Applied Surface Science Division
Room 13 - Session AS+MS-FrM

Unlocking the Sample History: Forensics and Failure Analysis

Moderators: Karen Gaskell, University of Maryland, College Park, Matthew Linford, Brigham Young University

8:20am **AS+MS-FrM-1 *In Situ* Diagnostics of the Coupled Mechanical and Electrochemical Degradation of High Capacity Electrode Materials in Lithium Ion Batteries*, Xingcheng Xiao,*** General Motors R&D Center **INVITED**

Higher capacity in electrode materials (such as Silicon) is always accompanied by higher volume expansion. Most of the efforts to date in Si based electrodes have been focused on architectural design to avoid Si cracking. To achieve high current efficiency and long cycle life, the solid-electrolyte interface (SEI) must be mechanically and chemically stable despite the large volume-change. In this presentation, I will show you a comprehensive set of *in-situ* diagnostic techniques we developed to understand the coupled mechanical/chemical degradation of SEI layers during cycling. Based on the learning from the in-situ diagnostics, I will discuss some coating design strategies to achieve high cycle efficiency and extend the cycle life of high energy density batteries for electrical vehicle applications.

9:00am **AS+MS-FrM-3 A Novel Approach to Characterizing the Silicon Anode Electrolyte Interface in Lithium Ion Batteries*, Caleb Stetson,*** Colorado School of Mines, National Renewable Energy Laboratory*; C Jiang, S Harvey, K Wood, G Teeter, C Ban, M Al-Jassim,* National Renewable Energy Laboratory*; S Pylypenko,* Colorado School of Mines

As the Lithium-ion battery (LIB) technology sector continues to develop, advances increasingly rely on innovative battery materials, particularly anode materials. Silicon has arisen as a frontier in anode material research mainly due to its high theoretical lithium capacity and the extensive knowledge regarding its processing and fabrication.

One of the principal challenges associated with the development of LIBs is the lack of understanding of the solid electrolyte interphase (SEI) layer that forms between the organic electrolyte and anode during the initial cycling of the battery. Formed from electrolyte decomposition products, this layer must be electronically insulating while still being permeable to lithium ions to allow for charge transport. This balance between differing properties is often difficult to maintain: if the SEI grows too thick, it loses its permeability to lithium; if it becomes too thin, the electronic resistance cannot be maintained and current will flow between the two electrodes. Measuring spatial variation in resistivity within this layer and correlating these data with chemical composition is of upmost importance to understanding SEI performance.

The SEI forms on the anode surface with thickness in the nanometer regime, which poses a challenge for finding the buried interface of the SEI with the Si anode. In order to locate and measure electronic properties at this interface, our group has utilized a scanning spreading resistance microscopy (SSRM) probe and scanner head to measure resistivity with nanometer-scale resolution. This system is installed in an argon glove box to minimize sample exposure to oxygen and humidity. The SSRM probe features a doped diamond-coated silicon probe that is both electronically conductive and wear resistant. The application of a sample-probe bias voltage while varying the force exerted on the probe in AFM contact mode allows for measurement of resistivity laterally and vertically.

Measurements of resistance vs. depth for SEIs demonstrate strong trends of resistance decrease as the probe penetrates deeper levels of the SEI. Several techniques are utilized to investigate the chemical composition at different depths of the SEI, including Time-of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS) and X-ray Photoelectron Spectroscopy (XPS). Combining resistance and chemical speciation data originating from specific depths provides an interesting basis for the study of SEIs and the evolution of Si anodes under different cycling conditions with distinct electrolyte solutions.

9:20am **AS+MS-FrM-4 In situ Liquid SIMS Investigation of Ion Solvation in Electrolytes for Lithium Ion Batteries*, Zihua Zhu,*** *Y Zhang, Z Xu, M Su, C Wang, X Yu,* Pacific Northwest National Laboratory*; J Wang,* Pacific Northwest National Laboratory, China

Ion-solvent interactions are of great fundamental and practical importance. However, many mysteries have long been existing in this field. For example, for the electrolytes used for Li ion batteries, preferential solvation and coordination number of a Li^+ ion are two interesting questions in hot debates so far. A major reason for above situation is lacking of reliable analysis techniques that can provide direct molecular information to elucidate ion-solvent interactions. In this work, in situ liquid SIMS was used to examine salt ion-solvent molecule interactions in several representative electrolytes used for Li ion batteries. Our data of the $LiPF_6$ in EC: DMC electrolyte show very strong molecular evidence that EC is preferentially solvated with Li^+, supporting previous ESI-MS and NMR results, but against recent Raman results. In addition, our data suggest that although the coordination number of a Li^+ ion can be as high as six in bulk electrolytes, three of them may be more stable than the remaining ones. In addition, it was observed that Li^+ and FSI^- ions tend to well-separated in 1.0 M LiFSI in DME electrolyte, consistent with our MD simulation results. As a comparison, many ion clusters were observed in the same concentration of $LiPF_6$ in EC: DMC electrolyte. The above findings suggest that in situ liquid SIMS can provide key evidence for better understanding of the ion-solvent interactions in the electrolytes for Li ion batteries.

