Chemical Analysis and Imaging at Interfaces
Room 205 ABCD W - Session CA-WeA

Advances in Experimental and Theoretical Insights Into Material Interfaces

Moderators: Jiyoung Son, Oak Ridge National Laboratory, **Samuel Tenney**, Brookhaven National Laboratory

2:15pm **CA-WeA-1 Optimizing in situ liquid ToF-SIMS using SALVI and IONTOF M5-NCS*, Jiyuong Son,*** *Anton Levlev, Jacob Shusterman, Xiao-Ying Yu,* Oak Ridge Natinal Laboratory

In situ time-of-flight secondary ion mass spectroscopy (ToF-SIMS) was enabled to study liquids using a vacuum compatible microfluidics device. This approach has brought a wider range of sample analysis capabilities in vacuum instrumentation, specifically applications in interfaces involving the condense liquid phase. The successful operation of in situ ToF-SIMS also has been presented previously using an IONTOF V instrument. We establish in situ liquid ToF-SIMS using the IONTOF MS-NCS instrument at the Oak Ridge National Laboratory (ORNL). Several parameters in the instrument setting (i.e., Primary beam current, voltage, pulse mode) were modified to optimize signal intensity and obtain more effective data collection in a wide mass range. A systematic study was performed including LMIG aperture, tip material of primary gun, primary beam current, voltage, and microfluidic device condition. If just following the procedure for the IONTOF V instrument, in situ liquid SIMS data suffered from low secondary ion intensity and only a narrow mass range was available for spectral and image collection. To acquire higher secondary ion counts, one procedure is not possible to “fit for all” for different ToF-SIMS instruments. In this work, we will present findings of in situ liquid ToF-SIMS optimization using the IONTOF M50NCS platform located in the center for nanophase materials science (CNMS) at ORNL. We demonstrated higher mass resolution in liquid SIMS spectral acquisition using the LIMG buncher voltage mode. Higher total secondary ion counts per sec (~40k ions / sec) with altering single pulse width of the LMIG primary beam was also achieved. The optimized in situ liquid SIMS procedure will be used to study complex interface chemistry in the future.

2:30pm **CA-WeA-2 First Principles-Based Defect Engineering to Enhance Layered Ni-rich Cathode Performance*, Sumaiyatul Ahsan,*** *Faisal M. Alamgir,* Georgia Institute of Technology, USA

We present a strategy to enhance the capacity retention of Ni-rich cathodes by modifying the electronic structure via an oxygen-vacant surface layer. Rather than addressing external factors that result in surface coatings for protection against electrolytic attack, we emphasize that intrinsic issues with electronic structure can also contribute to degradation, making materials more vulnerable in the first place. Our DFT calculations show that introducing oxygen vacancies (OV) in $LiNiO_2$ stabilizes reactive Ni^{2+} ions and reduces the overlap between O2p and Ni3d orbitals. To validate our predictions, we examined NMC811 ($LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$), known for its high initial capacity but tendency for capacity loss. An in-situ annealing XRD reveals the optimal temperature range for surface OV formation while retaining the layered bulk structure. Then, a one-step thermal treatment was employed to create a core-shell structure with 6.9% surface OV, resulting in a 9.4% improvement in capacity retention over 100 cycles at 1C compared to the unmodified sample. Scanning Transmission Electron Microscopy (STEM) visualized the vacancies and edge defects, and we implemented a quality control framework using XPS, tabletop XRD, and lab-scale h-XAS for efficient measurement of cation disorder, OV concentration, and bulk homogeneity. Our study on LNO and NMC811 demonstrates that employing OV to tune the electronic structure provides a universal solution for capacity fading in Ni-rich cathodes.

