Operando surface science – Atomistic insights into electrified solid/liquid interfaces

708. WE-Heraeus-Seminar

9 – 13 December 2019
at the Physikzentrum Bad Honnef/Germany

WILHELM UND ELSE
HERAEUS-STIFTUNG

Introduction

The Wilhelm und Else Heraeus-Stiftung is a private foundation that supports research and education in science with an emphasis on physics. It is recognized as Germany's most important private institution funding physics. Some of the activities of the foundation are carried out in close cooperation with the German Physical Society (Deutsche Physikalische Gesellschaft). For detailed information see https://www.we-heraeus-stiftung.de

Aims and scope of the 708. WE-Heraeus-Seminar:

The importance of solid/liquid interfaces for technological applications, e.g., in the fields of catalysis, energy conversion and storage or bio- and geophysical research has led to strong research initiatives to bridge the pressure and material gaps between classical surface science UHV studies and realistic working conditions. While the development of new experimental and simulation in-situ approaches have resulted in an enhanced understanding particularly of water at various surfaces ranging from metals to metal-chalcogenides to semiconductors, the interplay between dynamic operando conditions – including charge transfer and potential gradients – and interfacial atomic structure and reactivity have remained unresolved. Building up an atomistic picture of the complex interrelation between charge transfer, chemical conversion and interfacial potential in the presence of a solvent is one of the most imminent challenges that experimentalists and theoreticians working with solid/liquid interfaces are facing.

The WE-Heraeus seminar "Operando surface science – Atomistic insights into electrified solid/liquid interfaces" provides a discussion platform to assess the current state of art of the research on the dynamics of electrified interfaces with nanoscopic detail. As electrified solid/liquid interfaces play a key role in various disciplines, surface scientists with backgrounds in biology, chemistry and physics alike are welcome to exchange their complementary knowledge on the topic and pinpoint the challenges and opportunities that this research field entails. The seminar evolves around four subtopics, spanning from fundamental methodological and conceptual approaches to important technological applications in catalysis and energy conversion and storage as well as to interfaces of bio- or geophysical relevance.

Scientific Organizers:

Dr. Katrin F. Domke	MPI for Polymer Research, Germany E-mail: domke@mpip-mainz.mpg.de
Prof. Julia Kunze-Liebhäuser	Universität Innsbruck, Austria E-mail: julia.kunze@uibk.ac.at
Prof. Marialore Sulpizi	Universität Mainz, Germany E-mail: sulpizi@uni-mainz.de

Program

Program

Sunday, 8 December 2019

16:00 – 19:00	Registration	
18:00	*BUFFET SUPPER and get-together*	
19:15 – 20:15	R. Kramer Campen	**Towards a femtosecond resolved view of the hydrogen evolution reaction on Au and Pt**

Monday, 9 December 2019

08:00	*BREAKFAST*	
08:45 – 09:00	Scientific organizers	**Welcome words**
09:00 – 10:00	Ulrike Diebold	**Bridging ultrahigh vacuum surface science and liquid water: First steps and future opportunities**
10:00 – 10:45	Mira Todorova	**Predicting atomic structure and chemical reactions at solid-liquid interfaces by first principles**
10:45 – 11:15	*COFFEE BREAK*	
11:15 – 12:00	Fabiola Dominguez Flores	**Interaction of ions across carbon nanotubes**
12:00 – 12:45	Karla Banjac	**Emergence of potential-controlled Cu nanocubes under *operando* CO2 reduction**
12:45	*LUNCH / networking*	

Program

Monday, 9 December 2019

14:45 – 15:30	Marc Koper	**Electrochemical surface science of platinum**
15:30 – 16:15	Henrik Kristoffersen	**Modeling the liquid water-Pt(111) interface**
16:15 – 16:45	*COFFEE BREAK*	
16:45 – 17:30	Leon Jacobse	**Operando surface structure determination of Pt(111) under realistic oxygen reduction conditions using high-energy surface X-ray diffraction**
17:30-18:15	Jinggang Lan	**Ionization of water as an effect of quantum delocalization at aqueous electrode interfaces**
18:30	*DINNER*	
19:30	**Posterflash (1 min.) and postersession (even numbers)**	

Program

Tuesday, 10 December, 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Aliaksandr Bandarenka	**Why electrolytes can significantly control the catalytic activity. An experimental approach**
09:45 – 10:30	Jan Rossmeisl	**Electrocatalysis at the atomic scale**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Kristina Tschulik	**Electrochemical studies of nanoparticle observed with dark-field microscopy**
11:45 – 12:30	Karsten Reuter	**On the active site model in computational catalyst screening**
12:30 – 12:40	*Conference Photo (in the front of the lecture hall)*	
12:40	*LUNCH / networking*	
14:30	**Excursion: Wine tasting at the winery Broel**	
18:15	*DINNER*	
19:15 – 20:15	Daniel A. Scherson	**Electrode stimulation**

Program

Wednesday, 11 December, 2019

08:00	*BREAKFAST*	
08:45 – 09:45	Elena Savinova	***Operando* FTIR investigation of borohydride electrooxidation on nickel**
09:45 – 10:30	Stijn Mertens	**Electrochemical orbital imaging**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Markus Valtiner	**Angstrom-resolved characterization of electrochemical interfaces in real time during polarization**
11:45 – 12:30	Jun Cheng	**Ab initio modeling of electric double layers on single crystal electrodes**
12:30	*LUNCH / networking*	
14:45 – 15:30	Clotilde Cucinotta	**Improving the design of electrochemical materials and devices with theory and modelling**
15:30 – 16:15	Bridget Murphy	**Investigating atomic scale structure and kinetics of liquid metal–electrolyte interfaces**
16:15 – 16:45	*COFFEE BREAK*	
16:45 – 17:30	Vivek Sinha	**Towards multiscale modelling of the semiconductor electrolyte interface for oxygen evolution reaction**
17:30-18:15	Celine Merlet	**Exploring the properties of concentrated electrolyte / electrode interfaces in supercapacitors using idealised coarse-grained models**
18:30	*DINNER*	
19:30	**Posterflash (1 min.) and postersession (odd numbers)**	

Program

Thursday, 12 December, 2019

08:00	*BREAKFAST*	
08:45 – 09:00	**Poster awards**	
09:00 – 09:45	Marcella Iannuzzi	**Interfaces by ab initio molecular dynamics**
09:45 – 10:30	Olga Sambalova	**Magneto-optical Kerr effect set-up for operando probing of electrode surfaces**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Izabella Brand	**Investigating molecular scale changes at the electrode-electrolyte interface using polarization modulation infrared reflection absorption spectroscopy**
11:45 – 12:30	David Fermin	**Oxygen electrocatalysis at transition metal oxide nanostructures**
12:30	*LUNCH / networking*	
14:45 – 16:15	**Round table**	**Challenges and opportunities of solid/liquid operando surface science:method development, key applications and interdisciplinarity**
16:15 – 16:45	*COFFEE BREAK*	
16:45 – 17:30	Ismael Pérez Díez	**Mapping charge transport at electrode/liquid interfaces: from oxides films to biomolecules**
17:30-18:15	Ali Ismael	**Tuning the thermoelectric performance of aromatic molecules**
18:30	*HERAEUS DINNER* *(social event with cold & warm buffet with complimentary drinks)*	

Program

Friday, 13 December, 2019

08:00	*BREAKFAST*	
09:00 – 09:45	Harald Oberhofer	**Parametrizing implicit solvation models**
09:45 – 10:30	Manon Bertram	**Adsorbate properties on atomically-defined Co_3O_4(111) in UHV and the electrochemical environment**
10:30 – 11:00	*COFFEE BREAK*	
11:00 – 11:45	Andreas Erbe	**Probing water and surface oxides on electrodes by coupling in situ spectroscopic techniques**
11:45– 12:20	**Brainstorming**	
12:20 – 12:30	Scientific organizers	**Closing words**
12:30	*LUNCH*	

End of the seminar and departure

NO DINNER for participants leaving on Saturday morning

Posters

Posters

1	Yasmine Al-Hamdani Marcella Iannuzzi	**Computational materials science at the University of Zurich**
2	Albert C. Aragonès	**New spectroscopical tools for molecular circuitry**
3	Andrea Auer	**In-situ electrochemical STM imaging of Cu single crystal electrocatalysts**
4	Eric Borguet	**Impact of ions on structure and dynamics at charged solid - aqueous interfaces**
5	Angelika Demling	**Superoxide formation near DMSO/Cu(111) interfaces**
6	Katharina Doblhoff-Dier	**The influence of acetophenone adsorption on hydrogen underpotential deposition on Pt/Pd ML**
7	Dominik Dworschak	**Photochemical stability of polar and non-polar ZnO single crystal facettes during electrochemical polarization**
8	Johanna Eichhorn	**Impact of surface adsorbates on charge carrier transport in metal-oxides for solar water splitting**
9	Albert Engstfeld	**Disentangling hydrogen formation and anion coad-/ desorption phenomena on metal surfaces with electrochemical mass spectrometry**
10	Kai Exner	**A unifying material-screening approach**
11	Annette Foelske	**X-Ray photoelectron spectroscopy of ionic liquids – towards understanding of charging phenomena**

Posters

12	Giovanni Giuzio	**Determining redox-dependent Cu-ligand chelating behaviour in a single metallo-protein**
13	Akansha Goyal	**Towards the activity descriptor for HER at alkaline pH**
14	Francesco Greco	**Asymmetric potential screening at electrode/ionic liquid interfaces studied by *in situ* X-ray photoelectron spectroscopy**
15	Richard Haid	**In-situ identification of active sites using electrochemical scanning tunneling microscopy**
16	Haisheng Han	**Surface charge, surface hydration, and mineral flotation with vibrational sum-frequency generation spectroscopy**
17	Florian Hausen	**SEI formation vs. Lithiation: Insights from mechanical property measurements of anode materials by in-situ atomic force microscopy**
18	Hendrik Heenen	**Electrochemical CO_2 reduction from first principles: Electric field effects at the electrochemical interface**
19	Maren-Kathrin Heubach	**Sodium Deposition from [MPPI][TFSI] on Au(111): Initial Stages of the Deposition using *in-situ* STM**
20	Degenhart Hochfilzer	**Electrochemical characterisation of Cu model catalysts**
21	Nicolas Hörmann	**Ab-initio simulations of electrified interfaces under realistic conditions**

Posters

22	Nan Jiang	**Probing intermolecular and molecule-substrate interactions at angstrom scale via scanning tunneling microscopy and tip-enhanced Raman spectroscopy**
23	Franziska Karcher	**Microcalorimetric investigation of silver deposition from silver cyanide complexes**
24	Regina Kluge	**Identification of active electrocatalytic sites using electrochemical scanning tunneling microscopy**
25	Ritesh Kumar	**C_2N/WS_2 van der Waals Type-II heterostructure as a promising water splitting photocatalyst**
26	Haobo Li	**Ab initio thermodynamics insight into the surface structure of transition metal carbides in aqueous electrolyte**
27	Florian Maier	**Direct characterization of ionic liquid/graphene electrode interface by X-ray photoelectron spectroscopy**
28	Sabine Matysik	**Adsorption, decomposition and surface dynamics of formic acid on Cu{531}**
29	Jerome Mayer	**On the stability of gold electrodes in ionic liquids at very negative potentials**
30	Robert Meißner	**Molecular dynamics simulations of curved graphitic electrodes in supercapacitors**
31	Giacomo Melani	**From structural fluctuations to vibrational signatures of water at α-Al_2O_3(0001) Surface: Insights from ab initio molecular dynamics**

Posters

32	Daniel Ohm	**Electrochemical tip-enhanced Raman spectroscopy: Nanoscale reactivity mapping with chemical specificity**
33	Kasinath Ojha	**Complexity in the double layer of Pt(111)-aqueous electrolyte interface**
34	Pablo Ordejón	**Approaching electrochemistry with TranSIESTA**
35	Marco Schönig	**Entropy change during HER on Pt**
36	Georg H. Simon	***In situ* atomic force microscopy of copper surfaces for CO_2 electroreduction**
37	Corinna Stumm	**In-situ STM Studies of CoO_x nanoislands on Au(111): Potential dependent mobility and stability**
38	Yan Sun	**Towards ‘seeing’ the surfaces of oxide thin films using EC-STM**
39	Sudarsan Surendralal	**First-principles modeling of metal dissolution at Mg/H_2O interfaces**
40	Hsin-Yi Wang	**Constructing an *in-situ* electrochemical cell for soft X-ray study on CO_2 reduction over Cu**
41	Eva-Maria Wernig	**Electroreduction of water and CO_2: competition or synergism on Mo_2C film electrodes?**
42	Tim Würger	**A first principles analysis of the charge transfer in Magnesium corrosion**

Posters

43	Azade Yazdan Yar	**Electrified Au (111)-water interface studied by ab initio molecular dynamics**
44	Suhyun Yoo	**Selective stabilization of polar oxide surfaces in an electrochemical environment**
45	Taiki Yoshioka	**In situ AFM observation of Cu electrodeposition and dissolution on Au single crystal**
46	Jia-Xin Zhu	**Effects of adsorbates on Pt (100)**
47	Gregor Zwaschka	**Imaging of active sites for the oxygen evolution reaction on gold electrodes *operando***

Abstracts of Talks

(in chronological order)

Towards a Femtosecond Resolved View of the Hydrogen Evolution Reaction on Au and Pt

Yujin Tong[1], Gregor Zwaschka[1], François Lapointe[1], and R. Kramer Campen[1,2]

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[2] *Faculty of Physics, University of Duisburg-Essen, Lotharstraße 1, 47057 Duisburg, Germany*

Electrolytic water splitting, driven by a sustainable source of energy, is perhaps the most straightforward way of realizing a global energy economy based on hydrogen. Maximizing the efficiency of such devices requires understanding the *mechanism* of both halves of water splitting: oxygen and hydrogen evolution. While hydrogen evolution is the simpler half reaction experimental insight into even its mechanism on relatively simple metal electrodes has proven extremely challenging to obtain. This challenge is due to, at least, two factors: (i) an absence of analytical tools capable of fully describing molecular scale structure at the metal electrode/aqueous interface and (ii) the impossibility of directly inferring mechanism from steady-state measurements. We address challenge (i) by characterizing the electrode/electrolyte interface using the interface-specific, laser-based technique vibrationally resonant sum frequency generation spectroscopy and a novel, two-color, resonant photovoltage spectroscopy. We address the 'steady-state' limitation, challenge (ii), by perturbing electrode bias on femtosecond timescales using optical pulses and then characterizing interfacial structure, with femtosecond time resolution, as the voltage pulse dissipates.

On gold this approach allows us to track in real time the transfer of an electron from the metal to water, observe its ultrafast trapping (140 fs), localization (820 fs), characterize its resulting solvation structure and observe how it subsequently drives chemistry. On Pt(110) and (111), at steady-state, we have recently performed operando characterization of under potential deposited hydrogen and the the interfacial excess proton using VSFG spectroscopy. These observations offer a novel perspective on the electrolyte dependence of HER rates on Pt and, in particular, suggest a role for the interfacial solvated proton in the HER on Pt(111) absent on (110). In the perturbation approach described above we also examine femtosecond induced photovoltages on several different Pt electrodes [**?**]. This observable is a probe of ease of charge transfer on femtosecond timescales, *i.e.* a femtosecond resolved electrochemical charge transfer resistance. Intriguingly we find that, given appropriate electrolyte structure, relative ease of charge transfer on femtosecond timescales correlates with activity for H_2 evolution between Pt surfaces.

