

## Chemical Analysis and Imaging of Interfaces Room 121 - Session CA-ThM

### In Situ and Operando Analysis of Energy and Environmental Interfaces I

**Moderators:** Sefik Suzer, Bilkent University, Turkey, Xiao-Ying Yu, Oak Ridge National Laboratory, USA

#### 8:00am CA-ThM-1 Rationally Engineering Interfaces to Improve Performances of Li Metal Batteries, *Bin Li*, Oak Ridge National Laboratory, USA

INVITED

Lithium (Li) metal batteries have attracted world-wide attention due to its low density (0.534 g/cm<sup>3</sup>), high theoretical capacity (3,860 mAh/g), and low electrochemical potential (-3.04 V vs. SHE), enabling their potential to double the cell-level energy of the state-of-the-art lithium-ion batteries. However, there are still key materials issues that inhibit lithium metal from being commercialized as an anode for rechargeable battery applications. The chemical and morphological (e.g., grain distribution, surface roughness, etc.) non-uniformity, coupled with the high reactivity of lithium drive heterogeneous solid-electrolyte interphase (SEI) formation, poor ionic flux distribution, active material consumption, and rapid dendrite growth. Currently, there are ex-situ and in-situ approaches to address the above issues. For example, one of approaches is to coat artificial SEI layers on Li metal anode surfaces. The component, distribution and structures of SEI layers should be designed and well controlled. The other approach is to exploit advanced electrolyte to in-situ form high-performance SEI layers. In this talk, we will present our recent work from the two aspects: a) novel closed-host bi-layer porous/dense artificial SEI layers were designed<sup>[1]</sup>; b) the microstructures of localized high-concentration electrolyte were deeply understood and thus new electrolytes with high-performance SEI layers being formed were discovered.<sup>[2]</sup>

References:

[1] Efav, Corey M., et al. "A closed-host bi-layer dense/porous solid electrolyte interphase for enhanced lithium-metal anode stability." *Materials Today* 49 (2021): 48-58.

[2] Efav, Corey M., et al. "Localized High-Concentration Electrolytes Get More Localized Through Micelle-Like Structures." *Nature Materials*, 2023.

#### 8:30am CA-ThM-3 Dynamic Molecular Investigation of the Solid-Electrolyte Interphase of an Anode-Free Lithium Metal Battery Using in situ Liquid SIMS and Cryo-TEM, *Zihua Zhu, Y. Xu, P. Gao, C. Wang*, Pacific Northwest National Laboratory

A fundamental factor that governs the performance of a lithium battery is the formation and stability of the solid-electrolyte interphase (SEI) layer on the anode surface. Despite a large body of literature documenting the structural and chemical nature of the SEI layer, essentially three levels of information regarding the SEI layer have never been fully understood: the formation dynamics, the molecular nature, and the spatial configuration. In this work, we use *in situ* liquid secondary ion mass spectroscopy, cryogenic transmission electron microscopy, and density functional theory calculation to delineate the molecular process in the formation of the SEI layer under the dynamic operating conditions. We discover that the onset potential for SEI layer formation and the thickness of the SEI show dependence on the solvation shell structure. On a Cu film anode, the SEI is noticed to start to form at around 2.0 V (nominal cell voltage) with a final thickness of about 40–50 nm in the 1.0 M LiPF<sub>6</sub>/EC-DMC electrolyte, while for the case of 1.0 M LiFSI/DME, the SEI starts to form at around 1.5 V with a final thickness of about 20 nm. Our observations clearly indicate the inner and outer SEI layer formation and dissipation upon charging and discharging, implying a continued evolution of electrolyte structure with extended cycling.

#### 8:45am CA-ThM-4 Understanding the Surface and Bulk Transitions of Functional Inorganic Materials for Energy Applications, *Ajay Karakoti*, Pacific Northwest National Laboratory; *K. Thangaraj*, Washington State University, US; *T. Bathena*, Oregon State University; *V. Shutthanandan*, Pacific Northwest National Laboratory; *S. Lee, K. Ramasamy, V. Murugesan*, Pacific Northwest National Lab

The research encompassing the discovery of novel materials has been the cornerstone for multiple major advancements in energy storage, utilization, and conversion. However, the design and selection of materials has become highly challenging owing to the complex requirements of energy applications that requires the desired properties of materials to be maintained under dynamic operational conditions. The independent

characterization and property measurement of such materials can shed light on the structure-property correlations of materials in static conditions however, in-situ and operando measurements allow the researchers to understand the evolution of materials properties during the application of external stimuli such as temperature, pressure, voltage, and environment.

