

# Monday Afternoon, October 22, 2018

## Applied Surface Science Division Room 204 - Session AS-MoA

### Multitechnique Applications-When More techniques are Better than One

Moderator: Karen Gaskell, University of Maryland, College Park

#### 1:20pm AS-MoA-1 Overcoming Obstacles in Surface and Interface Characterization of All Solid-State Lithium Battery Materials, *Natalie Seitzman*, Colorado School of Mines; *H Guthrey*, *D Sulas*, *S Johnston*, National Renewable Energy Laboratory; *J Nelson Weker*, SLAC National Accelerator Laboratory; *H Platt*, Solid Power, Inc.; *M Al-Jassim*, National Renewable Energy Laboratory; *S Pylypenko*, Colorado School of Mines

Novel battery technologies are a key route to sustainable energy, but new chemistries come with new failure mechanisms that present characterization challenges. The nature of many promising next-generation batteries makes them inherently difficult to study, and multiple techniques must be combined to capture the relevant phenomena. For all-solid-state lithium batteries, one challenge is the reactivity of the battery components restrict which types of techniques may be used. Additionally, although the interfaces are of great interest, processes that expose them for characterization have unknown, likely deleterious effects on their integrity. Therefore, in order to understand characterization of surfaces and interfaces in batteries, bulk characterization and in situ characterization at multiple scales is also needed.

The focus of this work is probing the morphological evolution, including dendrite formation, of the electrode-electrolyte interface between lithium metal and  $\beta$ -Li<sub>3</sub>PS<sub>4</sub> solid electrolyte. This is done through a combination of lock-in thermography, x-ray tomography, in situ scanning electron microscopy (SEM), and x-ray absorption near edge structure (XANES). We used thermography as a first step to identify trends in location of dendritic features, to guide techniques with smaller fields of view and greater resolution, such as SEM. X-ray tomography enables characterization of the interfaces without deconstructing the device or exposing the interfaces needed for surface characterization. Therefore, micro-tomography was performed both to study morphological changes and to check that results observed in other experiments with modified samples—such as nanotomography, which required a focused ion beam to cut and lift out micron-scale samples—are consistent with the behavior of unaltered materials. In situ SEM cycling experiments and windowless energy dispersive spectroscopy (EDS) provided morphological and chemical characterization of the changing surfaces and interfaces with high spatial resolution. Detailed chemical characterization of the bulk material was obtained with XANES at the sulfur and phosphorus K-edges. This work furthers the development of surface and interface characterization of battery materials and moves toward localized, nanoscale characterization.

#### 1:40pm AS-MoA-2 In-situ Complementary XPS and Raman Analysis of Technologically Important Materials, *Paul Mack*, Thermo Fisher Scientific, UK

In this work, X-ray Photoelectron Spectroscopy (XPS) and Raman spectroscopy have been used to analyse technologically relevant materials. An XPS spectrometer (Thermo Scientific Nexsa) was configured with a Raman spectrometer, enabling *in-situ* complementary analysis. XPS is a surface sensitive technique, with an information depth between 0-10nm. It is chemically selective, allowing the use to investigate different bonding states of the same element. Raman is a vibrational spectroscopy, which is more bulk sensitive (typically on the  $\mu$ m scale). It can also give some information about chemistry, but it also yields complementary structural or bonding information.

The battery-relevant material, lithium cobaltite (LiCoO<sub>2</sub>) was analysed in the Nexsa spectrometer. LiCoO<sub>2</sub> is used in the cathode of some lithium-ion batteries. During charge/discharge cycling the cathode may degrade, causing the creation of the mixed oxide, Co<sub>3</sub>O<sub>4</sub>. XPS and Raman data were acquired from two different points on a LiCoO<sub>2</sub> cathode. Differences in cobalt and lithium bonding states at the surfaces of the two different points were analysed with XPS, before and after argon ion cleaning. Complementary Raman analyses were performed at the same points in the same instrument. The Raman data allowed identification of the bulk material, together with an evaluation of cobalt oxide degradation products.

The second sample analysed in this work was a boron nitride film deposited onto a copper substrate. The goal of the deposition was to create an atomically thin hexagonal boron nitride structure (h-BN), analogous to

graphene. It was found that the deposition created an inhomogeneous distribution of boron nitride, which was optically invisible. XPS mapping and imaging (Thermo Scientific SnapMap) was used to locate the boron nitride on the copper substrate. The XPS image was used to define the analysis points for further XPS and Raman analysis. XPS allowed the chemical bonding states of the boron and nitrogen to be identified, together with an identification of contaminants on the surface. The structure of the boron nitride, such an sp<sup>2</sup> and sp<sup>3</sup> configurations, was evaluated with Raman spectroscopy.

