

## O 45: Solid-Liquid Interfaces II: Reactions and Electrochemistry

Time: Tuesday 10:30–13:30

Location: WIL C107

O 45.1 Tue 10:30 WIL C107

**Photo-sensitive 2D-arrangement of -OH/H<sub>2</sub>O on brookite TiO<sub>2</sub> (210)** — •LEI YANG<sup>1</sup>, EERO HOLMSTROM<sup>2</sup>, TAKESHI FUKUMA<sup>3</sup>, and ADAM FOSTER<sup>2</sup> — <sup>1</sup>WPI Nano Life Science Institute, Kanazawa University, Kanazawa 920-1192, Japan — <sup>2</sup>COMP, School of Science, Aalto University, P.O. Box 11100, FI-00076 Aalto, Finland — <sup>3</sup>Division of Electrical Engineering and Computer Science, Kanazawa University, Kanazawa 920-1192, Japan

The brookite phase of TiO<sub>2</sub> is much less explored than the other two polymorphs (rutile and anatase), despite its potential applications in photocatalytic CO<sub>2</sub> reduction and water splitting. The first hydration layer and surface hydroxyl groups on brookite (210) surface and their structural changes under photo-irradiation have been considered to play significant roles in the process of such applications, thus will be elucidated at the atomic scale in this study by means of combining high-resolution liquid-environment atomic force microscopy (AFM) imaging using a custom-built equipment and *ab initio* molecular dynamics simulations. An interesting structural feature of the hydration layer of brookite TiO<sub>2</sub> (210) was observed by AFM imaging, which later disappeared under ultraviolet irradiation in preliminary results. The origins of the feature and its photo-switching behavior will be clarified.

O 45.2 Tue 10:45 WIL C107

**CPMD Performance Optimization for Large-Scale Simulations of Vibrational Spectra at Solid-Liquid Interfaces** — •TOBIAS KLÖFFEL<sup>1,2</sup>, PAUL SCHWARZ<sup>1</sup>, GERALD MATHIAS<sup>3</sup>, and BERND MEYER<sup>1</sup> — <sup>1</sup>ICMM and CCC, FAU Erlangen-Nürnberg — <sup>2</sup>HPC Group at RRZE, FAU Erlangen-Nürnberg — <sup>3</sup>LRZ, Garching

We present our recent optimizations of the ultra-soft pseudo-potential (USPP) code path of the *ab initio* Car-Parrinello molecular dynamics program CPMD (www.cpmc.org). All relevant USPP routines have been revised to fully support hybrid MPI+OpenMP parallelization. For two time-critical routines, namely the multiple distributed 3d FFTs of the electronic states and a key distributed matrix-matrix multiplication, we have implemented hybrid parallel algorithms with overlapping computation and communication. Our latest improvements include auto-tuning of overlapping computation and communication, communication avoiding, and node level MPI+MPI shared memory parallelization to fully exploit the powerful compute capabilities of SuperMUC-NG 48 core nodes. The achievements in performance and scalability are demonstrated on simulations of liquid water with 256 and up to 2048 molecules. With the improved CPMD code we were able to study the structural evolution of water on ZnO for increasing water coverage from the monolayer to thick water films by providing fingerprints of anharmonic vibrational spectra. Altogether, we performed 1 ns of *ab initio* simulations for systems with up to 368 atoms.

[1] X. Yu, P. Schwarz, A. Nefedov, B. Meyer, Y. Wang, Ch. Wöll, *Angew. Chem. Int. Ed.* **58** (2019) 17751.

**Invited Talk**

O 45.3 Tue 11:00 WIL C107

**In-situ identification of catalytically active surface sites using electrochemical STM** — •ALIAXSANDR BANDARENKA — Technical University of Munich, James-Franck-Str. 1, 85748 Garching, Germany

In the presentation, it will be demonstrated that common electrochemical STMs can be used to map the catalytic activity of the electrode surfaces with high spatial resolution. By monitoring relative changes in the tunnelling current noise, active sites can be distinguished in an almost quantitative fashion. Several important for energy provision reactions are used as model systems: the hydrogen evolution, oxygen reduction and oxygen evolution reactions. The above mentioned approach allowed to evaluate directly the nature of active sites at Pt(111), Pt<sub>3</sub>Ni(111), Pt and Pd monolayers on Au(111), HOPG, MoS<sub>2</sub>, MoSe<sub>2</sub> and IrO<sub>2</sub> electrodes in acidic and alkaline media.

