

In-situ Microscopy, Spectroscopy, and Microfluidics Focus Topic

Room 202B - Session MM+AS+NS+PC+SS-MoA

X-ray and Electron Spectromicroscopy in Liquids and Gases & Flash Networking Session

Moderator: Piran Kidambi, Vanderbilt University

1:20pm **MM+AS+NS+PC+SS-MoA1 Bridging the Material and Pressure Gap in Synchrotron based Photoelectron in Situ/Operando Studies**, **Luca Gregoratti**, M. Amati, P. Zeller, Elettra-Sincrotrone Trieste, Italy **INVITED**
Modelling the real behavior of technologically relevant materials at typical laboratory environmental conditions is a longstanding challenge. Not only classical pressure conditions are generally far from usual industrial environments (pressure gap) but also heterogeneous materials are very different from those often used to simplify the modelling strategies (material gap). For instance to monitor in-situ/operando the lateral distribution of the chemical state of surfaces and interfaces during a catalytic or electrochemical reaction at sub-micron level at environmental conditions as close as possible to the operational ones is of crucial importance to shed light on the running processes. But the possibility to investigate chemical reactions with X-ray photoelectron spectroscopies by overcoming material and pressure gaps is still a challenge also for modern experimental setups.

The Escamicroscopy team of Elettra which operates a Scanning Photoemission Microscope (SPEM) has recently developed novel concepts for a new generation of SPEM working under more realistic pressure conditions. The graphene sealed cells, combined for the first time with XPS by A. Kolmakov [1], allow the possibility to investigate systems which require an ambient pressure regime (e.g. liquid/solid interfaces). Despite the huge ongoing progress in the development and performance of these cells several crucial issues are unsolved and will be addressed by this presentation.

Another recent development is an effusive cell for near-ambient pressure SPEM setups where the highest static pressure achievable is around 1 mbar. Samples are encapsulated in a vacuum sealed cell and located behind a 200 μm diameter size pinhole through which the focused X-ray beam illuminates surfaces and photoelectrons reach the high vacuum path towards the electron analyzer [1].

2:00pm **MM+AS+NS+PC+SS-MoA3 Transition Metal Complexes in Aqueous Solutions Characterized by Liquid Jet Ambient Pressure X – ray Photoelectron Spectroscopy**, **Jared Bruce**, J.C. Hemminger, University of California, Irvine

Transition metals in aqueous solution have been investigated by a multitude of techniques and are a cornerstone of many aspects of chemistry. Recently, the atmospheric chemistry community has begun to shift their attention to iron, manganese and copper containing aqueous solutions due to their propensity to generate hydroxyl radicals at the air/water interface through a Fenton mechanism. Understanding the chemical state of the transition metal present at the air/water interface, in addition to the distribution as a function of depth, would provide critical insight to the active species of hydroxyl generation. Solvation effects have been shown to significantly affect the distribution of small ions as a function of depth from the vacuum/water interface; first through molecular dynamics (MD) simulations then corroborated by liquid – jet X – ray photoelectron spectroscopy (LJ-XPS). Solvation of transition metals in aqueous solution have added complexity compared to small ions because of complexation of ligands and equilibria with the surrounding solvent.

In our work, using both a lab – based LJ - XPS and synchrotron measurements at the Advanced Light Source, we have shown the distribution of chemical states on a model Fenton reagent, $\text{Fe}^{2+}_{(\text{aq})}$, change with depth relative to the air/liquid interface. The chemical state is also sensitive to “spectator” ions in the solution. The presence of Cl^- leads to a binding energy shift in the Fe 2p spectra and a change in the distribution as a function of depth. This is also observed in the Cl 2p spectrum where a binding energy shift of 0.3 eV indicates the presence of an inner sphere Cl that follows the distribution change in the Fe 2p spectrum

2:20pm **MM+AS+NS+PC+SS-MoA4 Interfacial Electrochemistry in Liquids Probed with Photoemission Electron Microscopy**, **S. Nemsak**, Forschungszentrum Juelich GmbH, Germany; **E. Strelcov**, NIST Center for Nanoscale Science and Technology; **Tomas Duchon**, Forschungszentrum Juelich GmbH, Germany; **H.X. Guo**, National Institute of Standards and Technology; **J. Hackl**, Forschungszentrum Juelich GmbH, Germany; **A. Yualev**, NIST Center for Nanoscale Science and Technology; **I. Vlasiouk**, Oak Ridge National Laboratory; **D.N. Mueller**, **C.M. Schneider**, Forschungszentrum Juelich GmbH, Germany; **A. Kolmakov**, NIST Center for Nanoscale Science and Technology

The use of photoemission spectromicroscopy as a probe of liquid electrolytes has been an elusive goal, motivated by the breadth of information the technique can provide, but hindered by many technical difficulties. Here, we present a universal multichannel array platform employing graphene capping that allows for investigation of interfacial liquid electrochemistry via soft x-ray absorption and photoemission spectromicroscopy. The methodology is demonstrated in the case of copper electroplating from a sulphuric acid solution, that, along with cycles of copper deposition on gold electrodes, reveals hindered nucleation at the electrified graphene membrane evidenced by the presence of stable Cu^+ ions.