#### 2:00pm AS-MoA-3 Integration of Laboratory Experiments. Spectroscopy, and Microscopy to Investigate the Reactivity of Metals in Mine Wastes, *José Cerrato*, University of New Mexico

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The reaction mechanisms affecting metal transport in mine waste sites was investigated by integrating laboratory experiments, microscopy, and spectroscopy. Metal release from these mine wastes could pose potential health risks for neighboring communities. Spectroscopy analyses on the first site located in Northeastern AZ (Navajo tribe) suggest that U-V phases are present in abandoned mine wastes; the dissolution of these U-V phases is relevant to U and V transport. Electron microprobe and electron microscopy analyses on the second site located in Laguna, NM (Pueblo tribe) suggest that U-Si and U-P phases on mine wastes from which could be a source for U in neighboring surface waters. The presence of U(VI) and U(IV) was detected with X-ray photoelectron spectroscopy (XPS) and X-ray absorption spectroscopy (XAS). The presence of coffinite encapsulated in particulate organic matter was identified in mine waste samples using X-ray diffraction (XRD) and transmission electron microscopy (TEM). Accumulation of U in roots of plants from these mine waste sites was also investigated.

#### 2:40pm AS-MoA-5 Degradation Methodology of Reinforced Concrete in South Asia analyzed using Surface Analysis and other Techniques, *Nirmalya Karar*, CSIR-National Physical Laboratory, India; *S Singh*, CSIR-CBRI Roorkee India, India

In the South Asian scenario, reinforced concrete was seen to degrade very fast. Reinforced concrete is also being extensively used in roads, bridges, tunnels and viaducts. So a detailed analysis was required to understand the reasons for the shortcomings. We have attempted to discuss contents for better standardization. Concrete is based on cement, steel, stone chips, sand and water to initiate the reaction process. Here, degradation is discussed keeping in mind every constituent materials' properties.

Cement is standardized by National Centre for Building Materials, Ballavgarh, Haryana through the BND program. Steel quality is standardized by Bureau of Indian Standards (BIS) and NML, through the BND program. Stone chips are not standardized for their chemical content as such stone based civil structures are historically quite stable in the Indian subcontinent.

Degraded concrete and rebars from areas of unusual degradation were collected and the rebars were analyzed across its cross-section using TOF-SIMS. It was seen that there were traces of halide and nitride ions in the periphery of the degraded steel rebars. It content were much less at the center of these degraded steel rebars. Such halide and nitride ions were also detected in soluble ground water residue in flake form in the same area. As ground water is used in most construction on sites, and as halide and nitride ions are known to act as wet chemical etchants of steel, it was concluded that ground water contributed to the steel rebar corrosion in concrete. It was speculated that the ground water slowly moved upwards by capillary action from the ground. But capillary action methodology was unknown.

An extensive analysis of the chemical content of sand used for civil construction was undertaken by analyzing the composition of representative sand samples used in civil construction using X-ray fluorescence (XRF) and powder x-ray diffraction (XRD). It was found that Indian sand always contains an appreciable amount of calcium carbonate. These calcium carbonate constituents of sand are easily soluble in the halides and nitrates of ground water. Thus capillaries can be slowly formed within the concrete after a few years which slowly increases with time and destroys the reinforced concrete. In contrast, sand samples in Europe and West Asia seem to be almost pure silica. So the effect of capillary action is also confirmed. Usage of potable water for civil construction along with sand free of calcium carbonate is a feasible solution.

Thus, based on our materials analysis, we have been able to evolve a methodology to substantially extend the life of reinforced concrete in South Asia.

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3:00pm AS-MoA-6 Surface Phase, Morphology, and Charge Distribution

**Transitions on Vacuum and Ambient Annealed Perovskites: A Case Study on SrTiO<sub>3</sub>(100), Omur Dagdeviren<sup>1</sup>, G Simon, K Zou, C Ahn, F Walker, E Altman, U Schwarz, Yale University**

