

## O 82: Structure of Solid/Liquid Interfaces I

Time: Thursday 10:30–13:00

Location: H6

O 82.1 Thu 10:30 H6

**Probing the TiO<sub>2</sub>/Liquid Interface of a Photoelectrochemical Cell by X-Ray Photoelectron Spectroscopy** — ●MICHAEL F. LICHTERMAN<sup>1,2</sup>, MATTHIAS H. RICHTER<sup>1,2,7</sup>, SHU HU<sup>1,2</sup>, ETHAN J. CRUMLIN<sup>3</sup>, STEPHANUS AXNANDA<sup>3</sup>, MARCO FAVARO<sup>3,4</sup>, WALTER DRISDELL<sup>3,4</sup>, ZAHID HUSSAIN<sup>3</sup>, BRUCE S. BRUNSWIG<sup>1</sup>, ZHI LIU<sup>3,5,6</sup>, NATHAN S. LEWIS<sup>1,2</sup>, and HANS-JOACHIM LEWERENZ<sup>1,2</sup> — <sup>1</sup>Caltech, Pasadena, USA. — <sup>2</sup>JCAP, Pasadena, USA. — <sup>3</sup>LBL, Berkeley, USA. — <sup>4</sup>JCAP, Berkeley, USA. — <sup>5</sup>Chinese Academy of Sciences, China. — <sup>6</sup>ShanghaiTech University, China. — <sup>7</sup>BTU C-S, Cottbus, Germany.

Amorphous TiO<sub>2</sub> coatings can stabilize semiconductor photoanodes such as Si, GaAs, and GaP that are otherwise unstable in aqueous media [1]. Using tender X-rays with their substantially increased inelastic mean free scattering length of photoelectrons and using the classical three-electrode potentiostatic arrangement allows one to follow of the influence of the applied potentials on the semiconductor electrode energetics such as band bending and band edge shifts directly [2, 3]. The observed shifts in binding energy with respect to the applied potential have directly revealed rectifying junction behavior on semiconducting samples. Accumulation, depletion and Fermi level pinning were observed. Additionally, the non-linear response of the core level binding energies to changes in the applied electrode potential has revealed the influence of defect-derived electronic states on the Galvani potential across the complete cell. [1] Science 344 (2014) 1005; [2] Sci Rep 5 (2015) 9788; [3] Ener & Env Sci 8 (2015) 2409

O 82.2 Thu 10:45 H6

**An Electrochemical, resonant Photoemission and Ambient Pressure-X-ray Photoelectron Spectroscopic Investigation of Si/TiO<sub>2</sub>/Ni/Electrolyte Interfaces** — ●MATTHIAS H. RICHTER<sup>1,2,7</sup>, MICHAEL F. LICHTERMAN<sup>1,2</sup>, SHU HU<sup>1,2</sup>, ETHAN J. CRUMLIN<sup>3</sup>, STEPHANUS AXNANDA<sup>3</sup>, MARCO FAVARO<sup>3,4</sup>, WALTER DRISDELL<sup>3,4</sup>, ZAHID HUSSAIN<sup>3</sup>, BRUCE S. BRUNSWIG<sup>1</sup>, ZHI LIU<sup>3,5,6</sup>, NATHAN S. LEWIS<sup>1,2</sup>, and HANS-JOACHIM LEWERENZ<sup>1,2</sup> — <sup>1</sup>Caltech, Pasadena, USA. — <sup>2</sup>Joint Center for Artificial Photosynthesis, Pasadena, USA. — <sup>3</sup>Lawrence Berkeley National Laboratory, Berkeley, USA. — <sup>4</sup>Joint Center for Artificial Photosynthesis, Berkeley, USA. — <sup>5</sup>Chinese Academy of Sciences, China. — <sup>6</sup>ShanghaiTech University, China. — <sup>7</sup>BTU C-S, Cottbus, Germany.

