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Fachbereich Chemie und Physik der Materialien
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Organisation:
Thomas Berger, Oliver Diwald, Günter Grampp

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Hörsaal C-3006, 3. Stock, Hellbrunnerstrasse 34/III, 5020 Salzburg

Donnerstag, 14. April		
12:00-13:00	Registrierung	
	Vorträge	
Electrochemistry and Energy Diskussionsleiter: Julia Kunze-Liebhäuser		
13:00-13:20	Gregor Walch *TU Wien*	Effect of light on mixed conducting electrodes in high-temperature solid oxide electrochemical cells
13:20-13:40	Michael Doppler *TU Wien*	Capacitive behavior of Nickel pattern electrodes on YSZ substrates
13:40-14:00	Wolfgang Preis *Uni Leoben*	Modeling of chemical diffusion and conductivity relaxation in electroceramic materials
14:00-14:20	Nina Schrödl *Uni Leoben*	Effects of Cr-poisoning on the performance of $La_2NiO_{4+\delta}$ anodes in solid oxide electrolyser cells
14:20-14:40	Martin Perz *Uni Leoben*	Degradation effects on a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ SOFC-cathode with Si-poisoned surface
14:40-16:40	**Postersitzung** (Getränke, Kaffee und Kekse)	
Surfaces and Interfaces Diskussionsleiter: Erminald Bertel		
16:40-17:00	Leonhard Grill *Uni Graz*	Assembly and Manipulation of Single Molecules on Surfaces
17:00-17:20	Martin Sterrer *Uni Graz*	Au(111) and supported Au model systems: CO_2 activation and gold mining
17:20-17:40	Günther Rupprechter *TU Wien*	Model catalysts for reforming reactions: water interaction with ultrathin films of zirconium oxide
17:40-18:00	Aida Naghilou *Uni Wien*	Spot Size and Pulse Number Dependence of Femtosecond Laser Modification and Ablation Thresholds
19:00	**Gemeinsames Abendessen im Gasthof Überfuhr**	

Freitag, 15. April		
	Vorträge	
Nanosized Matter Diskussionsleiter: Nicola Hüsing		
8:30-8:50	Julia Kunze-Liebhäuser *Uni Innsbruck*	Self-organized TiO_2 nanotubes as anode material for Li-ion intercalation – effect of preferential orientation and surface chemistry
8:50-9:10	Dominik Eder *TU Wien*	Interfacial dynamics in nanocarbon-inorganic hybrid photocatalysts
9:10-9:30	Gilles Bourret *Uni Salzburg*	Electrochemical approaches for controlling metal/semiconductor nanostructures
9:30-9:50	Cezarina Mardare *JKU Linz*	Synthesis, characterization and antibacterial properties of different molybdate powders
9:50-10:10	Markus Scharber *JKU Linz*	On the Efficiency Limit of Organic Solar Cells
10:10-11:00	**Postersitzung** (Getränke, Kaffee und Kekse)	
Dynamics and Kinetics in Solution Diskussionsleiter: Thomas Berger		
11:00-11:20	Alexander Wankmüller *TU Graz*	Magnetic field effect on p-type delayed fluorescence in organic systems
11:20-11:40	Josua Bächle *TU Graz*	Hydrogen Atom Self-Exchange Kinetics studied by CW-ESR Line Broadening
Corrosion Diskussionsleiter: Jürgen Fleig		
11:40-12:00	Jan Philipp Kollender *JKU Linz*	Online monitoring of metal dissolution during anodisation of valve metals
12:00-12:20	Sarah Walkner *JKU Linz*	µ-electrodes for measuring pH-value and chloride concentration in extraordinary surroundings
12:20-12:30	**Schlusswort**	

Posterbeiträge	
Christian Berger *Uni Leoben*	Mass and charge transport properties of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$
Erminald Bertel *Uni Innsbruck*	Complex Sulfur Chemistry on Cu and Cu/O Surfaces
Carina Grill *JKU Linz*	Cobalt-nickel material libraries fabricated by electrodeposition in the presence of various additives
Alexander Hutterer *TU Wien*	Al-doped ZnO as Current Collector in Ceria based Anodes for Solid Oxide Fuel Cells (SOFCs): Preparation, Stability and Electrochemical Properties
Krisztina Kocsis *Uni Salzburg*	Impact of interfacial changes on colloidal ZnO nanoparticle properties: spectroscopic studies on particulate model systems
Stephan Landgraf *TU Graz*	Time-Resolved Fluorescence HPLC Detection Using Semiconductor Light Sources: Principles and Applications
Matthias Niedermaier *Uni Salzburg*	Paramagnetic defects and adsorbates at aqueous interfaces: a comparative study on TiO_2 and ZnO nanoparticle systems
Daniel Rettenwander *Uni Salzburg*	Mircrocontanct impedance spectroscopy on Li- and Na-ion conducting solid electrolytes
Gabriela Schimo JKU Linz	Determination of hydrogen diffusion coefficients in metals using (scanning) Kelvin probe
Johannes Schneider *Uni Salzburg*	Porphyrin adsorption studies on MgO nanoparticles
Dominik Steiner *Uni Innsbruck*	Self-organized TiO_2 nanotubes as anode material for Li-ion intercalation – an XPS and electrochemical impedance spectroscopy study

VORTRÄGE

Effect of light on mixed conducting electrodes in high-temperature solid oxide electrochemical cells

Gregor Walch[a], Bernhard Rotter[b], Georg Brunauer[b], Esmaeil Esmaeili[b], Alexander Opitz[a], Johann Summhammer[c], Karl Ponweiser[b] and Jürgen Fleig[a]

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The effect of light on electrochemical processes is often investigated in cells using a liquid electrolyte (e.g. [1]). Work on solid state photoelectrochemical cells, such as the theoretical study by Ye *et al.* [2], however, is scarce but fundamentally interesting and might hold some potential for future applications in sensor or energy storage technology.

From literature the response of the oxygen incorporation kinetics to the irradiation with UV light on the “model materials” $SrTiO_3$ [3] and TiO_2 [4] is known. These studies suggest that UV light accelerates the oxygen incorporation into the material after a sudden increase in the oxygen partial pressure of the surrounding atmosphere.

In the present contribution these two oxides were investigated under constant atmosphere to check the effect of light on (more or less) equilibrated samples. The two materials were used as electrodes in high-temperature solid state photoelectrochemical cells that were exposed to UV radiation while monitoring the voltage change or performing electrochemical impedance spectroscopy (EIS).

$SrTiO_3$ samples were prepared by depositing an yttria-stabilized zirconia (YSZ) thin film on single crystalline $SrTiO_3$. The $SrTiO_3$ single crystal served as a working electrode and was contacted *via* a grid-like Pt or Au current collector. On the TiO_2 samples the working electrode was a titania thin which was deposited on single crystalline YSZ by sputtering and subsequent annealing in air. Again, metal current collectors were used. The electrochemical cells were completed by a porous Pt counter electrode.

