtures), thus providing a framework for simpler, more flexible and safer 2D graphene LPE development.

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Innovative coating technique to increase the electrochemical performance of thick electrodes for Lithium-ion batteries

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Increasing the energy density of Lithium-ion batteries is an important task to reduce greenhouse gas emissions arising from the transportation sector. Maximizing the ratio of active to inactive materials within the battery is one way to optimize this parameter. The fabrication of thick electrode coating layers can be considered a possible solution. Unfortunately, high-loading electrodes with thicknesses $> 150\ \mu\text{m}$ are difficult to process due to their mechanical instability and high probability of defect generation during manufacturing. Therefore, new process techniques need to be encountered to mitigate those effects. Carrying out multiple coatings on top of each other enables high-loading thick electrodes, accompanied by various other advantages. For example, material gradients can be introduced to the coating layer by separating the coating into multiple parts. Every component of the coating has a specific purpose and an ideal location in the cross-section of the electrode. The binder material is essential nearby the current collector to guarantee adhesion and a certain amount is also needed for particle cohesion. However, when highly concentrated, it can block Li-ion pathways and lead to reduced capacity.

In this work, this innovative coating technique was used to overcome the above-mentioned difficulties arising during high-loading electrode fabrication ($> 8.6\ \text{mAh cm}^{-2}$). Rate capability cycling tests and electrochemical impedance spectroscopy confirm the big improvements related to multi-layer coated electrodes even without introducing a material gradient [1]. Binder material reduction in the vicinity of the electrolyte interface was also established and tested [2]. Cycling performance was increased by more than 40% at C-rates of 1C compared to standard processed single-layer electrodes.

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In-situ experiments for identifying reaction mechanisms on solid oxide cell electrodes

High-temperature solid oxide cells are a highly promising technology for efficient, reversible electrochemical chemical energy conversion. Optimization of these cells requires knowledge of the oxygen exchange reaction mechanisms and kinetics at the electrode surfaces, such as oxygen anion incorporation and release on the air side and water splitting, H_2 oxidation, or CO_2 splitting on the fuel side. Although these reactions are seemingly simple, the reaction intermediates and rate-limiting steps are only partly resolved. These can be identified by combined ambient pressure XPS and electrochemical experiments on model cells with thin film electrodes, which reveal the surface chemistry as a function of cell voltage and atmosphere. This talk presents a survey of experiments that show the complex interplay of operation conditions, surface chemistry and electro-catalytic activity. Key results include tracking of cation segregation, sulphur impurity-driven degradation by modification of surface dipoles and the in-situ exsolution of catalytically active Fe nanoparticles.

Exploring the Role of Silver Birch and Scots Pine as Atmospheric INM Sources

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Silver birch (*Betula pendula*) and Scots pine (*Pinus sylvestris*) are prevalent tree species in the northern hemisphere, distributed across a wide range from Western Europe to Eastern Siberia. Past ice nucleation studies on birch trees identified them to have efficient ice-nucleating macromolecules (INMs) all over the surface.

In recent years, we focused on the INM distribution on the surface of Silver birch. We collected tissue samples (leaf, branch wood, bark), extracted the INMs from the intact surface, and found 10^5 to 10^{10} INMs per cm^2 Silver birch tissue surface. From the in-depth chemical analysis of Silver birch INMs, we conclude that the INMs are likely large aggregates with polysaccharide or proteinaceous subunits.

More recently, we conducted a similar study with Scots pine. We found that the INM concentrations range from 10^5 to 10^8 INMs per cm^2 Scots pine tissue surface.

In addition, we collected rain samples underneath both Silver birch and Scots pines and found them to contain INMs with similar freezing onset temperatures as the surface extracts. Thus, we show that INMs are easily released from the trees' surface.

Summarizing our results from the past years, we extrapolated our results to estimate that one square meter of birch stand can release 10^{13} to 10^{15} INMs, and one square meter of Scots pine stand can release about 10^9 to 10^{12} INMs. This highlights Silver birch and Scots pines as massive INM reservoirs, suggesting that forests with abundant birch and pine trees should be considered significant sources of atmospheric INMs. Our chemical analysis will further help to identify these potentially highly abundant INMs in various field measurements.

