Surface Science Division
Room 319 - Session SS-TuM

Liquid/Solid Interfaces and Electrochemistry

Moderators: Kathryn Perrine, Michigan Technological University, **Michelle Personick**, Wesleyan University

8:00am **SS-TuM-1 Investigating the Oxidation of Pt(111) Using High-Pressure Scanning Tunneling Microscopy, Force Field Calculations, and Ab Inito Thermodynamics***, D. Boden,* Leiden University, Netherlands*; M. van Spronsen,* Diamond Light Source, UK*; J. Frenken,* ARCNL*; J. Meyer, **Irene Groot**,* Leiden University, Netherlands

Platinum has always been an important catalyst for oxidation reactions in the automotive industry, but also for electrocatalysis. Therefore, oxidation of and on platinum surfaces has long been a favorite topic in the field of surface science.Recently, the development of in situ and operando techniques has shown that the classic ultrahigh vacuum (UHV) approach is inadequate to describe the catalyst at realistic catalytic conditions. We will show that under these conditions (>530 K and>1 bar O_2), the Pt(111) surface oxidizes and forms spoke wheel and stripe-like structures that are not stable under UHV conditions. The striped structures we found using high-pressure scanning tunneling microscopyhave since been investigated using a combination of density functional theory (DFT) and ab initio thermodynamics (AITD) to evaluate the surface free energy at realistic temperatures and pressures. Here we do the same for the spoke wheel structure. However, since even the smallest candidate structures are too large for ordinary DFT calculations, we employ a ReaxFF force field developed specifically for Pt and O. This force field is able to accurately reproduce results from DFT and allows us to obtain an atomic model for the spoke wheel structure that matches the experimental results closely. Using AITD we compare its relative stability to the stripe structures over a large range of temperatures and pressures. We show that the spoke wheel structure is more stable than the stripe structure if the surface is partially oxidized, while the stripe structure is more stable only if it covers the entire surface.

8:20am **SS-TuM-2 Operando Electrochemistry: NAP-XPS on Electrolyte/Electrode Interfaces - Studies of Liquid Electrolytes and Their Interfaces to Battery Cathodes for Lithium Ion Battery Applications***, **Francesca Mirabella**, P. Dietrich, A. Thissen,* SPECS Surface Nano Analysis GmbH, Germany

In this work, we present NAP-XPS results from model and commercial liquid electrolytes for lithium-ion battery production using an automated laboratory NAP-XPS system. As electrolyte solutions, we used LiPF6 in EC/DMC (LP30) as a typical commercial battery electrolyte and LiTFSI in PC as a model electrolyte. We analyzed the LP30 electrolyte solution, first in its vapor and liquid phase to compare individual core-level spectra. In a second step, we immersed a V_2O_5 single crystal as a model cathode material in this $LiPF_6$ solution. Additionally, the LiTFSI electrolyte model system was studied to compare and verify our findings with previous NAP-XPS data. Photoelectron spectra recorded at pressures of 2–10 mbar show significant chemical differences for the different lithium-based electrolytes.

8:40am **SS-TuM-3 AVS Dorothy M. and Earl S. Hoffman Scholarship Talk: Infrared Nanospectroscopy for Solid-Liquid Interface***, **Xiao Zhao***[1,2]*, M. Salmeron,* LBNL

Nanoscale properties and dynamical processes at solid-liquid interface are critical for many natural phenomenon and industrial applications, including energy storage, self-assembly and corrosion. However, fundamental study of those processes is often challenged by radiation damage from electron or X-ray probe, which may drive the structure and chemical states of interface away from its original state. Herein we demonstrate a new non-destructive platform that enables nanoscale interfacial sensitive Infrared (IR) spectroscopy for solid-liquid interface by combining graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). With that we investigated the nanoscale structural evolution and response of protein assemblies to external environments as well as dynamical interaction between nanoparticles with ligand capping layer for CO_2 electroreduction. The protein substructure and ordering, and specific adsorption configuration of ligand on nanoparticles are monitored by their characteristic IR vibrational bands at nanometer scale under realistic condition, which provides complimentary information to other operando techniques. Our platform opens broad opportunities for *operando* study of soft materials or nanostructures (membrane protein, virus, nanoparticles and plastic material) in their realistic condition and under external stimuli.