This talk will focus on the characterization of materials used in energy storage and catalysis under different stimuli such as high temperature and gaseous environment using multi-modal analytical capabilities. Specifically, we will demonstrate the temperature dependent phase transition of lead dioxide, critical to its application as an active electrode material in lead-acid batteries, using in-situ X-ray photoelectron spectroscopy (XPS) combined with residual gas analysis. We will follow this with the demonstration of high temperature X-ray diffraction (XRD) measurements of copper hydroxy chloride (CHC) along with thermogravimetric analysis for understanding its potential as a material for thermochemical energy storage (TCES) applications. We will demonstrate that CHC could be used for TCES based on its hydration and dehydration characteristics however, the hydration-dehydration reversibility is limited by the decomposition of CHC at higher temperatures. We also show that the decomposition of CHC at higher temperatures proceeds with loss of chlorine accompanied by the formation of copper oxide and that its application as a TCES material hinge on preventing its decomposition reducing the chlorine loss. Finally, we will conclude by demonstrating the use of in-situ XPS for understanding the changes in the oxidation states of bismuth and molybdenum in bismuth molybdate catalyst during its redox cycling. We show that the bismuth molybdate catalyst undergo surface oxidation state and stoichiometry changes during initial 3-5 redox cycles, which are also reflected in the dynamic phase changes observed by the X-ray Diffraction, before stabilizing into a temperature dependent equilibrium composition.

#### 9:00am CA-ThM-5 In situ Imaging and Spectroscopy of Boehmite Particles in Liquid, *Xiao-Ying Yu*, Oak Ridge National Laboratory

This work presents in situ imaging of boehmite ( $\gamma$ -AlOOH) particles, suspended in liquid, in a vacuum compatible microfluidic sample holder using a suite of tools including scanning electron microscopy (SEM) and time-of-flight secondary ion mass spectrometry (ToF-SIMS), highlighting the advantage of multiscale analysis in material sciences. Boehmite particles are known to exist in high-level radioactive wastes at the Hanford site. These particles are difficult to dissolve and cause rheological problems for processing in the nuclear waste treatment plant. Therefore, it is important to understand how boehmite particles form aggregates in waste tanks. Of particular interest is the pH effect on the boehmite aggregation and morphological change simulating tank waste relevant conditions. Polydisperse boehmite particles under different pH conditions in deionized (DI) water were studied using in situ SEM and liquid SIMS imaging in high vacuum, enabled via a transferrable and vacuum compatible microfluidic interface, System for Analysis at the Liquid Vacuum Interface (SALVI) [1, 2]. In situ liquid SEM provides descriptions of particle size, shape, morphology enhanced with elemental mapping [3]. When comparing particle morphology and shape changes under different pH conditions, more aggregates are seen. In situ liquid SIMS is used to study particle molecular structure and composition. In situ SIMS provides detailed submicron molecular mapping of the particle and its surrounding water cluster environments as well as molecular identification of small molecules in liquid. These new results demonstrate advancements of in situ correlative imaging of liquid surfaces and solid-liquid interfaces using a universal microfluidic interface [4].

References:

[1] L Yang *et al.*, *J. Vac. Sci. Technol. A* **29** (2011), art. no., 061101. doi: 10.1116/1.3654147.

[2] L Yang *et al.*, *Lab Chip* **11** (2011), 2481-4. doi: 10.1039/c0lc00676a.

[3] X-Y Yu *et al.*, *Surface Interface Analysis A* **51**(13) (2019), 1325-1331. doi: 10.1002/sia.6700.

[4] X-Y Yu, *J. Vac. Sci. Technol. A* **38** (2020), art. no., 040804. doi: 10.1116/1.5144499.