2:45pm **CA-WeA-3 Extending Ambient Pressure X-Ray Photoelectron Spectroscopy to Plasma Studies: A Custom-Built Plasma Source Apparatus*, Jun Cai,*** *Yang Gu,* Shanghaitech University, China*; Yong Han,* shanghaitech University, China*; Hui Zhang,* Shanghai Synchrotron Radiation Facility, China*; Zhi Liu,* Shanghaitech University, China

The characterization of the electronic structure and chemical states at heterogeneous interfaces (e.g., gas-solid or liquid-solid) can be effectively achieved using ambient pressure X-ray photoelectron spectroscopy (AP-XPS). However,acquiringthese properties under plasma conditions remains significant challenges. In this study, we introduce an AP-XPS system equipped with acustom-builtspatially confinedplasma source. This configuration confines the plasma to a controlled region, with the plasma intensity precisely regulated by adjusting either the working distance or the applied voltage. This system enables the direct detection of plasma electronsand real-time characterization of the surface states during plasma-surface interactions. To validate its efficacy and versatility, we conducted two proof-of-concept experiments: argon (Ar) plasma etching of graphene and oxygen plasma oxidation of platinum (Pt). The results demonstrate that Ar plasma effectively etches graphene, as evidenced by the distinct changes in the XPS spectra. Similarly, exposure of Pt surface to oxygen plasma induces pronounced surface oxidation. Thissystem significantly extends the operando capabilities of AP-XPS forin situ studies of plasma-enhanced reactions.Its application holds considerable promise for advancing fundamental and applied research in materials science and chemical engineering, particularly in the areas of surface modification and catalytic processes.

3:00pm **CA-WeA-4 Infrared Nanoscopy of Electron-Beam Modified Metal Organic Frameworks*, Samuel Tenney,*** Brookhaven National Laboratory*; Andrea Kraetz,* Johns Hopkins University*; Prerna Prerna, Ilja Siepmann,* University of Minnesota*; Michael Tsapatsis,* Johns Hopkins University

Metal organic frameworks (MOFs) are a class of porous materials that are promising for applications in many areas including gas separations and sorptions. Some MOFs, such as ZIF-L, can be chemically modified by exposure to an electron-beam to tailor their properties. This chemical modification by electron-beam exposure is known to modify their solubility among other properties. The modified MOFs have been characterized with nanoscale infrared techniques, namely photothermal infrared (PTIR) or AFM-IR and optical-photothermal infrared (O-PTIR), to understand the chemical changes that happen and the possible application of these materials towards gas separation. The results show a two-step process in the chemical modification of the MOFs with increasing electron-beam exposure.

3:15pm **CA-WeA-5 Probing the Electronic-Ionic-Mechanical Coupling at Solid-Electrolyte/Electrode Interfaces*, Yue Qi,*** Brown University **INVITED**

Electrochemical interfaces are critical components of energy conversion and storage devices. In solid-state batteries, the electrode/electrolyte interfaces must enable fast charge transfer reactions while maintaining physical contact throughout cycling. To probe the highly coupled electrochemical, mechanical, and physical responses and their evolution at these interfaces, multiscale modeling and multimodal characterization must work hand in hand.

At well-contacted interfaces, we draw an analogy to electron transport at metal/semiconductor interfaces and develop a density functional theory (DFT)-informed band-alignment model for intrinsic ionic resistance. This model incorporates DFT-computed electronic and point defect properties of the contacting phases to predict space-charge layer formation, potential drop, and electrostatic dipole at the electrode/solid-electrolyte interface. It is essential for interpreting *in operando* Kelvin probe force microscopy (KPFM) measurements of local potential profiles across interfaces of solid-state batteries—especially considering the dependence on lithium concentration and applied electric potential. To further probe band bending at buried interfaces, depth-resolved cathodoluminescence spectroscopy (DRCLS) is being developed to enable non-destructive characterizations.

Extrinsic interface resistance arises from changes in the contact area, which naturally decreases during Li stripping at Li/solid electrolyte interfaces. To capture the governing mechanisms across multiple length and time scales—including interface interactions, vacancy hopping, and plastic deformation, we integrated DFT simulations, kinetic Monte Carlo (KMC) methods, and continuum finite element modeling (FEM). By assuming the self-affine nature of multiscale contacts, we predicted the steady-state contact area as a function of stripping current density, interface wettability, and stack pressure. These predictions are supported by high-spatial-resolution operando scanning electron microscopy.

Together, these modeling advances are being integrated into a comprehensive framework to guide the design and development of next-generation all-solid-state batteries and electrochemical random-access memory (ECRAM) devices.

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