References

G Zwaschka, Y Tong, M Wolf, and R K Campen, *ChemElectroChem*, 6:2675–2682 (2019)

Bridging Ultrahigh Vacuum Surface Science and Liquid Water:

First Steps and Future Opportunities

Ulrike Diebold

[1]*Institute of Applied Physics, Vienna, Austria*

Transition metal oxides are promising materials for photo- and electrocatalysis. For a molecular-scale understanding of the underlying mechanisms and processes, experiments on well-characterized samples are necessary, i.e., specific facets of single crystals with a known composition, geometry and defect structure. Here the advanced methods of surface science, particularly Scanning Probe Microscopy (SPM) with atomic resolution, Thermally Programmed Desorption (TPD) with accurately-determined coverages, and X-ray Photoelectron Spectroscopy (XPS) with high resolution, together with first-principles computations based on Density Functional Theory (DFT) give unique insights. Bridging the gap to a (photo-) electrochemical environment is challenging, however.

In the talk we will address a first question, namely whether the atomic structure of oxide surfaces – once it is well-established in Ultrahigh Vacuum (UHV) – survives the exposure to liquid water. We use a novel apparatus that allows us to expose UHV-prepared samples to liquid water without exposure to air [1]. We find that the $TiO_2(110)$ surface maintains its (1x1) termination and that a (2x1) superstructure that is typically observed after water exposure in air stems from an ordered layer of carboxylates [2]. In contrast, the $TiO_2(011)$-2x1 reconstruction is lifted upon exposure to liquid water, and the surface is fully hydroxylated [3]. The $(\sqrt{2}\times\sqrt{2})R45°$ reconstruction [4] of the $Fe_3O_4(001)$ surface is also lifted in water, but the change proceeds slowly together with the growth of an oxy-hydroxide phase with a self-limiting coverage of 0.4 monolayers [5]. Fe_3O_4 was also tested for OER in alkaline conditions, and found to be stable at the nanoscopic scale, with a facet-dependent reactivity [6].

References

[1] J. Balajka, et al., Rev. Sci. Instr. **89,** 083906–6 (2018).

[2] J. Balajka, et al., Science **361,** 786–789 (2018). doi:10.1126/science.aat6752.

[3] J. Balajka, et al., J. Phys. Chem. C. **121,** 26424–26431 (2017).

[4] R. Bliem, et al., Science. **346,** 1212–1215 (2014).

[5] F. Kraushofer, et al., J. Chem. Phys., in press

[6] M. Müllner, et al., J. Phys. Chem. C **123**, 8304–8311 (2018).

Predicting atomic structure and chemical reactions at solid-liquid interfaces by first principles

M. Todorova, S. Yoo, S. Surendralal and J. Neugebauer
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Electrochemistry offers a direct route to tune materials properties, e.g. to address practical problems such as water electrolysis and batteries, electro-catalysis, photo-catalytic water splitting or corrosion. Utilizing these possibilities requires knowledge of the surface structures that form when a solid is immersed in an aqueous electrolyte, the identification of relevant mechanisms at the microscale and understanding how they influence properties at the macroscale.

Density functional theory (DFT) calculations are able to resolve processes at the microscopic scale and have proven immensely successful in providing insight into various areas of materials science, complementing experimental information. Electrochemical systems are, however, particularly challenging for DFT modelling, since they encompass different classes of materials, each imposing different requirements on the investigational approaches, and the necessity to perform DFT calculations under conditions of applied voltage.

In the presentation, it will be discussed how by utilizing DFT calculations to construct surface Pourbaix diagrams for the ZnO(0001)/H_2O system we are able to understand the role the solvent plays in shaping and stabilizing surface reconstructions [1]. Going beyond thermodynamic concepts, our recently developed novel potentiostat scheme [2] enables us to perform ab initio calculations under controlled bias conditions. Its application to Mg provides insights into the mechanisms of Mg corrosion [2], allowing us to solve a 150-year-old problem, which links H-evolution under anodic conditions to Mg dissolution .

References

[1] S. Yoo, M. Todorova and J. Neugebauer, Phys. Rev. Lett. **120**, 066101 (2018)
[2] S. Surendralal, M. Todorova, M. Finnis und J. Neugebauer, Phys. Rev. Lett. **120**, 246801 (2018)

Interaction of ions across carbon nanotubes

F. Dominguez-Flores[1], F. Juarez[1], Elizabeth Santos[1], W. Schmickler[1]

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Carbon nanotubes (CNT) are one of the most promising novel forms of carbon. Because of their high storage capacity for ions, they hold great promises for applications in Li-ion rechargeable batteries and supercapacitors [1]. The interaction of ions across the walls of CNTs is a key factor in the functioning of such devices. In a previous work [2], we discovered an unexpected effective attraction between two Li ions separated by a semiconducting nanotube. This results explained experimental evidence for an attractive interaction between Li-ions in batteries [3,4]. In the present work, we have systematically studied the inter-ionic interactions by changing the nature of the nanotube (semiconducting or conducting), as well as the type of ions. Thus we placed pairs of Li /Li and Li / Cl ions on opposite sides of the wall of a nanotube and investigated their interactions with density functional theory. Li donates an electron to CNTs. The adsorption of a first Li-ion increase the electronic density of states at the Fermi level of the CNT making the adsorption of a second ion more favorable. This effect is stronger for semiconducting (8, 0)CNT, but persists for conducting (5, 5) tubes. In contrast, Cl accepts an electron from the CNTs and forms a chemical bond. This induces an increase of the work function, which again favors the adsorption of a Li-ion on the other side of the wall. The direct Coulomb interaction between ions on opposite sides of the wall is small; the attraction or repulsion is caused by the modification of the electronic properties of the intervening CNT.

References

[1] Vatamanu, J., et al., Increasing Energy Storage in Electrochemical Capacitors with Ionic Liquid Electrolytes and Nanostructured Carbon Electrodes. The Journal of Physical Chemistry Letters, **4**, 2829 (2013).

[2] F. Juarez, F. Dominguez-Flores, A. Goduljan, L. Mohammadzadeh, P. Quaino, E. Santos, and W. Schmickler, Carbon, **139,** 808 (2018).

[3] M. D. Levi, and D. Aurbach, The mechanism of lithium intercalation in graphite film electrodes in aprotic media. Part 1. High resolution slow scan rate cyclic voltammetric studies and modeling, J. Electroanal. Chem. **79,** 421 (1997).

[4] J. S. Filhol, C. Combelled, R. Yazami, and K. L. Doublet, Phase Diagrams with Low Free energy Variation: A Coupled Theory/Experiments Method Applied to Li-Graphite, J. Phys. Chem. C. **112,** 3982(2008).

Emergence of Potential-controlled Cu Nanocubes under *Operando* CO_2 Reduction

K. Banjac, T. H. Phan, Y. Liang, F. Cometto, and M. Lingenfelder.[1]

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The electrochemical reduction of CO_2 (CO_2R) into added-value compounds is a promising pathway towards low-carbon fuels and renewable chemicals. While Cu is the only earth-abundant catalyst capable of CO_2-to-hydrocarbon conversion, its product selectivity is difficult to attain due to the lack of fundamental composition-activity-structure understanding. Only the recent development of *operando* spectroscopy and microscopy techniques has allowed systematic surface science studies of Cu catalysts during CO_2R. Here, we follow surface dynamics of Cu and graphene-protected Cu (G-Cu) surfaces during CO_2R using *operando* electrochemical scanning tunneling microscopy, *operando* electrochemical Raman spectroscopy and *quasi operando* x-ray photoelectron spectroscopy. Our first contribution to this field is the demonstration that both G-Cu and polycrystalline Cu reconstruct to Cu(100) nanocubic features during CO_2R via a potential-driven re-organization of Cu(0) atoms. These results show how Cu reconstructs in operando CO_2R conditions and how the reconstructions can be stabilized by graphene layer. This project is a part of large European effort to build an artificial leaf prototype, able to transform solar irradiation into fuels using CO_2 and water as feedstock (www.aleaf.eu).

Electrochemical surface science of platinum

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Platinum is the most used electrocatalyst in electrochemical energy conversion devices such as fuel cells and electrolysers. In this talk I will highlight the recent work of my group on understanding the surface chemistry of platinum in an aqueous electrolyte, by combining single-crystal electrochemistry, density functional theory calculations, ultra-high-vacuum modeling, in situ spectroscopy and in situ electrochemical scanning tunneling microscopy. I will challenge some existing explanations and interpretations of platinum electrochemistry, and show the sometimes surprising surface disordering of platinum that happens at both positive (anodic) and negative (cathodic) potentials.

Modeling the liquid water-Pt(111) interface

H. H. Kristoffersen

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We have studied the liquid water-Pt(111) interface with constant temperature *ab initio* molecular dynamics (AIMD) to explore the importance of liquid water dynamics on catalytic reactions such as the oxygen reduction reaction in PEM fuel cells. The structure and energetics of hydroxyl formation at the liquid water-Pt(111) interface is found to be significantly different from hydroxyl formation on a bare Pt(111) surface and hydroxyl formation on a Pt(111) surface with a static water layer. We identify 1/12 ML *OH, 5/12 ML *OH and 2/3 ML *OH as particular stable hydroxyl coverages in highly dynamic liquid water environments, which - contrary to static water-hydroxyl models - contain adjacent uncovered Pt sites. Atomic surface oxygen is found to be unstable in the presence of liquid water, in contrast to static atomic level simulations. These results give improved understanding of hydroxide and surface oxide formation in Pt(111) cyclic voltammetry and allow us to draw detailed connections between the electrostatic potential and the interface structure.[1]

Electrochemical reaction rates are also sensitive to interactions between electrolyte cations and adsorbed reaction intermediates, e.g., cation-*OH interactions in the oxygen reduction reaction on platinum. We have calculated the free energy interaction between adsorbed *OH and K^+/Li^+ situated at the liquid water-Pt(111) interface using AIMD and metadynamics. Li^+ stabilizes *OH by 0.1±0.1 eV and K^+ destabilizes *OH by 0.1±0.1 eV, in qualitative agreement with experimental cyclic voltammogram (CV) measurements. In contrast, the internal energy of *OH is stabilized by 0.3 eV and 0.4 eV for Li^+ and K^+, respectively. This demonstrates, that entropy significantly destabilizes cation-*OH interactions and is vital in order to understand even the relative influence of cations at interfaces.

References

[1] H. H. Kristoffersen, T. Vegge, H. A. Hansen, Chem. Sci. **9**, 6912-6921 (2018)

Operando surface structure determination of Pt(111) under realistic oxygen reduction conditions using High-Energy Surface X-Ray Diffraction

Leon Jacobse, Vedran Vonk, Andreas Stierle

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Platinum is the most widely used electrocatalyst driving water-splitting and (the reverse) hydrogen oxidation reactions, which are the processes occurring in electrolysers and fuel cells, respectively. Due to the material costs, it is of crucial importance to maximize the electrode stability. Experiments under static, oxygen-free conditions have provided a detailed description of the degradation of the Pt(111) electrode surface by applying highly oxidizing potentials. In our High-Energy Surface X-Ray Diffraction (HE-SXRD) experiments we have shown that the Pt(111) and Pt(100) surfaces change significantly at potentials above 1.1 V vs RHE. These changes depend on the potential, its scan rate and for how long it is applied. Despite extensive oxidation of the electrode, we did not observe any features indication the formation of an ordered (surface) oxide.

However, it is unclear how this degradation changes in case of a high oxygen chemical potential as during the oxygen reduction reaction. We have developed a Rotating Disk Electrode (RDE) setup that can be mounted on the beamline diffractometer, enabling us to perform operando HE-SXRD experiments. This setup has been used to determine the structure of a Pt(111) while a large current density for oxygen reduction is applied. The results are compared to measurements performed under static and oxygen-free conditions.

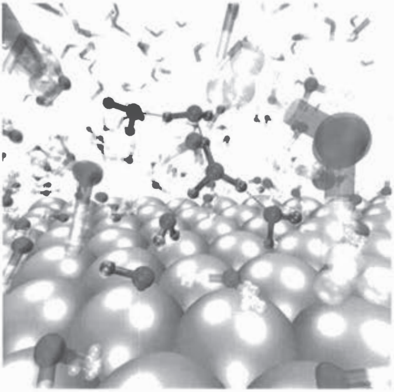
Like various other sample environments, the RDE setup is also available for users of the DESY NanoLab. Furthermore, to support the increasing demand for studying electrochemical systems using synchrotron radiation, we have recently set up a dedicated electrochemistry lab which is available as user facility.

Ionization of water as an effect of quantum delocalization at aqueous electrode interfaces

Jinggang Lan[1], Vladimir Rybkin[1], Marcella Iannuzzi[1]

[1]Univeristy of Zurich, Zurich, Switzerland

The enhanced probability of water dissociation at the aqueous electrode interfaces is predicted by path-integral ab initio molecular dynamics. The ionization process is observed at the aqueous platinum interface when nuclear quantum effects are introduced in the statistical sampling, while minor effects have been observed at the gold interface. We characterize the dissociation mechanism and the dynamics of the formed water ions. In spite of the fact that the concentration and lifetime of the ions might be challenging to be experimentally detectable at the neutral surfaces, we expect that they become measurable at an electrified interface. This might have a significant impact on electrochemical processes occurring at the metal electrode surface.



Why electrolytes can significantly control the catalytic activity. An experimental approach

Aliaksandr S. Bandarenka

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Electrocatalysis normally tries to find a link between the electrode surface structure, its composition and the resulting activity to improve the performance of electrolyzers, fuel cells, and batteries. However, this field currently encounters certain unexpected obstacles related to the prediction and explanation of a big influence of seemingly inert electrolyte components on the activity. In the presentation, results of systematic investigations of various electrocatalytic systems using a unique laser-induced current transient technique are discussed to approach the answer to a fundamental question: why can electrolytes control the activity so drastically? Different metal electrodes immersed in acidic solutions of different pHs and in near-to-neutral electrolytes containing Na^+ and K^+ served as model systems.

Electrocatalysis at the atomic scale

Jan Rossmeisl

University of Copenhagen, Department of chemistry, Copenhagen, Denmark

The chemical industry should in the future be based on renewable energy. Therefore, material development for environmentally friendly, electrocatalytic production of valuable chemicals is needed.

Chemicals could be produced using safe, cheap, more environmentally friendly and more abundant reactants than today. The products could be provided on demand at the place where they are needed, reducing expensive and hazardous transport of chemicals. However, stable, efficient and selective catalysts have to be discovered. This requires insight into the surface chemistry at the atomic scale.

The challenge of discovering new catalyst materials is twofold: Firstly, the properties or descriptors of the wanted catalyst have to be identified. Secondly, real materials with the wanted properties should be found.

I will give examples of determining descriptors for different reactions and a method for identify promising catalyst materials based on high entropy alloy, which is a new class of materials with the promise to change the way we discover interesting catalyst materials.

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Electrochemical studies of nanoparticle observed with dark-field microscopy

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Albeit nanoparticles, especially silver, are frequently used in medical applications and sportswear due to their antibacterial properties, their chemical reactivity and degradation is still insufficiently understood. Single noble metal nanoparticles can be studied with dark-field microscopy due to their localized surface plasmon resonance (LSPR). Thus, it is possible to observe their optical properties, that is, color, and scattering spectrum by hyperspectral dark-field imaging. This technique can be used for *operando* LSPR analysis of individual nanoparticles, for instance caused by their electrochemical transformation by tracking the scattering intensity and spectral position of the LSPR during electrochemical experiments.

With this newly established method, it becomes possible to obtain insights into in vivo and operando reaction dynamics and structural transformation of individual nanoparticles during charge transfer reactions.

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On the Active Site Model in Computational Catalyst Screening

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Over the last decade, a new theme has made a staggering appearance in theoretical surface catalysis research: computational screening as a means of catalyst discovery. The basis for such screening approaches is the realization that there are many dependencies in the adsorbate and transition state energetics, so-called scaling relations, that largely govern the microkinetics of a given catalyst material. Brønsted-Evans-Polanyi relationships link activation barriers to thermochemical reaction energies, while thermochemical scaling relations correlate the underlying adsorption strengths of reaction intermediates to those of their constituting base elements. Together with (sometimes drastic) assumptions on the reaction mechanism, these dependencies often allow for the description of the catalytic activity in terms of only a few simple parameters (descriptors).

