

## Chemical Analysis and Imaging at Interfaces Focus Topic Room On Demand - Session CA-Invited On Demand

### Chemical Analysis and Imaging at Interfaces Invited On Demand Session

**CA-Invited On Demand-7 Measuring the Depth Profiles of Surfactants, Ions, and Solvent at the Angstrom Scale**, *X. Zhao*, University of Wisconsin - Madison; *G. Andersson*, Flinders University, Australia; **Gilbert Nathanson**, University of Wisconsin - Madison

INVITED

We use neutral impact ion scattering spectroscopy (NICISS) to measure the depth profiles of ionic surfactants, their counterions and co-ions, and solvent molecules in liquid glycerol. The experiments yield an Angstrom-scale picture of how these species populate the interfacial region. The chosen surfactants are tetrahexylammonium bromide and sodium dodecyl sulfate in the absence and presence of additional sodium bromide. NICISS determines the depth profiles of the elements C, O, Na, S, and Br through the loss in energy of He<sup>+</sup> ions that travel into and out of the liquid, which is then converted into depth. In the absence of NaBr, we find that THA<sup>+</sup> and its Br<sup>-</sup> counterion segregate together because of charge attraction, forming a narrow double layer that is 10 Å wide and 150 times more concentrated than in the bulk. With the addition of NaBr, THA<sup>+</sup> is "salted out" to the surface, increasing the interfacial THA<sup>+</sup> and Br<sup>-</sup> concentration and spreading the ions over a ~30 Å depth. Added NaBr similarly increases the interfacial concentration of DS<sup>-</sup> ions and broadens their positions. However, the dissolved Br<sup>-</sup> ions are strongly repelled from surface DS<sup>-</sup> because of charge repulsion. These different interfacial Br<sup>-</sup> propensities correlate with previously measured gas-liquid reactivities: gaseous Cl<sub>2</sub> readily reacts with Br<sup>-</sup> ions in the presence of THA<sup>+</sup> but drops 70-fold in the presence of DS<sup>-</sup>, demonstrating that surfactant headgroup charge controls the reactivity of Br<sup>-</sup> ions through changes in its depth profile.

**CA-Invited On Demand-13 In-Situ/Operando Soft X-Ray Spectroscopy Characterization of Chemical Interfaces**, *Y. Liu, X. Feng*, Lawrence Berkeley National Laboratory (LBNL); **Jinghua Guo**, Lawrence Berkeley National Laboratory

INVITED

The energy materials and devices have been largely limited in a framework of thermodynamic and kinetic concepts or atomic and nanoscale. Soft x-ray spectroscopy characterization offers unique characterization in many important energy materials of energy conversion, energy storage and catalysis in regards to the functionality, complexity of material architecture, chemistry and interactions among constituents within.

It has been found that the microstructure and composition of materials as well as the microstructure have a great influence on performances of energy conversion and energy storage materials, chemical and catalytic processes. However, it is challenging to reveal the real mechanism of the chemical processes. In-situ/operando x-ray spectra characterization technique offers an opportunity to uncover the phase conversion, chemical speciation at the solid/gas and solid/liquid interfaces in real time.

I will give some basics on in situ/operando soft x-ray spectroscopy characterization of interfacial phenomena in energy materials and devices, and how to use the powerful in-situ/operando characterization techniques, e.g. soft x-ray absorption spectroscopy (XAS) and resonant inelastic soft x-ray scattering (RIXS) to investigate the real electrochemical mechanism during the operation. A number of electrochemical liquid cells will be presented with success in revealing the catalytic and electrochemical reaction at real time.

**CA-Invited On Demand-19 Direct-Write Electron Beam Processing of Topologically Complex Functional Nanomaterials using Thermo-Electrically Energized Multiphase Precursor Jets**, **Andrei Fedorov**, Georgia Institute of Technology