The voltage change upon irradiation with UV light was evaluated as a function of time and interpreted in defect chemical terms. The results were combined with those from EIS and suggest that apart from photovoltaic effects both materials seem to incorporate oxygen when irradiated with UV light. Accordingly, a battery-like voltage remains even after switching off UV light, indicating storage of chemical energy.

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[2] Ye, X., Melas-Kyriazi, J., Feng, Z. A., Melosh, N. A., & Chueh, W. C. *Physical Chemistry Chemical Physics* **2013**, 15, 15459-15469.

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[4] Gundlach, H. W. & Heusler, K. E. *Zeitschrift für Physikalische Chemie* **1980**, *119*, 213-224.

Capacitive behavior of Nickel pattern electrodes on YSZ substrates

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Solid oxide fuel cells are capable of converting chemical energy into electrical energy with high efficiency from a variety of C/H containing fuels. Modeling of such fuel cells requires detailed understanding of the fundamental properties of the system. In this study, the capacitive behavior of the state-of-the-art anode material – the Ni/yttria stabilized zirconia (YSZ) electrode – is investigated using structured thin film model electrodes.

It is shown that area specific capacitance (ASC) values are too high to be explained by a Helmholtz-type electrochemical double layer. A Gouy-Chapman type electrochemical double layer may explain the absolute value of the ASC, yet fails to explain the bias dependency of the capacitance. These facts and the dependency of the ASC on sulfur in the atmosphere indicate some sort of chemical capacitance. Potential types of chemical capacitances suggested in literature are discussed.

Modeling of chemical diffusion and conductivity relaxation in electroceramic materials

W. Preis

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A proper knowledge of the kinetics of oxidation / reduction (oxygen exchange) processes of oxide ceramics is inevitable for an improved understanding of the manufacturing as well as operation of various electroceramic components, such as $BaTiO_3$ - based PTC (positive temperature coefficient) resistors, ZnO - based varistors, and perovskite-type cathode materials for solid oxide fuel cells (SOFCs). Conductivity relaxation experiments represent a powerful technique for the experimental determination of the relevant kinetic parameters, viz. chemical surface exchange coefficient and chemical diffusion coefficient. A sudden change of the oxygen activity of the surrounding gas phase results in a chemical diffusion process in the electroceramic material which gives rise to a variation of the electrical conductivity with time (conductivity relaxation). Usually, the time dependence of the conductivity is correlated with the solution function for mass transport based on the diffusion equations.

It is the aim of this contribution to provide finite element simulations of chemical diffusion and conductivity relaxation in electroceramics. Basically, a simple relationship between the electrical conductivity and the total amount of exchanged oxygen (mass transport), $\sigma_{\mathrm{norm}} = m(t) / m(\infty)$, is strictly valid in the case of one-dimensional effective medium diffusion, where the relaxation curves for mass transport and dc conduction coincide perfectly. However, several examples will be provided where the conductivity relaxation curve deviates considerably from the relaxation curve for mass transport, i.e. $\sigma_{\mathrm{norm}} \neq m(t) / m(\infty)$. This peculiar deviation can be observed, when (i) extremely fast diffusion of oxygen along grain boundaries occurs and the (ii) electronic conductivities of grain boundaries (including core regions as well as electrically active space charge layers) and bulk (grain interior) differ remarkably from each other. This situation has been found recently with respect to conductivity relaxation experiments on PTC ceramics at 900°C [1]. Moreover, significant deviations between relaxation curves of mass transport and dc conduction have been reported previously for composite materials involving extremely fast diffusion along interfaces [2]. Even in the case of homogeneous samples the simple relationship $\sigma_{\mathrm{norm}} = m(t) / m(\infty)$ can only be expected, if one-dimensional diffusion is fulfilled which can be exemplified by finite element simulations regarding the van der Pauw method [3].

[1] W. Preis, W. Sitte, Solid State Ionics (2016), http://dx.doi.org/10.1016/j.ssi.2015.11.009 (in press).
[2] W. Preis, J. Solid State Electrochem. 15 (2011) 2013–2022.
[3] W. Preis, Computational Materials Science 103 (2015) 237–243.

Effects of Cr-poisoning on the performance of $La_2NiO_{4+\delta}$ anodes in solid oxide electrolyser cells

Nina Schrödl, Andreas Egger and Werner Sitte

Chair of Physical Chemistry, Montanuniversitaet Leoben, Austria

High temperature water electrolysis is regarded as a clean and sustainable way for hydrogen production as well as a means to store surplus energy from renewable energy sources. However, poisoning of the oxygen electrode with impurities released from stack or balance-of-plant components can limit the life-time of solid oxide cells. Although substantial efforts have been made to decrease the volatilization of Cr-compounds from interconnects using barrier coatings, Cr-poisoning still remains an issue for long-term operation.

The K_2NiF_4-type mixed conductor $La_2NiO_{4+\delta}$ (LNO) was investigated as anode material for solid oxide electrolyser cells. The fast oxygen exchange kinetics of LNO is related to its ability to incorporate excess oxygen on interstitial lattice sites. LNO has been considered to be more stable against Cr-poisoning than Ba- or Sr- substituted perovskite-type electrode materials, which are known to readily form insulating or catalytically inactive secondary phases with Cr-species [1].

The suitability and long-term stability of LNO under Cr-poisoning conditions was assessed at 800°C by monitoring the oxygen exchange kinetics via conductivity relaxation measurements for more than 3000 hours. Extensive post-test analyses from XPS and SEM-EDX depth profiling and AFM investigations showed that chromium can have a detrimental effect on the composition and morphology of the sample surface, leading to a decrease in oxygen surface exchange rates. In addition, impedance spectroscopy and current-voltage measurements on symmetrical and asymmetrical button cells were conducted at 800°C and 0.2 bar pO_2 [2,3]. Current densities of up to -410 $mAcm^{-2}$ were applied to simulate real-life SOEC-operating conditions. SEM-EDX/WDX analyses were performed on cross-sections of tested button cells and a number of impurities derived from different cell components have been identified.

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[2] Egger, A.; Schrödl, N.; Sitte, W. *Faraday Discuss.* **2015**, 182, 379.
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Degradation effects on a $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ SOFC-cathode with Si-poisoned surface

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The long-term stability of the cathode is an important requirement for a wider commercial utilization of the solid oxide fuel cell (SOFC) technology. In recent studies silicon, which was transported to the cathode surface by humid air has been found as a potential contaminant for the cathode, causing severe degradation of the oxygen exchange kinetics [1].

In the present work the influence of Si deposited on the surface of porous $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF) cathodes was investigated in a long-term experiment [2]. A symmetrical cell was fabricated by screen-printing porous LSCF layers on both sides of a solid electrolyte substrate of $Ce_{0.9}Gd_{0.1}O_{2-\delta}$. The evolution of the electrochemical behavior of the electrodes during 2000 hours at 700°C was characterized by impedance spectroscopy. In the first 1000 hours the as-produced cathodes were characterized. Afterwards Si-poisoning of the cathode surface was induced by sputtering Si-layers of approx. 10 nm on both sides of the sample. Impedance measurements on the contaminated cell for additional 1000 hours revealed a dramatical decrease of the electrochemical performance, causing an increase of the area specific polarization resistance (ASR) from 1.4 to 8 Ωcm^2 and changes in the shape of the impedance spectra. By SEM and STEM analyses of the degraded sample a 50 nm thick secondary silicate phase layer was found in a surface-near region of the cathode. It can be concluded that contamination with even small amounts of silicon drastically reduce the oxygen exchange reaction kinetics.