9:00am **SS-TuM-4 Methods for Exposing UHV-prepared Metal Oxide Surfaces to Liquid Water: A Comparison of TiO_2, Fe_2O_3, and Fe_3O_4***, **Jiri Pavelec**, J. Balajka, F. Kraushofer,* Vienna University of Technology, Austria*; Z. Jakub,* CEITEC, Czechia*; G. Franceschi, M. Schmid, G. Parkinson, U. Diebold,* Vienna University of Technology, Austria

The importance of bridging the pressure gap in studies of model catalysts has been recognized for decades. The investigation of surfaces under ambient conditions remains a challenge due to the restricted number of experimental techniques available and a high risk of contamination. The design of two working instruments for tackling the pressure gap in surface science will be presented: An apparatus for dosing liquid water in an ultrahigh vacuum [1,2] and a high-pressure cell [4]. The first instrument allows dosing a droplet of ultrapure liquid water on the surface of a sample without exposure to air. The second presented instrument is a novel design of a high-pressure cell, intended to expose metal-oxide single crystals to water vapour pressure up to the mbar range and elevated temperatures. Both instruments are coupled to an existing surface-science chamber, enabling reproducible sample preparation and sample characterization using UHV-based analytical techniques (q+AFM, XPS, LEIS). By exposing a number of metal oxides to liquid water we have learned that some surfaces stay intact, some are slightly modified, while some are completely changed. For example, no change is found after water drops or vapour exposure to rutile $TiO_2(110)$ [2], and it can be utilised as a benchmark system for clean liquid water dosing. The α-$Fe_2O_3(1\bar{1}02)$ surface exchanges oxygen with vapor and liquid water, but retains the UHV structure [3]. A more significant change was observed for $Fe_3O_4(001)$: Multi-Langmuir water doses do not change a $(\sqrt{2} \times \sqrt{2})R45°$ reconstruction under UHV conditions, but liquid water at room temperature lifts the reconstruction [4] followed by the formation of a partial oxyhydroxide layer.

References:

[1] J. Balajka, J. Pavelec , M. Komora, M. Schmid, U. Diebold (2018). Rev. Sci. Instruments 89: 083906.

[2] J. Balajka, M.A. Hines, W. DeBenedetti, M. Komora, J. Pavelec, M. Schmid, U. Diebold (2018). Science 361:786-789.

[3] Z. Jakub, M. Matthias, F. Kraushofer, J. Balajka, J. Pavelec, M. Schmid, C. Franchini, U. Diebold, G. S Parkinson (2021). Nature Commun. 12.

[4] F. Kraushofer, F. Mirabella, J. Xu, J. Pavelec, J. Balajka, M. Müllner, N. Resch, Z. Jakub, J. Hulva, M. Meier, M. Schmid, U. Diebold and G. S. Parkinson (2019). The J. Chem. Phy. 151:154702.

9:20am **SS-TuM-5 Interplay of Structure, Dynamics and Energetics of Alkali Metal Ions on Muscovite Mica Surfaces: Molecular Dynamics Simulation***, **Alper T. Celebi**,* Vienna University of Technology, Austria*; S. Reindl,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; M. Olgiati,* Vienna University of Technology, Austria*; T. Bauer,* Friedrich-Alexander-Universität Erlangen-Nürnberg, Germany*; L. Maers, M. Valtiner,* Vienna University of Technology, Austria