## References

- E. Mitterreiter, Y. Liang, M. Golibrzuch, D. McLaughlin, C. Csoklich, J.D. Bartl, A. Holleitner, U. Wurstbauer, A.S. Bandarenka. *NPJ 2D Materials and Applications* 3 (2019) 25 - Y. Liang, C. Csoklich, D. McLaughlin, O. Schneider, A.S. Bandarenka. *ACS Applied Materials and Interfaces* 11 (2019) 12476\*12480 - Y. Liang, D. McLaughlin, C. Csoklich, O. Schneider, A.S. Bandarenka. *Energy & Environmental Science* 12 (2019) 351-357 - J.H.K. Pfisterer, Y. Liang, O. Schneider,

A.S. Bandarenka. *Nature* 549 (2017) 74\*77

O 45.4 Tue 11:30 WIL C107

**In-situ STM imaging of self-activated CO oxidation on Cu(111) electrocatalysts** — ANDREA AUER<sup>1</sup>, EVA-MARIA WERNIG<sup>1</sup>, XING DING<sup>2</sup>, ALIAXSANDR BANDARENKA<sup>2</sup>, NICOLAS HÖRMANN<sup>3</sup>, KARSTEN REUTER<sup>3</sup>, and •JULIA KUNZE-LIEBHÄUSER<sup>1</sup> — <sup>1</sup>Institute of Physical Chemistry, University of Innsbruck, Innsbruck, Austria — <sup>2</sup>Physics of Energy Conversion and Storage, Technische Universität München, Garching, Germany — <sup>3</sup>Theoretical Chemistry, Technische Universität München, Garching, Germany

Carbon monoxide (CO) is a key intermediate in the electro-oxidation of energy carrying fuels. In this work, the ability of Cu(111) single crystals to electrochemically oxidize CO at low overpotentials is reported. In-situ infrared spectroscopy confirms weak adsorption of CO on Cu(111) as well as its oxidation to CO<sub>2</sub>. Electrochemical scanning tunneling microscopy (EC-STM) reveals that during CO oxidation the Cu(111) surface reconstructs and concomitantly adsorbs OH, while forming low-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. The potential of maximum entropy which is closely associated with the potential of zero charge (pzc) has been determined for Cu(111) and correlated with the corresponding surface structures through EC-STM studies. In combination with DFT calculations that include the effects of applied potential and the solvent environment, this helps to achieve a true atomistic understanding of the interfacial structures and the electrocatalytic activity.

O 45.5 Tue 11:45 WIL C107

**Electrically triggered reactions at interfaces** — •FLORIAN DEISSENBECK<sup>1</sup>, LEI YANG<sup>1</sup>, MARC PANDER<sup>1</sup>, FANG NIU<sup>2</sup>, ANDREAS ERBE<sup>1</sup>, CHRISTOPH FREYSOLDT<sup>1</sup>, MIRA TODOROVA<sup>1</sup>, JÖRG NEUGEBAUER<sup>1</sup>, and STEFAN WIPPERMANN<sup>1</sup> — <sup>1</sup>Max-Planck-Institut für Eisenforschung, Germany — <sup>2</sup>NTNU Trondheim, Norway

Presently, few experimental techniques are able to directly probe the microscopic structure of solid-liquid interfaces. In order to develop robust strategies to interpret experiments and validate theory, we carried out *ab initio* molecular dynamics (AIMD) calculations for interfaces between liquid water and well-controlled prototypical semiconductor substrates, supplemented by attenuated total internal reflection (ATR-IR) spectroelectrochemical measurements. We introduce a potentiostat scheme, allowing us to perform MD simulations either at constant electric field or constant dielectric displacement. We discuss interactions between commonly used thermostats and the potentiostat, and suggest to introduce temperature-induced dipole fluctuations directly into the potentiostat scheme. This new approach has been validated by extensive benchmarks and is shown to not affect the vibrational spectra at the solid-liquid interface. Support from BMBF NanoMatFutur grant No. 13N12972 is gratefully acknowledged.