9:40am **AS+MS-FrM-5 Determining Bulk and Interface Chemical Damage Regimes in XPS Depth Profiling using Cluster Ion Beams*, Benjamin Schmidt*,** *J Newman, J Moulder, J Mann,* Physical Electronics

The development of gas cluster ion beams (GCIB) has provided fresh opportunities to study materials that exhibit chemical changes under monatomic argon ion bombardment during XPS surface cleaning or depth profiling. This is especially important as mixed inorganic/organic structures are increasingly used in applications such as OLED display devices and medical implants.

Several variables are available to fine tune cluster energy and size, which provides high levels of control to the user, but can present an overwhelming parameter space for practical use. For example, previous studies have shown that there is a relationship between the GCIB energy/atom and observed chemical changes. In the case of depth profiling bulk HfO_2, Barlow [1] observed that no change in Hf 4f peaks was detected for argon GCIB settings of 6 eV/atom, whereas a decrease to 2 eV/atom was required to minimize indium reduction in InAs. In a similar study on HfO_2, we observe similar results. By varying beam conditions, no Hf 4f reduction is observed at nominal 5.6 eV/atom, but is seen with an nominal 8 eV/atom beam. We discuss bulk and interface effects under these various conditions. For example, while no peak shape changes were observed in bulk HfO_2 at 5.6 eV/atom, reduced Hf oxide species are observed near the Si substrate, broadening the measured HfO_2/Si interface. We have investigated several other material systems, including polymers and Ti compounds, to provide guidance on general user settings.

[1] AJ Barlow, JF Portoles, PJ Cumpson. Observed damage during Argon gas cluster depth profiles of compound semiconductors. J App Phys 116, 054908 (2014)

10:00am **AS+MS-FrM-6 In Situ Studies on Radiation Resistance of Nanoporous Metals*, Jin Li*[1]*,*** Texas A&M University*; C Fan,* Purdue University*; Y Chen,* Los Alamos National Laboratory*; X Zhang,* Purdue University

High energy particle radiation induces severe microstructural damage in metallic materials. Void swelling is a general consequence of radiation damage and can drastically degrade the mechanical integrity of irradiated materials. Nanoporous (NP) materials have great potentials to alleviate irradiation-induced damage due to their giant surface-to-volume ratio. Here we show, by using in situ Kr ion irradiation of nanoporous Au in a transmission electron microscope, nanopores shrink during radiation, and their shrinkage rate is pore size dependent. In addition, from temperature-dependent studies, we found that both defect density and nanopores evolve with radiation temperature. Higher temperature results in lower defect density and reduced shrinkage rate of nanopores. The sink strength of nanopores as a function of temperature is estimated. Moreover, NP Au exhibits significantly enhanced swelling resistance compared to coarse-grained Au. This study sheds light on the design of radiation-tolerant nanoporous metallic materials.

[1] **ASSD Student Award Finalist**

10:20am **AS+MS-FrM-7 Surface Analysis in the World of Fine Art**, ***Thomas Beebe, Jr.***, *Z Voras, C Goodwin, K deGhetaldi, B Baade, J Mass,* University of Delaware **INVITED**

Connections between the science of surface analysis and the science of cultural heritage, such as it is, have been neither historically strong nor particularly productive, unfortunately for both fields. We are developing new collaborations aimed at changing this. Not all cultural heritage conservators adopt a scientific approach, and not all of those that do are willing to expand their scientific approaches to include surface-sensitive techniques such as XPS and TOF-SIMS, in many cases because their backgrounds have not led them to know about such methods. To be fair, we surface scientists don't have all the answers and often can't get them. Not all surface scientists are interested in pushing the boundaries of their sample types into such unconventional realms, and not all of those that are interested have the patience to develop the new sample-handling and sample-preparation techniques applicable to XPS and TOF-SIMS analysis, not to mention dealing with the ultra-small sample sizes of such precious works of art. This presentation will draw upon several recent examples from the speaker's research team to show how XPS and TOF-SIMS can be used to shed some light on mechanisms of chemical and physical degradation, proposed and applied methods of stopping such degradation, and proposed and applied methods of repairing such degradation. The examples will come from a range of paintings and other art objects spanning from the Italian Renaissance to the post-Modern era.