[1] E. Bucher et al: Solid State Ionics 191 (**2011**), 61–67
[2] M. Perz et. al.: Solid State Ionics (2016), in press, http://dx.doi.org/10.1016/j.ssi.2016.01.005.

Assembly and Manipulation of Single Molecules on Surfaces

Leonhard Grill,[a]

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Functional molecules on surfaces and their assembly into pre-defined architectures are key challenges in nanotechnology and of interest in various fields from molecular electronics over novel materials to molecular machines. Various examples of functional molecules, ranging from molecular wires to molecular switches that are studied by scanning tunneling microscopy (STM) under ultrahigh vacuum conditions, will be discussed. Specifically designed molecular building blocks are connected to two-dimensional networks or one-dimensional chains [1], which can act as molecular wires. When pulling a single molecule with the STM tip, we measured not only the current flowing through the wire [2,3] but also the forces that are active during the conformational changes in the single oligomer when using an atomic force microscope [4].

An important issue for any functional molecule is the role of the direct environment for the molecular function. We have studied the atomic scale surroundings of individual molecules and found that the electronic structure of molecules [5] or chemical processes within individual molecules can be controlled by single atoms. This was observed for molecular switches, where the atomic-scale surroundings cause drastic changes in their switching probability, leading to periodic switching patterns [6]. In the case of porphycene molecules, the rate of an intramolecular hydrogen transfer reaction can be tuned up and down by only one single atom in the vicinity of the molecule [7]. The same effect is then extended to molecular assemblies where cooperative effects in single molecules are directly observed.

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[4] Kawai S. et al., *PNAS* **2014**, *111*, 3968.
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[6] Dri C. et al., *Nature Nanotech.* **2008**, *3*, 649.
[7] Kumagai T. et al., *Nature Chem.* **2014**, *6*, 41.

Au(111) and supported Au model systems: CO_2 activation and gold mining

Martin Sterrer

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In this talk, I present results of recent STM and IR experiments aiming at CO_2 activation on gold surfaces. We have studied MgO-supported Au nanoparticles and 1-dimensional metal-organic chain structures formed by 1,4-Phenylene-Diisocynanide (PDI) and Au atoms on an Au(111) surface and found activation of CO_2 on both surfaces. The formation of the CO_2 anion is facilitated by charge transfer, which in the case of MgO-supported Au clusters is provided by the substrate and on the metal-organic overlayer through electron donation from the isocyanide group into the Au adatom.

In addition, I will present results of the coverage dependence of PDI assembly on Au(111) in UHV, their stability of the metal-organic overlayer structures in air, and the tip-induced Au nanoparticle formation on PDI-Au(111) surfaces in ambient environment, which was investigated using scanning tunneling microscopy (STM) and vibrational sum frequency generation (SFG) spectroscopy. This study reveals that the distribution of Au nanoparticles created during tip-induced release of Au atoms from molecule-Au adatom complexes shows strong dependence on the PDI coverage, with the possibility of creating highly ordered Au nanoparticle arrays in the medium coverage regime, and more disordered distributions at low and saturation coverage, respectively.

Model catalysts for reforming reactions: water interaction with ultrathin films of zirconium oxide

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It is well accepted that surface science based planar model catalysts are well-suited for fundamental studies of surfaces processes, despite the inherent differences between model and technological catalysts [1-3]. Methodological advances also allow to examine active functioning model catalysts, at (near) atmospheric pressure and at elevated temperature. Frequently applied methods encompass polarization-modulation infrared reflection absorption spectroscopy (PM-IRAS), sum frequency generation (SFG) laser spectroscopy and near atmospheric pressure X-ray photoelectron spectroscopy (NAP-XPS). In the current contribution this approach is utilized to examine Ni-ZrO_2 „cermet“ anodes that are employed in Solid Oxide Fuel Cells (SOFCs) for CH_4 reforming to H_2 and/or H_2 oxidation.

In order to model SOFC anodes well-ordered ultrathin films of ZrO_2 were grown in UHV by oxidation and annealing of $Pt_3Zr(0001)$ single crystals [4]. Ni was deposited by physical vapor deposition. Low Energy Electron Diffraction (LEED), Scanning Tunneling Microscopy (STM), high resolution X-ray Photoelectron Spectroscopy (XPS) and Density Functional Theory (DFT) indicated the formation of a well-structured ZrO_2 trilayer film, corresponding to the (111) facet of cubic ZrO_2. Whereas the interaction of the ZrO_2 film with CO or CO_2 was very weak (desorption temperatures of 155 and 117 K, respectively), its interaction with water was very strong (desorption temperature of 485 K). NAP-XPS (O1s and Zr3d) and PM-IRAS were thus applied to examine water adsorption/dissociation and hydroxylation of the O-Zr-O film. Backed by DFT, three channels of water adsorption (molecular vs. dissociative, reversible vs. non-reversible) could be identified. Creation of defects by ion bombardment strongly enhanced water dissociation.

Once hydroxylated the ZrO_2 film exhibited exceptional activity for reaction with CO_2 (whereas the non-hydroxylated film did not). IRAS, using formic acid (HCOOH) and formaldehyde (HCHO) as reference, was used to identify the functional groups of the species formed. Ni nanoparticles grown on the ZrO_2 trilayer were examinded by PM-IRAS and XPS.

Support by the Austrian Science Fund (FWF SFB-F45 FOXSI) is gratefully acknowledged.

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Spot Size and Pulse Number Dependence of Femtosecond Laser Modification and Ablation Thresholds

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Modification fluence thresholds are core parameters in laser materials processing as well as for optical components and telecommunication systems. The threshold energy density (fluence) was found to be an unambiguous material property for a given set of experimental parameters such as pulse duration, wavelength, number of pulses, and pulse repetition rate.

The modification threshold fluence however shows a dependence on the irradiated area, both for femtosecond and nanosecond pulses. However, existing models cannot explain this crucial phenomenon. The results show incubation behaviours depending on the material class. The spot size dependence of pulse laser-induced ablation thresholds of solid materials could not be satisfactory described by the two existing quantitative models based on defect densities and on heat accumulation.

In the present study, the heat accumulation model was amended but still yielded results in contradiction to experimental observations. The existing defect model was extended to account for incubation at metals, semiconductors, and polymers to a new generic model combining the spot size and pulse number dependence of femtosecond pulse laser-induced ablation thresholds.