# Thursday Morning, November 7, 2024

9:15am **CA-ThM-6 Square Wave Modulated Xps Enables Capturing Dynamics of Local-Electrical Potential Variations of Solid-Liquid Interfaces**, *E. Kutbay*, Bilkent University, Ankara, Turkey; *P. Aydogan-Gokturk*, Koc University, Istanbul, Turkey; *S. Ergoktas*, *C. Kocabas*, Manchester University, UK; *Sefik Suzer*, Bilkent University, Chemistry Department, 06800 Ankara, Turkey

X-Ray Photoelectron Spectroscopy (XPS) has been utilized to extract local electrical potential profiles by recording core level binding energy shifts upon application of a DC and/or AC [Square Wave (SQW)] bias with different frequencies. In this work, to carry out these measurements on a co-planar capacitor with a polyethylene membrane (PEM) coated with a 1:1 by volume mixture of Ionic Liquids (ILs) N,N-Diethyl-N-methyl-N-(2-methoxyethyl) ammonium bis(trifluoromethanesulfonyl)imide (DEME-TFSI) and N,N-Diethyl-2-methoxy-N-methylthamaminium tetrafluoroborate (DEME-BF<sub>4</sub>). Analyses were carried out in-operando; such that XPS measurements were carried out simultaneously with current measurements. ILs have complex charging/discharging processes and they induce formation of the Electrical Double Layer (EDL) at the interface of the electrode. Certain properties of this process can be extracted via AC modulation under appropriate time windows. Here, two frequencies, 10 kHz and 0.1 Hz, were selected to investigate the effects of the fast polarization and the slow migratory currents, respectively. Local electrical potential developments were extracted at different locations of the device, from the variations in binding energies before and after adding two equivalent resistors in series to the device. This simple modification of the circuit allows us to quantify the AC currents passing through the device as well as the system's resistance and capacitance under specific conditions. Moreover, we were able to detect differences in the time-behavior of the two anionic (BF<sub>4</sub><sup>-</sup> and TFSI<sup>-</sup>) moieties. With this relatively non-invasive methodology, XPS becomes a useful tool for extracting localized electrochemical information and may be of great importance in better understanding of energy harvesting and storage systems.

9:30am **CA-ThM-7 Infrared Spectro-Microscopy of Solid-Liquid Interfaces**, *Xiao Zhao*, *M. Salmeron*, Lawrence Berkeley National Laboratory

Nanoscale properties and dynamical processes at solid-liquid interface are critical for many natural phenomenon and industrial applications, including catalysis, energy storage and self-assembly. However, fundamental study of those processes is often challenged by radiation damage from electron or X-ray probe, which may drive the structure and chemical states of interface away from its original state. Besides, most imaging techniques offer morphological information at the interfaces, while the chemical and structural information is lacking. Herein we demonstrate a new non-destructive platform that enables nanoscale interfacial sensitive Infrared (IR) spectroscopy for solid-liquid interface by combining a graphene liquid cell and Fourier Transform Infrared Nanospectroscopy (nano-FTIR). With that we investigated the nanoscale dynamic structural evolution of protein assemblies to external environments as well as dynamic interaction between nanoparticles with electrolyte and ligand capping layer for CO<sub>2</sub> electroreduction. The protein substructure and ordering, specific adsorption configuration of ligand on nanoparticles and interfacial water structure are monitored by their characteristic IR vibrational bands at nanometer scale under realistic condition, which provides complimentary information to other operando imaging techniques. Our platform opens broad opportunities for *operando* chemical imaging of soft materials or nanostructures (membrane protein, virus and nanoparticle) in their realistic condition and under external stimuli.

