

## O 8: Poster Session I: Solid-liquid interfaces: Structure, spectroscopy

Time: Monday 10:30–12:30

Location: P

O 8.1 Mon 10:30 P

**Interface Composition of Pure and Mixed Ionic Liquid Films on Metal Surfaces** — ●STEPHEN MASSICOT<sup>1</sup>, TOMOYA SASAKI<sup>2</sup>, MATTHIAS LEXOW<sup>1</sup>, SUNGHWAN SHIN<sup>1</sup>, FLORIAN MAIER<sup>1</sup>, SUSUMU KUWABATA<sup>2</sup>, and HANS-PETER STEINRÜCK<sup>1</sup> — <sup>1</sup>Lehrstuhl für Physikalische Chemie 2, Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany — <sup>2</sup>Department of Applied Chemistry, Graduate School of Engineering, Osaka University, Japan

Ionic liquids (ILs) are salts with melting points below 100°C and extremely low vapor pressure. Thin films of ILs are of utmost interest in potential applications, e.g. in the fields of catalysis and electrochemistry. In this context, we investigate mixed ultrathin films of two ILs on metal surfaces. The molecular composition of the IL/solid and IL/vacuum interfaces is studied by angle-resolved and temperature-programmed X-ray photoelectron spectroscopy on the molecular scale. We observe phenomena of ion exchange and preferential enrichment at the interfaces, and selective desorption which opens pathways for on surface formation of new ILs by metathesis at IL/metal interfaces. In particular, we address mixtures of the protic IL diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) and the aprotic IL 1-methyl-3-octylimidazolium hexafluorophosphate ([C8C1Im][PF6]).

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O 8.2 Mon 10:30 P

**bias- and concentration- dependent switching of supramolecular nanostructures at the solid-liquid interface** — ●BAOXIN JIA<sup>1</sup>, MIHAELA ENACHE<sup>1</sup>, SANDRA MIGUEZ-LAGO<sup>2</sup>, MILAN KIVALA<sup>2</sup>, and MEIKE STÖHR<sup>1</sup> — <sup>1</sup>Zernike Institute for Advanced Materials, University of Groningen, Netherlands — <sup>2</sup>Institute of Organic Chemistry, University of Heidelberg, Germany

Research into the controlled switching between different molecular phases at the solid-liquid interface induced by an external trigger has gained increasing attention over the past years, also in view of application as smart surfaces. Here we discuss the bias- and concentration-dependent switching of a carboxy-functionalized triarylamine derivative at the HOPG/nonanoic interface studied by scanning tunneling microscopy. For a fully saturated solution, a porous phase (chicken-wire) was observed for negative sample bias and a close-packed phase was observed for positive sample bias. For a 50% saturated solution, a second porous phase (flower) coexisted with the chickenwire phase at negative sample bias, while the close-packed phase was still observed at positive sample bias. For a 20% saturated solution, the two porous phases and the close-packed phase coexisted at positive sample bias because of the low molecule concentration in the solution. By changing the sample bias from negative to positive, an electric field-induced phase transition from the porous phases to the close-packed phase was accomplished, which was fully reversible by changing the bias back. Our study demonstrates that switching can be accomplished by changing the polarity of the applied external electric field.

O 8.3 Mon 10:30 P

**Stability and Exchange Processes in Ionic Liquid/Porphyrin Composite Films on Metal Surfaces** — ●MATTHIAS LEXOW, STEPHEN MASSICOT, FLORIAN MAIER, and HANS-PETER STEINRÜCK — Lehrstuhl für Physikalische Chemie II, Friedrich-Alexander-Universität Erlangen-Nürnberg, Egerlandstr. 3, 91058 Erlangen

In the context of organic-organic multicomponent heterostructures on metals, we studied prototypical composite systems of ultrathin porphyrin and ionic liquid (IL) films on metallic supports – Ag(111) and Au(111) – by means of angle-resolved X-ray photoelectron spectroscopy under well-defined ultrahigh vacuum conditions. After deposition of an IL on top of a monolayer of porphyrin, we observe changes in the growth behavior and thermal stability of the IL compared to deposition directly on the metals. Upon adsorption of a porphyrin layer on top of a frozen IL film at around 90 K, the porphyrin molecules replace the IL at the IL/metal interface upon heating above 240 K, a process likely driven by a larger adsorption energy of the porphyrin molecules on the Ag(111) and Au(111) surfaces.

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Lexow *et al.*, *J. Phys. Chem. C*, **2019**, 123, 29708.