O 45.6 Tue 12:00 WIL C107

**Dependence of Electron and Ion Transport on the Intermolecular Coupling in Fluorinated Phthalocyanine Thin Films as Electrochromic Materials** — •THI HAI QUYEN NGUYEN<sup>1</sup>, MARIUS PELMUS<sup>2</sup>, SERGIU M. GORUN<sup>2</sup>, and DERCK SCHLETTWEIN<sup>1</sup> — <sup>1</sup>Justus Liebig University Gießen, Institute of Applied Physics — <sup>2</sup>Seton Hall University, Department of Chemistry and Biochemistry

Phthalocyanines as organic ionic and electronic conductors are of great interest for the application in electrochromic devices. An influence of the degree of fluorination in copper phthalocyanines on the intermolecular coupling of the molecules in the solid state and, thus, on the rate of electron and ion transport was observed: For *F*<sub>16</sub>*PcCu* the transport of electrons was faster than the diffusion of ions as opposed to *F*<sub>64</sub>*PcCu*. In this work, thin films of a new type of fluorinated phthalocyanine (*F*<sub>40</sub>*PcCu*) were prepared by physical vapor deposition. The dependence of the intermolecular coupling on the film thickness was analyzed by in situ UV/Vis spectroscopy. The transport of electrons and ions in these films as well as their electrochromic behaviour were investigated by electrochemical and spectroelectrochemical measurements with an aqueous solution of *KCl* as electrolyte. The films provided a well-balanced, equally fast transport of electrons and ions. The op-

tical absorption spectra revealed reversible changes of the films upon reduction with intercalation of the  $K^+$  counter ions and re-oxidation with extraction of the counter ions. Fast and stable electrochromic switching of the films was achieved over at least 200 cycles.

O 45.7 Tue 12:15 WIL C107

**Ab initio thermodynamics study of two-dimensional Ir and Ru oxide nanosheets as active oxygen evolution reaction catalyst in acidic media** — ●PO-YUAN HUANG, YONGHYUK LEE, CHRISTOPH SCHEURER, and KARSTEN REUTER — Technical University of Munich, Germany

Iridium and ruthenium oxides are among the most active oxygen evolution reaction (OER) catalysts in acidic media, with iridium oxide exhibiting somewhat lower activity, but higher durability. As one promising strand to maximize precious atom efficiency, highly active two-dimensional hexagonal nanosheets of both oxides have recently been reported [1,2]. Here, we use density-functional theory based *ab initio* thermodynamics to systematically compare the stable surface terminations of the isostructural Ir and Ru nanosheets as a function of the applied potential. Extending our investigation over both the sheet surface and the sheet edge, we find the Ir nanosheet to deprotonate already at much lower potentials. Thermodynamic Gibbs free energy barriers along the generally accepted OER reaction pathway are investigated to gain insight into the overpotentials and assess whether the earlier deprotonation can rationalize the different Tafel slopes measured for the two oxide nanosheets.

[1] D. Weber *et al.*, *J. Mater. Chem. A* **6**, 21558 (2018).

[2] S. Laha *et al.*, *Adv. Energy Mater.* **9**, 1803795 (2019).

O 45.8 Tue 12:30 WIL C107

**Chemistry and phase transition of pyridine derivatives on gold electrode probed by vibrational sum frequency generation** — XIN GONG, MARTIN WOLF, R. KRAMER CAMPEN, and ●YUJIN TONG — Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany

Pyridine and its derivatives are of both practical and fundamental importance in electrochemistry. While the flat to vertical phase transition has been extensively studied and well understood, knowledge on the deprotonation and protonation chemistry at the electrode/solution interface in aqueous solution is still very limited. In the current study, we employed vibrational sum frequency generation (VSFG) to monitor both the structural and chemical evolution of 4-(dimethylamino)pyridine (DMAP) adsorbed on a gold electrode as a function of external bias. Significant spectral changes are observed as a function of the applied bias voltage in the cyclic voltammetry. These features can be unambiguously assigned to the protonation/deprotonation and orientational changes respectively. The information revealed by this study is essential for the application of pyridine derivatives in nanoparticle manipulation, enhancement of  $CO_2$  reduction, formic acid electro-oxidation, etc.