The surface structures of SrTiO<sub>3</sub>(100) single crystals were examined as a function of annealing time and temperature in either oxygen atmosphere or ultrahigh vacuum (UHV) using noncontact atomic force microscopy (NC-AFM), Auger electron spectroscopy (AES), and low-energy electron diffraction (LEED) [1]. Samples were subsequently analyzed for the effect the modulation of their charge distribution had on their surface potential. It was found that the evolution of the SrTiO<sub>3</sub>surface roughness, stoichiometry, and reconstruction depends on the preparation scheme. LEED revealed phase transitions from a (1x1) termination to an intermediate c(4x2) reconstruction to ultimately a ( $\sqrt{13} \times \sqrt{13}$ )-R33.7° surface phase when the surface was annealed in an oxygen flux, while the reverse transition from ( $\sqrt{13} \times \sqrt{13}$ )-R33.7° to c(4x2) was observed when samples were annealed in UHV. When the surface reverted to c(4x2), AES data indicated decreases in both the surface Ti and O concentrations. These findings were corroborated by NC-AFM imaging, where initially TiO<sub>2</sub>-terminated crystals developed half-unit cell high steps following UHV annealing, which is typically attributed to a mix of SrO and TiOSrO and TiO<sub>2</sub>terminations. Surface roughness evolved nonmonotonically with UHV annealing temperature, which is explained by electrostatic modulations of the surface potential caused by increasing oxygen depletion. This was further corroborated by experiments in which the apparent roughness tracked in NC-AFM could be correlated with changes in the surface charge distribution that were controlled by applying a bias voltage to the sample. Based on these findings, it is suggested that careful selection of preparation procedures combined with application of an electric field may be used to tune the properties of thin films grown on perovskite substrates. application of an electric field may be used to tune the properties of thin films grown on perovskite substrates.

[1] O. E. Dagdeviren et al., Physical Review B **93**, 195303 (2016)

3:40pm AS-MoA-8 In-situ Characterisation of Graphene using combined XPS and Raman Spectroscopy: Removal of Polymer Residue by Ar Gas Cluster Ion Beams, Barry Brennan, National Physical Laboratory, UK; P Mack, Thermo Fisher Scientific, UK; A Centeno, A Zurutuza, Graphenea, Spain; A Pollard, National Physical Laboratory, UK

The transfer of chemical vapour deposition grown 2D materials to a relevant substrate material typically involves deposition of a thin polymer layer, usually PMMA, as a handle to transport the 2D material, which is then dissolved in solvent. Any polymer residue is then typically further reduced in a thermal annealing step, designed to break down the polymer chain and remove it from the surface. However, this is rarely fully effective, with trace PMMA residue usually detected. This can then affect the electrical and physical properties of the 2D layer, and prevent consistency in the final material. Recently, a number of mechanisms have been explored to further improve the quality of the transferred layer, from introducing further solvent and annealing steps, to the use of plasmas, and argon gas cluster ion beams (GCIB), to remove any remaining residue. In this study, we explore in detail the use of size selected argon GCIBs to clean polymer residue from a CVD-grown graphene surface. Due to the distribution of the charge applied to the cluster over the individual argon atoms, the energy per atom can be tuned to <0.5 eV/atom, significantly below the bond strength of the graphene, but sufficiently energetic to remove polymeric material.

In order to characterise this, a combination of techniques are needed to thoroughly confirm the removal of polymer material, as well as show there is no impact to the underlying graphene. Ideally these techniques would be in-situ and confocal in nature in order to prevent modifications to the sample surface after cleaning, as well as provide confidence in the measurements. To this end, in this study we used the Thermo Scientific Nexsa X-Ray Photoelectron Spectrometer (XPS) system which allowed us to carry out correlative XPS, REELS and Raman spectrometry in-situ from the same area of a graphene sample during GCIB cleaning. This meant we could examine changes in the chemical composition of the graphene surface as polymer material was removed, while monitoring changes in the Raman spectra to determine whether any defects were being generated in the graphene during the cleaning process. The changes in the sample were further probed using 3D time of flight secondary ion mass spectrometry (ToF-SIMS) imaging, to clearly show the removal of polymer materials during GCIB cleaning, while leaving the underlying graphene layer intact.

Through the combination of these measurements, we are able to determine that by keeping the energy per argon atom less than 1 eV, we can prevent the introduction of defects to the graphene layer, as well as significantly decrease the level of contamination present on the graphene surface.

4:00pm AS-MoA-9 Topography-corrected TOF-SIMS Chemical Imaging of Chip Interconnect Surfaces, Conor Thomas, B Singh, R Wang, IBM Systems Division

Next generation computing systems are driving increasingly complex packaging architectures and interconnection techniques to meet higher performance and bandwidth requirements at smaller feature sizes. First-level packaging techniques that incorporate controlled collapse chip connections (C4) in flip-chip applications have become critical to enable near-future microelectronics packaging. Conventional C4 technology uses solder bumps for off-chip interconnections after back end of line wafer fabrication. Solder-based flip-chip technology is currently the industry standard with a proven track record of performance, reliability, and ease of manufacturing at low-cost. However, increasing I/O requirements are pushing the limits of interconnection pitch scalability below 50μm, resulting in a higher spatial density of solder bumps and reduction in solder volume per bump.