One can hardly overstate the impact that this type of work has made in recent years. Computational screening is now a widely accepted (sometimes already considered essential) strategy to guide experimental catalyst synthesis. Reports on the corresponding identification of improved catalyst materials are already piling up. That said, it is however also clear that the approach necessarily has limitations – even though this is less emphasized in the wake of its current of success. In this talk I will argue that our still limited understanding of the structure of active sites is actually one of the major bottlenecks towards an ever extended and reliable use of such computational screening for catalyst discovery [1]. For low-index transition metal surfaces, the prevalently chosen high-symmetry (terrace and step) sites offered by the nominal bulk-truncated crystal lattice might be justified. For more complex surfaces and composite catalyst materials, computational screening studies will need to actively embrace a considerable uncertainty with respect to what truly are the active sites – especially when considering the possibility of *operando* changes to the catalyst (surface) structure and composition. In my talk I will survey this context and discuss possible directions how to actively embrace this uncertainty.

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Electrode Stimulation

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According to Newman[1], the rates of heterogeneous redox reactions can be written $i = i_o \{\exp(\alpha_a nF\eta_s/RT - \exp(-\alpha_c nF\eta_s/RT)\}$, where η_s is defined as "the potential of the working electrode, relative to a reference electrode of the same kind placed in the solution adjacent to the surface of the working electrode." On this basis, η_s can modify the current flowing across the electrode-electrolyte interface. Due to its intrinsic resistive character, the flow of electricity through the electrolyte will elicit changes in the electrostatic potential within that phase, which can be measured using reference electrodes, as has been shown in this[2-4] and other laboratories[5]. To be described in this presentation is a novel means of inducing local changes in η_s by passing current between a ***stimulating*** electrode, SE, and a distant counter electrode in the same solution. The overall tactic was demonstrated using a redox active self-assembled monolayer of N-ethyl-N'-octadecyl-4,4'-bipyridinium dibromide (EOB) adsorbed on a Au(poly) disk electrode as the WE and a Au(poly) disk of larger diameter placed parallel to the WE with its normal axis aligned along the corresponding axis of the WE, as the SE. The potential of the WE, E_{WE}, was set at E_{WE}= -0.35 V, while the SE placed at a distance d = 0.5 mm from the WE was scanned from 0.65 V up to 0.8 V, and back at ν = 1 V/s, yielding a i_{SE} vs time curve shown in red dots in Fig. 1. The response of the WE is shown in blue in Fig. 1. As clearly indicated, $i_{SE} > 0$ elicits a corresponding $i_{WE} < 0$ due to the change in the electrostatic potential in the vicinity of the WE. Once i_{SE} is reversed, the previously reduced fraction of EOB is oxidized returning the redox layer to its original fully oxidized state. This explanation is also consistent with the increase in i_{WE} induced by a decrease in d. Implementation of this tactic will enable application of a local potential in a region next to a working electrode and thus promote electrochemical processes in that region without the need of a mask.

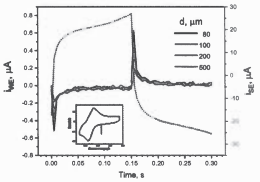

Figure 1. Currents flowing through the WE, i_{WE}, polarized at E_{WE}= -0.35 V, in aqueous 0.5 M $NaClO_4$ while scanning the potential of the SE, E_{SE}, at ν = 1 V/s between 0.65 and 0.8 V for various d, The red dotted line (see right ordinate) is the i_{SE} vs t profile during the stimulation. **Insert**: Cyclic voltammogram of a self-assembled EOB adsorbed on a Au(poly) disk electrode recorded in the same media at ν = 0.5 V/s.

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Operando FTIR investigation of borohydride electrooxidation on nickel

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Direct Borohydride Fuel Cells (DBFCs) are considered as promising power sources for portable and mobile applications. Their advantages are high theoretical specific energy, and high theoretical cell voltage. However, currently available noble metal-based (Pt, Pd) electrocatalysts do not allow one to take full advantage of the low standard potential of the BH_4^-/BO_2^- couple (-1.24 V vs NHE, pH = 14) due to the competing faradaic hydrogen evolution reaction and to the nonfaradaic heterogeneous hydrolysis of BH_4^- [1].

We have recently demonstrated that electrodeposited Ni greatly outperforms Pt in the borohydride oxidation reaction at overpotentials as low as 0.2 V, both in half-cell and in unit fuel cell configurations [2].

Here we apply *operando* Fourier-Transform infrared (FTIR) spectroscopy to study the products and intermediates of the borohydride oxidation reaction on Ni. We supplement FTIR data with the differential electrochemical mass spectrometry to detect hydrogen evolution and with DFT calculations to propose a tentative mechanism of the borohydride oxidation reaction on Ni.

Acknowledgments

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Electrochemical Orbital Imaging

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Since the invention of scanning tunnelling microscopy (STM) in the 1980s, this technique has enabled the observation of atomic, molecular and supramolecular structures under both vacuum and electrochemical conditions [1]. However, the significant electronic interaction between the orbitals of the adsorbates under study and those of the conducting supporting surface often causes image distortion and limits the spatial resolution that can be achieved.

In my talk, I will discuss experiments that reveal the direct observation of individual, unperturbed molecular orbitals by electrochemical STM [2]. This result opens the door to studying catalytic reactions under electrochemical *in situ* and *in operando* conditions with single-orbital resolution.

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Angstrom-Resolved Characterization of Electrochemical Interfaces in Real Time during Polarization

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Electrochemical solid|liquid interfaces are critically important for energy conversion, biosensing and biodegradation processes. Yet, a real-time visualization of dynamic charging processes at electrified solid|liquid interfaces with close to atomic resolution is extremely challenging.

I will discuss a unique real-time atomistic view into dynamic charging processes at electrochemically active metal interfaces using white light interferometry in an electrochemical surface forces apparatus. This method allows simultaneous deciphering of both sides of an electrochemical interface; the solution and the metal side; with microsecond resolution under dynamically evolving reactive conditions that are inherent to technological systems in operando. The real-time capability of this approach reveals significant time lags between electron transfer, oxide reduction/oxidation, and solution side reaction during a progressing electrode process. In addition, the developed approach provides detailed insight into the structure of the electric double layer under varying charging conditions.

I will also discuss how we can complementary use high resolution in-situ AFM imaging to further characterize ion layering at charged surfaces. The presented work may have important implications for designing emerging materials utilizing electrified interfaces and may apply to bio-electrochemical processes, signal transmission and pore charging.

Ab initio modeling of electric double layers on single crystal electrodes

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Single crystal electrochemistry plays significant role in providing microscopic understanding of electrified interfaces. Atomically flat single crystal electrode surfaces can be made with high precision and cleanness. Equipped with highly sensitive spectroscopic and microscopic techniques, one could investigate these highly complex electrochemical interfaces. The interpretation of spectra however is not always straightforward, which often can be complemented with computation. We have developed ab initio methods simulating electrochemical interfaces using density functional theory based molecular dynamics (DFTMD). Electrochemical environments can be simulated with well-defined (computed) voltage conditions, so that the computed structures and electrochemical properties of interfaces can be directly compared with experiment. In this talk, I will present some of our recent work on simulation of electric double layers on single crystal electrode surfaces (e.g. Au, Pt and Ag), and their comparison with available experiment.

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Improving the design of electrochemical materials and devices with theory and modelling

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In this talk I will highlight my research on materials and fundamental atomic process that underpin different areas of energy and nanotechnology, such as in electrolysers, batteries and memristors. I will introduce some issues connected with the simulation of electrified interfaces at the nanoscale focusing on modelling the effect of an applied potential to a cell. I will present some recent progress in our understanding of the interactions of the electrolyte with the metal under applied potential in the technologically relevant Pt-water interface.

Investigating atomic scale structure and kinetics of liquid metal–electrolyte interfaces

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Electrochemical interfaces between immiscible liquids have lately received renewed interest, both for gaining fundamental insight as well as for applications in nanomaterial synthesis. In this contribution, we demonstrate that the atomic scale structure of these previously inaccessible interfaces nowadays can be explored by in situ synchrotron based X-ray scattering techniques. Exemplary studies of a prototypical electrochemical system – a liquid mercury electrode in pure NaCl solution – reveal that the liquid metal is terminated by a well-defined atomic layer. This layering decays on length scales of 0.5 nm into the Hg bulk and displays a potential and temperature dependent behaviour that can be explained by electrocapillary effects and contributions of the electronic charge distribution on the electrode [1]. In similar studies of nanomaterial growth, performed for the electrochemical deposition of PbFBr, a complex nucleation and growth behaviour is found, involving a crystalline precursor layer prior to the 3D crystal growth. Operando X-ray scattering measurements provide detailed data on the processes of nanoscale film formation [2,3].
We also report the successful implementation of a method that enables the measurement of liquid–liquid X-ray reflectivity [XRR] curves using simply a fixed, horizontal source beam, a vertical translation stage and a two-dimensional detector [4].

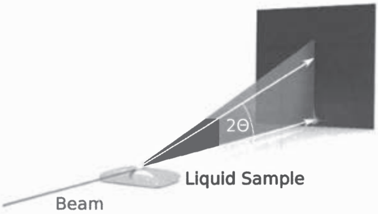

Figure 1. A horizontal X-ray beam reflected from the surface of a liquid drop and detected by a two-dimensional detector.

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Towards Multiscale Modelling of the Semiconductor-Electrolyte Interface for Oxygen Evolution Reaction

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Photoelectrochemical (PEC) cells that produce hydrogen from water are highly relevant in transition to a clean energy economy. Hematite is a promising semiconductor for PEC cells due to its suitable band gap (2.1 eV), availability, stability and non-toxicity. The oxygen evolution reaction (OER) largely determines the energy efficiency in PEC cells. Computational modelling of OER, a multiscale modelling problem, can improve the efficiency of PEC cells by mechanistic insight which is unavailable from experiments[1].We present a multiscale model of the semiconductor-electrolyte interface. We combine density functional theory (DFT) and DFT based molecular dynamics (DFT-MD) calculations including explicit solvation[2] with kinetic Monte Carlo (kMC) simulations. Assuming a four-step proton coupled electron transfer (PCET) mechanism and its slightly extended version[3], we estimate the rate constants for elementary steps in the OER over hematite 110 surface. These rate constants are input for the kMC simulations which are run to laboratory time scales (~2000 s) to get surface coverage of different intermediates at various applied potentials. This data is experimentally not available and represents mechanistic data under operando conditions. Furthermore, we simulate the polarization curve for OER and determine the onset potential which allows us to validate our model against experimental data. With our multiscale model we also examine the impact of individual elementary steps on the semiconductor-electrolyte interface under operando conditions which will pave the way to identify the limitations at the solid-liquid interface.

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Exploring the properties of concentrated electrolyte / electrode interfaces in supercapacitors using idealised coarse-grained models

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Supercapacitors are energy storage systems in which the energy is stored by ion adsorption at the electrode/electrolyte interface. In order to optimise these systems, it is important to characterise precisely the electrolyte structure at the interface and how it is affected by the application of a potential difference. In this talk, I will focus on carbon-carbon supercapacitors and explain how a combination of simulations and *in situ* NMR experiments can be used to improve our understanding of the interface between a solid electrode and a concentrated electrolyte. In particular, I will show results from molecular simulations describing the change in electrolyte structure between planar and porous electrodes, and between pure ionic liquids and organic electrolytes. I will then report on the development of a mesoscopic approach to model ion diffusion in carbon particles and predict NMR spectra of such ions.

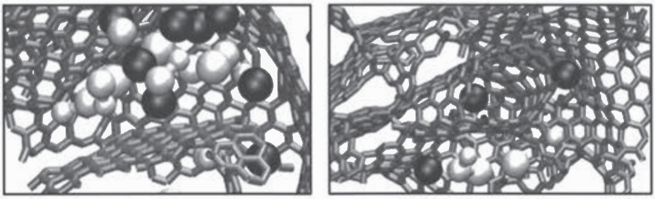

Figure: Local structure of a pure ionic liquid in pores of various geometries, charged positively (black: anions, white: cations, grey: carbon atoms).

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Interfaces by ab initio molecular dynamics

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The fundamental understanding of interfaces at the atomic level would greatly help in predicting the stability and reactivity of materials and eventually would lead to the rational tuning of the different components for example for heterogeneous catalysts, nano-electronics, photocatalysis. One important field where this knowledge is especially needed is electrochemistry, where most of the relevant processes occur at solid/liquid interfaces. Unfortunately, the direct observation of these processes and the characterisation of the interfaces under operating conditions are still challenging for both experimental and modeling approaches. On the other hand, modelling of materials properties and processes from first principles is becoming sufficiently accurate as to facilitate the design and testing of new systems in silico. Computational materials science is both valuable and increasingly necessary for developing novel functional materials and composites that meet the requirements of next-generation technology. In order to shed some light on selected functionalised interfaces, we employ electronic structure calculations based on density functional theory, combined with the simulation of spectroscopic properties and with ab initio molecular dynamics (AIMD)[1]. In particular, we present our studies on the functionalisation of supported hexagonal boron nitride (h-BN)[2], which modifies the interaction of ad- sorbing species on the metal, their reactivity and spectroscopic signature

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Magneto-optical Kerr effect set-up for *operando* probing of electrode surfaces

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Electrolysis offers an attractive up-scalable solution for sustainable production of hydrogen. However, the challenge of increasing efficiency of the process still remains. It has recently been reported that applying external magnetic field to an oxygen evolution electrode can increase current flowing through the electrochemical cell [1]. This process is currently not understood, as calculations predict virtually zero effect on current by applied magnetic field [2]. Operando surface-sensitive analysis of electrodes is a great challenge, as most surface-sensitive techniques are not compatible with in situ measurements (e.g. high vacuum requirement for XPS).

Here, we present an optical approach based on magneto-optical Kerr effect that allows for *in situ* probing of local magnetisation within top 5 nm of magnetically active electrodes (archetypically: Co, Ni or Fe). The spin carries information on the electronic structure [3]. Although the interpretation is not straightforward, the advantage of the method lies in the compatibility of optics with an electrochemical setup. The design includes an integrated polypropylene electrochemical cell optimized for optical probing and a software that allows for simultaneous detection of optical images of the electrode surface, electric flow through the cell and applied magnetic fields.

Gradient-coated samples are used to differentiate between the bulk-influenced spectral response and the chemical changes of the catalytically active surface. Here, we demonstrate the applicability of the electrochemical MOKE set-up for the surface monitoring of the electrode as a function of applied potential.

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Investigating molecular scale changes at the electrode-electrolyte interface using polarization modulation infrared reflection absorption spectroscopy

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Electrochemistry belongs to the fastest developing braches of physical chemistry due to its enormous importance in the research on renewable energy storage and conversion. Charged interfaces occur commonly in nature and appear commonly at technologically important devices such as batteries, fuel cells, photovoltaic devices, sensors or implants. Clearly, molecules present at charged interfaces are exposed to strong static electric fields, which affect their structure, orientation and reactivity, comparing to the situation in a bulk phase. *In situ* studies of structural changes in functional molecular systems fabricated on electrode surfaces bring a need of use analytical methods which would allow for carrying out sensitive, selective, reproducible, measurements of the composition and function of these complex systems. Reflection-based IRS techniques such as the polarization modulation infrared reflection-absorption spectroscopy (PM IRRAS) have been successfully applied for the electrode-electrolyte interface.

