

# Tuesday Morning, October 20, 2015

## In-Situ Spectroscopy and Microscopy Focus Topic

Room: 211C - Session IS+AS+SA+SS-TuM

### In-situ Studies of Solid-liquid Interfaces

**Moderator:** Anatoly Frenkel, Yeshiva University, Franklin (Feng) Tao, University of Kansas

8:20am **IS+AS+SA+SS-TuM2 Water at Ionic Liquid Interfaces Probed by APXPS, John Newberg, Y. Khalifa, A. Broderick, University of Delaware**

Ionic liquids (ILs) have a wide array of applications in biotechnology, coatings, synthesis, separations, and energy sciences. Many of these processes involve either IL-solid or IL-vapor interactions. It is therefore critical we understand the fundamental interfacial properties of ILs on a molecular level. Due to the ubiquity of water, its influence on the properties of ILs has been the focus of many bulk studies and, more recently, surface science studies. Here we will highlight the use of a recently commissioned ambient pressure X-ray photoelectron spectroscopy setup in our laboratory and its application in characterizing the interfacial region of hydrophilic and hydrophobic ILs upon interaction with water vapor as a function of increasing pressure.

8:40am **IS+AS+SA+SS-TuM3 Probing the Liquid-Solid Interface of polycrystalline Pt in 1.0 M KOH using Ambient Pressure Photoemission Spectroscopy and "Tender" X-rays, Marco Favaro, B. Jeon, P.N. Ross, Z. Hussain, J. Yano, Z. Liu, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

With the previous success in soft X-ray AP-XPS gas-solid interface<sup>1a-e</sup> probing, researchers have started to gain insights into the liquid-solid boundaries<sup>1d</sup>. Taking the cue from these new research frontiers, we have developed on BL 9.3.1 at the Advanced Light Source (LBNL) a new liquid phase AP-XPS system (based on a Scienta R4000 HiPP-2 analyzer) that will shed new light on the understanding of the chemical changes at the electrode surfaces during normal working conditions, leading to a great enhancement of our knowledge on the most important processes in energy conversion and storage<sup>2a,b</sup>. The combination of this new system with synchrotron radiation in the "tender" X-ray region (between 2 and 7 keV), allows us to probe the interface between thin liquid and solid phases using high kinetic energy photons and then, thanks to the *in operando* approach, directly track the phenomena occurring at the electrode liquid-solid interface during the electrochemical reactions of interest. The technique developed at BL 9.3.1 allows the study of both gas-liquid and liquid-solid interfaces, for pressures up to a hundred of Torr<sup>2a</sup>.

In order to deeply investigate the possibilities offered by this new technique and, at the same time, to establish a benchmark, a reference material such as polycrystalline Pt has been studied in 1.0 M KOH electrolyte. In this talk we will demonstrate that it is possible to have fine control of the applied potential<sup>2a,b</sup>, measuring the core level binding energy shift of the oxygen 1s and potassium 2p photoemission lines, according to the applied external potential. Moreover we will discuss the observation, under *in operando* conditions, of the changes of the surface oxidation state<sup>2b</sup> of Pt triggered by the applied potential. Thanks to the innovative experimental approach, we have observed the *in situ* formation of Pt(II) and Pt(IV) species during the oxygen evolution reaction (OER), as well as the reversibility of the surface chemistry passing from anodic to cathodic potentials (up to the hydrogen evolution reaction, HER).

[1] a. Lu et al., *Sci. Rep.* **2**, 715 (2012); b. Zhang et al., *Nat. Mat.* **9**, 944 (2010); c. Axnanda et al., *Nano Lett.* **13**, 6176 (2013); d. Starr et al., *Chem. Soc. Rev.* **42**, 5833 (2013); e. Mudiyansele et al., *Angew. Chem. Int. Ed.* **52**, 5101 (2013).

[2] a. S. Axnanda, E. Crumlin et al., *Sci. Rep.*, accepted; b. E. Crumlin et al., *in preparation*.