Self-organized TiO_2 nanotubes as anode material for Li-ion intercalation – effect of preferential orientation and surface chemistry

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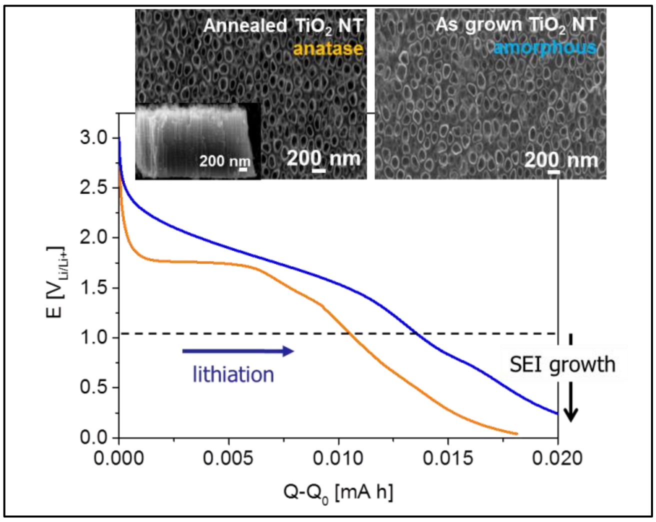
[c] *Technische Universität München, Experimentalphysik E12, Germany*



Model electrodes of self-organized anodic titania nanotubes are produced and studied in terms of their lithiation/ delithiation characteristics. The nanotube array provides direct one dimensional electron transport to the current collector, without the need of adding binders or conductive additives [1,2]. Quantitative determination of the lithiation degree is performed at different stages of lithiation by the use of cold neutrons [3], X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS).

In TiO_2 anatase nanotubes, the orientation of grains is found to influence the lithiation behavior of the material.

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Interfacial dynamics in nanocarbon-inorganic hybrid photocatalysts

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Hybridising nanocarbon materials, i.e. CNTs and graphene, with active inorganic nanomaterials constitutes a powerful strategy towards designing new-generation functional materials for many applications where efficient charge separation and extraction is required, including photovoltaics, photocatalysis, batteries, supercapacitors and biosensors [1]. In contrast to nanocomposites, which merely combine the intrinsic properties of both compounds, nanocarbon hybrids additionally provide access to both a large surface area required for gas/liquid-solid interactions and an extended interface, through which charge and energy transfer processes create synergistic effects that result in unique properties and superior performances.

In this talk, I will briefly introduce the concept of nanocarbon-inorganic hybrids, discuss various hybridisation strategies and present intriguing examples for the photocatalytic performance of nanocarbon hybrids (i.e. water purification [2] and water splitting [3]). In particular, I will demonstrate how their activity can be further enhanced through purposefully engineering interfaces and morphology. For example, growing ultra-thin single-crystalline Ta_2O_5 films on the surface of CNTs has increased the activity for hydrogen evolution remarkably compared to hybrids with the typical polycrystalline oxide coatings. This improvement is attributed to fewer grain boundaries, which alleviates electron transport to the interface, and the formation of a Ohmic junction, which facilitates charge transfer and separation at the interface. Finally, I will discuss the nature and extent of interfacial charge and energy transfer and elaborate on their impact on the hybrids' properties using electrochemical (i.e. chronoamperometry, EIS) and photoluminescence techniques.

[1] D. Eder, *Chem. Rev.*, **2010**, 110, 1348; C. Shearer et al. *Adv. Mater.*, **2014** 26, (15), 2295-2318;
[2] Z. Ren et al, *Chem. Sci.*, **2012**, 3, 209-216.
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Electrochemical approaches for controlling metal/semiconductor nanostructures

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The optical and electrical properties of heterogeneous nanowires are profoundly related to their composition and nanoscale architecture. However, the intrinsic constraints of conventional synthetic and lithographic techniques have limited the types of multi-compositional nanowires that can be created and studied in the laboratory. Our recent progress in templated syntheses of one-dimensional nanostructures will be briefly discussed in the context of plasmonics.[1-3] In particular, we report a high-throughput technique that can be used to prepare coaxial nanowires with sub-10 nm control over the architectural parameters in both axial and radial dimensions. The method, which is termed coaxial lithography (COAL),[3] relies on templated electrochemical synthesis and can create coaxial nanowires composed of combinations of metals and semiconductors. The optoelectronic properties of a plasmonic nanoring embedded hybrid core-shell semiconductor nanowire were studied. This demonstrates the potential of this new synthetic technique to radically change nanowire fabrication.

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[3] Ozel, T.; Bourret, G. R.; Mirkin, C. A. *Nature Nanotech.* **2015**, *10*, 319.

Synthesis, characterization and antibacterial properties of different molybdate powders

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Recent studies of molybdenum oxides and molybdate compounds showed that this class of materials has great potential for being used as antibacterial agents [1,2]. In the same time, Ag and Cu compounds are known as bactericidal [3], whereas CaOH is traditionally used in endodontic treatment against infections [4]. Based on these premises, different molybdate powders (Ag_2MoO_4, $CuMoO_4$, $Cu_3Mo_2O_9$ and $CaMoO_4$) were produced via chemical synthesis using non-harsh conditions and in the range of temperatures from room temperature up to 100 °C, and for selected samples post-synthesis heat treatments were performed. Their crystallographic characterization revealed the presence of fully crystalline phases with no spurious compounds. Morphological investigations showed grain sizes ranging from nanometer ($Cu_3Mo_2O_9$) to micrometer (Ag_2MoO_4, $CaMoO_4$ and $CuMoO_4$). The suspensions of synthesized powders with different concentrations (1, 5 and 10 mM) were tested for antibacterial activity against transformed *E. coli* BL21DE3 (kanamycin resistant) by mixing them with the bacterial culture and spreading them onto agar plates with nutrient medium. Optical density measurements of the suspensions, as well the observation of colonies grown on the agar plates after defined times showed extremely high antibacterial activity in the presence of some of the tested molybdates (Ag_2MoO_4, $CaMoO_4$ and $CuMoO_4$), whereas $CaMoO_4$ did not inhibit the growth of *E. coli*.

Acknowledgements

The financial support by the Austrian Federal Ministry of Science, Research and Economy and the National Foundation for Research, Technology and Development is gratefully acknowledged.

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On the Efficiency Limit of Organic Solar Cells[1,2]

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Organic photovoltaic cells (OPVs) are promising and relatively new devices for the conversion of light into electricity. Today the technology has demonstrated moderate power conversion efficiencies and operational stabilities which have not qualified OPV for rapid, large scale commercialization. In this contribution the conversion efficiency limit of OPVs will be discussed. Based on these findings absorber material properties required for higher PCEs will be developed. It will be demonstrated that OPVs could be as efficient as solar cells based on inorganic semiconductor absorber materials.