3:40pm **MM+AS+NS+PC+SS-MoA8 Practical Liquid Cell Microscopy - Opportunities and Challenges**, **Daan Hein Alsem**, **K. Karki**, Hummingbird Scientific; **J.T. Mefford**, **W.C. Chueh**, Stanford University; **N.J. Salmon**, Hummingbird Scientific **INVITED**

Transmission electron microscopy (TEM), scanning electron microscopy (SEM) and synchrotron X-ray microscopy (XRM) are powerful characterization tools and are routinely used to study a wide range of material-systems at the nanoscale. This has generated strong interests in acquiring more reliable quantitative *in-situ* and *operando* measurements in realistic reaction environments, as is possible with liquid environmental cells. This approach has already started to produce new insights on the dynamics and structural changes during electrochemical processes as lithium ion insertion/extraction, dendrite formation, metal nucleation and corrosion. However, practical aspects of replicating representative electrochemical data reminiscent of bulk behavior are still a challenge in these systems.

Here, we will discuss practical aspects of conducting *operando* liquid cell microscopy experiments relating to the typical geometry of these liquid-cell microscopy systems as well as artifacts coming from the microscope during *operando* experiments. We will also present a TEM/SEM/XRM microscopy platform that enables true electroanalytical measurements mimicking bulk behavior of the material system.

The example study shown here is performed using electrochemical cells, which consist of two microfabricated chips sandwiched with transparent SiN_x membranes for encapsulating liquid and viewing in the microscope. A newly developed hardware system and specially optimized electrochemistry chips with a custom configuration for working electrode (WE), counter electrode (CE) and reference electrode (RE) allows quantitative measurements of electrochemical processes with details resembling the complete cycle of the bulk. As illustrations, we present cyclic voltammetry (CV) studies of some model compounds such as 0.1M CuSO_4 and 20 mM $\text{K}_3\text{Fe}(\text{CN})_6$ /20 mM $\text{K}_4\text{Fe}(\text{CN})_6$ in 0.1M KCl solutions. In the former case, the copper deposition and stripping occurs at the working electrode at distinct redox peaks in liquid cell and the result mimics the bulk electrochemical cells with large electrode areas and larger volume of electrolyte solution. This work highlights the fact that with suitable hardware systems and with knowledge and correction of microscope-induced artifacts, bulk behavior of the electrochemical processes can be both observed and measured quantitatively.

4:20pm **MM+AS+NS+PC+SS-MoA10 Observation of Electric Double Layer under Graphene by Scanning Electron Microscopy**, **Hongxuan Guo**, **A. Yulaev**, **E. Strelcov**, National Institute of Standards and Technology (NIST)/University of Maryland, College Park; **A. Tselev**, CICECO and Department of Physics, University of Aveiro, Portugal; **A. Kolmakov**, National Institute of Standards and Technology

The formation of the electric double layer is a fundamental phenomenon occurring at electrified solid-liquid electrolyte interfaces and which has a key importance for energy devices, chemical engineering and biomedical applications. The structure and composition of electric double layer can be accessed using optical methods ¹, and more recently with X-ray spectroscopy ^{2,3}, as well as scanning probe microscopy⁴.

Monday Afternoon, October 22, 2018

In this presentation, we demonstrate the feasibility of *in-situ* scanning electron microscopy to observe the changes in electric double layer in different electrolytes upon polarization. We designed an electrochemical liquid cell with electron transparent electrode made of bilayer graphene.^{5,6} We monitored the changes in secondary electron yield from the graphene-liquid interface upon electrolyte polarization. We found that the normalized SEM image contrast is linear with the applied bias voltage and is related to the concentration and distribution of the ions at the interface. The analysis of SEM videos provide insight on long term kinetics of ionic moieties in electrolyte during polarization. This experimental methodology will be helpful for understanding the structure, property, and dynamics of the electric double layer at solid -electrolyte interfaces.

Reference

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