9:45am **CA-ThM-8 Scanning Photoelectron Spectro-Microscopy – Opportunities and Possibilities of Operando Micro-Imaging and Chemical Analysis**, *Zygmunt Milosz*, *M. Amati*, *L. Gregoratti*, Elettra-Sincrotrone Trieste, Italy

Due to the short escape depth of electrons X-ray Photoelectron Spectroscopy (XPS) is the best surface sensitive analytical techniques for probing surface and interface chemical composition. The Scanning PhotoEmission Microscope (SPEM) uses a direct approach to add the spatial resolution and characterize materials at the submicron scale i.e. the x-ray photon beam is downsized to a submicron spot and the sample surface is mapped by scanning the sample with respect to the focused beam. With the SPEM hosted at the Escamicroscopy beamline (Elettra-Sincrotrone Trieste) the beam can be downsized, by using Zone Plates, to a diameter of up to 150 nm with overall energy resolution better than 200 meV [1].

Investigation of complex systems in electrochemistry and catalysis often requires Near Ambient Pressure (NAP) conditions. Due to samples

inhomogeneity in submicron scale conventional XPS systems did not allow to examine them in proper way. We present an alternative way for operando XPS measurements based on a special NAP cell [2] (SI fig. 1) with working pressure up to 2x10<sup>-1</sup> mbar and temperature range from room temperature (RT) up to 550°C. The NAP cell combined with focused synchrotron beam allows for continuous operando chemical characterization of the systems and imaging the surface within scanning areas of 450 μm<sup>2</sup> [1]. It opens new opportunities for operando measurements on the systems in micro- and nanometric scale.

Fuel cells are electrochemical devices providing efficient and environmentally-friendly production of electricity directly converting the electrons exchanged in a redox reaction (such as a combustion) into electric current. One of the still unresolved issues that impedes their widespread applications is related to the limited durability of crucial components and mass transport events that deteriorate the performance.

Recent achievements in the chemical and electronic characterization of fuel cell components will be presented providing an overview of the capabilities of The NAP cell technique. For example the in situ characterization of novel non-noble metal catalysts for the Oxygen Reduction Reaction (ORR) and the characterization of a Self-Driven Single Chamber SOFC in operando condition will be shown [3].

[1] <https://www.elettra.eu/elettra-beamlines/escamicroscopy.html>

[2] H. Sezen et al. *ChemCatChem*, Vol. 7 - 22, pp. 3665-3673 (2015)

[3] B. Bozzini et al. *Scientific Report* 3, 2848, 2013

11:00am **CA-ThM-13 The Dynamics of Encapsulated Clusters Under the Microscope**, *Barbara A.J. Lechner*, Technical University of Munich, Germany

**INVITED**

Catalysts on reducible oxide supports often change their activity significantly at elevated temperatures due to the strong metal-support interaction (SMSI), which induces the formation of an encapsulation layer around the noble metal particles. However, the impact of oxidizing and reducing treatments on this encapsulation layer remains controversial, partly due to the 'pressure gap' between surface science studies and applied catalysis.

In the present work, we employ near-ambient pressure scanning tunneling microscopy (NAP-STM) and X-ray photoelectron spectroscopy (NAP-XPS) to study the effect of reducing and oxidizing atmospheres on the SMSI-state of well-defined oxide-supported Pt catalysts at pressures from UHV up to 1 mbar. On a TiO<sub>2</sub>(110) support, different sintering and encapsulation dynamics are observed in O<sub>2</sub>, H<sub>2</sub> and CO<sub>2</sub> environments, respectively, and we show that the degree of support reduction plays an important role. We also compare the encapsulation of nanoparticles, which is well established, with that of small clusters, where no satisfying atomistic model exists to date. On Fe<sub>3</sub>O<sub>4</sub>(001), encapsulation stabilizes small Pt clusters against sintering [1]. Moreover, the cluster size and the cluster footprint on the support affect its diffusivity and can therefore be used to tune the sintering mechanism. Interestingly, small clusters of up to 10 atoms even still diffuse intact after encapsulation, and we can observe and track this diffusion in real time using our FastSTM [2].

[1] S. Kaiser et al., *ACS Catalysis* 13, 6203-6213 (2023).

[2] C. Dri et al., *Ultramicroscopy* 205, 49-56 (2019).