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Magnetic field effect on p-type delayed fluorescence in organic systems

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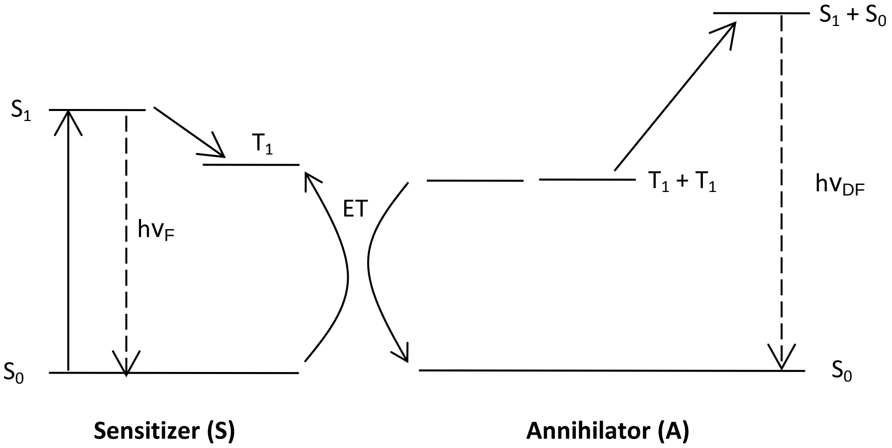
Delayed Fluorescence is a well known process since the late 70s. It has been proved that an external magnetic field has an influence on the delayed fluorescence yield. [1] Whereas this phenomenon has been studied extensively in the solid state, almost no experiments were done in solution. [2] This work intends to explore the influence of the magnetic field on a process that leads to delayed fluorescence in solution.

The sensitized delayed fluorescence reaction can be summarized by the following equations:

$S_{0,S} + h\nu_F \rightarrow S_{1,S}$
$S_{1,S} \rightarrow T_{1,S}$
$T_{1,S} + S_{0,A} \rightarrow S_{0,S} + T_{1,A}$
$T_{1,A} + T_{1,A} \rightarrow {}^{1,3,5}[T_1T_1]_A$
${}^{1}[T_1T_1]_A \rightarrow S_{1,A} + S_{0,A}$
$S_{1,A} \rightarrow S_{0,A} + h\nu_{DF}$



A magnetic field can influence the 4th reaction, as it splits the energy levels of triplet pairs, which can either be in singlet, triplet or quintet state. Whereas in a zero field situation all states are accessible, the number of attainable states in a high field situation differs.

We studied the magnetic field effect on the lifetime and the intensity of different sensitizer/annihilator pairs in different solvents.

In the ZnTPP and Perylene system an additional emission, which does not belong to the normal delayed fluorescence, was observed. This signal shows a viscosity dependence that we analysed and are going to present.

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Hydrogen Atom Self-Exchange Kinetics studied by CW-ESR Line Broadening

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The process of hydrogen atom transfer (HAT) is the simplest kind of proton coupled electron transfer (PCET) which plays an important role in a wide range of chemical, biological and industrial processes. These include reactions related to the interconversion of chemical and electrical energy, water splitting and fuel cells. [1] All state of the art theories predict strong medium effects on the kinetics of such processes [2] and propose an analogy to the Marcus Cross Relation. [3]

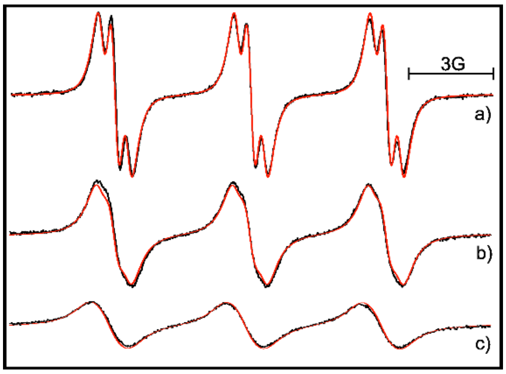

Figure 1. CW-ESR spectra (black) of (a) 0.5 mM PINO in MeCN containing 0.1 M NaClO4 (b) with 5 mM NHPI and (c) with 10 mM NHPI and corresponding simulations (red).

In our current research we successfully reported the first successful CW-ESR line-broadening experiments to determine the kinetics of hydrogen atom self-exchange which is displayed in figure 1. The system N-hydroxyphtalimid/ phtalimide-N-oxyl (NHPI/PINO) was investigated at room temperature in different organic solvents that cover a range of one order of magnitude in dynamic viscosity. [4] These first results were interpreted by a theoretical description derriced from statistical dynamics by Alexandrov and Gold´anskii. They predict a linear dependence of the rate k on the inverse of the mediums dynamic viscosity η, which manifests in the preexponential factor of an Arrhenius type description:

$$k = \frac{A}{\eta}\, e^{\frac{-\Delta G^{*}}{kT}}$$

This type of behaviour was found in a viscosity range of 0.3 – 2.8 Pa s. [5]

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Online monitoring of metal dissolution during anodisation of valve metals

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Valve metals are non-noble metals which are spontaneously reacting with water or oxygen forming dense oxide layers on their surface. These thin passive layers are protecting the metals from further corrosion. The thickness of the passive layers can be artificially increased for improved corrosion and wear resistance using an electrochemical process called anodisation. It is commonly accepted that the oxide growth during anodisation occurs via ion transport through the oxide film under high field conditions.

Many aspects of the oxide growth process during anodisation of valve metals have been investigated in the past. The most widely used model for description of the oxide growth mechanism during anodisation is the high field model [1]. One parameter that cannot be described by the high field model or any other existing model is the metal dissolution during oxide growth. Until now the metal dissolution during anodisation of valve metals has also never been experimentally observed or quantified. To investigate this phenomenon a flow-type scanning droplet cell microscope (FT-SDCM) [2] which is directly coupled to inductively coupled plasma mass spectrometry (ICP-MS) [3] was used. Using this technique we investigated the time and potential dependent metal dissolution during anodisation.

During all experiments an overshoot in metal dissolution was observed during the initial stage of oxide growth. After the initial oxide growth the dissolution rate stabilized into a constant plateau (stationary dissolution) for all investigated materials. A constant increase of the overall amount of dissolved metal was observed when increasing the anodisation potential.

Additionally, a direct potential - independent proportionality between the amount of charge carriers crossing the electrolyte-oxide interface and the amount of dissolved metal during anodisation was observed. The observed dissolution rates were highest for Ti and lowest for Ta under all investigated conditions.

To better understand the observed dissolution behaviour electrochemical impedance spectroscopy was performed under oxide formation conditions for each investigated material. Significant differences in film resistance depending on the applied potential were found and could be used to rationalise the observed dissolution behaviour.

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µ-electrodes for measuring pH-value and chloride concentration in extraordinary surroundings

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To improve stability of metal sheets, they are often coated with different kinds of alloys. Additionally, organic coatings are used to protect steel components from atmospheric corrosion and give them long term stability. Different ways of de-adhesion of organic coatings of a metal substrate are known like cathodic or anodic delamination, filliform corrosion and blister formation. Ongoing processes in these blisters are very interesting and also diffusion of certain anions plays a main role. Changing of pH during a corrosion process often gives an evidence for formation of precipitates. In an alkaline pH-region hydroxide ions are consumed during film formation, which shifts the pH-value to more acidic values. Ion selective electrodes, more in detail pH-sensitive microelectrodes, are used to test pH-changes over certain time periods. Chloride often plays a key role for starting of corrosion mechanism and µ-chloride sensitive electrodes gives the chance to investigate chloride concentration in very small electrolyte volumes and in extraordinary surroundings like in a formed blister.