Methods of fabrication of redox-inactive and redox-active supramolecular films on electrode surfaces will be presented. Electrochemical properties: electron transfer reactions, capacitance, surface charge density and potential window of the films adsorption on the electrode surface depend on the composition and structure of the molecules present in the film. In the first example electrical properties of models of cell membranes will be presented. Biological cell membranes react to changes in static electric fields. PM IRRAS with electrochemical control allows the analysis of potential-driven changes in the orientation and conformation of the hydrophobic hydrocarbon chains and of the orientation and hydration of the carbonyl ester groups in lipid molecules forming the model membrane. A redox-active five-coordinate iron(III) surfactant shows some unusual redox and spectroscopic behavior. This amphiphilic molecule acts as diode-like metallosurfactant capable of current rectification, or unidirectional transfer of electrons, when deposited as Langmuir-Blodgett (LB) monolayers between two electrodes. Changes in molecular orientation triggered by electrochemical reduction of an iron-containing surfactant in LB films deposited onto gold electrodes are determined by the application of in situ PM IRRAS.

Oxygen Electrocatalysis at Transition Metal Oxide Nanostructures

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The establishment of structure-activity relationships between transition metal oxide and the oxygen evolution (OER) and reduction reactions (ORR) is one of the grand challenges in the field of electrochemical energy conversion. The vast majority of studies examine links between bulk structural properties and conventional electrochemical descriptors, largely disregarding the complex surface structure of these materials. We have shown that perovskites such as $LaMnO_3$ are uniquely active towards the ORR reaction due to the changes in the redox state of Mn sites at potentials close to the formal ORR potential [1-4]. More recent works have shown that the activity is closely linked to the coordination of surface Mn sites, which is undetectable employing conventional tools such as XRD and EXAFS [5]. In the case of OER, highly active Ni sites in perovskite lattice also undergoes changes in their electronic configuration at the onset potential. In this contribution, I will share new data illustrating the link between density of states associated with these redox transitions and electrocatalytic activity, making the case for developing effective surface sensitive tools for *operando* probing of these processes.

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Mapping Charge Transport at Electrode/Liquid Interfaces: from Oxides Films to Biomolecules

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Solid/liquid interfaces are the scenario for many important processes with outstanding technological implications in Material Science, Chemistry and Biology. To mention some, corrosion and passivation processes, electrochemical and catalytic reactions or molecular recognition and/or molecular sensing are processes involving heterogeneous interactions between a solid surface and a wide variety of chemical species dissolved in a liquid environment. The need to understand the fundamental mechanisms behind these processes, and having the ability to control them, has been in the scope of scientists for centuries. As in other scientific fields, with the advent of Nanoscience, new capabilities to study solid/liquid interfaces with nanoscale resolution emerged, fact that opened new ways to approach the study of dynamic heterogeneous processes taking place at surfaces in contact to liquid media including electrolytes. In this presentation, a quick overview of the use of electrochemical scanning probe techniques (SPM) to explore a large variety of electrode/liquid interfaces will be given. From the study of technological semiconducting oxide films [1,2] to the electrical characterization of more complex electrode/(bio)molecule interfaces [3-5], this contribution will try to summarize our long journey seeking for quantitative understanding of charge transport through various hybrid electrode/electrolyte interfaces that directly impacts on a large variety of fields; from surface sciences [1-5] to biological electron transfer [6-8]. Along this journey, we will show bits on how our electrochemical SPM approaches have been shaping to adapt to the particular studied phenomena, as well as the level of overlapping with other distinct disciplines.

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Tuning the Thermoelectric Performance of Aromatic Molecules

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Molecular junctions are a versatile test bed for investigating nanoscale thermoelectricity [1-2] and contribute to the design of new cost-effective environmentally-friendly organic thermoelectric materials [3]. It was suggested that transport resonances associated with discrete molecular levels would play a key role in thermoelectric performance [4], but no direct experimental evidence has been reported.

Here we present four different studies of single-molecule junctions formed from crown-ether bridged anthraquinones (sensing and thermoelectric properties theoretical studies [5-6]), endohedral fullerene $Sc_3N@C_{80}$. In the first two studies, the novel design feature is the presence of either (1) a crown-ether or (2) a diaza-crown ether bridge attached to the side of the current-carrying anthraquinone wire. The crown-ether side groups selectively bind alkali-metal cations and when combined with TCNE or TTF dopants, provide a large phase-space for sensing and optimising thermoelectric properties.

For the third study [7], we investigate the endohedral fullerene $Sc_3N@C_{80}$ connected to gold electrodes using a scanning tunnelling microscope (STM). We find that the magnitude and sign of the thermopower depend strongly on the orientation of the molecule and on applied pressure. Our calculations show that Sc_3N inside the fullerene cage creates a sharp resonance near the Fermi level, whose energetic location and hence the thermopower can be tuned by applying pressure. These results reveal that $Sc_3N@C_{80}$ is a bi-thermoelectric material, exhibiting both positive and negative thermopower, and provide an unambiguous demonstration of the importance of transport resonances in molecular junctions.

The last project [8], about answering the question. Do side groups have effect on *G* or *S* for fluorene derivatives? Theoretical calculations predict no effect on G and an increase of %80 for *S*. Experimental measurements prove the predictions to be corrected

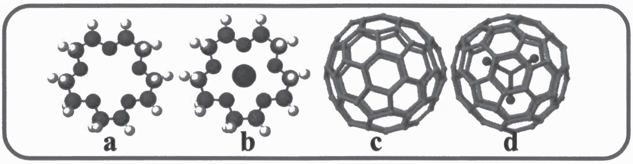

Figure: (a) Schematic of crown ether (15-Crown-5), (b) Host-guest complex, (c) Fullerene C_{60} and (d) Endohedral fullerene $Sc_3N@C_{80}$ used in this work.

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Parametrizing Implicit Solvation Models

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The importance of solvation effects on electrochemical reactions is by now a widely accepted fact. On the other hand, sampling all solvent degrees of freedom at potentially expensive levels of electronic structure is often not a feasible approach either. For this reason, implicit solvation models, first pioneered over 80 years ago, are currently undergoing a strong renaissance. Such models generally treat the electrostatic response and possibly dissolved electrolytes on the level of a polarised continuum and the ions' Boltzmann distributions, respectively. The downside to this is that the accuracy of such models generally depend very strongly on a number of effective parameters which, in most cases, cannot be derived from first principles, but rather have to be fitted to a suitable training set.

In my talk I present two implicit solvation models, differing in computational cost and complexity, which we implemented in the full-potential numeric atomic orbital code FHI-AIMS. Thereby, I will focus on the parametrisation of the models based on the recently presented Solv@TUM database of experimental solvation free energies. I will highlight some of the intricacies involved the application of popular non-electrostatic correction terms, generally applied to include interactions other than pure electrostatics and to compensate for errors in the solvation model itself. I will also present a new descriptor which to a certain degree can account for structuring of the solvent otherwise absent in pure continuum models. Finally, I will discuss new non-electrostatic corrections derived from a compressed sensing machine learning approach used to identify cheaply accessible descriptors for the missing interactions.

Adsorbate Properties on Atomically-Defined Co_3O_4(111) in UHV and the Electrochemical Environment

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Functional organic/inorganic hybrid materials are in the focus of current research. In our work, we employed the (electrochemical) surface science approach to study the interaction of different adsorbates with atomically-defined Co_3O_4(111) thin films on Ir(100) prepared in UHV. We performed comparative studies and investigated the adsorbate properties in UHV by infrared reflection-absorption spectroscopy (IRAS). Further, we transferred our systems into the electrochemical environment under ultraclean conditions and analyzed them using (photo)electrochemical infrared reflection-absorption spectroscopy (PEC-IRRAS).

First, we investigated the surface interactions of phosphonate anchor groups and deposited a monolayer of phenylphosphonic acid (PPA) at 380 K in UHV. At sub-monolayer coverages PPA binds to the surface as fully deprotonated chelating tridentate, which is replaced by partially protonated bidentates at full monolayer coverages. Upon deposition in the EC environment (pH 10, ammonia buffer), PPA shows a potential-dependent behavior An increase of the potential leads to surface oxidation. PPA and ammonia compete in taking up the released protons. At low buffer concentrations surface-anchored phosphonates are protonated forming singly-protonated surface phosphonates. At high buffer concentrations the preferred adsorption motif of the phosphonate changes from bidentate to tridentate. [1]

Further, we functionalized the Co_3O_4(111) surface with a norbornadiene (NBD) derivative. With the valence isomers NBD and quadricyclane (QC) solar energy conversion, storage, and energy release can be combined in a single molecule system. We followed the photochemical conversion from 2-cyano-3-(4-carboxyphenyl)NBD to 2-cyano-3-(4-carboxyphenyl)QC in UHV, in dichloromethane, and in the EC environment. Photoconversion was triggered by illumination at 365 nm and was observed for all three environments. [2]

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Probing water and surface oxides on electrodes by coupling in situ spectroscopic techniques

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Solvent structure and surfaces during running electrochemical reactions can only be fully understood when analyzing electrodes in situ and operando. These two aspects serve as illustration of the power of and need for operando characterization.

In the first part, the electrode-potential dependent structure of water in contact with Ge(100) single crystal electrodes will be discussed, as probed by classical IR absorption spectroscopy in attenuated total reflection (ATR) geometry. The well-defined illumination geometry of an evanescent wave together with continuum spectral simulations using bulk optical constants enables a subtraction of the remaining bulk water background in the ATR-IR spectra [1,2]. Spectra treated in this way reveal the appearance of the spectral signature of non H-bound water at potentials were Ge(100) is H-terminated. Important electrode potential dependent trends agree with trends obtained from spectra from electrode-potential dependent ab initio molecular dynamics simulations [1].

A much more challenging situation for spectroscopic experiments arises when looking at water splitting, discussed in the second part. For the oxygen evolution reaction (OER) as one important partial reaction of water splitting the challenge persists of finding surfaces which are active and stable under the conditions of the OER. Here, the OER on two different metals, Cu [3] and Mn [4], was investigated by combining spectroscopic ellipsometry in the UV/VIS and Raman spectroscopy; the analysis of the photoluminescence background in the latter also provides important information. On Cu, a passivating oxide forms at intermediate electrode potentials. Above a certain potential, this oxide layer breaks down, probably because the oxide becomes unstable towards defect formation. OER sets in at the breakdown potential. On Mn, on the other hand, OER sets in on an oxide-covered surface, leading to very fast dissolution at the same time as oxide grows [4].

The contribution shall highlight how different analysis methods contribute to understanding of interfacial water in different systems.

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Abstracts of Posters

(in alphabetical order)

Computational Materials Science at the University of Zurich

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We are interested in the development and application of computational methodologies for the atomistic simulations of condensed matter. Our research is often strongly related to open questions on the fundamental understanding of physical and chemical properties and of the microstructural evolution of systems of interest in technologically relevant fields. We have specialised in the investigation of complex interface systems, combining the accurate description of the interatomic interactions, including environment effects, with the sampling of the accessible phase space. These are the necessary ingredients in order to reproduce and characterise molecular processes, like structural rearrangements, transport, assembly, reactions.

The fundamental understanding of interfaces at the atomic level would greatly help in predicting the stability and reactivity of materials and eventually would lead to the rational tuning of the different components, for example in heterogeneous catalysis, nano-electronics, photocatalysis. Most of the relevant processes in an electrochemical cell occur at solid/liquid interfaces. However, the direct observation of these processes and the characterisation of the interfaces under operating conditions are still challenging for both experimental and modelling approaches. By developing efficiently scaling computational strategies [1], modelling of materials properties and processes from first principles is becoming sufficiently accurate as to facilitate the design and testing of new systems in silico. We present a few examples where computational materials science turns out to be valuable and necessary for developing novel functional materials.

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New spectroscopical tools for molecular circuitry

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Biological charge transport (CT) is the key step in many basic cellular processes such as respiration or photosynthesis and nature has developed highly specialized molecular building blocks to achieve it with unprecedented efficiency. Understanding the mechanisms behind biological CT is key to elucidate the changes in its regimes caused by specific structural variations of the associated molecular machinery. Such knowledge will ultimately lead us to tailor its electrical properties and exploit them as high performance bioelectronic devices with a wide variety of applications in organic electronics, sensing, biomanufacturing etc.

To investigate CT in single-molecule bioelectronic devices, we exploit Scanning Tunnelling Microscopy-based approaches in the break-junction mode (STM-BJ)[1,2] under electrochemical control (EC-STM) to trap individual molecules in a junction under electrochemical control to characterize their main electrical signatures.[3] The first block of this contribution will present novel electrochemical studies carried out with native and mutated Azurines (blue copper proteins) and the effects over the electron transport mechanism as a function of the redox state of the central Cu.[3] Our results show a clear transition from a two-step mechanism of the native Azurin to an almost fully coherent direct tunnelling mechanism, invariant to electrochemical gate voltage and temperature for the mutant. Thanks to the chosen point-site mutagenesis, the intervention of the redox center in the CT was totally neglected due the slight reduction of its charge density.

We will end this contribution by showing the work in progress on the development of a new hybrid platform with spectro-electrical single-molecule detection capabilities under ambient conditions. It aims to explore several key structural and physicochemical aspects that remain unknown during the single-molecule electrical contact formation. This is possible thanks to the operando capabilities of the hybrid platform to work in the near-field Raman between the two STM electrodes (TERS),[4] a high ultrasensitive non-destructive spectroscopic method with molecular resolution. The new platform opens the gates to obtain detailed insights into the molecular junction structure by simultaneously capturing the current during the spontaneous formation of a molecular junction, i.e. the evolution of spectro-electrochemical characteristics of the junction.

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In-situ electrochemical STM imaging of Cu single crystal electrocatalysts

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Carbon monoxide (CO) is a key intermediate in the electro-oxidation of energy carrying fuels and in the electroreduction of carbon dioxide. Ideally, heterogeneous catalysts should be able to catalyze the reverse of a given reaction under nearly the same conditions, which is, however, rarely observed. In this work, the ability of Cu(111) single crystals to electrochemically oxidize CO at low overpotentials of 350 mV is reported for the first time. In-situ infrared spectroscopy confirms weak adsorption of CO on Cu(111) as well as its oxidation to carbon dioxide which directly reacts to carbonate in solution. Electrochemical scanning tunneling microscopy (EC-STM) reveals that during CO oxidation the Cu(111) surface reconstructs and concomitantly adsorbs OH, while forming one- and two-dimensional Cu nanostructures that are effectively stabilized through the presence of CO. Therefore, CO itself activates the (111) surface of Cu and enhances its own oxidation. This self-activation makes it a promising candidate for the oxidation of small organic molecules, e.g. hydrocarbons or alcohols.

Knowledge of the electrified solid/liquid interface is key for a true understanding of electrocatalytic processes, i.e. CO oxidation. Laser-induced current transient (LICT) measurements allow the investigation of interactions between the electrode and the electrolyte at the interface.[1] The interface undergoes a sudden change of temperature induced by application of a short laser pulse, which leads to (re)orientation of interfacial water. The potential at which the measured current transient changes its sign, is the so-called potential of maximum entropy (pme), where there is no net orientation of water dipoles. This parameter is crucial for understanding electrosorption and the actual charge of the metal electrode. In this work, the pme for a Cu(111) electrode in different electrolytes has been determined and correlated with the corresponding surface structures through EC-STM investigations.

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Impact of ions on structure and dynamics at charged solid - aqueous interfaces

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Interfacial water structure is key to many chemical and physical processes. It can be probed by vibrational sum-frequency generation (vSFG) spectroscopy as well as ultrafast time-resolved vSFG. However, a more complete microscopic understanding requires additional techniques such as molecular dynamics simulations. Our experiments show that in the absence of surface charge (pH 2), water at silica surfaces exhibits significantly slower OH stretch vibrational relaxation (~600 fs) compared to bulk water.[1] However, at charged SiO_2 surfaces (e.g., pH 6), bulk-like fast dynamics (~200 fs) are observed at low ionic strength. This decelerates to ~600 fs with the addition of NaCl.[2] In parallel, vSFG results demonstrated that SiO_2 interfacial water structure is most sensitive to ions at pH=6-8, correlating with the known salt and pH dependence of silica surface reactivity. Consequently, it is unclear whether the observed slowing of the vibrational dynamics is due to the reduction in the Debye length, or because of changes in the local hydrogen bonding environment caused by the electrolyte and how this might depend on the identity of the ions or the solid surface. The combination of molecular dynamics simulations with spectroscopic and time-resolved vSFG experiments on aqueous Al_2O_3 interfaces,[3-5] along with the use of a molecular probe SCN^-, sheds light on the ongoing debate on the role of ions in interfacial water structure and whether the observed behavior is specific to SiO_2/water interfaces or can be generalized to other charged aqueous interfaces.