11:00am **AS+MS-FrM-9 Surface Characterization of Acrylic Artists' Paints After Wet Cleaning with Water-in-Oil Microemulsions.**, ***Michael Clark***, *M Keefe,* The Dow Chemical Company; *T Learner,* The Getty Conservation Institute; *B Ormsby,* Tate, UK; *A Phenix,* The Getty Conservation Institute; *E Willneff,* University of Leeds, UK

This paper reports on developments from collaboration between The Dow Chemical Company, Tate and the Getty Conservation Institute to improve cleaning systems for unvarnished modern painted surfaces. Increased use of new artistic paints since the 1950s has created a need for new cleaning approaches as traditional wet and dry cleaning systems have been found to be unsuitable in many cases.

This body of research has focused on the development of improved wet cleaning systems for artists' acrylic emulsion paints. The present study describes novel microemulsion systems based on water and mineral spirits, each formulated with different anionic or non-ionic surfactants. For this application, water-in-oil microemulsions were designed to capture the positive aspects of water-based cleaning systems (good pick-up and dispersion of soils; control over the conductivity and pH) while limiting, to a degree, the risks associated with exposure to aqueous cleaners. These notable cleaning solutions have been found to be very effective at removing surface soiling on acrylic paintings and other water sensitive works of art. A range of spectroscopic techniques have been employed to characterize the paint surface for changes induced treatment with different cleaning solutions. TOF-SIMS and XPS results show that trace amounts of surfactant residues from cleaning formulations remain on paint surfaces in some cases. Amounts vary depending on the surfactant type, inherent surfactant solubility, in addition to the clearance steps undertaken.

11:20am **AS+MS-FrM-10 Surface and Depth Profiling of Soft Organic Thin Films. X-Ray Photoelectron Spectroscopy Study**, ***Tatyana Bendikov***, Weizmann Institute of Science, Israel; *S Hutton,* Kratos Analytical Ltd, United Kingdom of Great Britain and Northern Ireland; *R Balgley, G de Ruiter, M Lahav, M Van der Boom,* Weizmann Institute of Science, Israel

X-ray Photoelectron Spectroscopy (XPS) is uniquely suited for the direct characterization of nanomaterials and thin films in terms of layer thicknesses, elemental composition and, frequently, the depth-distribution profile of elements across the film. In general, XPS is limited to probe the top <15 nm of a sample, and for thicker structures a digging-like etching process is needed.

Recent advances in depth profiling of organic and biological materials are based on sputtering with large Argon ion clusters (Ar_n^+).[1] Unlike monoatomic ions (Ar^+), large cluster ions do not penetrate deeply into the material, therefore sputter material from the near-surface region only, leaving the subsurface layers undisturbed and undestroyed.

Here we present two examples of successful XPS depth profiling of composite metal-organic architectures self assembled on the pyridine terminated silicon/ ITO substrates. The samples consist of four main components: metal complexes ($[M(mbpy\text{-}py)_3][PF_6]_2$, M = Ru (**1**) or Os (**2**); $Pd(PhCN)_2Cl_2$ (**3**) and (1,4-bis[2-(4-pyridyl)ethenyl]benzene, **BPEB**, (**4**) spacer molecules.

The first system was prepared by sequential immersion of the substrate in solution **1** (alternating with solution **3**) (4 layers) followed by **2** (alternating with **3**) (4 layers). Each layer is ~ 6 nm thick, thus the consequent total thickness of the organic film reaches 40-50 nm.[2]

In the second example molecular assemblies consist of different layers of metal complexes **1** and **2**, separated by repetitive spacers **4** alternated with **3**. Total thickness of the analyzed **[Ru-BPEB$_{12}$-Os]** assembly is ~20 nm.[3]

1. P. J. Cumpson et. al., *Surf. Interface Anal.*, **2013**,45, 1859-1868.

2. G. de Ruiter et. al., *J. Am. Chem. Soc.*, **2013**, 135, 16533-16544.

3. R. Balgley et. al., *J. Am. Chem. Soc.*, **2016**,138, 16398-16406.

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