INVITED

Focused Electron Beam Induced Processing (FEBIP) is a powerful method for atom-by-atom fabrication of topologically complex nanostructures from a variety of materials. It provides a complete processing environment for emerging electronic and quantum devices based on 2D materials.[1] Energized micro/nano-jets of thermally or electro-kinetically energized precursors in both gas [2-4] and liquid [5] phase provide unique capabilities for localized delivery of precursor molecules to the substrate, thus establishing locally controlled deposition/etching site for FEBIP. This enhances the growth rate and purity by selectively tuning of precursor and contaminant sticking and surface diffusion coefficients as well as adsorption/desorption activation energies.[6] Expanding on gas-phase jet

delivery of precursors, we recently demonstrated a new approach to FEBIP using liquid phase precursors delivered via a nanoelectrospray jetting process into a vacuum environment.[5] This enabled (1) dramatically increasing the growth rate of deposition/etching, (2) enabling deposition of composite materials and alloys with tailored electromechanical properties, and (3) fabrication of new, truly 3D topologies of nanostructures that are fundamentally out of reach of current gas-phase FEBID techniques. These unique new capabilities of NESA-FEBIP are matched by the complexity of the underlying physics and chemistry of ion transport and electrochemical reaction interactions, which need to be understood on the most fundamental level in order to take full advantage of and further develop new FEBIP modes and applications to emerging electronic and quantum devices based on 2D materials. I will highlight development and demonstration of a complete set of processing capabilities using FEBIP to fabricate devices from monolayer graphene, including high resolution, high speed etching [4], dynamic patterning and n-p-n junction formation [7,8], low resistance, Ohmic contact at the metal-graphene junctions [9], and "direct-write" reduction of graphene oxide, forming high electronic mobility conductive line patterns on the substrate. [10]

DOE BES Grant Support (DE-SC0010729) is acknowledged.

[1] Fedorov et al, Appl. Phys. A – Mat. Sci. & Proc., 117 (2014), 1659; [2] Henry et al, Phys. Chem. Chem. Phys., 21, 10449 - 10456 (2019); [3] Henry et al, Appl. Phys. Lett., 98 (2011), 263109; [4] Kim et al, Appl. Phys. Lett., 107, (2015), 233102; [5] Fisher et al, Nano Lett., 15 (2015), 8385; [6] Henry et al, J. Phys. Chem. C (2016), 120 (19), 10584-10590 (2016); [7] Kim et al, ACS Nano 8 (7), (2014) 6805; [8] Kim et al, Nanoscale 7 (2015), 14946; [9] Kim et al, ACS Nano 10 (2016), 1042; [10] Kim et al, Appl. Phys. Lett. 106 (2015), 133109.

**CA-Invited On Demand-25 From Bulk to Constriction: Scaling Analysis of Ionic Transport Through Nanopores and Channels**, **Michael Zwolak**, NIST; **S. Sahu**, University of Colorado at Boulder

INVITED

Single pores through 2D materials, such as graphene and MoS<sub>2</sub>, provide new opportunities for biochemical analysis and probing fundamental transport mechanisms of ions and molecules through confined environments [1]. For these "atomically thin" membranes, ion transport depends on dynamics both inside and outside the geometric volume of the pore due to several commensurate length scales, such as the effective membrane thickness, radii of the first and the second hydration layers, pore radius, and Debye length. We will demonstrate that a novel scaling analysis [2] and associated golden aspect ratio [3] enable all-atom molecular dynamics and other simulations to capture the transition between pore- and access-dominated ionic conductance as the pore radius increases beyond the effective membrane thickness (around 1 nm). In the pore-dominated regime, the physics of ion transport subdivides into mechanisms controlled by the free-energy landscape and diffusion. The latter again depends strongly on the flow of ions from bulk to the pore, just as in the access-dominated regime but now due to diffusive limitations and giving rise to sub-ohmic transport. A small strain applied to the 2D membrane can tune transport between these two mechanisms by modulating the balance of dehydration and electrostatic interactions via picometer changes in atomic positions and giving rise to optimal transport (and selectivity) regimes [4]. Overall, these concepts tie transport in nanoscale synthetic pores to transport in biological ion channels, as well as provide several tools for the rigorous simulation and modeling of biological and synthetic pores alike.

[1] *Colloquium: Ionic phenomena in nanoscale pores through 2D materials*, S. Sahu and M. Zwolak, *Reviews of Modern Physics* 91, 021004 (2019).

[2] Maxwell-Hall access resistance in graphene nanopores, S. Sahu and M. Zwolak, *Physical Chemistry Chemical Physics* 20, 4646 (2018).

[3] Golden aspect ratio for ion transport simulation in nanopores, S. Sahu and M. Zwolak, *Physical Review E* 98, 012404 (2018).

[4] Optimal transport and colossal ionic mechano-conductance in graphene crown ethers, S. Sahu, J. Elenewski, C. Rohmann, and M. Zwolak, *Science Advances* 5, eaaw5478 (2019).

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