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Superoxide formation near DMSO/Cu(111) interfaces

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DMSO is a common non-aqueous solvent with the potential to be used in lithium-oxygen batteries due to its ability to catalyze the superoxide formation [1]. In this study we investigate the electron dynamics in DMSO films on Cu(111) using time- and angle-resolved two-photon photoemission and disentangle the individual steps of charge transfer leading to superoxide formation:

Electrons are injected from the metal to the DMSO, where they form small polarons on sub-picosecond time scales. The subsequent trapping extends the electronic lifetimes to several seconds [2]. Co-adsorption of O_2 quenches the trapped electron signal and leads to the appearance of an occupied state whose binding energy is in good agreement with electrochemical data of superoxide [3].

These results may contribute to a basic understanding of charge transfer processes in novel battery systems.

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The influence of acetophenone adsorption on hydrogen underpotential deposition on Pt/Pd ML

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The adsorption of graphene or benzene derivatives on metallic surfaces typically blocks other species from the surface, thereby hindering them from being adsorbed, and/or reacting at the surface. Interestingly, while most other species are blocked from the surface, hydrogen underpotential deposition (HUPD) and hydrogen evolution are still possible.

As shown in Fig. 1, in the case of acetophenone (AP) adsorption, the peak associated to HUPD is not only shifted, but the integrated charge delivered to the surface in the potential window assigned to the HUPD process also increases with the organic substrate concentration. This strongly suggests that AP is reduced concomitantly to hydrogen adsorption at the surface and thus actively takes part in the charge transfer within the HUPD window.

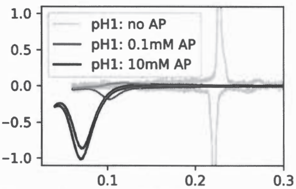

Figure 1: CV for Pt/Pd ML in the presence and absence of AP.

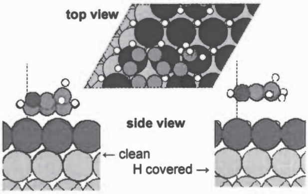

Figure 2: AP on Pt(111)/Pd ML.

In the aim of clarifying this and other observations, we present a detailed DFT study.

We find AP to strongly bind to Pt(111)/Pd ML in a flat geometry. As the potential decreases, it becomes energetically more favorable to co-adsorb hydrogen. As shown in Fig. 2, even at full hydrogen coverage, AP still binds preferentially in a horizontal geometry, but at much larger binding distances.

The reduction process of AP is investigated as a function of applied potential, as shown exemplarily for the clean surface in Fig. 3. Nudge elastic band calculations will shed some light on the most likely pathway to AP reduction on Pt(111)/Pd ML.

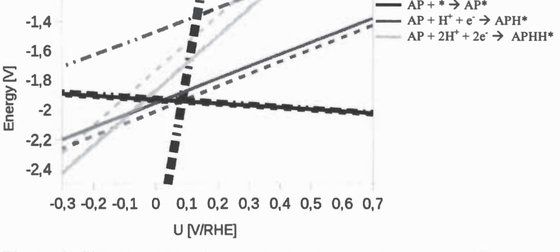

Figure 3: Simulated binding strength of AP on Pt(111)/Pd ML as a function of potential. (full line: ring on bridge site, 30° tilted; dashed: ring on hcp, 0°; dash-dot: ring on hcp, 30°; bold: with adsorbed H)

Photochemical stability of polar and non-polar ZnO single crystal facettes during electrochemical polarization

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Degradation of transparent oxides is a main challenge for designing catalysts and catalysis conditions, or for passivation of metal surfaces. Photocorrosion can be significant and plays a central role during photoelectrochemical water splitting, contributing to enhanced degradation of oxides during illumination with UV light. Here, we utilize an electrochemical flow cell combined with an inductively coupled mass spectrometer (ICP-MS) to enable the in-situ study of the time-resolved release of zinc into solution under radiation of UV-light. We study zinc oxide single crystals of the orientation 0001 and 10-10. Under several pH conditions both the oxygen and the hydrogen evolution were studied. Quantification of dissolved zinc from zinc oxide crystals during water splitting allows us to enhance our understanding of catalyst degradation. A significant influence of the UV radiation and the pH of the electrolyte was observed.

Impact of surface adsorbates on charge carrier transport in metal-oxides for solar water splitting

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Photoelectrochemical water splitting is a promising route for efficient conversion of solar energy into chemical fuels. The chemical transformation of water into oxygen and hydrogen takes place at the photoelectrode surface. Consequently, the activity, efficiency, and reaction pathway are critically controlled by the material surface properties. Under operating conditions, surface properties depend on the surrounding environment, and may be altered in the course of the reaction. Thereby, absorption of molecules can modify the chemistry at the surface, for example by influencing the kinetics of reactants, products, or reaction intermediates, but they can also directly impact the electronic transport properties by acting as surface trap states. In this context, improved understanding of these complex surface interactions will aid the development of highly efficient light absorbers as well as the integration of effective passivation and catalyst layers for these materials.

Among different photoelectrode materials, bismuth vanadate ($BiVO_4$) is one of the most actively investigated oxide semiconductors. Here, we employ photoconductive AFM under controlled *in-situ* conditions to gain insight into the relationship between surface interactions and interfacial charge transport characteristics in polycrystalline $BiVO_4$ thin films. We demonstrate that the low intrinsic bulk conductivity of $BiVO_4$ limits charge transport through the film, and that the transport mechanism can be attributed to space charge limited current in the presence of trap states.[1] By analyzing the space charge limited current in selective gas environments, we are able to quantify the impact of surface adsorbates on bulk transport properties. We find that surface adsorbed oxygen acts as a shallow trap state and accounts for 40% of the effective trap density in $BiVO_4$ thin films.[2]

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Disentangling hydrogen formation and anion coad-/desorption phenomena on metal surfaces with electrochemical mass spectrometry

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Over the last decades, fundamental research on the electrochemical/-catalytic properties of low index single crystals has played an important role for the understanding and improvement of industrially relevant and more complex (electro-)catalyst materials. A common approach to study the electrochemical (EC) properties of these systems is cyclic voltammetry (CV). Based on the metal and the respective surface orientation a so-called fingerprint region appears in the CV, with distinct peaks which are associated with the oxidative/reductive adsorption and desorption of ions from the electrolyte solution (H^+, OH^-, $HSO4^-$, ...). Especially on Pt the peaks related to individual processes in specific electrolytes are almost perfectly separated and well understood. Other metals, such as Ru and Cu, however, have received less attention. The interpretation of the CVs of these metals is particularly complicated since the regions of anion ad-/desorption overlap with the regions of hydrogen underpotential deposition (H_{UPD}) or the hydrogen evolution reaction (HER). Focusing on Ru(0001), we show in a combined ultrahigh vacuum (UHV) and differential electrochemical mass spectrometry (DEMS) study, that H_2 is detected by DEMS at potentials positive of 0 V vs. the reversible hydrogen electrode (tentatively called "anodic H_2"). This phenomenon was observed in 0.5 M H_2SO_4, 0.1 M $HClO_4$ and 0.1 M NaOH electrolyte. So far it was generally accepted that H_2 evolution only occurs at potentials more negative than 0 V, which reflects the equilibrium potential of $E(½H_2/H^+) = 0$ V under standard conditions. Based on a careful evaluation of CVs and the H_2 mass signals we suggest that this surprising result is caused by the displacement of adsorbed H* to form H_2 by adsorbing anions such as (bi-)sulfate or hydroxide, while the formation of H^+ from H* under these conditions is kinetically limited by the co-adsorbed anions. To ascertain the stability of the electrodes, we performed scanning tunnelling microscopy (STM) measurements under UHV conditions (new peaks in the CV can be associated with structural changes) before and after EC measurements. In total, these findings lead to a reinterpretation of the CVs of Ru(0001) in these electrolytes. Finally, in a related CV study on polycrystalline Cu electrodes in 0.1 M KOH, we also observe "anodic H_2". Hence we suggest that this phenomenon is a general process for systems where regions of H_{UPD} or HER overlap with regions of strongly adsorbing anions in the CVs.

A Unifying Material-Screening Approach

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The oxygen evolution reaction (OER) is the bottleneck in proton-exchange membrane (PEM) electrolyzers as substantial overpotentials are required for the formation of gaseous oxygen at anode side to reach a satisfying current density. In past years, significant research efforts were dedicated to search for electrode materials with an ameliorated OER activity. Therein, different frameworks can be found in the literature: the conventional method, based on the computational hydrogen electrode approach,[1] relies on an assessment of simple binding energies by deriving linear scaling relationships that translate to a Volcano plot at zero overpotential.[2] Recently, the traditional Volcano concept was extended, in that the applied overpotential and kinetics were accounted for by deducing overpotential-dependent Volcano curves[3,4] or kinetic scaling relations,[5] respectively. An alternative framework corresponds to the electrochemical-step symmetry index (ESSI),[6] which was proposed as an improved measure within the search of potential OER electrocatalysts. Hitherto, there is no connection between these diverse methods and it remains elusive, which of these approaches is most suitable for material screening. On the example of the OER over transition-metal oxides, porphyrins, perovskites, metal oxides, and functionalized graphitic materials a powerful combination of linear scaling relationships, kinetic scaling relations, overpotential-dependent Volcano plots, and ESSI is suggested as a unifying theory.[7] While the computational costs of this advanced approach are identical to the traditional Volcano analysis, the inclusion of a single experimental input parameter in the underlying material-screening framework enables gaining unprecedented insights in catalyst design, thereby considering various aspects, such as binding energies, rate-determining reaction step, applied overpotential, and catalytic symmetry.

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X-Ray Photoelectron Spectroscopy of ionic liquids – towards understanding of charging phenomena

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Ionic liquids (IL) are ultra-high vacuum (UHV) compatible, thus allowing for performing X-ray Photoelectron Spectroscopy (XPS) measurements of the IL/UHV interface in the analyzer chambers of the spectrometers. In recent years, controversial observations related to charging phenomena were reported for different IL and measurement configurations, thus leading to different explanations of respective charging mechanisms.

We follow the thesis that the origin of charging can be largely explained by means of the electronic properties of the solid/liquid interface.

The thesis has been supported by several experimental approaches, i.e.:

- X-ray induced open circuit potential (OCP) measurements of high and low surface area working electrodes using an in situ electrochemical XPS cell [1]
- flood gun induced charging of core level data of the IL [EMIM][Tf_2N] supported by metals, high and low surface area glassy carbon, and a semiconductor [2]
- flood gun induced charging of core level data of the IL [EMIM][Tf_2N] supported by Si and Ge semiconductors with different charge carrier densities [3]

It has been shown, that no significant charging occurs on activated carbon supports with high double layer capacitance. Furthermore it was found that magnitude of charging increases in the order of metal < carbon < semiconductor as the space charge layer capacitance becomes pre-dominant with decreasing charge carrier concentrations of the solid substrates.

In this contribution experimental details and results will be summarized and qualitatively explained by means of double layer phenomena and respective energy schemes.

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Determining redox-dependent Cu-ligand chelating behaviour in a single metallo-protein

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The copper metallo-protein azurin is a widely studied system due to the characteristic coupling of electron transfer (ET) with optical and vibronic properties. ET is performed under physiological conditions by switching the oxidation state of the Cu center between +1 and +2. [1]

In the presented project, we study individual azurin proteins bound to a Au(111) surface combining scanning tunneling microscopy and tip-enhanced Raman spectroscopy (TERS) under electrochemical conditions. [2] In-air TER spectra show that the electronic, optical and vibrational properties of the azurin Cu center are preserved upon molecule conjugation with the Au surface. STM images proove that we TERS-probe individual proteins at a time.

Under EC conditions, we control the Au(111) potential which in turn regulates the oxidation state of the Cu center. The results show a potential-dependent behavior of the TER spectra. Comparing the S/N of in-air and in-liquid EC-experiment, a drastic signal reduction is observed under *operando* conditions. To improve the EC-TERS sensitivity, we use a spatial light modulator to optimize the laser-tip coupling, using either the focus size or the TER signal as a feedback. TERS potentiodynamic mapping of a single molecule switch and extracting structural information about the metallo-protein under switching conditions can be expected to provide unprecedented insights into ET transfer characteristics in biomolecular switches. [3]

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Towards the activity descriptor for HER at alkaline pH

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Hydrogen evolution reaction (HER) is perhaps the most studied reaction in the field of electrocatalysis, both from a fundamental standpoint and for application purposes, namely, in water splitting electrolysers. However, a caveat in the present understanding arises from the solitary focus on the Pt surface, where this reaction proceeds with an almost negligible overpotential. While at the acidic pH a single activity descriptor i.e. hydrogen binding energy seems to suffice for understanding the HER on all metal surfaces, at the alkaline pH this picture becomes more two dimensional. In this work we show that at alkaline pH values, the HER activity on Au (111) surface improves with increasing alkalinity. This delineates strongly from the previously reported trend for the Pt (111) surface[1], clearly showing that the descriptor for HER at alkaline pH goes beyond the hydrogen binding energy. Further probing shows that water reduction activity scales linearly with the cation concentration in the electrolyte, which indicates a possible correlation between the cation concentration in the double layer region and the "apparent" pH dependence of water reduction activity. This is further validated by determining the double layer capacitance at different pH values, which varies as a function of the cation concentration in the double layer, in accordance with the Gouy-Chapman model. Hence, we show that the activity descriptor for HER at alkaline pH is a function of the interfacial electrode-electrolyte properties, in a way that is different for different metals.

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Asymmetric Potential Screening at Electrode/Ionic Liquid Interfaces Studied by *In Situ* X-ray Photoelectron Spectroscopy

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Ionic liquids are suitable candidates to perform electrochemistry due to their large electrochemical window, good ionic conductivity and extremely low vapor pressure. The interface between an IL and an electrode plays a crucial role in capacitor charging and redox reactions, hence the investigation of this region is of great interest to understand and control electrochemical phenomena in ILs. We introduce a new approach to study the ILs/electrode interface by *in situ* X-ray photoelectron spectroscopy by using two-identical electrodes under non-faradic conditions.[1] The potential screening (PS) given by the electrical double layer at the counter and working electrode is deduced as a function of the applied bias from the potential change of the bulk IL, as derived from corresponding core level binding energy shifts for different IL/electrode combinations. On Pt electrodes we measure a considerably larger PS at the anode than at the cathode for imidazolium-based ILs, which we attribute to strong attractive interactions between the imidazolium cation and Pt. In contrast, for $[C_4C_1Pyrr][Tf_2N]$ without delocalized π orbitals, the PSs at the anode and at the cathode are identical. For Au electrodes, ILs with similar size of anion and cation show nearly identical PSs at cathode and anode, consistent with the fact that specific adsorption is not as strong on Au as on Pt. Asymmetric PS on gold was observed for $[C_8C_1Im][Cl]$ in which cation and anion have different sizes. In combination with classic electrochemical techniques, our findings provide an excellent starting point for investigations at polarized IL/metal interfaces under ultraclean vacuum conditions.