Adsorption of ions at the solid-liquid interface is of great importance in various physical processes such as corrosion of metals, electrochemical energy storage, swelling of clays, biofouling in the marine environment and transport in shale rocks. In these processes, the type of cation in an electrolyte solution has a profound influence on the hydration structure, dynamics and energetics of the ions at the interface. Atomistic simulations are practical to properly explore such influences at the molecular resolution. In this study, we performed molecular dynamics (MD) simulations of different aqueous salt electrolytes confined between two negatively charged mica surfaces. As the electrolyte, we used chlorides of different alkali metals, namely Cs^+, K^+, and Li^+. We explored the variations in interfacial water density, ion concentrations, structural orientations, ion mobilities and hydration energies. Our simulations show that Cs^+ has prominent concentration peaks at the surface, indicating very strong ion adsorption. Unorthodoxly, there are more counter-charges at the interface than is on the mica surface, which result in non-classical charge overscreening. However, this is not the case for Li^+ ions. They bound less strongly to the surface. Thus, Li^+ concentrations at the interface are lower than for Cs^+ and K^+ at the same molar concentration. This behavior is further supported by the ion mobilities at the interface where Cs^+ ions are found to be more stagnant while Li^+ ions are more mobile and K^+ ions have intermediate characteristics. Another interesting finding is that Cs^+ and K^+

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[1] **SSD Morton S. Traum Award Finalist**

[2] **AVS Dorothy M. and Earl S. Hoffman Scholarship Recipient**

ions predominantly sit at the cavity center of muscovite mica, creating a diamond-shape pattern. On the contrary, Li$^+$ cations are located on the charged oxygen site of the mica with slit-like formation. We asses that such structural orientations are mainly due to the differences in the ion sizes and electron densities. Moreover, water densities for Li$^+$ solution show the most pronounced oscillatory layering at the interface. Although there are less Li$^+$ ions at the surface compared to K$^+$ and Cs$^+$,more water molecules come near to the surface depleting the center of the channel for Li$^+$ case. This clearly points out that hydration forces are more effective for the aqueous Li$^+$ solution while the surface and metal ion interactions are the driving forces of Cs$^+$ and K$^+$ solutions. We also found out that the effect of the molar concentration has a negligible role on structure and energetics of mica and electrolyte interfaces. High-resolution atomic force microscopy imaging is being performed in parallel to further support our MD simulations.

9:40am **SS-TuM-6 Corrosion Mechanism of Aluminum Alloy at Grain Boundaries Investigated by in-Liquid Nanoscale Potential Measurement Technique***, **Shinnosuke Yamamoto**, D. Taniguchi, T. Okamoto, K. Hirata,* Kanazawa University, Japan*; T. Ozawa,* Kobe Steel, Ltd., Japan*; T. Fukuma,* Kanazawa University, Japan

Al-Zn-Mg alloys are used as a structural material for automobiles and aircraft due to their outstanding strength. However, the high susceptibility to the local corrosion and stress corrosion cracking of the Al-Zn-Mg alloys limits their applications. The high susceptibility of Al-Zn-Mg alloy to the local corrosion is caused by the microstructural inhomogeneities such as the grain boundaries (GBs) and intermetallic particles. Along GBs of these alloys, a line-shaped precipitate free zone (PFZ) made of aluminum is formed. In addition, inside the PFZ, granular precipitates made of MgZn$_2$ are distributed along the GBs. The coexistence of these different materials forms corrosion cells to induce corrosion at the GBs. However, nanoscale mechanisms of such corrosion have been elusive. To solve this problem, we have directly imaged the corrosion behavior near the GBs of Al-Zn-Mg alloys in liquid on a nanoscale using a local potential measurement technique referred to as open-loop potential microscope (OL-EPM) (Fig.1).We imaged the changes in topography and potential at the same location during and after replacing the solution from water to pH 2.2 H$_2$SO$_4$ solution by OL-EPM. At 28 min after the immersion of an Al-Zn-Mg alloy sample, high potential spots were observed inside the GBs (Fig. 2 (a) and (b), red arrows), which probably correspond to the MgZn$_2$ precipitates. Meanwhile, the relatively low potential area around MgZn$_2$ precipitates should correspond to the PFZ (Fig.2 (a) dotted line). Previous studies showed that the high potential area has high corrosion activity. Thus, the observed high potential areas suggest the anodic dissolution of the MgZn$_2$ precipitates. Indeed, the height profiles measured across one of the precipitates reveal a 10 nm height decrease caused by replacing water with the H$_2$SO$_4$ solution (Fig.2 (c)). At 97 min, the bright spot was not observed at the GB (Fig.2 (b) (iii)). This disappearance suggests the complete dissolution of the MgZn$_2$ precipitate. Consequently, the PFZ area shows a lower potential than the surrounding matrix. In addition, small anodic and cathodic regions are formed all over the matrix, forming many local corrosion cells. The dissolution of these anodic areas increased the surface roughness as confirmed in the height profile shown in Fig.2 (c). Based on these observations, we found that the MgZn$_2$ and PFZ areas respectively serve as the anode and cathode in the initial stage of the corrosion at GBs. After the complete dissolution of MgZn$_2$ precipitates, the matrix starts to serve as an anode instead of the MgZn$_2$ precipitates.