9:00am **IS+AS+SA+SS-TuM4 Toward Ambient Pressure Electron Spectroscopy with Conventional XPS Instrumentation, Andrei Kolmakov, National Institute of Standards and Technology (NIST)**

The current state of the art instrumentation for ambient pressure electron spectroscopy requires highly specialized sophisticated laboratory equipment or dedicated synchrotron radiation facilities. The limited access to these equipment impedes *in situ* (*in vivo*) studies under realistic conditions in catalysis, energy, environmental and bio-(medical) fields. We propose a new sample platform which enables ambient pressure XPS to be conducted using conventional XPS instrumentation. The core of the sample platform is

microchannel environmental cells sealed with electron transparent, molecularly impermeable, mechanically and chemically stable graphene layer. The channels can be impregnated with liquids or gases and yet be vacuum compatible. Two major wafer scale fabrication strategies: (i) transferred graphene and (ii) as grown graphene layer were described. The coverage yield, membrane cleanness and leaking rates were comparatively studied. The feasibility tests of the platform included *in situ* XPS and electron microscopy studies of the water radiolysis and electrochemical processes taking place at liquid electrolyte-solid interface.

9:20am **IS+AS+SA+SS-TuM5 Solvation and Chemistry at the Interface: Near Ambient Pressure Electron Spectroscopy Studies of Aqueous Solution Interfaces, John Hemminger, University of California, Irvine**

INVITED  
We have combined liquid-jet photoelectron spectroscopy coupled with classical molecular dynamics simulations to study the composition and chemistry of the liquid/vapor interface of aqueous solutions. Our experiments take advantage of the variable x-ray energy capability of synchrotron radiation and the kinetic energy dependence of the electron inelastic mean free path to carry out experiments with different probe depths. At low x-ray energy the low energy photoelectrons are detected primarily from the surface region of the solution. At higher x-ray energy our experiments probe more deeply into the solution. This allows us to directly compare the liquid/vapor interface with the bulk of the aqueous solution. We will present recent results on aqueous solutions of organonitrile compounds (acetonitrile and propionitrile). Our experiments and MD simulations show that both acetonitrile and propionitrile accumulate at the liquid/vapor interface—even though both nitriles are fully miscible with water. We have also studied the salting in and salting out effects for nitriles in water. We also have studied the effect of ion size on the surface propensity of cations in alkali halide aqueous solutions.

11:00am **IS+AS+SA+SS-TuM10 In situ Single-molecule Microscopy of Photoelectrocatalysis for Solar Water Oxidation, Peng Chen, Cornell University**

INVITED  
This talk will present our recent results in using single-molecule super-resolution fluorescence microscopy to image photoelectrochemical reactions on single semiconductor nanostructures *in situ* under photoelectrochemical water oxidation conditions. We separately image hole and electron induced reactions, driven by light and electrochemical potential, and map the reactions at single reaction temporal resolution and nanometer spatial resolution. We also correlate the surface hole and electron reactivity with the local water oxidation efficiency using sub-particle level photocurrent measurements. By depositing oxygen evolution catalysts in a spatially controlled manner, we further identify the optimal sites for catalyst deposition for photocurrent enhancement and onset potential reduction.

11:40am **IS+AS+SA+SS-TuM12 In Situ and Operando AP-XPS for the Oxidation State of Pd at Solid/Liquid Interface, Beomgyun Jeong, M. Favaro, P.N. Ross, Z. Hussain, Lawrence Berkeley National Laboratory (LBNL), Z. Liu, Shanghai Institute of Microsystem and Information Technology, China, B.S. Mun, J. Lee, Gwangju Institute of Science and Technology, Republic of Korea, E.J. Crumlin, Lawrence Berkeley National Laboratory (LBNL)**