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In-situ Identification of Active Sites Using Electrochemical Scanning Tunneling Microscopy

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Many devices that are essential in a sustainable energy system, most importantly fuel cells and batteries, rely on the interplay of solid/liquid interfaces. In order to comprehend the processes at these heterogeneous interfaces on a nanoscopic level, special in-situ investigation techniques are necessary. Recently, Electrochemical Scanning Tunneling Microscopy (EC-STM) has been utilized as a means to observe the behavior of electrode surfaces under reaction conditions. The technique allows experimental distinction between non-active and active sites of a catalytic system by comparison of the recorded noise level. If the scanning tip is positioned over a non-active site the tunneling current will be stable. Over an active site, on the other hand, reactions occurring within the tunneling gap will distort the EC-STM signal. The technique has been successfully employed to differentiate between the activity of steps and terraces on Pt(111) towards the oxygen reduction and hydrogen evolution reaction (ORR, HER). Further investigated materials include graphene, Pt3Ni(111), as well as dichalcogenides.

Here, we demonstrate one of the most powerful aspects of EC-STM, its capability to obtain information on an atomic level. For the HER on the carbon based material highly ordered pyrolytic graphite, it was possible to identify individual active sites on the atomic pattern of the substrate surface, located primarily near steps and defects. Furthermore, we show that the technique can even be used to obtain quantitative information of the local activity. This was done for Pt(111) under ORR conditions, by relating the recorded noise level to its turn-over frequency.

The approach has led to significant experimental insights into the origin of catalytic activity on important electrode materials. Combined with theoretical calculations it can be an exceptionally valuable tool to guide catalyst design towards maximum efficiency and minimize the need for rare and expensive materials.

Surface charge, surface hydration, and mineral flotation with vibrational sum-frequency generation spectroscopy

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Adsorption of collectors and modifying reagents in the flotation of oxide and silicate minerals is controlled by the electrical double layer at the mineral–water interface. In systems where the collector is physically adsorbed, flotation with anionic or cationic collectors depends on the mineral surface being charged oppositely, and water layer on mineral surface also plays an important role. The vibrational sum-frequency generation spectroscopy (SFG) technique is an exceptionally useful tool for investigating surfaces and molecules within interfacial regions, and being increasingly applied to provide molecular-level understanding of the behavior of water and adsorbates at interfaces. This review is not going to repeat the successful stories of the SFG technique, but aims to connect the molecular microscopic reality in the solid/aqueous interface to macroscopic adsorption phenomena, especially for mineral flotation. In this article, we reviewed the relationship between surface charge, surface hydration, and flotation behavior of minerals. And this review also provides insight into recent applications and advances of SFG to the mineral/aqueous interface with particular focus on neat water structure, specific ion, and surfactants at interfaces. Specially, SFG, as an in-situ technique, can be potentially applied to study monolayer and multilayer adsorption, self-assembly behavior of surfactant, and the dynamic process of adsorption. The information on interfacial water and surfactant structure will help to explain the hydrophobic or hydrophilic phenomenon and the film rupture during bubble attachment in the flotation process. Moreover, some of the challenges and opportunities on SFG study of mineral/water interface are highlighted. We hope that what we discussed here can help break some limitations to some extent and provide new ideas for any other field involving solid/liquid interface.

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SEI formation vs. Lithiation: Insights from mechanical property measurements of anode materials by in-situ atomic force microscopy

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Formation of the solid-electrolyte interphase (SEI) layer on anode materials such as graphite or silicon as well as lithiation and delithiation of these materials are the fundamental and inevitable mechanisms in lithium ion batteries (LIB). However, the interplay between both processes is not yet fully understood on sufficiently small scales. Atomic Force Microscopy (AFM) is an ideal technique to study the mechanisms at the electrode-electrolyte interface in-situ and down to the nanometer level.

Within this contribution a combined AFM and electrochemical (de)lithiation study of two types of anode materials is presented. Highly oriented pyrolytic graphite (HOPG) as a model system has been investigated in order to observe the topographical, mechanical and electrochemical properties simultaneously. Secondly, the structural and mechanical behavior of silicon anodes during charging and discharging will be discussed. To avoid strain and crack formation [1] sputtered silicon thin film electrodes have been employed [2]. We find that AFM measurements enable a differentiation between SEI formation and expansion of the silicon electrode upon lithiation in our system. Significant variations in the elastic modulus during the lithiation processes can be directly attributed to the formation of an SEI layer as well as to the expansion of the electrode due to the lithium insertion. [3]

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Electrochemical CO_2 reduction from first principles: Electric field effects at the electrochemical interface

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The electrochemical conversion of CO_2 (CO_2RR) to fuels and chemical feedstocks has become a central research activity in renewable energy technologies. To date, copper (Cu) (or Cu-based materials) are the only catalysts that show substantial selectivity towards high value C-C coupled (C_{2+}) products. Despite tremendous recent research efforts, the mechanistic understanding of the reaction pathways remains controversial. One undisputed main characteristic is an apparent pH independence on the SHE scale of C_{2+} products. This indicates that the rate-determining step (RDS) for C_{2+} products is not electrochemical. Since C_{2+} products still show a potential dependence, it is hypothesized that key intermediates are strongly stabilized by electric field effects at the electrochemical double layer [1]. In this work, we use computational methods to investigate this field effect stabilization and its influence on the CO_2RR reaction kinetics. On the atomistic level, DFT is combined with continuum solvation models to obtain an accurate description of the electrochemical interface. This enables grand canonical DFT calculations that couple charge transfer reactions and field effects into one comprehensive free energy description [2]. Going beyond the standard approaches, the detailed atomistic model reveals new insights. We find that the OC-CO coupling reaction and its related intermediates are significantly stabilized by the applied electric potential. We integrate this finding into a microkinetic model and recover the experimentally known potential dependence and pH-insensitivity of the C_{2+} pathway, rationalizing its enigmatic behavior.

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Sodium Deposition from [MPPI][TFSI] on Au(111): Initial Stages of the Deposition using *in-situ* STM

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Sodium batteries are a promising alternative for lithium based battery systems.[1,2] Metallic sodium has a reduction potential of -2.71 V *vs.* SHE.[3] In addition, it is much more abundant and thus cheaper than lithium.[4,5] In order to enable secondary sodium metal batteries, it is crucial to understand the fundamental processes of the sodium deposition and dissolution. In this work we investigated the initial stages of the sodium deposition from the ionic liquid (IL) *N*-methyl-*N*-propylpiperidinium (MPPI) bis(trifluoromethanesulfonyl)imide (TFSI) on a Au single crystal surface. Cyclic voltammetry and *in-situ* scanning tunnelling microscopy (STM) are used to characterise the deposition behaviour of sodium on a Au(111) substrate.

The deposition follows several stages: (i) Formation of a surface alloy of sodium and gold at the initial stages of the sodium deposition. A change of the atomic step height is clearly observed in the STM images. (ii) Monoatomic high islands form on top of the surface at 0.5 V vs. Na/Na^+. The islands are observed to coalesce and grow with time to form smooth layers which cover the complete scanned area of 200 nm × 200 nm. (iii) Small nuclei in form of islands grow onto the previously formed layers, resulting in a three-dimensional growth of cauliflower-like structures.

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Electrochemical Characterisation of Cu Model Catalysts

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Copper (Cu) is the only monometallic electrocatalyst that can reduce carbon dioxide (CO_2) into hydrocarbons and alcohols [1]. The selectivity towards certain products is thereby dependent on the properties of the electrolyte as well as the catalyst itself [2]. While electrolyte properties such as cation and anion identity are determined by the choice of the electrolyte and remain constant during the reaction the catalyst is prone to morphological changes [3,4]. In general detection of these structural changes relies on in situ experiments at the synchrotron or operando electrochemical scanning tunneling microscopy [3,5]. Herein we demonstrate an electrochemical approach to characterise Cu electrocatalysts based on measurements performed over well defined extended Cu surfaces. Furthermore, these measurements shall be extended to investigate the transient morphological changes experienced by nanoscopic Cu clusters during CO reduction.

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Ab-initio simulations of electrified interfaces under realistic conditions

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An in-depth, atomic-level characterization of solid-liquid interfaces is crucial for the design of a wide range of energy conversion systems such as electrocatalysts, batteries or fuel cells. Predictive-quality quantum mechanical (QM) simulations can make most valuable contributions to this end, but are challenged by the treatment of the liquid environment – even when relying on computationally most efficient approaches like semi-local density-functional theory (DFT). Traditionally, the electrochemical stability and activity at such interfaces has therefore been analyzed from charge-neutral DFT calculations, often considering only a very reduced set of interfacial degrees of freedom, e.g. only adsorbates that are chemically bound to the electrode surface.

Recently, it has been shown that an inclusion of mean-field solvation and electrolyte effects via hybrid QM/continuum models allows to determine electrochemical properties with much better accuracy and at only marginally higher computational costs [1,2]. We will present recent developments in simulation strategies of electrochemical interfaces within such implicit solvation schemes, using the ENVIRON [3] module of Quantum ESPRESSO, and assess its accuracy by comparison to experimental and theoretical results. In particular, we will analyze how the application of a potential via explicit variation of the electronic surface charge affects the energetics of electrosorbed adsorbates on metallic surfaces.

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Probing Intermolecular and Molecule-Substrate Interactions at Angstrom Scale via Scanning Tunneling Microscopy and Tip-Enhanced Raman Spectroscopy

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My research group is broadly interested in spectroscopically determining how local chemical environments affect single molecule behaviors. We focus on highly heterogeneous systems such as molecular self-assembly and bimetallic catalysis, developing and using new imaging and spectroscopic approaches to probe structure and function on nanometer length scales. We are using Tip-Enhanced Raman Spectroscopy (TERS) which affords the spatial resolution of traditional Scanning Tunneling Microscopy (STM) while collecting the chemical information provided by Raman spectroscopy. By using a plasmonically-active material for our scanning probe, the Raman signal at the tip-sample junction is incredibly enhanced, allowing for single-molecule probing. This method, further aided by the benefits of ultrahigh vacuum, is uniquely capable of obtaining (1) single molecules chemical identification; (2) the molecular mechanism of chemical bond formation under near-surface conditions using self-assembly concepts; (3) adsorbate-substrate interactions in the ordering of molecular building blocks in supramolecular nanostructures. By investigating substrate structures, superstructures, and the adsorption orientations obtained from vibrational modes, we extract novel surface-chemistry information at an unprecedented spatial (<1nm) and energy (<10 wavenumber) resolution. We are able to interrogate the impact of changes in the chemical environment on the properties of supramolecular nanostructures, and thereby lay the foundation for controlling their size, shape and composition.

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Microcalorimetric investigation of silver deposition from silver cyanide complexes

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Electrochemical silver deposition from cyanide containing solutions is one of the most common methods for producing thin Ag-deposits on different substrates. Therefore, electroplating of silver from cyanide electrolyte is of great technical importance [1]. However, the use of such plating-bathes involves a high risk for the environment due to the potential release of toxic CN^-. The knowledge of the detailed reaction mechanism of silver deposition would substantially simplify the development of alternative plating methods. Despite intensive efforts it could not be determined yet if the reduction of Ag^+ proceeds via an adsorbed species or by direct discharge of a solvated complex compound [2,3].

Measuring the heat evolution of electrochemical reactions enables the determination of the reaction entropy, which, in turn, allows conclusions on the reaction mechanism. Therefore, cyclovoltammetric and microcalorimetric measurements were performed to detect the reversibly exchanged heat at a single Ag-electrode during short potential pulses in cyanide electrolyte.

In solutions with low (0.008 M) or no amounts of additional cyanide the $[Ag(CN)_2]^-$-complex is the predominant species. The results show that silver deposition at negative potentials takes place by direct reduction of this complex probably without any adsorption step. In solutions with higher cyanide concentration (0.1 M) the dissociation of the $[Ag(CN)_3]^{2-}$-complex precedes the charge transfer step. At more positive potentials a passivating surface layer on the Ag-electrode is formed. Based on the microcalorimetric measurements it can be shown that this surface layer results from the formation of solid AgCN.

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Identification of Active Electrocatalytic Sites Using Electrochemical Scanning Tunneling Microscopy

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In order to economize the resources of our world, research should focus on the use of widely abundant and environmentally friendly materials and techniques. In terms of energy supply, a “hydrogen economy” would provide such a sustainable and worldwide accessible energy system. However, for such electrochemical energy provision devices to become competitive, suitable catalysts have to be developed. The performance of such a heterogeneous catalyst is highly dependent on the electronic structure of specific surface sites, so-called active sites, which offer optimal binding of reaction intermediates. Commonly, Sabatier-type volcano plots are used to predict the geometric structure of optimal active sites [1]. Combining theoretical predictions with a technique that is able to directly identify and monitor these sites in-situ would therefore be a powerful tool to advance the performance and rational design of catalysts.

Here we demonstrate the potential of a conventional scanning tunneling microscope (STM) to spatially map and in-situ identify active sites on a catalyst's surface with resolutions down to the nanometer or even atomic scale. In the course of a reaction, reactants and products ad- and desorbing on and from the surface present in the tunneling gap, change the composition of the tunneling medium, and thus have an influence on the tunneling current. By monitoring relative changes in the tunneling current, an increased noise level was detected over active centers, confirming electrochemical STM (EC-STM) as a powerful tool to determine the position of active sites [2].

We have successfully applied EC-STM to model catalytic systems such as Pt(111) and Pt3Ni(111) for the oxygen reduction reaction and Ir oxide for the oxygen evolution reaction. Furthermore, we turned our interest towards carbon-based catalytic materials, as they are potentially more environmentally friendly. Here we were able to resolve active sites with down to atomic resolution.

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C_2N/WS_2 van der Waals Type-II Heterostructure as a Promising Water Splitting Photocatalyst

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Increasing global warming and diminishing fossil fuel reserves have led to extensive research in finding sustainable resources of energy like hydrogen production from water using sunlight. In this direction, we proposed C_2N/WS_2 van der Waals heterostructure as a possible photocatalyst for water splitting. The C_2N/WS_2 heterostructure was found to satisfy many of the required properties of an efficient photocatalyst[1], which were evaluated using first-principles calculations. For instance, band edges of the heterostructure were found to satisfy both water oxidation and reduction energy levels, ensuring the occurrence of these two reactions. Additionally, it was found to be a type-II heterostructure, thus enabling the separation of electrons and holes into two different layers upon light irradiation and thereby facilitating water oxidation on WS_2 layer and water reduction on C_2N layer. The interlayer charge transfer from WS_2 to C_2N monolayer could serve the dual purpose of separating photoinduced charge carriers and extending their lifetimes. Most importantly, light absorption in visible range for the heterostructure was significantly enhanced compared to the constituent monolayers, rendering it to be a good sunlight absorber. The heterostructure also exhibited large charge carrier mobilities, indicating the high probability of utilization in reduction and oxidation reactions before recombination. Apart from fulfilling the required physical properties for an efficient photocatalyst, a facile hydrogen generation on the heterostructure was also observed, based on the free energy calculations. Therefore, this study explains the underlying mechanism of the enhanced photocatalytic activity of the proposed C_2N/WS_2 heterostructure, which could further lead to the designing of wider range of type-II photocatalysts.

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Ab Initio Thermodynamics Insight into the Surface Structure of Transition Metal Carbides in Aqueous Electrolyte

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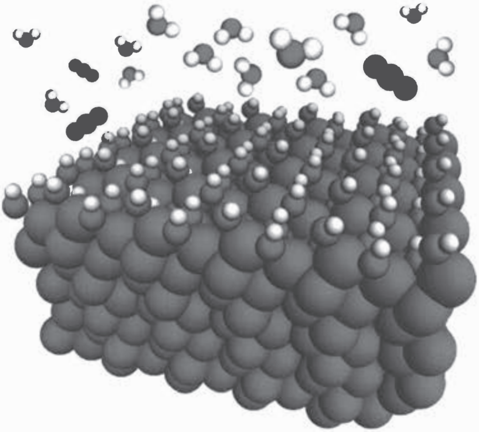
A drastic reduction of CO_2 is urgently needed to fight climate change and enable a sustainable growth. The electrochemical reduction of CO_2 (CO_2RR) is a promising approach to generate chemical energy carriers from renewable electricity [1]. Transition metal carbides (TMCs) are a promising non-noble material class, with e.g. Mo_2C recently reported to convert CO_2 into CH_4 at low potentials of ~0.55 V [2]. Understanding the surface structure and composition of TMCs under working conditions in the aqueous electrolyte is a prerequisite for ensuing CO_2RR mechanistic studies. We therefore conduct ab initio thermodynamic calculations to investigate the atomic structure of Mo_2C/aqueous interfaces as a function of potential and pH. Based on these insights, we further determine the adsorption properties of key CO_2RR reaction intermediates on these surfaces.