Different measuring ways are possible, like dotting of the blisters, coming from the backside of the sample or removing electrolyte by a specially designed sucking system (Figure 1). More information can be gained by directly inserting microelectrodes into the formed blisters by sealing the blisters with wax. The free metal surface in a blister acts as working electrode. All kind of electrochemical measurements are possible, like for example CV, OCP and even electrochemical impedance measurements (EIS). If the area of the free metal is well known even thickness of the formed corrosion products can be calculated.

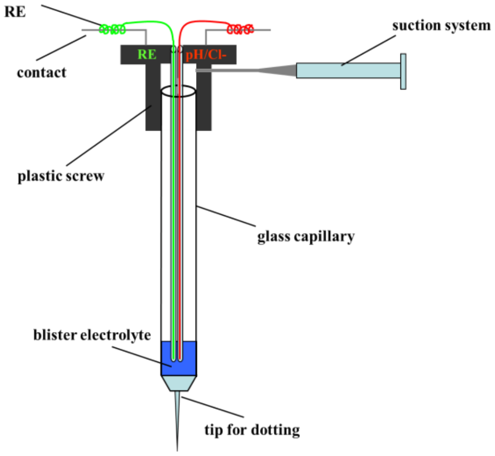

Figure 1 Sketch of the dotting system

POSTER

Mass and charge transport properties of $La_{0.9}Ca_{0.1}FeO_{3-\delta}$

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Mixed ionic-electronic conducting perovskites from the series (La,Sr)(Co,Fe)$O_{3-\delta}$ have a wide range of applications, for example as cathodes for solid oxide fuel cells (SOFCs), gas sensors or catalysts. Unfortunately, the long-term stability of these materials is insufficient. Thermodynamic considerations guide to the conclusion that the replacement of Sr with Ca and of Co with Fe will result in more stable compounds. Furthermore, only a few studies on the mass and charge transport properties of (La,Ca)$FeO_{3-\delta}$ are found in the literature. By now, no data on the oxygen exchange kinetics of these materials are available. In the present work, the composition $La_{0.9}Ca_{0.1}FeO_{3-\delta}$ (LCF91) was synthesized via a glycine-nitrate process. XRD measurements and Rietveld analysis showed LCF91 as the main phase and a minor amount of brownmillerite $Ca_2Fe_2O_5$ as secondary phase. The electronic conductivity and the oxygen exchange kinetics of LCF91 were determined as functions of oxygen partial pressure ($1\text{x}10^{-3} \leq pO_2/\text{bar} \leq 0.1$) and temperature ($600 \leq T/°C \leq 800$). In-situ dc-conductivity relaxation experiments revealed the chemical surface exchange coefficient k_{chem} and the chemical diffusion coefficient of oxygen D_{chem}. High values of $k_{chem}=9\text{x}10^{-4}$ cm s^{-1} and $D_{chem}=7\text{x}10^{-6}$ cm^2 s^{-1} were obtained at 800°C and $pO_2=0.01$ bar. The activation energies for k_{chem} and D_{chem} were in the range of $33 \leq E_a/\text{kJ mol}^{-1} \leq 43$ and $61 \leq E_a/\text{kJ mol}^{-1} \leq 67$, respectively. To obtain the thermodynamic factor of oxygen and to estimate the self-diffusion coefficients of oxygen, data on the oxygen nonstoichiometry of LCF91 from the literature were utilised [1]. In addition, the ionic conductivity of LCF91 was calculated via the Nernst-Einstein relation.

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Complex Sulfur Chemistry on Cu and Cu/O Surfaces

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Sulfur dioxide is still one of the major air pollutants despite the industrial clean-up in the 1980s. Thus the interaction of S and SO_x with surfaces remains a significant environmental problem. Copper is an important catalyst in desulfurization prozesses, a major constituent of cultural artifacts and an electrode material. Therefore, the surface reactions of Cu with S and SO_x are of particular interest. In the present study we have investigated the adsorption of pure sulfur and the reaction with oxygen on a Cu(110) surface by scanning tunneling microscopy (STM).

A surprisingly complex pattern of reactions is found including the adsorption of atomic sulfur, the formation and migration of Cu/S clusters and the growth of polymer-like structures, which is catalyzed by the presence of oxygen. The reaction products observed by STM are interpreted in the light of DFT calculations. The results cast new light on the catalytic processes involved, i.e. the important role of shape changes and compositional variation under reaction conditions.

Cobalt-nickel material libraries fabricated by electrodeposition in the presence of various additives

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Cobalt-nickel electrodeposition can be characterised as an anomalous co-deposition system, due to the fact, that cobalt is deposited preferentially under most plating conditions [1]. A modified Hull cell made of acrylonitrile butadiene styrene (ABS) was constructed by 3D printing. The inclined electrodes in the Hull cell allow the establishment of a current density gradient, which leads to electrodeposition of a cobalt-nickel coating with a composition gradient. Different additives (glycine, trisodium citrate, tetrasodium pyrophosphate, tartaric acid and malic acid) in the electrolyte solution were evaluated in terms of their effects on the properties and composition of the cobalt-nickel samples.

Especially glycine and trisoidium citrate showed positive effects on the appearance and uniformity of the cobalt-nickel coatings, therefore these samples were further investigated by scanning droplet cell microscopy (SDCM) concerning their electrocatalytic activity for non-enzymatic sensing of glucose [2].

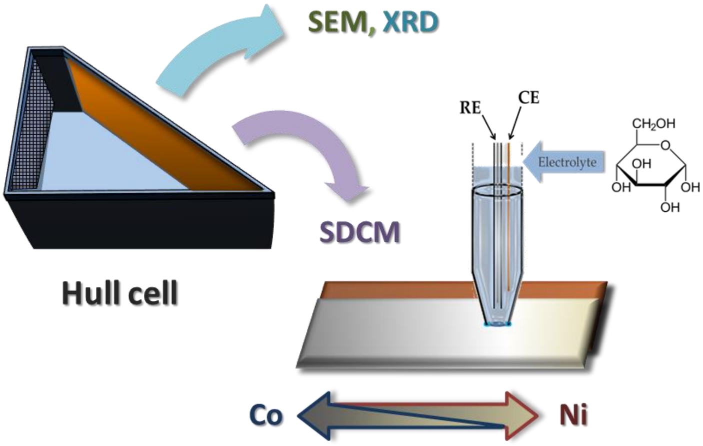

Figure 1: Electrodeposition of cobalt-nickel material libraries using a Hull cell and further characterization including glucose sensing experiments by means of SDCM.

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Al-doped ZnO as Current Collector in Ceria based Anodes for Solid Oxide Fuel Cells (SOFCs): Preparation, Stability and Electrochemical Properties

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Solid oxide fuel cells (SOFCs) are highly efficient electrochemical energy conversion systems. Fuel reduction takes place at the anode which is usually based on a composite of Ni (for electron conduction and steam reforming) and the electrolyte (usually yttria stabilized zirconia for ion conduction). The electrochemical reaction is believed to take place at three phase boundaries (TPB). An extension of the reaction zone is possible when using mixed conducting oxides. Such oxides – when used as single phase anodes – would also no longer suffer from the known redox cycle instability of Ni. Under reducing conditions, mixed conducting oxides are often excellent ion conductors, but suffer from a reduced electron conduction. A possible solution is the use of a second, highly electronically conducting phase in the oxide anode.