11:00am **SS-TuM-10 Identifying Available Adsorption Sites on Au-Ps Alloys by FTIR Spectroscopy and Monte Carlo Simulations***, S. Manzi,* Dep. de Física, Universidad Nacional de San Luis, Instituto de Física Aplicada, CONICET, Argentina*; M. Bosco, M. Brites Helú,* Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina*; A. Baldo,* Fac. de Ingeniería Química (FIQ), Universidad Nacional del Litoral (UNL), Argentina*; S. Collins, **Florencia Calaza**,* Instituto de Desarrollo Tecnológico para la Industria Química (INTEC), UNL/CONICET, Argentina

Available adsorption sites on the surface of bimetallic AuPd compounds were studied by comparison of experimental results of CO adsorption, used commonly as a probe site molecule, on catalysts (powders) AuPd/CZ (ceria-zirconia) prepared in a relation 1:1 (Au:Pd), and on catalyst model surfaces prepared over single crystals. On both systems the sites exposed for CO adsorption are modified by calcining or heating the material to specific temperatures, allowing surface and bulk Au and Pd reordering. The spectroscopy results from both systems present some degree of agreement supporting in this way the need for interdisciplinary research to study catalytic systems. Furthermore, the system was also characterized by Monte Carlo simulations, which give an explanation for the increased availability of Pd atop sites experimentally observed, by forming Pd chains across the surface and avoiding 3-fold site formation due to agglomeration of Pd atoms.

11:20am **SS-TuM-11 Role of Chemisorbing Species in Growth at Liquid Metal-Electrolyte Interfaces Revealed by in Situ X Ray Scattering***, **Andrea Sartori**,* ESRF, France

Liquid-liquid interfaces offer intriguing possibilities for nanomaterials growth. Especially, growth at liquid metal surfaces has recently received renewed interest. Here, fundamental interface-related mechanisms that control the growth behavior in these systems are studied for the case of Pb halide compound formation at the interface between liquid mercury electrode and aqueous salt solutions, using in situ X-ray reflectivity and grazing incidence X-ray diffraction, supplemented by electrochemical measurements and optical microscopy. The nucleation and growth of these compounds at potentials in the regime of Pb de-amalgamation was investigated in NaX + PbX$_2$ (X = F, Cl, Br) to systematically explore the role of the halide species. X-ray reflectivity studies reveal the rapid formation of well-defined ultrathin precursor adlayers in Cl- and Br-containing solution. This adlayer formation is followed by subsequent quasi-epitaxial growth of Pb(OH)X bulk crystals, that are oriented with the c-axis along the surface normal. In contrast, growth in F-containing solution proceeds by slow formation of a more disordered deposit, resulting in random bulk crystal orientations on the Hg surface. A detailed structural analysis of the Pb(OH)Br and Pb(OH)Cl precursor adlayers reveals that they determine the orientation of the subsequently formed bulk crystals, with the arrangement in the adlayer providing a template. Together with our previous results on the pseudo-epitaxial growth of PbFBr on Hg (A. Elsen, et al., Proc.Nat.Acad.Sci., 2013, 110, 6663), these data reveal the decisive role of the interface chemistry, especially the strong chemisorption of the anions bromide and chloride, in steering the formation of these textured deposits at the liquid metal surface.