O 8.4 Mon 10:30 P

**Chemistry and phase transition of pyridine derivatives on a gold electrode probed by vibrational sum frequency generation** — XIN GONG<sup>1</sup>, MARTIN WOLF<sup>1</sup>, R. KRAMER CAMPEN<sup>1</sup>, and ●YUJIN TONG<sup>1,2</sup> — <sup>1</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, 14195 Berlin, Germany — <sup>2</sup>Fakultät für Physik Universität Duisburg-Essen, 47057 Duisburg, 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<sub>2</sub> reduction, formic acid electro-oxidation, etc.

O 8.5 Mon 10:30 P

**Water structure at Pb(100) and (111) surfaces studied with the interface force field** — ●OSKAR CHEONG<sup>1,3</sup>, MICHAEL H. EIKERLING<sup>1,2</sup>, and PIOTR M. KOWALSKI<sup>1,2</sup> — <sup>1</sup>Theory and Computation of Energy Materials (IEK-13), Forschungszentrum Jülich, 52425 Jülich, Germany — <sup>2</sup>Jülich Aachen Research Alliance, JARA-CSD and JARA-ENERGY, 52425 Jülich, Germany — <sup>3</sup>Chair of Theory and Computation of Energy Materials, Faculty of Georesources and Materials Engineering, RWTH Aachen University, 52062 Aachen, Germany

The activity and selectivity of vital electrochemical reactions such as the oxygen evolution reaction or the CO<sub>2</sub> reduction reaction strongly depend on the solvent structure at the metal-electrolyte interface. In this realm, ab initio as well as classical molecular dynamics (AIMD and CMD) simulations are harnessed to study the structure and dynamics of water at metal surfaces. AIMD provides high accuracy but is restricted to short time- and length-scales. CMD allows simulating larger scales. However, the accuracy of CMD depends on the force field applied to describe interatomic interactions. We present results of CMD investigation of water structures on Pb metal surfaces performed with the interface force field [1]. On comparable time- and length-scales, AIMD water structures were reproduced. However, on much larger scales CMD yields different, more stable and better equilibrated water structures [2]. This clearly shows the large potential of CMD for efficient statistical sampling of atomic structures at the interfaces. [1] Heinz *et al.*, *Langmuir*. 29, 1754 (2013). [2] Cheong *et al.* submitted (2021).

O 8.6 Mon 10:30 P

**Solving Catalyst Degradation: Platinum Stability for Fuel Cell Operation** — ●FRANCESC VALLS MASCARÓ<sup>1</sup>, MARC T. M. KOPER<sup>1</sup>, and MARCEL J. ROST<sup>2</sup> — <sup>1</sup>Leiden Institute of Chemistry, Leiden University — <sup>2</sup>Huygens-Kamerlingh Onnes Laboratory, Leiden Institute of Physics, Leiden University

The longevity of a catalyst plays a crucial role for many industrial scale applications. Platinum is the best candidate to be used in electrochemical energy conversion systems due to its high activity. However, platinum suffers from degradation during fuel cell operation. This degradation is caused by the nucleation and growth of nanoislands, which roughen the surface [1, 2]. It is known that the extend of this roughening can be tuned by including additives, changing the electrolyte pH or working within different potential windows [3, 4]. In this work, we study the degradation of different platinum stepped surfaces under potential cycling to oxidative potentials. Interestingly, we quantify significantly less degradation for the surfaces with shorter terraces: Pt(111) > Pt(15 15 14) > Pt(554). We present here a model that explains this trend, in which steps act like sinks for both adatoms and vacancies, slowing down the nucleation and growth of the mentioned nanoislands. Finally, we do not observe roughening at all for platinum surfaces with only four atoms terrace width: Pt(553) and Pt(533).

- [1] Jacobse, L. et al., ACS Cent. Sci. 5 (12), 1920 (2019)  
 [2] Rost, M.J. et al., Nat. Commun. 10, 5233 (2019)  
 [3] Topalov, A. et al., J. Chem. Sci., 5, 631 (2014)  
 [4] Ruge, M. et al., J. Am. Chem. Soc., 139, 4532 (2017)

O 8.7 Mon 10:30 P

**TiO<sub>2</sub>(110) in Liquid Water, Air, and Solution** — ●JAN BALAJKA<sup>1,2</sup>, MELISSA HINES<sup>2</sup>, WILLIAM DEBENEDETTI<sup>2</sup>, JIRI PAVELEC<sup>1</sup>, MICHAEL SCHMID<sup>1</sup>, and ULRIKE DIEBOLD<sup>1</sup> — <sup>1</sup>Institute of Applied Physics, TU Wien, Vienna, Austria — <sup>2</sup>Department of Chemistry and Chemical Biology, Cornell University, Ithaca NY, USA

Our understanding of metal oxide surface chemistry arises from studies under highly idealized ultrahigh vacuum (UHV) conditions, that cannot be extrapolated to the complex reaction environments of real industrial processes. Material properties, such as chemical reactivity, are determined by the nature of individual surface sites and thus related to the detailed atomic configuration. Yet, the interfacial structure under application conditions remains largely unexplored.