Photoelectrochemical cells based on semiconductor-liquid interfaces provide a method of converting solar energy to electricity or fuels. Recently, we have demonstrated operational systems that involved stabilized semiconductor-liquid junctions [1]. The electrical and spectroscopic properties of the TiO<sub>2</sub>/Ni protection layer system have been investigated in contact with electrolyte solutions [2, 3, 4]. From the response of the photoelectron binding energies to variations in applied potential the energetics of the solid/electrolyte interface are elucidated. The degree of conductivity depended on the chemical state of the Ni on the TiO<sub>2</sub> surface. The combinations of these techniques provide a powerful tool for the investigation of hybrid electrode/solution contacts. [1] Science 344 (2014) 1005; [2] Sci Rep 5 (2015) 9788; [3] Ener & Env Sci 8 (2015) 2409; [4] J Electrochem Soc 162 (2016) H1

O 82.3 Thu 11:00 H6

**Model free method to measure the surface potential of colloidal particles in aqueous solution** — ●GRAZIA GONELLA<sup>1</sup>, CORNELIS LÜTGEBAUCKS<sup>2</sup>, and SYLVIE ROKE<sup>2</sup> — <sup>1</sup>Max Planck Institute for Polymer Research, Ackermannweg 10, 55128 Mainz, Germany — <sup>2</sup>Laboratory for fundamental BioPhotonics (LBP), Institute of Bioengineering (IBI), and Institute of Materials Science (IMX), School of Engineering (STI), and Lausanne Centre for Ultrafast Science (LA-CUS), École Polytechnique Fédérale de Lausanne (EPFL), CH-1015 Lausanne, Switzerland

Retrieval of information regarding properties of, and processes at, interfaces is notoriously difficult especially at the surface of colloidal particles in solution. Determination of the surface potential,  $\Phi_0$ , is a particularly important albeit difficult task. For instance  $\Phi_0$  affects the stability of a colloidal suspension and in turn is affected by the opening of ion-channels in a membrane, just to cite two core problems in colloids and soft matter. Computations have shown that in theory the SH scattering pattern contains enough information to determine  $\Phi_0$

without making any assumptions on the structure or state of the interface. We implement this theory and extend it to low ionic strengths and use it to determine the surface potential of a variety of colloidal systems in aqueous solution.

O 82.4 Thu 11:15 H6

**Adsorption of Organic Molecules on Iron Oxide Model Surfaces in Solution** — ●PETER SEIDEL<sup>1,2</sup> and MARTIN STERRER<sup>1,2</sup> — <sup>1</sup>Institute für Physik, Universität Graz, Universitätsplatz 5, 8010 Graz, Österreich — <sup>2</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Faradayweg 4-6, 14195 Berlin, Deutschland

Single-crystalline oxide thin films supported by metals are a well-accepted class of model system for studying fundamental aspects of oxide surface and thin oxide layer chemistry and physics. In the present contribution, we report on our efforts to expand this model approach to electrochemical studies on well-ordered oxide surfaces. Single-crystalline FeO(111) and Fe<sub>3</sub>O<sub>4</sub>(111) films were grown under ultrahigh vacuum (UHV) conditions on a Pt(111) substrate and subsequently transferred into air or brought into contact with aqueous solutions. We have tested the stability of the oxide layers in these environments and characterized their electrochemical properties by cyclic voltammetry. Two different organic compounds (Catechol and Aminophthalic acid) were deposited from solution and investigated by electrochemical and UHV methods. Finally, the surface morphology and potential-dependent surface structure changes were investigated in-situ by electrochemical scanning tunneling microscopy.

O 82.5 Thu 11:30 H6

**Quantitative Measurements of Electrochemical Strain using Atomic Force Microscopy** — ●VALON LUSHTA<sup>1,2</sup>, THOMAS GÖDDENHENRICH<sup>1</sup>, BERNHARD ROLING<sup>2</sup>, and ANDRÉ SCHIRMEISEN<sup>1</sup> — <sup>1</sup>Institut für Angewandte Physik, Justus-Liebig-Universität Gießen, D-35392 Gießen — <sup>2</sup>Physikalische Chemie, Philipps-MarburgUniversität Marburg, D-35032 Marburg

Electrochemical Strain Microscopy (ESM) has emerged as a powerful tool for probing ionic transport in battery cathode. A biased AFM tip concentrates an electric field in a nanometer-scale volume of the sample, inducing ionic intercalation or deintercalation. The intrinsic link between concentration of ionic species and the molar volume of the material results in electrochemical strain and surface displacement. The magnitude of this displacement is lower than the sensitivity of modern AFMs. The excitation signal at the tip is chosen at contact resonance frequency in order to amplify the displacement by the Q factor of the AFM cantilever. The ongoing challenges in ESM are the quantitative measurement of the displacement and understanding delocalized electrostatic forces effecting the cantilever motion. Both challenges are linked to the uncertainty of contact resonance dynamics. We demonstrate a technique to quantify the displacement and estimate the electrostatic contribution without loss of resonance amplification.