11:40am **SS-TuM-12 In Situ Electrochemical STM Imaging of an Au Electrode Identifying the Active Sites during the Electrocatalytic Process***, **Yongman Kim**,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea*; Y. Jeong,* Institute for Basic Science (IBS), Republic of Korea*; Y. Kim, J. Park,* Korea Advanced Institute of Science and Technology (KAIST) & Institute for Basic Science (IBS), Republic of Korea

Understanding the influence of surface structural features is important for guiding mechanistic proposals for electrocatalytic reactions of the electrode. However, atomistic knowledge of the actual active sites remains elusive, because of the complicated relationship between structural stability and catalytic activity. With this in mind, we have focused on the fundamentals of the electrocatalytic process, using in situ electrochemical STM, and on locating the real active sites, a longstanding issue. In this work, we present STM results on two-dimensionally well-ordered manganese porphyrin structures on Au(111). We show that manganese porphyrins are oxidized after water oxidation and promptly decompose into catalytically active species as bright protrusions. These newly formed active species have dramatically lost their catalytic activity, either by acid treatment, one of the oxide removal methods, or by deposition of phosphonic acid, one of the oxide–favoring materials. This confirms that the active species are composed mainly of manganese oxides as a water oxidation catalyst. We extended our study to examine the surface structural sensitivity of Au single crystals itself for electrocatalytic CO$_2$ reduction as a simple model study. As the most active electrocatalyst for CO$_2$ conversion into CO, Au(*hkl*) shows structural dependency on coordinated sites, such as the terrace of Au(111) and the steps of Au(332). Through real-time electrochemical STM measurements, we have confirmed that these are the actual active sites for CO$_2$ reduction. A remarkable finding of our work provides the molecular evidence for Au and modified-Au electrode's active sites, providing impetus for future application in water oxidation and CO$_2$ reduction catalysts, as the data establishes a relationship between catalytic activity and structural changes.

12:00pm **SS-TuM-13 Extreme Atomic-Scale Surface Roughening: Amino Acids on Ag on Au(111)***, E. Cook, K. P.S. Boyd, M. Paszkowiak, **Erin Iski**,* The University of Tulsa

A clear description of how surface morphology is affected by the bonding of biomolecules, like amino acids, with metal surfaces is critical to identify due to the potential applications in microelectronics, medical devices, and biosensors. Amino acids (AAs) on clean Au(111) were previously observed to trap Au adatoms, eventually leading to the formation of one atom high metal islands whose area was related to the amino acid molecular weight. To better understand the role of surface identity, L-Isoleucine on Au(111) modified with a Ag thin film was investigated at ambient conditions with Electrochemical Scanning Tunneling Microscopy (EC-STM). The atomically-thin Ag films were deposited on the Au(111) using Underpotential Deposition. The mere presence of a Ag monolayer drastically changed the amino acid/surface interactions despite the chemical similarity of Au and Ag. The adsorption of the AAs on the Ag monolayer drastically altered the surface and caused significant surface roughening distinct from 2D growth which had previously existed only on top of the surface. This roughening occurred layer-by-layer and was not restricted to the first layer of the surface as seen with sulfur containing molecules. Notably, this study demonstrates surface roughening that is occurring under extremely mild conditions highlighting the ability of Ag thin films to markedly alter surface chemistry in concert with biomolecules.

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