In this contribution, the applicability of Al-doped ZnO (AZO) is investigated for the purpose of electron conduction in mixed conducting oxide anodes. AZO thin films were prepared by pulsed laser deposition at room temperature. Chemical and structural stability on the electrolyte was analyzed as well as electrical conductivity by 4 point van-der-Pauw measurements. The conductivity turns out to be sufficiently high for a use in SOFCS anodes. Thus, Al-doped ZnO was employed as an electronic current collector in model-type ceria-based anodes. Electrochemical tests of these model thin film anodes were performed successfully and revealed the possibilities and limits of AZO current collectors in SOFC anodes.

Impact of interfacial changes on colloidal ZnO nanoparticle properties: spectroscopic studies on particulate model systems

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Despite the fact that surfaces and interfaces of colloidal ZnO nanoparticle systems have a key influence on their optoelectronic properties, their chemical and physical properties have remained unspecified for most cases. Considering that minor changes in colloidal processing correspond to substantial changes in the interfacial properties, a particularly unsatisfactory situation is created where an increasing number of publications report discrepant results for one and the same well-established nanomaterial. [1] In this contribution we will discuss for vapor phase grown ZnO nanoparticles how defect related spectroscopic fingerprints such as photoluminescence emission from oxygen interstitials [2] or paramagnetic oxygen vacancies in the surface and subsurface region can be used as probes for interfacial changes in the colloidal system. We will focus on the interplay between particle interface condition and spectroscopic properties for originally dry nanoparticle systems that became converted into colloids by step wise water addition via the gas phase. [3] Aiming at a more consistent and robust assessment of ZnO nanoparticle properties in aqueous dispersions this work also explores the spectroscopic response of nanoparticle interfaces to small molecules such as oxygen and formic acid.

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Time-Resolved Fluorescence HPLC Detection Using Semiconductor Light Sources: Principles and Applications

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Simultaneous static and time-resolved fluorescence detection in HPLC systems using time-correlated single photon counting and modulation techniques is a very recent topic in analytical and physical chemistry. Whereas most commercial systems use simple intensity detection in fluorescence systems or fluorescence spectra with very low sensitivity, here real-time time-resolved fluorescence counting with on-the-fly data evaluation and display like a typical chromatogram are applied [1]. Both results are independent and characteristic for the fluorescent analytes and exhibit equal sensitivity. For ns resolution, modern semiconductor light sources are used. Modern electronics allow a setup in typical HPLC component size and the measuring procedure requires no adjustment or calibration for the chromatogram. Rapid modification for new applications is possible due to the flexible modular design. The application is patent pending [2].

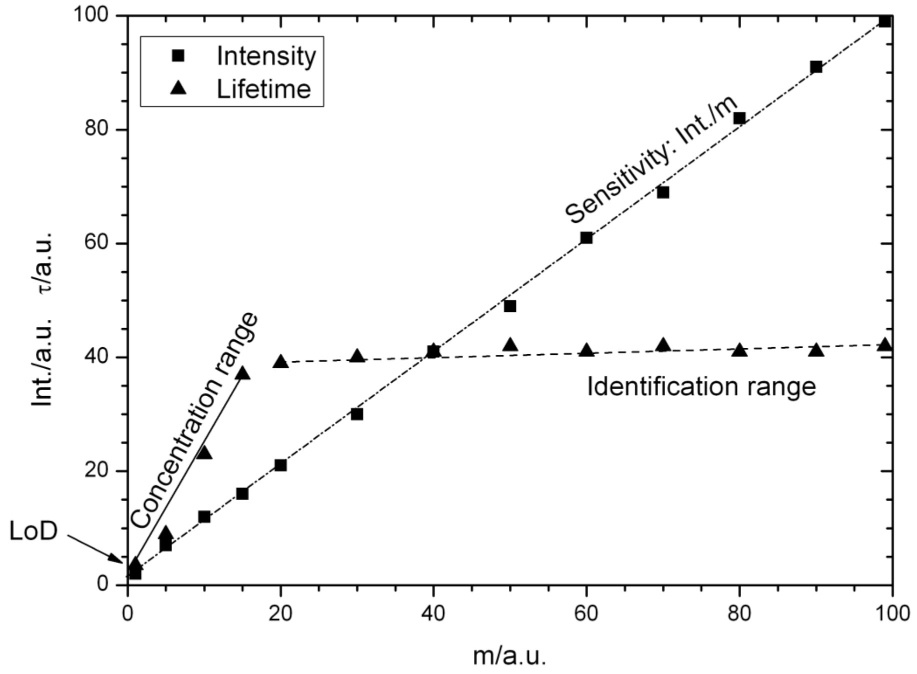

Figure 1: Intensity and lifetime trace in chromatographic fluorescence detection.

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Paramagnetic defects and adsorbates at aqueous interfaces: a comparative study on TiO_2 and ZnO nanoparticle systems

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Properties of semiconducting metal oxide nanoparticle systems are determined by nature and abundance of point defects. Their characterization and manipulation is challenging and requires the comprehensive discussion of the entire materials' situation. Electron paramagnetic resonance (EPR) spectroscopy is an excellent technique to investigate paramagnetic defects and, in particular, to characterize the electronic structure of electron centers in metal oxide particle systems such as TiO_2 or ZnO [1,2].

ZnO and TiO_2 nanoparticle systems were prepared by metal-organic chemical vapor synthesis and characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD) and UV-Vis spectroscopy. Different procedures for defect generation, e.g. annealing under high vacuum conditions ($p < 10^{-6}$ mbar) or in controlled gas atmospheres (O_2, H_2) were applied and the paramagnetic properties of resulting particle powders were described. As a result of electron transfer reactions between reactive defects present on non-stoichiometric and defective metal oxide samples and molecular oxygen, superoxide species (O_2^-) are generated and utilized as paramagnetic surface probes. We tracked these processes with EPR spectroscopy and explored the impact of adsorptive water condensation in detail. The comparison of dry particle powders with colloidal particle systems underlines the critical importance of the surrounding continuums phase on the electronic properties of ZnO and TiO_2 nanoparticle systems and constitutes an important step to translate results from studies on model systems to the more realistic situation present on more complex materials systems. [2]

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Mircrocontanct impedance spectroscopy on Li- and Na-ion conducting solid electrolytes

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NASICON-type structured materials (**Na S**uper-**I**onic **Con**ductor, with space group $R\bar{3}c$) are promising solid electrolytes with total ion conductivity of about 10^{-4} to ~10^{-2} S cm^{-1}. [1]
Due to the very high bulk Li^+/Na^+ conductivity in this class of materials the corresponding arc in the complex impedance plane response in the high MHz range and can be only resolved at very low temperatures. [2,3] Determination of the ionic bulk conductivity is strongly simplified when large sized single crystals are available; as for polycrystalline pellets macroscopic electrodes may be used in electrical measurements and electrical properties can be determined without being restricted by the need for a proper separation of partly large grain boundary resistances. Here, a modification of conventional impedance spectroscopy comes into play: microelectrodes deposited on large single crystals or grains of a polycrystalline sample still allow impedance measurements which are unaffected by the resistivity of grain boundaries. [4-6] This is caused by the spatially very constricted current distribution between neighboring microelectrodes. However, so far this technique of local impedance measurements was rarely applied to determine bulk Li^+/Na^+ conductivities.
In this contribution microcontact impedance spectroscopy was applied to small $Li_{1+x}Al_xTi_{2-x}(PO_4)_3$, and $Na_3Sc(PO_4)_3$ single crystals to exactly determine the ionic bulk conductivity at room temperature. This enables a precise analysis on transport properties and a better understanding of the structure–property relationship of Li^+/Na^+-based NASICON-structured materials.