11:30am **CA-ThM-15 Scanning Tunneling Microscopy for High Entropy Materials**, *TeYu Chien*, University of Wyoming

High entropy materials, including high entropy alloys (HEAs), high entropy Van der Waals materials, and high entropy oxides, have drawn the attention of scientists and engineers for their various functionalities and properties. While a wide variety of properties are being studied in these materials, microscopic understanding is still challenging. In this talk, I will talk about our recent efforts in using scanning tunneling microscopy (STM) based techniques to study this intriguing material system. Including synchrotron X-ray STM (SX-STM) in which combining the atomic scale spatially resolving STM with the elemental resolving X-ray absorption spectroscopy (XAS) to achieve distinguishing elements at sub-nm scale on the surface of HEA; revealing short-range order and local lattice distortion; and revealing gap features in high entropy alloys and compounds, which might originate from strong correlation physics in the high entropy materials.

11:45am **CA-ThM-16 in-Situ Observation of Chemical and Morphological Transformations by Multi-Modal X-Ray Characterization**, *Slavomir Nemsak*, Lawrence Berkeley National Laboratory

In the last two decades, Ambient Pressure X-ray Photoelectron Spectroscopy (APXPS) in both soft and tender/hard X-ray regime has

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established itself as a go-to technique to study heterogeneous and complex materials under reaction environments. Multimodal approaches, which correlate information from two or more complementary techniques, are currently one of the forefronts of the APXPS development [1]. In the past three years, the ALS contributed one such setup: a combined Ambient Pressure PhotoEmission and X-ray Scattering (APPEXS) instrument commissioned and operated at beamline 11.0.2 of the Advanced Light Source [2]. The combination of the two in-situ techniques allows correlating structural and chemical information. By using APPEXS, we observed dynamics of the exsolution process of catalyst metallic nanoparticles [3]. To expand the capabilities of APPEXS further, we introduced a new platform using arrays of patterned nanoparticles to study the evolution of catalytic systems under reaction conditions [4]. Future developments of the technique(s) and the beamline will be also discussed.

## References

[1] H. Kersell, L. Falling, A. Shavorskiy, S. Nemsak, *Ambient Pressure Spectroscopy in Complex Chemical Environments*, 333-358 (2021).

[2] H. Kersell, P. Chen, H. Martins, Q. Lu, F. Brausse, B.-H. Liu, M. Blum, S. Roy, B. Rude, A. Kilcoyne, H. Bluhm, S. Nemšák, *Rev. Sci. Instr.* **92**, 044102 (2021).

[3] H. Kersell, M.L. Weber, L. Falling, Q. Lu, C. Baeumer, N. Shirato, V. Rose, C. Lenser, F. Gunkel, S. Nemšák, *Faraday Discussions* **236**, 141-156 (2022).

[4] H. Kersell, S. Dhuey, D. Kumar, S. Nemsak, *Synchr. Rad. News* **35**, 61-66(2022).

12:00pm **CA-ThM-17 NO Adsorption on Pd(111): A Relationship between Coverage and Spectral Shift**, *Sayantani Sikder*, Stony Brook University; *E. Fornero*, Universidad Nacional del Litoral (UNL), Argentina; *A. Boscoboinik*, Center for Functional Nanomaterials, BNL

Understanding the adsorption of nitric oxide (NO) on catalytic surfaces like Pd (111) is crucial for environmental and health reasons. Despite previous research, there is a gap in understanding spectral changes across different coverage ranges. Addressing this, we investigate the relationship between spectral shifts, integrated intensity, and coverage of NO on Pd (111) in IRRAS (Infra-red reflection Adsorption Spectroscopy). We conducted experiments at 200 K under ultra-high vacuum conditions to high doses of NO  $\sim$  5L, to ensure precise control over NO exposure and adsorption. A mathematical expression was developed for the relationship of coverage & dose. We observed that as we approach the saturation coverage, the coverage/dose correlation changes from linear (0.3 to 0.6 ML), when NO adsorbs in three-fold and bridge sites, to a more complex correlation above 0.6 ML, when the adsorption is a combination of atop and bridge sites. The IRRAS peak positions are useful in providing insights toward this conclusion. In short, our research provides valuable insights into NO adsorption dynamics on Pd (111), advancing our comprehension of surface adsorption phenomena with implications for catalytic converter design and environmental mitigation strategies.

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