Methane partial oxidation on Ni nanoparticles supported by MgO-ZrO₂ mixed oxides

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Syngas can be produced from biomethane via Partial Oxidation of Methane (POM), as an ecofriendly and sustainable route. In this work, catalysts of Ni supported on MgO-ZrO₂ solid solutions, prepared by a one-step polymerization method, were characterized by HRTEM/EDX, XRD, XPS, H₂-TPR, in situ XRD and tested for POM. NiO/MgO/ZrO₂ contained two solid-solutions, MgO-ZrO₂ and NiO-MgO. Ni supported on MgO-ZrO₂ solid solution exhibited high CH₄ conversion and H₂ selectivity. However, depending on the MgO amount, major differences in NiO reducibility, Ni⁰ crystallite growth, and carbon deposition rates were observed. Interestingly, catalysts with lower MgO content achieved the highest CH₄ conversion and selectivity to H₂ and CO, and low carbon deposition rates, with Ni₄MgZr (4 mol% MgO) turning out to be the best catalyst. In situ XRD during POM indicated metallic Ni nanoparticles, supported by MgO-ZrO₂ solid solution, with small amounts of NiO-MgO present. MgO also influenced the morphology of the carbon deposits, leading to filaments instead of amorphous carbon. A combustion-reforming mechanism is suggested and using a MgO-ZrO₂ solid solution support strongly improves catalytic performance, which is attributed to effective O₂, CO₂ and H₂O activation at the Ni/MgO-ZrO₂ interface.

Sr₂NiMoO₆ and Sr₂CoMoO₆ Double Perovskites as Catalyst Precursors in Methane Dry Reforming

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Abstract: The double perovskites materials Sr₂NiMoO₆ (SNMO) and Sr₂CoMoO₆ (SCMO) were tested as precursor materials in the methane dry reforming reaction to eventually yield defined and active metal-perovskite or metal-oxide interfaces upon Ni and Co exsolution. After solid-state synthesis at 1623 K in air, both structures feature a rock-salt ordered double perovskite structure. During treatment in a 1:1 CH₄:CO₂ atmosphere SNMO shows spontaneous activation between 1013 K and 1073 K due to the decomposition of the perovskite into SrMoO₄, SrCO₃ and metallic Nickel particles. In comparison, pre-treated/reduced SNMO samples, either by prior heating in the CH₄:CO₂ atmosphere or pure H₂ at 1073 K, shifts the onset of the reaction to 773 K accompanied by a more gradual activation. For all SNMO experiments, we experience the competing reverse water gas shift reaction affecting both reactant conversion and product yield.

In contrast, Co exsolution and self-activation in the CH₄:CO₂ atmosphere is strongly suppressed for SCMO. Pre-reduction of SCMO in pure H₂ up to 1173 K results in partial SCMO decomposition into Sr₁₁Mo₄O₂₃ and metallic Cobalt. Several approaches are currently tested to activate SCMO, including adding H₂ to the DRM reaction mixture to suppress Co oxidation, co-alloying of Co and Ni and introducing A-site vacancies to induce the easier structural breakdown of the double perovskite.

Disclaimer: Results are still partially preliminary.

Laser spectroscopy and the interfacial structure at the spinel-water interface

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Several spinel oxides have shown promising catalytic activity for the photolytic conversion of H₂O to H₂ and O₂. Catalyst improvement is predominantly based on trial and error rather than rational optimization, as fundamental insights into the spinel oxide-water interface, the actual position of the reaction, are still lacking. To shed light on the spinel oxide-water interfacial structure we apply phase resolved sum frequency generation spectroscopy. As a model system single crystalline MgAl₂O₄, the eponym of the spinel group, is used, where the (001) surface is in contact with water. It is observed that the interfacial molecular structure depends on the pH value of the aqueous solution. At pH 3 water molecules are net oriented with the oxygen atom towards the MgAl₂O₄ surface. On the flipside, at pH 11 the water molecules are pointing with the hydrogen atoms more likely towards the surface. Besides interfacial water, the spectra provide also evidence for the presence of surface hydroxy groups. Furthermore, it is evaluated if the interfacial structure changes when probing not the MgAl₂O₄ (001) but the (110) and (111) surfaces in contact with water.

