

Wednesday Afternoon, November 12, 2014

In-Situ Spectroscopy and Microscopy Focus Topic Room: 313 - Session IS+2D+MC+NS+SP+SS-WeA

In-Situ Scanning Microscopy

Moderator: Markus Ammann, Paul Scherrer Institut

2:20pm IS+2D+MC+NS+SP+SS-WeA1 *In Situ* Studies of Model Fuel Cells, *Zhi Liu*, Lawrence Berkeley National Laboratory **INVITED**

The ambient pressure x-ray photoelectron spectroscopy (AP-XPS) endstations based on differentially pumped electron energy analyzers have been recognized by scientific communities as an important in-situ tool to study water, environmental science, catalysis and many other important fields. Multiple new AP-XPS endstations are currently under planning or development at US and international synchrotron light sources. Recently we have installed a new hard x-ray AP-XPS endstation at ALS Beamline 9.3.1 (2.5keV- 5keV). By using X-ray up to 5KeV, we can perform AP-XPS at a pressure up to 110 torr. The probing depth of photoelectrons also increases to >10 nm, which will allow us to study not only the gas/solid interface but also the liquid/solid interface. In this talk, I will give an overview of science projects at ALS BL9.3.2 in heterogeneous catalysis and electro-chemistry using these new systems. Furthermore, I will present results of our in-situ study on the electrolyte/electrode interface of a working model electrochemical cell at ALS BL9.3.1. We believe the successful development of soft and hard X-ray APXPS endstations will provide energy research community a powerful in-situ tool to directly study the electrolyte/electrode interface of many important electrochemical devices.

3:00pm IS+2D+MC+NS+SP+SS-WeA3 Probing of Nanoscale Objects in Reactive Liquids through Membranes using Near-Field Microwave Microscopy, *Alexander Tselev*, Oak Ridge National Laboratory, *A. Komakov*, National Institute of Standards and Technology (NIST)

Many functional objects (and interfaces) have to be studied in situ when the object is immersed in liquid environment. In addition, for energy, chemical, (bio-) medical and other applications, there is a need to study the encapsulated objects, which otherwise can be chemically reactive or toxic. These samples are often mesoscopically small or exist in minuscule quantities. Recently, we have developed a process for preparation of liquid-filled cells sealed with ultrathin membranes. Such cells can be implemented for in-situ studies using, for example, electron or soft x-ray microscopy due to a high transparency of these membranes to electron beams. However, in many cases electron microscopy is an invasive technique due to various electron beam induced parasitic effects (e.g. radiolysis or beam induced deposition). To overcome these impediments, we demonstrate the scanning microwave impedance microscopy (sMIM) to image different nanoscale objects immersed in the liquid environment through 30 nm SiN membranes. In the sMIM, microwaves of a frequency of 3 GHz are sent through a coaxial cable connected to a shielded cantilever probe fully compatible with an AMF microscope. The sharp probe tip provides "focusing effect" for the electric component of the microwave. For imaging, the tip is brought into gentle mechanical contact with a membrane. Amplitude and phase of microwaves reflected from the probe are monitored. Since the wave reflection is dependent on the tip-sample system impedance, reflected waves carry information about sample local properties. The effective distance into the sample depth, where the tip-induced field enhancement takes place, is approximately equal to the tip apex radius. Since the membrane thickness is smaller compared to the tip radius of a typical probe (about 50 nm for a fresh tip), the tip-sample impedance is dependent on the dielectric properties of the material beneath membrane, and therefore, it is possible to "see" through the membrane. We demonstrate imaging of different combinations of model liquids and nanoparticles: water and water-based solutions ($\epsilon \sim 80$), organic solvents ($\epsilon \sim 10-25$), and oils ($\epsilon \sim 2-3$) containing Ni metal, polystyrene ($\epsilon \sim 2.5$) and PbO ($\epsilon \sim 25$) particles. This technique can be further implemented for a broad range of objects in confined liquids, and can be used to monitor interfacial electrochemical reactions. Imaging with sMIM was performed at CNMS, which is sponsored at ORNL by the SUFD, BES, US DOE.

4:20pm IS+2D+MC+NS+SP+SS-WeA7 Caught in the Act! Live Observations of Catalysts Using High-Pressure Scanning Probe Microscopy, *Irene Groot*, Huygens-Kamerlingh Onnes Laboratory, Leiden University, Netherlands **INVITED**

Recently it has become clear that essential differences can exist between the behavior of catalysts under industrial conditions (high pressure and temperature) and the (ultra) high vacuum conditions of traditional laboratory experiments. Differences in structure, composition, reaction

mechanism, activity, and selectivity have been observed. These observations indicated the presence of the so-called pressure gap, and made it clear that meaningful results can only be obtained at high pressures and temperatures. However, most of the techniques traditionally used to study catalysts and their reactions were designed to operate under (ultra) high vacuum conditions. To bridge the pressure gap, the last years have seen a tremendous effort in designing new instruments and adapting existing ones to be able to investigate catalysts *in situ* under industrially relevant conditions.

