

Chemical Analysis and Imaging Interfaces Focus Topic Room A120-121 - Session CA+2D+AS+BI+NS-ThM

Chemical Analysis and Imaging of Liquid/Vapor/Solid Interfaces II

Moderators: Utkur Mirsaidov, National University of Singapore, Xiao-Ying Yu, Pacific Northwest National Laboratory

8:00am CA+2D+AS+BI+NS-ThM1 From Surfaces to Solid-Gas and Solid-liquid Interfaces: Ambient Pressure XPS and Beyond, **Miquel B. Salmeron**, Lawrence Berkeley Lab, University of California, Berkeley **INVITED**

The rapidly increasing field of surfaces under ambient conditions of temperature and pressure, in gas and liquid environments, reflects the importance of understanding surface properties in conditions closer to practical situations. A lot of progress has been made in the last two decades, enabled by the emergence of a number of new techniques, both spectroscopy and microscopy, that can deliver atomic scale information with the required surface/interface sensitivity. I will present recent advances with examples that illustrate the novel understanding derived from the use of new techniques. One in the gas–solid interface where two important barriers have been bridged: the pressure gap, and the temperature gap. These gaps are very important when dealing with weakly bound molecules, where only in the presence of gas at a suitable pressure, or at low temperatures, a non-negligible coverage of adsorbed molecules can be achieved. The temperature gap manifests also in the removal of kinetic barriers. By bridging these two gaps a host of new interface structures have been unveiled that bring new understanding to catalytic phenomena. This will be illustrated with the examples of Cu and CuCo alloys in the presence of CO. In the case of solid-liquid interfaces, the introduction of new methods using well established x-ray spectroscopies is opening the way to the study of the important electrical double layer structure as a function of applied bias, as I will illustrate with the application of X-Ray absorption and IR to sulfuric acid-Pt and Ammonium Sulfate-graphene interfaces.

8:40am CA+2D+AS+BI+NS-ThM3 Probing Solid-liquid Interfaces with Tender X-rays, **Zbynek Novotny**, *N. Comini, B. Tobler*, University of Zuerich, Switzerland; *D. Aegerter, E. Fabbri*, Paul Scherrer Institute, Switzerland; *U. Maier*, Ferrovac GmbH, Switzerland; *L. Artiglia, J. Raabe, T. Huthwelker*, Paul Scherrer Institute, Switzerland; *J. Osterwalder*, University of Zuerich, Switzerland

Many important chemical and biological processes occur at the interface between a solid and a liquid, which is difficult to access for chemical analysis. The large inelastic scattering cross section of electrons in the condensed matter makes X-ray photoelectron spectroscopy (XPS) highly surface sensitive but less sensitive to buried interfaces. This limitation can be overcome by stabilizing an ultrathin layer of liquid with a thickness in the order of a few tens of nanometres and by employing tender X-rays (photon energy ranging between 2-8 keV) that can be used to probe the buried solid-liquid interface. We have recently built and commissioned a new instrument at the Swiss Light Source that combines ambient-pressure XPS with in-situ electrochemistry. With this new setup, we can stabilize a thin liquid layer on a solid surface by a dip&pull method [1], and by using tender X-rays (2-8 keV) from the Phoenix beamline, we can probe the properties and chemistry at the solid-liquid and liquid-gas interface while having a potential control over the ultrathin electrolyte film. The capabilities of this new instrument were demonstrated during the first commissioning beamtime, where we stabilized a thin electrolyte layer (0.1 M KOH) over the Ir(001) electrode. The dip&pull technique was used for the first time using well-defined single-crystalline surfaces (see Supplementary document). Core-level binding energy shifts following the applied potential were observed for species located within the electrolyte film. This included the oxygen 1s level from liquid water, potassium, and, interestingly, also an adventitious carbon species, while the interface was carbon-free. We will present the results from the first commissioning beamtime and outline the future directions we are going to pursue using this new instrument.

[1] S. Axnanda, E. J. Crumlin et al., *Sci. Rep.* 5, 09788 (2014).