The surface cleanliness of fine-pitch solder bumps before chip attachment plays an important role in the solder wetting and reliability of the chip-package interconnect structure. In both flip-chip mass reflow and thermo-compression bonding techniques, the solder bump surfaces go through several assembly steps before chip join and are exposed to potential sources of contamination. Unfortunately, the solder bump surfaces are challenging to study by traditional surface characterization techniques like x-ray photoelectron spectroscopy, Auger electron spectroscopy, and secondary ion mass spectrometry due to the relatively small size of the bumps, the mixed conducting and insulating environments of the sample, and the high curvature of the bumps, respectively. These challenges have only been exacerbated by the decreasing size of the bumps.

Here we describe a new approach to characterize modern solder bumps using a time-of-flight secondary ion mass spectrometer (TOF-SIMS) with an atomic force microscope (AFM) integrated in the same vacuum chamber. We can correlate high spatial resolution TOF-SIMS images with AFM topography images to generate topography-corrected chemical images. With this method we can chemically and spatially characterize the contaminants on solder bump surfaces. This method will be compared with results from Auger electron spectroscopy, our standard method of characterizing solder bump surfaces. We will discuss the important considerations for TOF-SIMS imaging of these highly curved surfaces and approaches to correlate images taken by TOF-SIMS and AFM.

4:20pm AS-MoA-10 Combining the Benefits of GCIB-ToF-SIMS, MALDI-FTICR-MS and LC-MS/MS for Location specific Lipid Identification in Planarian Flatworm Tissue Sections, Tina Angerer, University of Washington; D Velickovic, C Nicora, C Anderton, Pacific Northwest National Laboratory; D Graham, L Gamble, University of Washington

*Phagocata gracilis* are planarian, non-parasitic flatworms. Planarians are best known for their fascinating regenerative abilities, requiring a complex interplay of a wide range of molecules. The regeneration process and the molecules involved are still poorly understood. Most notably there is a lack of lipid and fatty acid data, a diverse group of molecules fulfilling numerous functions such as energy storage and cell signaling.

To gain a better understanding of the lipidomic landscape in planarians we analyzed positive and negative ions from longitudinal sections of *P. gracilis* with MALDI-FTICR-MS and ToF-SIMS along with homogenized whole worm extracts with LC-MS/MS.

Imaging MALDI-FTICR-MS (15T, Bruker Solarix) provides location specific (50 μm/pixel), ultra-high mass resolution (R=250,000 @m/z=400) and ultra-high accuracy (<1ppm) lipid data capable of distinguishing intact lipid species of similar exact mass and showing their distribution in the tissue. The drawbacks for this technique are that the spatial resolution is too low to clearly identify features within the worm and its low fragmentation rate. While beneficial for molecular peak intensities, the lack of fragments does not allow for specific lipid assignments with structural information (e.g. lipid headgroup and both fatty acid chains identified).

Imaging GCIB-ToF-SIMS (J105, Ionoptika) generates high mass accuracy (< 5ppm), cell/organ-specific data (3 μm/pixel) consisting of intact lipids, lipid fragments and fatty acids. The moderate mass resolution (R~10,000@m/z=700) is sufficient to resolve most lipid species. Mass peaks

<sup>1</sup> NSTD Student Award Finalist

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consisting of more than one species are indicated by broad and/or asymmetric peaks with poor mass accuracy. However co-localizing fragments can add confidence for the assignment of overlapping species, provide us with structural information and allow for unambiguous identification of resolved peaks.

LC-MS/MS (Thermo Velos Pro Orbitrap ) separates different lipid species prior to fragmentation so, in contrast to SIMS, the observed lipid fragments are guaranteed to stem from the analyzed species. The drawback with this technique is that it provides no location specific information. Similar to SIMS, lipids with similar mass are not separated leading to mixed fragments in the MS/MS data. Comparing LC-MS/MS to SIMS data shows that the same lipid fragment species are present in both spectra.

This work demonstrates that only by correlating all 3 techniques can we get highly accurate, high mass, high spatial resolution, structural and location specific lipid information. Together this data provides detailed information about all major structures and organs within planarians.

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