This talk focuses on the development of scanning probe microscopy for *operando* observations of active model catalysts. In our group, we have developed set-ups that combine an ultrahigh vacuum environment for model catalyst preparation and characterization with a high-pressure flow reactor cell, integrated with either a scanning tunneling microscope or an atomic force microscope. With these set-ups we are able to perform atomic-scale investigations of well-defined model catalysts under industrial conditions. Additionally, we combine the structural information from scanning probe microscopy with time-resolved mass spectrometry measurements on the gas mixture that leaves the reactor. In this way, we can correlate structural changes of the catalyst due to the gas composition with its catalytic performance.

This talk highlights a short overview of the instruments we developed and illustrates their performance with results obtained for different model catalysts and reactions. As a proof of principle, results for the fruit fly of surface science, *i.e.* CO oxidation, will be shown. But additionally, results for more complex reactions such as NO reduction, Fischer-Tropsch synthesis, desulphurization, and production of chlorine will be discussed.

5:00pm IS+2D+MC+NS+SP+SS-WeA9 X-ray Photoelectron Spectroscopy Studies of H₂O Dissociation on Pre-oxidized Al (111) and Cu (111) Single Crystal Surface, *Qianqian Liu*, SUNY, Binghamton University, *X. Tong*, Brookhaven National Laboratory, *G.W. Zhou*, SUNY, Binghamton University

Dissociation of H₂O molecules on ultrathin oxide overlayers formed on metal surfaces plays a critical role in many catalytic reactions. However, the effects of chemical states and thickness of oxide overlayers on the microscopic process of H₂O dissociation are still poorly understood. In this work, X-ray photoelectron spectroscopy (XPS) is employed to study H₂O dissociation on oxidized Al (111) and Cu (111) surfaces with controlled chemical states and thicknesses of the oxide films. For Al (111), the experiment was performed under two water vapor pressures (10⁻⁶ Torr and 5 Torr) on aluminum oxide films with the thicknesses varying from 2.47 Å to 5.14 Å; for Cu (111), the experiment was performed by varying the water vapor pressure from 10⁻⁷ Torr to 10⁻⁵ Torr and temperature from 100°C to 450°C on the oxide film with a constant thickness. Al (2p), Cu (2p), Cu (LMM) and O (1s) spectra were monitored by XPS after each oxygen exposure followed by subsequent H₂O exposure. Upon exposing the oxide to water vapor, the O (1s) peak shifts to a higher energy and becomes broader. A detailed analysis of the spectra indicates that H₂O molecules dissociate into OH groups for both oxidized Al and Cu surfaces. However, the subsequent reaction of OH groups with the oxide films on Cu (111) and Al (111) surfaces are dramatically different. On the oxidized Al(111) surface, OH is further incorporated into the aluminum oxide that results in the thickening of the oxide film, whereas on the oxidized Cu (111) surface, OH works as a reducing agent to remove oxygen from the oxide film that results in the thinning of the Cu oxide film. The microscopic processes underlying the differences in H₂O dissociation on oxidized Al (111) and Cu (111) will be described in detail.

5:20pm IS+2D+MC+NS+SP+SS-WeA10 Operando APXPS of the Liquid-Solid Interface: Au Oxidation, *Ethan Crumlin*, *S.A. Axnanda*, *P.N.R. Ross*, *Z.L. Liu*, Lawrence Berkeley National Laboratory

Interfaces play an important role for many reaction processes and are essential for electrochemistry. Electrochemical systems ranging from high temperature solid oxide fuel cells (SOFC) to lithium ion batteries to capacitors have a wide range of important interfaces between solids, liquids, and gases which play a pivotal role in how energy is stored, transferred, and/or converted. Previous capabilities of ambient pressure X-ray Photoelectron Spectroscopy (APXPS) have primarily only been able to observe the gas-solid and gas-liquid interfaces. However, recent enhancements now enable new APXPS systems to work at pressures larger than 20 Torr, and utilize 'Tender' X-rays (2.5 – 7 keV). These features provide new capabilities and opportunities for probing the liquid-solid and solid-solid interfaces. Using synchrotron X-rays at Lawrence Berkeley National Laboratory, the Advanced Light Source and our 'Tender' X-ray APXPS endstation that is outfitted with various *in situ/operando* features such as electrical leads to apply electrical potentials and operates at

pressures >20 Torr, to observe the liquid-solid interface of a gold foil electrode that has been immersed and partially removed from a liquid electrolyte. This talk will provide details on how we used this technique to probe liquid-solid interface and in real-time observe the oxidation of the gold foil electrode under varying applied potentials and different electrolyte solutions.

5:40pm **IS+2D+MC+NS+SP+SS-WeA11 Water on ZnO(10-10) Investigated by Ambient Pressure X-ray Photoelectron Spectroscopy.**
Chris Goodwin, University of Delaware, *A. Boscoboimik*, Brookhaven National Lab, *C. Arble*, *J.T. Newberg*, University of Delaware

The extent to which ZnO hydroxylates under ambient conditions can significantly influence catalytic properties. Thus, it is critical to understand the composition of different ZnO terminations as a function of relative humidity (RH) in order to elucidate the true interfacial surface terminations. In this talk we present results of ambient pressure XPS (APXPS) for water exposures to a ZnO(10-10) single crystal. It will be shown that ZnO(10-10) extensively hydroxylates at the interface, and both molecular and dissociative water increase as the RH increases. These results are consistent with simulations in the literature that highlight the efficacy for ZnO(10-10) to dissociate water.

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