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Direct Characterization of Ionic Liquid/Graphene Electrode Interface by X-ray photoelectron spectroscopy

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Ionic liquids (ILs), salts with low melting points, have drawn significant interest in electrochemistry due to their enormous potential as solvent-free electrolytes for applications in batteries, supercapacitors, and electrodeposition. The IL/electrode interface plays a crucial role in these electrochemical phenomena and requires atomic-scale understanding but has not been explored due to the lack of experimental methods. Here, we report an X-ray photoelectron study on the IL/electrode interface with atomic-scale depth resolution by using an electron-transparent graphene electrode.

The main body of the electrochemical cell is made of PEEK and the cell holds three electrodes: Pt quasi-reference electrode, stainless steel counter electrode, and the terminating graphene working electrode, which is supported by a porous silicon nitride membrane. The IL in the cell is separated from the vacuum measurement chamber by the graphene. X - rays irradiate the IL through the graphene and the photoelectrons from the IL can penetrate the electrode and be detected on the vacuum side. The atomic-scale depth information of the interface was obtained using (angle-resolved) X-ray photoelectron spectroscopy. Due to the high concentration of electrolytes in IL, our approach does not require an intensive synchrotron source, which has advantages for avoiding beam damage.

We directly observed the potential screening and the change of counterions at the IL/graphene interface from the binding energy shifts and the intensity changes of IL as a function of the applied potential.

Adsorption, Decomposition and Surface Dynamics of Formic Acid on Cu{531}

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The decomposition of formic acid has been studied on numerous low-index metal and metal oxide surfaces, both for its industrial relevance and as a model system for the catalytic properties of various surfaces. In this dispersion-corrected density functional theory study, we focus on the adsorption of HCOOH and formate as its first decomposition intermediate on the chiral Cu{531} surface. The interplay between chirality and surface dynamics is explored by using the transition state of this dissociation reaction as a starting point for *ab initio* molecular dynamics simulations. Special focus in the analysis of these reactive trajectories lies on the time evolution of rotational momenta.

On the Stability of Gold Electrodes in Ionic Liquids at Very Negative Potentials

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It is well-known that the electrochemical stability of room temperature ionic liquids (RTILs) is dramatically decreased after the addition of water.[1,2] While this effect is highly detrimental to applications in electrodeposition and energy storage, the increased conductivity and lower viscosity of mixtures with water are still highly desired. For this reason, previous studies investigated the electrochemical stability of many RTILs and mixtures of water in great detail.[3] However, the stability of the electrode itself has not been addressed systematically. This holds especially true for noble metal electrodes for which degradation is usually only achieved by strongly oxidizing agents or anodic treatment and not under a highly reductive environment, which is necessary for electrodeposition.

In this study, we present the electrochemical behavior of a polycrystalline gold electrode in multiple RTILs at highly negative potentials and highlight the impact of trace amounts of water on degradation processes. Scanning electron microscopy is employed to determine structural changes of the electrode surface, revealing the occurrence of faceting phenomena. Electrochemical characterization provides evidence for the enhancement of specific crystallographic features and facets compared to the pristine polycrystalline gold electrode.

This research aims at presenting a new perspective on noble metal electrode stability for strongly negative polarizations and how these findings can be compared to studies of noble metal electrode stability in aqueous electrolytes.[4,5]

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Molecular Dynamics Simulations of curved graphitic Electrodes in Supercapacitors

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Supercapacitors are promising storage devices for electrical energy that offers a high power density but typically low energy density. Their storage performance is due to a reversible ion absorption by forming an electric double layer on the electrode surface. Molecular dynamics (MD) simulations offer the possibility to gain deep insights into the molecular mechanisms of forming electric double layers and the pore filling. However, simulations show that in supercapacitors with an ionic liquid as electrolyte, the mean-field approach for calculating the differential capacitance leads to false results due to the strong correlation of ions. By using a free energy approach for the calculation of the differential capacity from the fluctuating charge density on the electrode surfaces, it is possible to show a non-linear behavior of the ionic liquid on the capacitance [1]. Furthermore, MD-Simulations show a different orientation of the ionic liquid to the electrode interface depending on the applied potential, which can be a reason for the fluctuation of the capacity. By simulating curved graphitic electrodes, with a convex and concave pore-like structure, in combination with a diluted ionic liquid as electrolyte it is possible to examine the impact of curvature on the orientation of the ionic liquid, and finally the resulting capacity [2].

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From Structural Fluctuations to Vibrational Signatures of Water at α-Al_2O_3(0001) Surface: Insights from Ab Initio Molecular Dynamics

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Atomistic description of water adsorption on metal oxide surfaces like α-Al_2O_3 is of crucial importance for many research areas, from geochemistry to heterogeneous catalysis [1]. In particular, water can adsorb molecularly or dissociatively onto different sites of metal oxide surfaces [2]. These adsorption sites can be disentangled using surface-sensitive vibrational spectroscopy, as Vibrational Sum Frequency (VSF) generation [3]. The spectroscopic assignment is often corroborated by theoretical calculation of vibrational frequencies, which, in may cases is limited to static Normal Mode Analysis (NMA). To go beyond this approach, classical time-correlation functions [4] obtained from Ab Initio Molecular Dynamics are the perfect tools to include anharmonicity, line broadening, surface thermal motion and spectroscopic selection rules.

Here, using an efficient scheme based on velocity-velocity autocorrelation functions from DFT-based AIMD trajectories [5], we report vibrational signatures of water on α-Al_2O_3(0001) surface: from Vibrational Density Of States (VDOS) curves, to InfraRed (IR) and VSF spectra. We consider two representative cases for low and medium coverage regimes: first, describing deuterated water dissociative adsorption on the thermodynamically most stable Al-terminated surface [6] and then simulating a reconstructed, O-terminated hydroxylated surface, with or without additional water. While the first example allows for analysis of dissociated OD species at sub-monolayer coverages and comparison with experimental VSF spectra in UHV, the second corresponds to a stable situation in environmental conditions, towards the description of a solid / liquid interface [7]. For the hydroxylated surface model, we highlight high-frequency vibrations of interfacial OH bonds, disentangling their spectral features in terms of their local hydrogen bonding environment and their average orientation. Both cases are directly tested again previous experiments [2, 8, 9] with an overall good agreement.

While sampling of equilibrium trajectories provides information about vibrational frequencies and spectra, a non-equilibrium picture is required to describe adsorbate-surface couplings and energy transfer at the interface. Together with pump-probe VSF experiments, non-equilibrium AIMD simulations are employed considering a water-covered hydroxylated (0001) surface model. Our aim is to reproduce the dynamics of vibrationally excited OH bonds and to follow their behaviour upon IR-light absorption. The corresponding trajectories are then analyzed either by looking at the kinetic energy decay of selected OH bonds or by calculating transient VDOS spectra, in order to extract vibrational lifetimes which are also determined experimentally. Overall, we find that interfacial OH groups with stretching frequencies above 3700 cm^{-1} decay with a timescale between 2 and 4 ps. This observation is in good agreement with experiments, especially for vibrational lifetimes obtained for the air/α-alumina and the liquid/α-alumina interfaces. Moreover, we can also dissect pathways for vibrational energy redistribution, where the adsorbed water layer and hydrogen-bonded surface OH groups play the most prominent role.

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Electrochemical Tip-Enhanced Raman Spectroscopy: Nanoscale Reactivity Mapping with Chemical Specificity

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Identification and local detection of reaction intermediates during electrochemical reactions is crucial to develop rational design principles to engineer future highly-efficient fuel cell catalysts. However, simultaneous acquisition of nanoscale topographic as well as chemical information under electrochemical reaction conditions represents a major challenge in electrocatalysis. We have proposed electrochemical tip-enhanced Raman spectroscopy (EC-TERS) as a potential future nano-tool to address this challenge.[1] EC-TERS is a combination of a conventional electrochemical scanning tunneling microscopy setup and a Raman platform, combining the advantages of scanning probe microscopies, electrochemistry and Raman spectroscopy. The STM-tip acts as a nano-antenna that amplifies, via a surface plasmons generated near-field, the otherwise weak Raman signals of few molecular adsorbates in close proximity to the tip apex, while maintaining the EC-STM imaging capabilities.

We have mapped the water splitting reaction at the reversible electro-oxidation potential of Au(111) nano-defects in contact with sulfuric acid, and correlate surface topography and electrochemical reactivity with a chemical feature sensitivity of 9.4 nm. Delivering such information, we provide the proof-of-concept that EC-TERS can be utilized for nanoscale chemical reactivity mapping under reaction conditions.

We have built platinum group metal islands with controllable size and island distribution on Au(111) by copper underpotential deposition and galvanic metal displacement reaction. The catalytic properties of these islands can be used in EC-TERS experiments to investigate the active catalyst sites for electrochemical prototype reactions like formic acid oxidation.

With further methodology development and continuous technical setup improvement, EC-TERS can provide insights on a wealth of (electro)chemical reactions occurring at the nanoscale, possibly approaching the single active site in the future.

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Complexity in the Double Layer of Pt(111)-Aqueous Electrolyte Interface

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Atomic/molecular level understanding of the double layer, interfacial water structure such as organization and orientation, H-bonding network at the metal-electrolyte interface is of utmost importance for fundamental science as well as for technological applications[1–3]. These water structures is the important part of the double layer structure of electrode-aqueous electrolyte interfaces. However, the double layer of Pt (111) is not well understood yet while Pt is the most studied and applied metal in energy, catalysis, sensing and electrochemistry. Here, we investigated the double layer and discovered the minimum of the Gouy-Chapman capacitance on Pt (111) for the first time and directly identify the potential of zero charge of Pt(111)[4] which is an important intrinsic property of an electrode material. Similar experiments were demonstrated to observe the GC capacitance and pzc of Au(111) which is in good agreement with the literature[5]. The complexity arises when non-specifically adsorbing anions (e.g. perchlorate, fluoride, methanesulfonate) and their concentration change the double layer capacitance of Pt(111). Moreover, the inner layer and diffuse layer capacitance of Pt(111) is higher than that of Au(111). Here we will be discussing the effect of anions on the water structure and the reorganization of the water at the interface around the pzc of Pt(111).

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Approaching electrochemistry with TranSIESTA

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The TranSIESTA code [1,2] was developed within the SIESTA project and code [3] to study problems involving steady-state non-equilibrium problems in nanoscale constrictions, where an external electric bias is imposed between the two sides of the constriction, and a steady electric current is established. Non-equilibrium Green Functions are used to solve the problem, as they can deal with open, non-periodic systems out of equilibrium. This machinery can be also used for the study of electrified solid/liquid interfaces [4], where an external bias is applied to the solid electrode. I will show examples of application of this idea, as a proof of concept for future realistic atomistic first-principles simulations of electrochemistry.

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Entropy change during HER on Pt

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We measure the heat evolution during pulsed hydrogen evolution (HER) on platinum foil in pure and H_2 saturated 0.1 M H_2SO_4. The measured heat is directly correlated with the reaction entropy of the half-cell reaction. Employing the thermal response function of the electrochemical cell we can reconstruct the time-resolved heat/entropy flux during the reaction [1].

Since the HER has been one of the most investigated reactions many mechanistic details are known. We want to compare the measured heat flux to the currently accepted mechanistic concepts and extract thermodynamic data of the involved species.

Upon application of 10 ms current pulses in pure 0.1 M H_2SO_4, we initially observed positive heat flux, which turned into negative heat flux after 4 ms. In contrast, when the solution was saturated with H_2 we obtained only negative heat flux. From the determination of the total entropy change caused by the reaction, we were able to match these observations with the formation of dissolved H_2 in pure and gaseous H_2 in H_2-saturated solution.

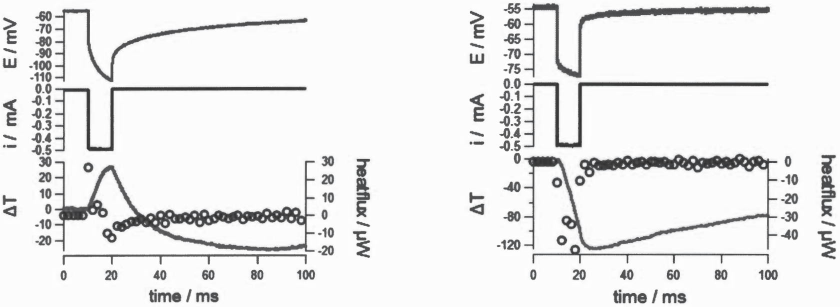

Figure 1: Potential (blue) and temperature response (red) to a 10 ms 500 µA current pulse (black). Left: pure 0.1 M H_2SO_4 solution; right: H_2 saturated 0.1 M H_2SO_4 solution. The black dots represent the reconstructed heat flux.

The entropy flux during the first 2ms after starting the reaction is considerably lower than during the rest of the pulse, which may result from the initial adsorption step of the HER. From the disentanglement of the heat flux, we hope to calculate the entropy of the reactive hydrogen species.

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In situ Atomic Force Microscopy of Copper Surfaces for CO_2 Electroreduction

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Insufficient knowledge of nanoscale materials properties and structure-property relationships under (electro-)chemical reaction conditions greatly hampers advances in rational design of materials for key catalytic reactions including electrochemical CO_2 conversion. As many catalysts undergo substantial morphological, structural and chemical changes during reactions operando methods that allow real-space analysis of electrode surfaces in fluids while reactions proceed are considered a keystone in future catalysis research.

In this work we employ *in situ* electrochemical atomic force microscopy (EC-AFM)[1] for the study of copper crystal surfaces under CO_2 electroreduction conditions. We focus on UHV-prepared single crystalline copper surfaces, which are suitable to model morphological aspects relevant to CO_2 electroreduction.[2] On Cu(hkl) single crystal faces, large morphological changes are observed upon exposure to aqueous electrolyte. Under reducing conditions, atomically stepped surfaces can be established.[3] From this starting point, we follow *in situ* morphological changes in potentiostatic and potentiodynamic image series. Preliminary results show drastic and at least partially reversible processes over the potential range, which proceed at largely different rates during anodic and cathodic scans. With the combination of electrochemical electrode characterization and local real space morphology information, this work sheds light on the general behaviour of polarized electrode surfaces, as well as on interface dynamics associated with electrochemical potential pulses used to enhance product selectivity in copper CO_2 reduction.[4] Product analysis for correlation with surface reactivity is under development. We will further discuss the broader relevance and applicability of introduced *in situ* EC-AFM techniques on the route toward rationally designing catalytic materials featuring enhanced stability and product selectivity.

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In-Situ STM Studies of CoO_x Nanoislands on Au(111): Potential Dependent Mobility and Stability

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Cobalt oxide is one of the most intensively studied oxides in electrocatalysis, as it is a promising earth abundant electrocatalyst e.g. for water splitting. In spite of the importance of this oxide material, it has been a challenge to understand the functionality and structure of the oxide interface under reaction conditions. Oxide interfaces are highly dynamic, responding to the reaction environment, such as pH, solvents and electrochemical potential. In this study we investigated an atomically defined CoOx/Au(111) model system in-situ in a 0.1 M phosphate buffer solution at pH 10. The samples were prepared by physical vapor deposition (PVD) in an ultrahigh vacuum (UHV) chamber following a preparation procedure previously reported by J. Lauritsen and coworkers. Changes in the morphology of the model system were followed by electrochemical scanning tunneling microscopy (EC-STM). The dissolution behavior of cobalt was monitored by on-line inductively coupled plasma mass spectrometry (ICP-MS).