O 82.6 Thu 11:45 H6

**Solvent- and deposition temperature-dependent 2D supramolecular assemblies of trimesic acid at the liquid-graphite interface revealed by scanning tunneling microscopy** — ●YEN D.C NGUYEN, LARS SMYKALLA, HA N.T NGUYEN, and MICHAEL HIETSCHOLD — TU-Chemnitz, Institute of Physics, D-09107 Chemnitz, Germany

By using scanning tunneling microscopy (STM), the polymorphism of self-assembly of trimesic acid molecules at the liquid-solid interface to graphite was investigated for different kind of solvents and temperatures of the pre-heated during deposited substrate. TMA was dissolved in phenyloctane, octanoic acid and undecanol, which have different polarity. At elevated substrate temperatures, various periodic assemblies of TMA can be obtained. By increasing the temperature of the pre-heated substrate, the specific 2D supramolecular network structure and the corresponding packing density can be precisely tuned in each kind of the solvents studied. The results found by STM are explained by the increased concentration of the solution at the pre-heated substrate as well as the higher mobility of the solute molecules enforcing the interactions between the molecules, in particular different hydrogen bonding motifs. Our interpretation is supported by optimizing each

structure and comparing their total interactions energy calculated by PM6-DH+.

O 82.7 Thu 12:00 H6

**Self-assembly of 2,2'-spirobi[4H-1,3,2-benzodioxasiline] at the solid-liquid interface controlled by solvent polarity** — •THI NGOC HA NGUYEN<sup>1</sup>, DOAN CHAU YEN NGUYEN<sup>1</sup>, THOMAS EBERT<sup>2</sup>, STEFAN SPANGE<sup>2</sup>, and MICHAEL HIETSCHOLD<sup>1</sup> — <sup>1</sup>Professur Analytik an Festkörperoberflächen, Institut für Physik, Technische Universität Chemnitz, Chemnitz, Germany — <sup>2</sup>Professur Polymerchemie, Institut für Chemie, Technische Universität Chemnitz, Chemnitz, Germany

Self-assembled molecular architectures at solid-liquid interfaces are mainly governed by the chemical nature of solute, solvent as well as the substrate properties. When molecules solved in a solution are adsorbed at a liquid-solid interface, in addition to molecule-molecule and molecule-substrate interactions, the solvent itself can also play an important role in the formation of self-assembled monolayers. In this paper, the influence of solvent polarity on self-assembly of the 2,2'-spirobi[4H-1,3,2-benzodioxasiline][1] is investigated. Such spiro molecules are useful monomers for the so-called twin polymerization. Spiro molecules consist of two different parts, - organic and inorganic - linked together by Si-O units, which can be cleaved under the same conditions but at different rates resulting in organic and inorganic precursors for the formation of two different kinds of polymers. In this way, there are created two different types of polymers out of one kind of monomer which are interlinked together on the nanoscale creating a real nanocomposite material. The self-assembly at the liquid-solid interface of these spiro molecules reveals different adsorbate patterns driven by solvent polarity.

O 82.8 Thu 12:15 H6

**Porphyrimetalation at the Solid-Liquid Interface** — •MATTHIAS FRANKE<sup>1</sup>, FLORENCIA MARCHINI<sup>2</sup>, HANS-PETER STEINRÜCK<sup>1</sup>, OLE LYTKEN<sup>1</sup>, and FEDERICO JOSÉ WILLIAMS<sup>2</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie II, Universität Erlangen-Nürnberg, Germany — <sup>2</sup>Departamento de Química Inorgánica, Analítica y Química Física, Universidad de Buenos Aires, Argentina