9:00am CA+2D+AS+BI+NS-ThM4 X-ray Photoelectron Spectroscopy Insight into X-ray Induced Radiolysis at Heterogeneous Liquid Electrolyte Interface, **Christopher Arble**, National Institute of Standards and Technology (NIST); *H. Guo*, Southeast University, China; *E. Strelcov, B. Hoskins*, National Institute of Standards and Technology (NIST); *M. Amati, P. Zeller, L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy; *A. Kolmakov*, National Institute of Standards and Technology (NIST)

Assessing chemical processes of electrolyte interfaces under operando conditions is an aspirational goal of great importance to many industrial applications¹ that remains technically challenging to investigate. XPS is a powerful characterization tool that can probe elemental and chemical information of atoms with nanoscale depth sensitivity but has traditionally been restricted to UHV conditions. There has been a concerted effort to enable quantitative in-situ measurements of gas and liquid interfaces under realistic environments.²⁻⁴ Recently, advances in 2D materials, i.e., graphene, have been utilized to probe heterogeneous interfaces through molecularly impermeable, electron transparent membranes to maintain UHV pressure in the analysis chamber.⁵

Herein we apply photoemission spectromicroscopy to study the electrochemical dynamics of an array of several thousand individual electrolyte cells encapsulated with electron transparent bilayer graphene.⁶ We monitored the chemical speciation at the electrode- aqueous CuSO₄ electrolyte interface as a function of potential. During the electrochemical experiments, the effects of irradiation upon the solution were observed to influence the system, and spectral deconvolution identified oxidized species of copper and oxygen as well as reduced states of sulfur that were connected to reaction pathways tied with radiolysis. Corresponding SEM images and subsequent EDS spectral maps display spatially confined irradiated byproducts which can be associated with the species observed in with XPS.

Observations of XPS spectroscopic regions in the system were taken at varied X-ray dosages to probe the impacts of radiolysis on the liquid solution concerning the spectroscopic observation of electrochemical deposition of Cu. This experimental methodology imparts a greater understanding of the influence of X-ray induced water radiolysis processes towards the quantification of the electrode/electrolyte interfaces and the underlying dosages necessary for artifact-free data acquisition in condensed media.

References:

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4. Starr, D.; et al., *Chem. Soc. Rev.* **2013**, 42, (13), 5833-5857
5. Kraus, J.; et al., *Nanoscale* **2014** 6, (23), 14394-14403
6. Yulaev, A.; et al., *ACS Appl. Mater. Interfaces* **2017**, 9, (31) 26492-26502

9:20am CA+2D+AS+BI+NS-ThM5 Theoretical Investigation of Reactivity at Complex Solid-Liquid Interfaces, **R. Rousseau, Manh Nguyen**, Pacific Northwest National Laboratory **INVITED**

Contrary to solid/gas interfaces, in solid/liquid interfaces the molecules in the liquid can be organized such that those near the surface are appreciably different from the bulk. This can be impacted by: the composition of the liquid phase, the size shape and loading of nanoparticles and the hydrophilicity of the support. In this talk, we will outline the findings from our ongoing studies of both thermal and electrochemically driven hydrogenation of organic molecules. We will present both classical and ab initio molecular dynamics calculations that simulate the structure and composition within the double both at the support as well as on surface of catalytic nanoparticles. The calculations explicitly identify the different roles of entropy and binding energy on the activity and selectivity of solution phase hydrogenation. A first example [1] shows how phenol/water mixtures behave on hydrophilic and lipophilic surfaces, and provides a possible explanation as to why a higher phenol hydrogenation conversion is observed [2] on Pd catalysts on hydrophilic surfaces than on lipophilic surfaces. We show how reaction rates can be manipulated by changing the concentration of phenol adjacent to the catalysts through modification of the degree of support hydrophilicity, size and loading of nanoparticles, and temperature. In a second example [3], we simulate the speciation on a Au and graphitic carbon cathodic surface of a complex solvent mixture containing organics, salts, acids, as a function of cathode charge and temperature. Here we show that the ability to transfer an electron to the organic is governed by the amount of organic in

the double layer as well as its orientation with respect to the electrode surface. While both examples included have been drawn from the upgrading of bio-oil ex pyrolysis, the principles shown are relevant to any application in heterogeneous catalysis with condensed reaction media.

References

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2. Perez Y, Fajardo M, Corma A. 2011, *Catalysis Communications*, 12, 1071-1074.
3. Padmaperuma AB, Cantu DC, Yoon Y, Nguyen MT, Wang YG, Glezakou VA, Rousseau R, Lliga MA. Manuscript in preparation, to be submitted.