Operando spectroscopy of working VOC nanocomposite sensors

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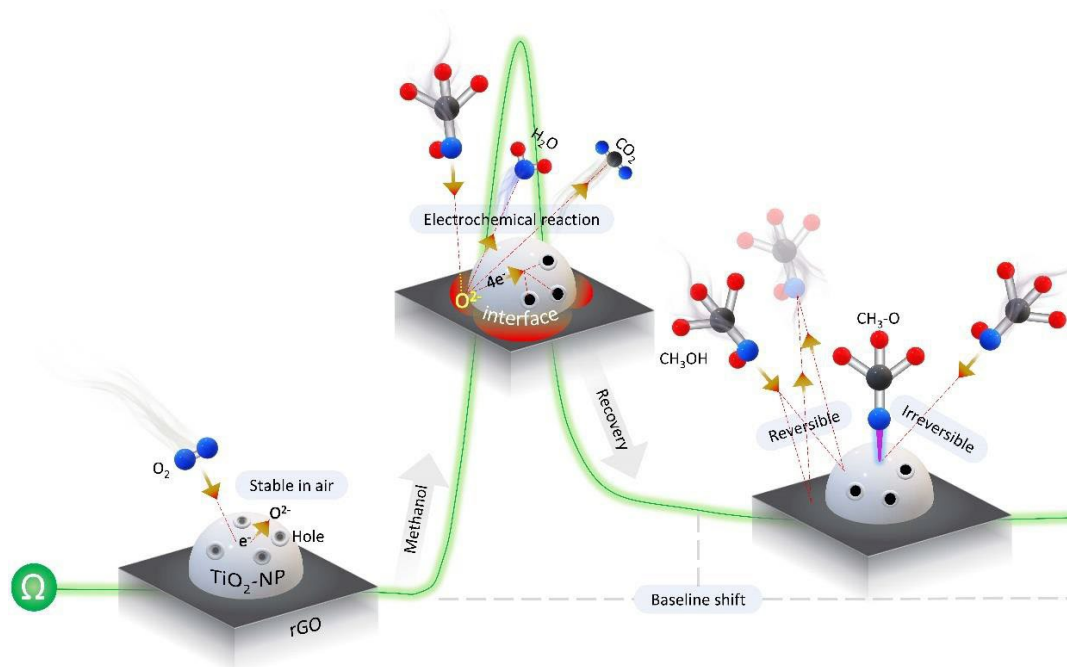
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The interaction of volatile organic compounds at room temperature (RT) with metal oxide semiconductor-based sensing materials can irreversibly affect the sensor performance. Unfortunately, the analysis of molecular processes on chemiresistive gas sensors is often based on indirect evidence, whereas *in situ* or *operando* studies monitoring the gas/surface interactions enable direct insight. Here we report a multidisciplinary approach employing *operando* spectroscopy of working sensors to investigate RT methanol detection, contrasting well- characterized nanocomposite (TiO₂@rGO-NC) and reduced-graphene oxide (rGO) sensors. Methanol interactions with the sensors were examined by (quasi) *operando*-DRIFTS and *in situ*-ATR-FTIR spectroscopy, the first paralleled by simultaneous measurements of resistance. The sensing mechanism was also studied by mass spectroscopy (MS), revealing the surface electrochemical reactions. The *operando* and *in situ* spectroscopies demonstrated that the sensing mechanism on the nanocomposite relies on the combined effect of methanol reversible physisorption and irreversible chemisorption, sensor modification over time, and electron/O₂ depletion-restoration due to a surface electrochemical reaction forming CO₂ and H₂O.



MOF BASED SINGLE-SITE PHOTOCATALYSIS USING ANCHORED MOLECULAR CLUSTERS

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Over the past few years, metal-organic frameworks (MOFs) have emerged as efficient photocatalyst systems with uniformly distributed catalytic active centres. However, they often suffer from a limited number of these active centres and/or insufficient catalytic activity of the intrinsic metal centres; therefore need a co-catalyst to overcome these limitations and enhance their overall performance. MOFs are usually very porous thereby having large surface areas and tunable pore size, which makes them versatile and great candidates to design catalysts that bear single-metal sites. By choosing an appropriate ligand, the MOF can be designed to have co-catalyst anchoring sites for immobilization via electrostatic or photo-deposition. One such MOF is the recently reported COK-47 consisting of a Ti-oxo secondary building unit linked via biphenyl-4,4-dicarboxylate ligands^[1]. The 2D structure of this MOF provides a channel for efficient charge transfer and additionally, its organic ligand can be modified to have –N- sites acting as co-catalyst anchor points.

Among many non-noble metal-based co-catalysts, exfoliated MoS₂ has proven to be an excellent alternative in many cases. It is also established that the edge sites are the active centres for catalysis whereas the basal plane largely remains unreactive. Therefore, molecular analogues that mimic the edge sites of MoS₂ were probed and shown to perform better than MoS₂ under similar testing conditions. Batool et al. demonstrated that [Mo₃S₁₃]²⁻ (**Mo₃**), one of the most active molecular inorganic catalysts for the photocatalytic hydrogen evolution reaction, covalently anchors onto a model TiO₂ substrate exhibiting a stable and excellent HER performance; falling short by a mere threefold when compared to the most efficient Pt nanoparticle^[2]. In our work, we probe the photocatalytic performance of Mo₃ clusters anchored onto modified COK47. We partially replace the biphenyl-4,4-dicarboxylate ligand, with a pre-modified ligand anchored with the cluster at the –N atom. This covalent attachment provides better charge transfer and thereby enhances the activity in comparison to pristine Mo₃-COK47 composite where the cluster is attached via weak van-de Waals interactions. We use a variety of characterization methods such as Raman, XPS, NMR etc. to confirm the attachment of these molecular clusters onto the MOFs. We then test them for the photocatalytic hydrogen evolution reaction and compare their performance to other known Ti-based MOFs prepared using alternate strategies for preparing single-site catalysts.

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