Porphyrimetals are large organic molecules with potential in numerous technical applications. Especially metalloporphyrins are promising, since the metal center coordinated to the central cavity strongly influences the functionality of these molecules. So far, on-surface metalloporphyrin synthesis in ultrahigh vacuum has been achieved by codeposition of metal atoms and subsequent annealing. However, the common way to metalate porphyrins in liquid medium is through deprotonation and coordination of a dissolved metal ion. We have transferred the liquid phase synthesis approach to the surface by metalating a free-base porphyrin (2HTPP), adsorbed on an Au(111) single crystal, by exposure to aqueous zinc acetate solution, yielding ZnTPP.[1] This reaction happens at room temperature, in contrast to the higher temperatures required for metalation by codeposited metal atoms. Metalation was followed spectroscopically by means of X-ray photoelectron spectroscopy (XPS). The project is supported by the DFG through FOR 1878 (funCOS) and by the DAAD.

[1] Franke, M.; Florencia, M.; Steinrück, H.-P.; Lytken, O.; Williams, F.; *J. Phys. Chem. Lett.* 2015, accepted, DOI: 10.1021/acs.jpcllett.5b02218

O 82.9 Thu 12:30 H6

**Potential step experiments on Ag<sub>x</sub>Pt<sub>1-x</sub>/Pt(111) surface alloys - the influence of the upper potential limit on surface structure** — •STEPHAN BECKORD, SYLVAIN BRIMAUD, and R. JÜRGEN BEHM — Ulm University, Institute of Surface Chemistry and Catalysis, 89069 Ulm

Ag<sub>x</sub>Pt<sub>1-x</sub>/Pt(111) surface alloys exhibit electrochemical and catalytic properties which differ significantly from those of the individual metals. Studies in our institute revealed them as a very promising candidate for the oxygen reduction reaction [1]. To unveil possible restructuring or corrosion processes during the electrocatalytic reaction, which could strongly influence the electrocatalytic characteristics of the surface alloy, we investigated the electrochemical corrosion behavior of structurally well-defined Ag<sub>x</sub>Pt<sub>1-x</sub> surface alloys on Pt(111) with different Ag contents. The surface alloys were prepared under ultrahigh vacuum (UHV) conditions and structurally characterized by STM before and after electrochemical investigation. Electrochemical characterization was performed in a flow cell set up, which also allows measuring the dissolution of surface atoms during corrosion by a collector electrode. Additionally the corroded surfaces were electrochemically characterized by basic cyclic voltammetry (BCV) in supporting electrolyte (0.5 M H<sub>2</sub>SO<sub>4</sub>). We demonstrate that the sensitivity of the surface structure towards corrosion depends sensitively on the surface composition. The role of Pt atoms for stabilizing the Ag surface atoms is discussed. [1] S. Beckord, S. Brimaud, R.J. Behm, *ORR on Structurally well-defined Ag<sub>x</sub>Pt<sub>1-x</sub>/Pt(111) surface alloys* (in preparation)

O 82.10 Thu 12:45 H6

**Surface engineering of nanomaterials for electrochemical energy conversion and storage** — •MIN ZHOU and YONG LEI — Institute for Physics and IMN MacroNano\*, Ilmenau University of Technology, Ilmenau 98693, Germany

In view of the worldwide energy challenge in the 21st century, the electrochemical technologies have received considerable attention for energy conversion (i.e. photoelectrochemical water splitting) and storage (i.e. secondary ion battery). Nearly all chemical transformations related to energy conversion and storage take place at the surfaces and interfaces between electrode and electrolyte. Hence, surface engineering of nanomaterials offers the possibility to optimize the final electrochemical devices. We employ three-dimensional (3D) ordered porous architectures to illuminate the important role of surface science for energy conversion and storage. For example, a 3D ordered macro-mesoporous architecture of BiVO<sub>4</sub> is first fabricated through a modified colloidal crystal template method. Superior photocurrent densities are achieved in return for controllable surface-to-volume ratio. This advantage can be further enhanced within the photoelectrodes of faster charge transport. As for electrochemical storage, 3D ordered porous architecture of amorphous TiO<sub>2</sub> is chosen as a proof-of-concept prototype to illuminate the importance of surface design for rate capability in sodium ion batteries. The enhancement is primarily attributed to effective surface ion availability by increasing the roughness of the electrode surface. Both the results of energy conversion and storage highlight the great significance of surface engineering for energy-related area.