The model system was investigated in a potential window ranging from -0.4 V_{RHE} to 1.8 V_{RHE}. At 0.8 V_{RHE}, both CoO bilayer and CoO double-bilayer nanoislands are stable and show no mobility in subsequent STM images. In the anodic scan, the CoO islands retained their morphology up to a potential of 1.5 V_{RHE}, above which the Au(111) undergoes oxidation and roughening. In the cathodic scan at potentials of 0.5 V_{RHE} and below, the CoO bilayer islands show increased mobility and eventually undergo partial dissolution. ICP-MS indicates an onset of Co dissolution at 0.5 V_{RHE}, in good agreement with the increased mobility of the CoOx nanoislands as recorded by EC-STM. Stepping the potential from 0.8 V_{RHE} to more negative potentials leads to decreasing dissolution of cobalt, which shows that Co dissolution is a largely transient process. In contrast to the CoO bilayer islands, the CoO double bilayer islands retain their morphology up to even lower potentials. Close to the reduction potential of Co^{2+} to Co^0, we observe the re-deposition of (adsorbate covered) Co aggregates on the Au surface. Further reduction and subsequent reoxidation leads to dissolution of most Co containing deposits.

Towards ‘seeing’ the surfaces of oxide thin films using EC-STM

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Oxides, specially oxide surfaces play a significant role in photo- and electro-catalysis. There are many reviews involving the role of oxides. Most oxides photo-catalysis reviews adopt an application-driven perspective, but a few approached the field from a surface science perspective. [1] We chose titanium dioxide (TiO_2) as a typical model system to explore the role of oxides surface in photo-catalytic process due to its wide application in the process.

Scanning tunneling microscopy(STM) is of great importance in situ studies of single molecule photo-catalysis. A part of small molecules adsorption on model TiO_2 surface have been observed by using STM in ultrahigh vacuum(UHV). [2] Moreover, in contrast to UHV, much less is achieved in solid/liquid interfaces, which is a more realistic environment. To our knowledge, the study of surface processes is different between UHV and solid/liquid system. Serrano et al. highlighted high-resolution situ STM images of the rutile TiO_2(110) surface in direct contact with bulk liquid water for the first time. [3] And electrochemical scanning tunneling microscopy(EC-STM), which can provide structural morphology within potential range, is often used in metal surface study and very less in oxides surface study. Therefore, it is promising to explore the role of oxides/liquid interface science in photo- and electro-catalysis by using EC-STM.

In this work, we choose pulsed laser deposition (PLD) to prepare TiO_2 single-crystal thin films with different doping and defects, which possess simple structural arrangements and are of great value in experimental and calculation process. X-ray diffraction(XRD) and atomic force microscope(AFM) are used to analyze the crystal structures. Finally, we study the structure of TiO_2 and adsorption of small molecules under different electrochemical conditions in TiO_2/liquid system by using EC-STM, and combine density functional theory based molecular dynamics(DFTMD) simulations to reveal the electrochemical behavior in TiO_2/liquid interface system.

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First-principles modeling of metal dissolution at Mg/H_2O interfaces

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Knowledge of the atomistic mechanisms of reactions at electrified electrochemical interfaces are important in understanding critical processes relevant to electrochemistry and corrosion. Using our recently developed ab initio potentiostat scheme [1], we study the process of metal dissolution at the vicinal Mg(1 2 -3 15)/water interface using DFT based ab initio molecular dynamics simulations under conditions of applied anodic bias. We observe that water dissociation and the subsequent adsorption of OH groups at low coordinated "kink" sites of the electrode makes this site more susceptible to dissolution. This kink atom gradually dissolves during the course of the simulation, forming a 6 fold solvation shell. The anomalous hydrogen evolution reaction, which is also observed during the simulations appears to happen independently of the dissolution reaction. Based on these observations, a possible reaction mechanism of Mg dissolution involving water dissociation is proposed.

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Constructing an *in-situ* electrochemical cell for soft x-ray study on CO_2 reduction over Cu

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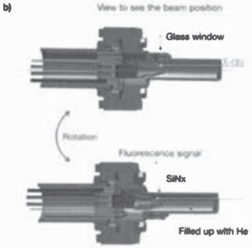
By coupling to the green electricity resource, electrochemically converting CO_2 into value-added chemical products (i.e., CO_2 reduction reaction, CO_2RR) is a cost effective way to facilitate a net-neutral CO_2 emission future. So far, copper (Cu) is the only known catalyst that is capable to simultaneously produce a mixture of C_1 to C_{2+} oxygenates and hydrocarbons. However, the underlying mechanism is still elusive. Despite a hard X-ray investigation on nanostructured copper cathodes has showed the precursor oxidation state does not affect the electro-catalytic selectivity,[1] the structural transformation does not provide enough information about the correlation between the product formation and Cu substrate under a real CO_2RR process. It is believed that a soft x-ray study could provide more detailed insight because the electronic interaction between the Cu valance band and the 2p orbital of carbon and oxygen from the reactants could thus be monitored during the *operando* condition.

Our team has built an endstation denoted as **TI**me resolved x-ray s**T**udies of re**A**ctio**N**s (TITAN) equipped with x-ray absorption detector and x-ray emission spectrometer **that fits the VERITAS beamline's open**-port branch (B branch) in MAXIV (Figure 1a), and our *in-situ* electrochemical cell (Figure 1b) can perfectly be adopted into TITAN with a 360° azimuthal rotating freedom. The cell has two **symmetric sides: one for optimizing the cell's position to the beam, and the other for** performing the XAS for Cu L edge and XES measurements on O or C Kα. The incident beam will come from a sharp angle of 15° to amplify the interaction between the beam and the substrate. The challenges of the cell construction/design, including the x-ray transmission, surface contamination, and beam damage will be discussed and the usability of the cell will be verified during the commissioning beamtime (week 6, 2020). The first experimental beamtime will be on week 8, 2020.



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Electroreduction of water and CO_2: competition or synergism on Mo_2C film electrodes?

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The materials class of transition metal carbides (TMCs) has gained importance among electrocatalysts for reduction processes such as the hydrogen evolution reaction (HER) and the CO_2 reduction reaction (CO_2RR). In the CO_2RR, theoretical calculations [1] predict that TMCs are promising alternatives to Cu catalysts due to their ability of breaking the binding energy scaling relations for the corresponding reaction intermediates, which has been experimentally shown to result in less negative onset potentials for hydrocarbon formation on Mo_2C compared to Cu [2]. For a comprehensive understanding of the electrocatalytic properties of Mo_2C towards the CO_2RR and the competing HER in aqueous electrolytes, the present study merges materials science and interface analytics with electrochemistry to unravel the pathways of these complex reactions.

We report on the synthesis of Mo_2C films using direct carburization of polycrystalline Mo substrates through carbothermal conversion. Cyclic voltammetry, complemented by rotating ring disc electrode (RRDE) measurements, was used to investigate the electrocatalytic activity of Mo_2C films towards the HER in the absence and presence of CO_2, while changes of the chemical composition at the surface were analyzed with *ex-situ* emersion X-ray photoelectron spectroscopy (XPS). Subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) enabled the *in-situ* determination of reaction intermediates at the solid/liquid interface while gas chromatography was used for the detection of hydrogen. The activity of Mo_2C film electrodes towards the HER was observed to be enhanced in the presence of CO_2.

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A First Principles Analysis of the Charge Transfer in Magnesium Corrosion

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Magnesium is the lightest structural engineering material and bears high potential in areas such as the automobile industry, medical engineering and energy storage systems. However, untreated magnesium alloys are prone to corrosion, restricting their practical use. In order to prevent or control corrosion and degradation processes, a deeper understanding of the underlying reaction pathways is crucial. Recent studies about the hydrogen evolution in magnesium corrosion suggested gaseous hydrogen to form according to the Volmer-Heyrovski pathway, rather than the Volmer-Tafel pathway as previously assumed. Still, there is no real consensus about the involved energetic and electronic states, and questions about the charge state of dissolved magnesium remain. This study lies a focus on the energetics and charge transfers in the major magnesium corrosion mechanisms, thus answering open questions and supporting recent claims[1,2] in the realm of magnesium corrosion research.

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Electrified Au (111)-water interface studied by ab initio molecular dynamics

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Metal-water interfaces are present in many experimental settings and are of great relevance to various fields of study including electrochemistry. Therefore, a thorough understanding of water structure on the surface is essential and yet missing for many systems. Due to the exceptional properties of water and its complex behavior, computational methods can be great assets in providing unique insights to the metal-water interfaces, which may not be easily accessible via experiment.

Here, we study the Au (111)-water interface in the presence of an electric field using ab initio molecular dynamics simulations. The effect of the presence of the electric field and its strength on the interfacial water is studied. Our results so far show that in the absence of an electric field, the interfacial water has no preferential orientation with respect to the surface. Upon applying the electric field towards the surface, the interfacial water seems to re-orient towards the surface, with the hydrogens closer to the surface. This re-orientation is very weak and we believe that the re-orientation of the interfacial water is dominated by the hydrogen bonding. This is in agreement with previous studies where it was shown that the gold surface causes the hydrogen bonding to become stronger [1]. To test our hypothesis further, the influence of the electric field on a single water molecule on the gold surface was studied, where clear re-orientation of the molecule with respect to the presence, strength and direction of the electric field was observed.

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Selective stabilization of polar oxide surfaces in an electrochemical environment

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Solid-electrolyte interfaces are at the heart of various areas of application, such as batteries, electrolysis, photo catalytic water splitting or metal corrosion. Understanding what surface structures form in contact with an electrolyte is therefore very important. Focusing on the ZnO(0001) surface as a typical example of a polar oxide surface, we study the thermodynamic stability of its surface reconstructions in the electrochemical environment using density functional theory calculations. We find that the effect of the solvent is highly selective. Semiconducting surfaces are significantly influenced by the presence of the solvent, while the impact on metallic surfaces is less pronounced. In particular, semiconducting surfaces which experience a high electrostatic penalty in vacuum, experience a large stabilization by solvation. We will show that this selectivity has direct consequences for the surface phase diagram and discuss the mechanisms by which it is triggered.

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In situ AFM observation of Cu electrodeposition and dissolution on Au single crystal

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Research on the electrodeposition mechanism of copper has been carried out by time course of precipitation current during constant potential electrolysis, ex-situ and in-situ observation. Among them, we have conducted in-situ observation using high-speed AFM[1, 2].

A three-electrode electrochemical AFM cell was used for in-situ observation. In the cell, the working electrode was single crystal Au(111) substrate (φ= 3 mm). The reference electrode was a copper wire and the counter electrode was a platinum wire. Potentiostatic electrodeposition was carried out in an aqueous electrolyte containing 3 mM $CuSO_4$ and 50 mM H_2SO_4 at room temperature. The high-speed AFM image area (500×375 nm^2) was recorded at 1 flame s^{-1}.

Before electrodeposition, a smooth substrate without any irregularities was observed. At a deposition potential(- 0.08V), it was confirmed that a few nanometer size nucleation occurred and the precipitates grew in the plane direction along the steps(Figure 1.(a)~(d)). In addition, the surface of the electrodeposits showed a very small irregularity. At a dissolution potential(0.05V), it was observed that the electrodeposits dissolved from the edge surface(Figure 1.(e)~(h)). As a result, regular growth and irregular dissolution was confirmed during electrodeposition and dissolution process.

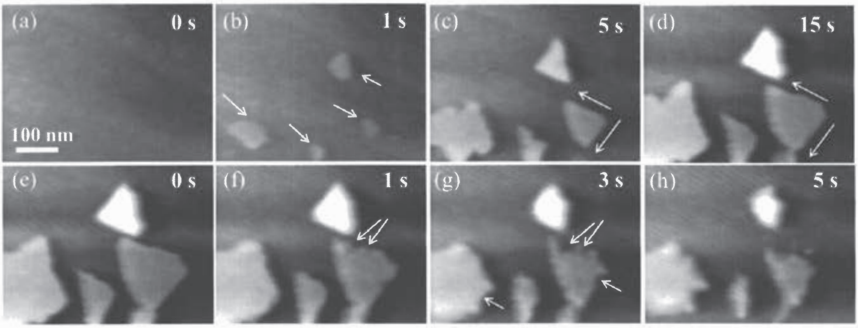

Figure 1. Series of high-speed AFM images of Cu growth((a)~(d)) and dissolution((e)~(h)) on Au(111) at (a) 0 s , (b) 1 s , (c) 5 s (d) 15 s and (e) 0 s, (f) 1 s, (g) 3 s, (h) 5 s after starting Cu electrodeposition and dissolution (Electrode potential = - 0.08 V, 0.05 V) Image acquisition rate = 1 flame s^{-1})

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Effects of Adsorbates on Pt (100)

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Generally speaking, there exists visible double layer region, which is hard to be observed on other surfaces' counterparts, in cyclic voltammograms (CVGs) of Pt (111) surface. The explanation is the co-adsorption of hydrogen and hydroxide (cations also participate in basic condition), which is presumed by many researchers[1] [2]. According to deconvolution of CVGs, the CVGs of Pt (100) at 0-0.6V (v.s. RHE) consists of a broad peak and a sharp peak, corresponding to adsorption of hydrogen and replacement of H* by OH* respectively.

The starting point of my project is modelling electrical double layer (EDL) on clean Pt (100) surface. By adding counter ions on the surface, we can adjust the electrode potential (v.s. SHE) and construct the model near the pzc (potential of zero charge). The potential of model is calculated with the computational standard hydrogen electrode method[3]. The density and orientation of water on Pt (100) is similar to its counterpart on Pt (111). The water can be divided into three parts, chemisorbed water, physisorbed water and bulk water respectively.

Then, the adsorbates, including hydrogen and hydroxide, will be added into the model and simulate the real surface step by step. According to theoretical derivation [1], the potential region for co-adsorption is 0.4-0.5V (v.s. RHE). The pzc is slightly negative to this region, so we start with a hydrogen-covered surface. The coverage of hydrogen is 1ML, determined by the surface energy calculation[4]. The calculation hasn't been finished and we expect the surface will be more hydrophobic.

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Imaging of Active Sites for the Oxygen Evolution Reaction on Gold Electrodes *Operando*

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Many mechanistic aspects of the oxygen evolution reaction (OER) remain unknown, partially because the most frequently employed methods are either indirect (electrochemistry) or ensemble averaging (spectroscopy), partially because the reaction happens on oxide surfaces which are inherently more complicated to characterize than metals. We overcome these difficulties by combining second harmonic imaging with electrochemical methods and address the so far neglected aspect of spatial heterogeneity of OER activity on Au. We investigate the OER operando on polycrystalline Au foils and homogeneous thin films and by observing where on the surface oxygen bubbles are formed, we find that the activity is highly local and confined to two distinct types of active areas which account for the majority of the activity. The first type, tens of square micrometers big, is observed at potentials positive of the OER onset, its formation is linked to a thicker oxide layer and a defect penetrating to the bulk which is why it is stable with respect to surface atom reconstruction. The fractional coverage of this active area we observe operando is similar to previously reported active site coverages of gas phase catalysts, but lower than ex-situ measured values for electrocatalysts. The OER current that is passed through it as a function of potential correlates well with the measured electrochemical current, suggesting that the latter is a sum of the contributions of only a few active areas. The second type of active area is observed at potentials negative of the OER onset, linked to a highly active surface motive, it is transient and not stable with respect to surface atom reconstruction. It possibly is the catalytically active species (hydrous oxide) in the incipient hydrous oxide/adatom mediator model of electrocatalysis[1].

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