A catalyst is defined as a substance that enhances a reaction rate without changing its chemical state. However, often the chemical state of a catalyst surface undergoes changes during the reaction, leading to the degradation of catalyst performance. These phenomena are particularly significant in electrocatalysis in which reaction occurs at solid/liquid interface with electrical potential as an activation energy to drive the reaction. In order to understand the mechanism of catalyst degradation, it is important to have a capability to observe the chemical states of electrode and various chemical species in electrolyte during the reaction taking place at the solid/liquid interface. In order to explore this region, we have developed a new experimental approach [1], using ambient pressure XPS (AP-XPS) coupled with "tender" X-rays (in the range between 2.5 and 7.0 keV) at the Advanced Light Source BL 9.3.1, Lawrence Berkeley National Laboratory. Because of the relatively high kinetic energy of the incoming photons, "tender" X-rays allow probing solid/liquid interfaces through thin electrolyte films characterized by a thickness of 10-30 nm. This unique functionality allows the ability to simultaneously correlate the electrocatalytic activity of electrodes to both the chemical modifications of the electrode surface, and the electrolyte.

This talk will provide details on *in-situ* and *operando* AP-XPS measurements on the chemical modifications of polycrystalline Pd surface studied at different electrochemical potentials. Pd is a cost-effective materials alternative to Pt showing similar electrocatalytic property of Pt in

various reactions, such as oxygen reduction and electrooxidation of hydrogen and formic acid. On the other hand, it is well known that the Pd activity decreases faster than that of Pt especially in formic acid oxidation [2]. This phenomenology could be understood by the direct observation of the Pd surface chemistry evolution at electrified solid/liquid interface. We will discuss the performance of the Pd electrode in two different aqueous electrolytes, in particular in an alkaline medium and in a formic acid solution, an electroactive liquid organic molecule. We believe that our findings represent a step forward in the rationalization of the electrocatalytic behavior of Pd.

[1] S. Axnanda, E.J. Crumlin *et al.*, *Sci. Rep.* 5 (2015) 9788.; b. E.J. Crumlin *et al.*, in preparation.

[2] H. Jeon, S. Uhm, B. Jeong, J. Lee, *Phys. Chem. Chem. Phys.* 13 (2011) 6192.

12:00pm **IS+AS+SA+SS-TuM13 In situ Characterization of Switchable Ionic Liquids by Liquid ToF-SIMS and SALVI**, *Juan Yao, X. Sui, D. Lao, Y. Zhou, S. Nune, D. Heldebrant, Z. Zhu, X.-Y. Yu*, Pacific Northwest National Laboratory

A vacuum compatible microfluidic reactor, SALVI (System for Analysis at the Liquid Vacuum Interface) was employed for *in situ* chemical imaging of switchable ionic liquids (SWILs) using time-of-flight secondary ion mass spectrometry (ToF-SIMS). A model SWIL system consisting of 1,8-diazabicycloundec-7-ene (DBU) and 1-hexanol with CO<sub>2</sub> gas to change solvent polarity was selected. A series of ionic liquids with different CO<sub>2</sub> loading was analyzed. Spatial chemical differences were observed within the same ionic liquid, indicating inhomogeneity of the ionic liquid. Spectral principal component analysis (PCA) was conducted using both positive and negative ToF-SIMS data. Clear distinctions were observed among SWILs of different CO<sub>2</sub> loadings. The loading plots strongly indicate that fully loaded SWILs share similar spectral components as those of the non-loaded ILs. This finding confirms the hypothesis of the biphasic structure in the fully loaded IL predicated by molecular dynamic simulation and presents the first physical evidence of the liquid microenvironment of IL determined by liquid ToF-SIMS. Various ion pairs were also observed in addition to the known SWIL chemistry of the DBU and 1-hexanol system, indicating the complexity of the ionic liquid previously unknown. The vacuum compatible microchannel in SALVI provides a new way to study ionic liquids in vacuum by sensitive surface techniques. Our approach directly visualized spatial and chemical heterogeneity within the SWILs by dynamic liquid ToF-SIMS for the first time.

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