11:00am **CA+2D+AS+BI+NS-ThM10 In-situ/Operando Soft X-ray Spectroscopy for Interfacial Characterization of Energy Materials and Devices**, Y.-S. Liu, X. Feng, *Jinghua Guo*, Lawrence Berkeley National Laboratory

In-situ/operando soft x-ray spectroscopy offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure evolution process have a great influence on performances in a variety of fields, e.g., energy conversion and energy storage materials, chemical and catalytic processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical environment of elements and other critical information of solid/liquid interfaces in real time. We will present soft x-ray spectroscopy characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS), and the development of in situ/operando capabilities for the characterization of interfacial phenomena in energy materials and devices.

A number of the experimental studies, which revealed the catalytic and electrochemical reactions in real time, will be presented, e.g. solid (metal film)/liquid (water) electrochemical interface, Mg-ion batteries, and Li-S batteries [1-5]. The experimental results demonstrate that in-situ/operando soft x-ray spectroscopy characterization provides the unique information for understanding the real reaction mechanism.

References:

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2. "The structure of interfacial water on gold electrodes studied by x-ray absorption spectroscopy", J. J. Velasco-Velez, C. H. Wu, T. A. Pascal, L. F. Wan, J.-H. Guo, D. Prendergast and M. Salmeron, *Science* **346**, 831 (2014)
3. "Nucleophilic substitution between polysulfides and binders unexpectedly stabilizing lithium sulfur battery", M. Ling, L. Zhang, T. Zheng, J. Feng, J.-H. Guo, L. Mai, G. Liu, *Nano Energy* **38**, 82 (2017).
4. "Interfacial insights from operando sXAS/TEM for magnesium metal deposition with borohydride electrolytes", T. Arthur, P.-A. Glans, N. Singh, O. Tutusaus, K. Nie, Y.-S. Liu, F. Mizuno, J.-H. Guo, D. H. Asem, N. Salmon, R. Mohtadi, *Chem. Mater.* **29**, 7183 (2017).

"Revealing the Electrochemical Charging Mechanism of Nanosized Li₂S by in Situ and Operando X-ray Absorption Spectroscopy", L. Zhang, D. Sun, J. Feng, E. Cairns, J.-H. Guo, *Nano Lett.* **17**, 5084 (2017).

11:20am **CA+2D+AS+BI+NS-ThM11 The Importance of Amino Acid Adsorption on Polymer Surfaces in *P. Aeruginosa* Biofilm Formation**, *Olutoba Sanni*, University of Nottingham, UK

High throughput materials discovery screens have revealed polymers that reduce bacterial surface colonization which have progressed to currently ongoing clinical trials [Hook *et al.* *Nature Biotech* 2012]. These novel poly (meth)acrylate coatings reduced biofilm formation by *Pseudomonas aeruginosa*, *Staphylococcus aureus* and *Escherichia coli* in laboratory cultures *in vitro* and *in vivo* in a mouse foreign body infection model. These coatings are known to function by preventing biofilm formation, however why the bacterial cells respond in this way to these polymers has yet to be elucidated. The initial interaction between bacteria and surfaces has been identified as a key determining factor when bacteria decide to either irreversibly attach and colonise a surface or not.

The exposure of most materials to biological milieu is accompanied by adsorption of biomolecules. In protein containing media there is a strong relationship between the adsorbed protein layer formed on materials and

mammalian cell attachment. However, in protein-free media such as used by Hook *et al.*, this cannot be a contributor to early bacterial cell attachment. Consequently, here we carry out careful surface chemical analysis on two polymers known to exhibit drastically different biofilm formation in a standard protein-free, amino acid containing bacterial culture medium (RPMI).

Time of flight secondary ion mass spectrometry (ToF-SIMS) and X-ray photoelectron spectroscopy (XPS) analysis determined that high amino acid adsorption correlates with the surface exhibiting low *P. aeruginosa* colonisation. A total of 10 peaks characteristic of specific amino acids were identified by ToF-SIMS to be adsorbed on polymer. We successfully fitted the Freundlich and Langmuir adsorption isotherm models from which we determined adsorption capacity of polymers, calculated the on/off rate of amino acid adsorption on both anti-biofilm and pro-biofilm surfaces. With XPS, the overlay coverage of amino acids on the polymer surface was established to be approximately 0.2 nm.

The study was extended to quantify in high throughput manner the adsorption of amino acids from RPMI media onto surfaces of 288 polymer materials printed onto a microarray. Ion fragments generated from ToF-SIMS were used to produce a regression model from which we identified polymers with cyclic moieties as major promoters of amino acid adsorption.

This is the first report suggesting adsorbed amino acids or other adsorbed nutrients may correlate with the biofilm formation tendency of materials.

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