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Determination of hydrogen diffusion coefficients in metals using (scanning) Kelvin probe

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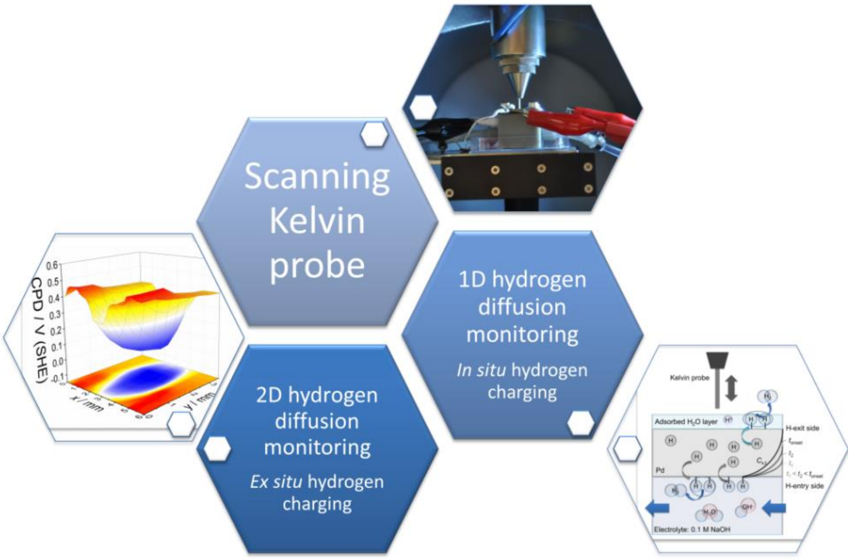
Determination of hydrogen diffusion coefficient in metals and alloys, like steel, are essential in investigations related to hydrogen embrittlement. The hydrogen diffusion coefficient enables characterization of hydrogen mobility within a material and is strongly influenced by the material's microstructure: Metal lattice defects like grain boundaries, phase boundaries, inclusions etc. can act as traps for hydrogen causing a decrease of the apparent diffusion coefficient. Kelvin probe microscopy represents a novel technique allowing visualization of hydrogen within a metal by monitoring its contact potential difference (CPD), which is lowered in the presence of hydrogen [1]. Different methods to determine the hydrogen diffusion coefficient based on the Kelvin probe technique are presented. As deformation drastically affects the microstructure, the influence of cold-rolling on the hydrogen mobility within a ferritic steel sheet was evaluated by performing a 2D analysis of hydrogen diffusion within a deformed sample [2]. Furthermore, approaches to study hydrogen trapping and distinguish the apparent diffusion coefficient from the real, only diffusion related coefficient, are presented [3-5].



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Porphyrin adsorption studies on MgO nanoparticles

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The technological exploitation of porphyrin functionalized oxide nanostructures and their successful implementation in macroscopic, functional devices still requires a better understanding of the microscopic interaction between porphyrins and inorganic components [1, 2]. We prepared MgO nanocubes by chemical vapor synthesis and larger MgO cubes by magnesium combustion in air and subsequently annealed and oxidized them under high vacuum conditions to achieve clean and dehydroxylated surfaces. The functionalization of these well-defined particle systems with free-base porphyrin (2H-tetraphenylporphyrin, 2HTPP) was studied by DR-UV/Vis and photo-luminescence emission spectroscopy. We followed two different functionalization protocols such as a) porphyrin adsorption on nanoparticle powders at high vacuum conditions and b) porphyrin adsorption out of colloidal toluene based nanoparticle dispersions. For both adsorption protocols we observed ion exchange reactions between the two aminic protons of the porphyrin molecule and Mg^{2+} ions from the surface and the persistent adsorption of MgTPP at the oxide surface [3, 4]. From studies at high vacuum conditions (protocol a) we learned that low-coordinated surface cations like corners, edges or step-edges serve as reactive sites for porphyrin metalation. The impact of interface type, composition and temperature on the reactive adsorption of porphyrins will be discussed.

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Self-organized TiO_2 nanotubes as anode material for Li-ion intercalation - an XPS and electrochemical impedance spectroscopy study

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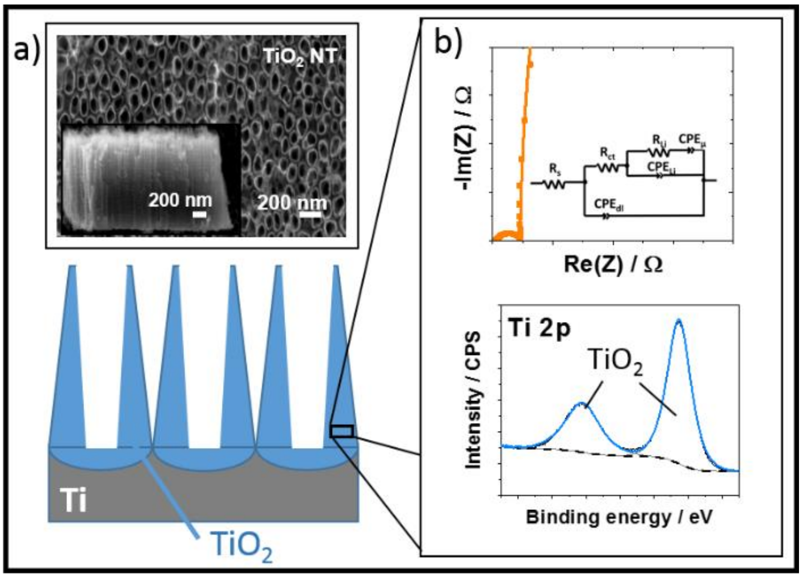

Research on nanostructured intercalation compounds as anode materials in Li-ion batteries revealed that their morphology has advantages in terms of improved rate capability and specific capacity. Titania is especially interesting due to its cost effectiveness, safety and environmental compatibility.

Model composite electrodes of anodically grown, self-organized TiO_2 nanotubes [1,2] are produced and studied by X-ray photoelectron spectroscopy (XPS) and electrochemical impedance spectroscopy (EIS) to gain further insight and fundamental understanding of lithiation/ delithiation characteristics and surface chemistry.

Preferential crystallographic orientation in anatase TiO_2 nanotubes is found to influence the lithiation behavior.

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