I will review our work on the prototypical TiO<sub>2</sub>(110) surface in ambient and aqueous environments. Using a UHV-compatible dispenser of ultrapure liquid water, we demonstrated that the TiO<sub>2</sub>(110) surface is not altered upon contact with clean liquid water. However, when exposed to air, low-concentration atmospheric species, such as carboxylic acids, adsorb with high affinity and form an ordered overlayer at the surface, effectively passivating the undercoordinated Ti surface sites.[1]

I will further discuss a chemical functionalization of the TiO<sub>2</sub>(110) surface by a monolayer of terephthalic acid (1,4-benzenedicarboxylic acid) deposited from solution and intended to serve as a growth template for three-dimensional metal-organic networks (MOFs).

- [1] J. Balajka, *et. al.*, Science 361, 786 (2018)

O 8.8 Mon 10:30 P

**How surface oxides determine the activity of Mo<sub>2</sub>C electrocatalysts** — ●CHRISTOPH GRIESSER<sup>1</sup>, HAOBO LI<sup>2</sup>, EVAMARIA WERNIG<sup>1</sup>, DANIEL WINKLER<sup>1</sup>, DAVID EGGER<sup>2,3</sup>, CHRISTOPH SCHEURER<sup>2,3</sup>, KARSTEN REUTER<sup>2,3</sup>, and JULIA KUNZE LIEBHÄUSER<sup>1</sup> — <sup>1</sup>Department of Physical Chemistry, Universität Innsbruck, Austria — <sup>2</sup>Chair of Theoretical Chemistry and Catalysis Research Center, Technische Universität München, Germany — <sup>3</sup>Fritz-Haber-Institut der Max-Planck-Gesellschaft, Berlin, Germany

Transition metal (TM) compounds are widely applicable as materi-

als in heterogeneous catalysis, due to their compositional and structural diversity. TM carbide compounds are praised as electrocatalysts for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), due to a possible break of key adsorption energy scaling relations, predicted by density-functional theory studies. Mo<sub>2</sub>C was classified as highly suitable for the CO<sub>2</sub>RR in an active-site computational screening study. Here we assess the activity of hexagonal Mo<sub>2</sub>C towards the CO<sub>2</sub>RR in aqueous electrolyte by a multimethod experiment and theory approach. We find, that an ultrathin oxide film persists at the surface of this catalyst material and completely suppresses any CO<sub>2</sub>RR activity. The one monolayer thin oxide films are stable down to -1.9 V<sub>SHE</sub>, and exclusively the hydrogen reduction reaction is found to take place. This points to the necessity of considering the true interface, forming under operando conditions, in computational screenings for catalyst materials. Preliminary experiments performed under protection of Mo<sub>2</sub>C from ambient air in non-aqueous electrolyte indeed reveal CO<sub>2</sub>RR activity.

O 8.9 Mon 10:30 P

**Hydration of Polyvinyl Alcohol Surfaces Mediated by Ammonia** — TAKAHIKO IKARASHI<sup>1</sup>, TAKUMI YOSHINO<sup>1</sup>, NAOKI NAKAJIMA<sup>1</sup>, KAZUKI MIYATA<sup>1</sup>, KEISUKE MIYAZAWA<sup>1</sup>, ●YGOR MORAIS JAQUES<sup>2</sup>, ADAM S. FOSTER<sup>2</sup>, MEGUMI UNO<sup>3</sup>, CHIKAKO TAKATO<sup>3</sup>, and TAKESHI FUKUMA<sup>1</sup> — <sup>1</sup>Kanazawa University, Japan — <sup>2</sup>Aalto University, Finland — <sup>3</sup>EBARA Corporation, Japan

Chemical mechanical planarization (CMP) is a process that smooths silicon wafers surface for their efficient use in electronics. This procedure results in the surfaces being covered by silica nanoparticles. An effective way of removing these debris is by scrubbing polyvinyl alcohol (PVA) brushes on the wafer's surface in an aqueous solution. However, this can cause cross-contamination between wafers due to debris adhesion into the PVA surface. Thus, for an optimal technical setup, the interactions between silica nanoparticles and PVA as well as PVA's hydration in different liquids have to be properly addressed. Here, we investigate the hydration of PVA in NH<sub>3</sub> aq. and pure water. Using atomic force microscopy, we found that the adhesion force between a silica tip and a PVA surface in NH<sub>3</sub> aq. is drastically reduced when compared to the system immersed in water. Using molecular dynamics simulations, we have found that this happens because the NH<sub>3</sub> molecules perturb the hydrogen bond networks formed between water and the PVA hydroxyl groups, promoting faster interactions and diffusion. This central role of ammonia in the inhibition of nanoparticle adhesion can further improve post CMP cleaning processes.