O 45.9 Tue 12:45 WIL C107

**Influence of surface coating on electrochemical performance of Ni-rich NCM cathodes for Lithium ion batteries** — ●RAJENDRA SINGH NEGI and MATTHIAS T. ELM — Center for Materials Research, Justus-Liebig-University Gießen, Germany, Heinrich-Buff-Ring 16, 35392 Gießen

The Ni-rich NCM based cathode material has allured great research interest owing to its high energy density, high capacity and low costs. Nonetheless, the rapid capacity fading still hinders its wide range application. Surface modification became a feasible approach to handel this issue. However, achieving a homogenous coating using a simple

approach is still challenging. In this work, a surface-active -OH group assisted homogenous  $Al_2O_3$  coating on the NCM have been achieved. The  $Al_2O_3$  coated cells show improved capacity retention (89.5% after 130 cycles) during long-term cycling test compared to pristine cells (i.e. 38.3% after 130 cycles). In addition, Electrochemical Impedance Analysis (EIS) showed the tremendous increase in cell resistance of uncoated electrodes compared to coated electrodes after long-term cycling.

O 45.10 Tue 13:00 WIL C107

**Influence of Porosity on the Protonic Surface Conductivity of Yttria-Stabilized Zirconia Thin Films** — ●ERDOGAN CELIK<sup>1</sup>, TORSTEN BREZESINSKI<sup>2</sup>, and MATTHIAS T. ELM<sup>1</sup> — <sup>1</sup>Center for Materials Research, Justus-Liebig-University Gießen, Germany, Heinrich-Buff-Ring 16, 35392 Gießen — <sup>2</sup>Institute of Nanotechnology; Karlsruhe Institute of Technology (KIT), Hermann-von-Helmholtz-Platz 1, 76344 Eggenstein-Leopoldshafen

Yttria-stabilized zirconia (YSZ) is among the best-performing solid-state electrolytes for applications in fuel cells or heterogeneous catalysis because of its outstanding ionic conductivity at high temperatures. In addition, nanostructured oxides exhibit an even enhanced protonic conductivity at low temperatures. Nevertheless, the influence of material morphology on the protonic transport is still controversially discussed. To study the effect of surface and porosity on the protonic conductivity, porous YSZ thin films were prepared pulsed laser deposition. Such films represent an ideal model system because of their high surface-to-volume ratio. Electrochemical impedance spectroscopy was carried out as a function of temperature, oxygen activity and humidity of the surrounding atmosphere. The total conductivity is found to increase under humidified atmosphere conditions at all temperatures due to protonic surface conduction, especially below 100 °C. When coating a nanometer-thick layer of titania ( $TiO_2$ ) on the porous YSZ network using atomic layer deposition (ALD), the proton transport is suppressed, thus indicating the significant influence of surface properties on the protonic transport.

O 45.11 Tue 13:15 WIL C107

**A DFT study of early steps of Au island nucleation on  $c(2 \times 2)$ -Cl Au(001) surface** — ●ALEXANDRA C. DÁVILA and ECKHARD PEHLKE — Institut für Theoretische Physik und Astrophysik, CAU Kiel, Germany

Electrodeposition experiments of Au on a Au(001) electrode in a  $Cl^-$  containing electrolyte have shown a dependence of the growth mode on sample potential and Au deposition rate [1]. While island nucleation is essential for layer-by-layer growth, a detailed atomic-scale description of the early steps leading to the formation of Au ad-structures on the  $c(2 \times 2)$ -Cl covered Au(001) electrode surface is still lacking (for Au adsorption structures at low Cl coverage see [2]). We present DFT calculations, carried out with PWscf [3], of  $Au_n$  adatom structures for  $n \leq 4$  on the  $c(2 \times 2)$ -Cl Au(001) surface without as well as in the presence of a small number of Cl vacancies, and investigate the stability as a function of Cl chemical potential. The electrolyte has not been included in the simulations. In the absence of Cl vacancies  $Au_{ad}Cl_2$  chains form on the surface. In the range of Cl chemical potential where Cl vacancies become part of the equilibrium atomic adsorption structure, we find Cl vacancies to modify and to bind to the Au ad-structures. In this case, the energy gain due to the addition of a  $Au_{ad}$  monomer increases from about 0.06 eV to about 0.23 eV. I.e., the presence of Cl vacancies tends to promote Au ad-structure formation.

[1] K. Krug *et al.*, *Phys. Rev. Lett.* **96**, 246101 (2006).

[2] Mesgar *et al.*, *ChemPhysChem* **11**, 1395 (2010).

[3] P. Giannozzi *et al.*, *J. Phys. Condens. Matter* **21**, 395502 (2009).