

Processing and Characterization of Air-Liquid, Solid-Liquid and Air-Solid Interfaces Focus Topic

Room 202A - Session PC+AS+BI+NS+PB+SS-TuM

Solid-Liquid and Gas-Liquid Interfacial Processes and Characterization

Moderators: Stephen Nonnenmann, University of Massachusetts - Amherst, Juan Yao, Pacific Northwest National Laboratory

8:00am **PC+AS+BI+NS+PB+SS-TuM-1 Liquefied Gas Electrolytes for Electrochemical Energy Storage Devices, Y. Shirley Meng**, University of California San Diego; **Y Yang**, University of California at San Diego **INVITED** Electrochemical energy storage devices, such as Li-ion batteries and electrochemical capacitors, have seen little change in their electrolyte chemistry since their commercialization. These liquid electrolytes often limit the energy density and low-temperature operation of these devices, which hinder many potential applications. Our work uses electrolytes based on solvent systems which are typically gaseous under standard conditions and show excellent performance in electrochemical energy storage devices. It has demonstrated that these novel solvents have superior physical and chemical properties which are attributed to excellent performance over an extended temperature range and a wide potential window of stability with unique safety features. The use of fluoromethane as solvent for lithium batteries shows excellent low-temperature operation down to -60 °C with high capacity retention. The liquefied gas electrolytes also show a high coulombic efficiency for cycling dendrite-free lithium metal anodes.

8:40am **PC+AS+BI+NS+PB+SS-TuM-3 An In situ Molecular-scale View of Nucleation and Self-assembly at Solid-liquid Interfaces, James De Yoreo**, Pacific Northwest National Laboratory **INVITED**

Nucleation and self-assembly from solutions are seminal processes in the formation of ordered structures ranging from simple inorganic crystals to macromolecular matrices. Observations over the past fifteen years have revealed a rich set of hierarchical nucleation pathways involving higher-order species ranging from multi-ion clusters to dense liquid droplets, as well as transient crystalline or amorphous phases. Despite their complexity, a holistic framework for understanding particle-based pathways to crystallization that extends classical concepts emerges when the coupled effects of complexity of free energy landscapes and the impact of dynamical factors that govern particle formation and interaction are considered. Here I use a series of in situ TEM and AFM studies on inorganic, organic, and macromolecular systems to illustrate that framework via the evolution in nucleation and growth processes as these complexities and dynamical factors come into play. The results show that the introduction of either size-dependent phase stability associated with the high surface-to-volume ratios of nanoparticles, or high driving force coupled with the existence of metastable polymorphs leads to two-step pathways characterized by the initial appearance of a bulk precursor phase. The creation of micro-states, which represent local minima in free energy stabilized by configurational factors associated with structural elements of molecules, can also lead to hierarchical pathways, but the intermediates are microscopic transient states that do not appear on a bulk phase diagram. However, small changes in molecular structure can eliminate these transient states, leading to a direct pathway of nucleation. Limitations on molecular mobility, either through large barriers to changes in coordination or conformation, reduced temperature, or introduction of ion-binding polymers, can freeze non-equilibrium states into place for dynamical reasons. Analysis of sub-critical cluster evolution and subsequent nucleation shows that these dynamical constraints can lead to density fluctuations in accordance with classical descriptions even when non-classical pathways dominate. The findings from these in situ studies provide a common basis for understanding the development of order in systems as diverse as simple salt crystals, branched semiconductor nanowires, and microbial membranes.

9:20am **PC+AS+BI+NS+PB+SS-TuM-5 Non-linear Surface Spectroscopy at the Aerosol Particle/Gas Interface, F Geiger, Ariana Gray Be**, Northwestern University **INVITED**

While the interface of the aerosol gas and particle phase is the first entity encountered by incoming gas phase species, accessing it with bond-specific methods has been hindered due to a lack of tools that can operate under ambient pressure and temperature conditions. Here, we overcome this

hurdle by using nonlinear optics and demonstrate the utility of vibrational sum frequency and second harmonic generation for probing the surfaces of sea spray aerosol, secondary organic aerosol, and anthropogenic influence on them. By following the heterogeneous physical and chemical processes that drive gas-to-particle conversion, aerosol formation, their transformations and phase transitions, and reactivity, we provide the molecular origin for cloud activation.

11:00am **PC+AS+BI+NS+PB+SS-TuM-10 The Influence of Electrochemical Potential and Water Vapor on Ionic Liquid Binding Energy Shifts Examined by AP-XPS, Meng Jia**, University of Delaware; **A Broderick, J Newberg**, University of Delaware

Ionic liquids (ILs) have relatively high electrochemical and thermal stability, good conductivity and low volatility, making them inherently “greener and safer” compared to the conventional electrolytes. The application of ILs in the field of electrochemistry has identified many opportunities for their use as electrolytes in electrochemical devices. Due to the ubiquity of water and the hydrophilic nature of ILs, water can either be unintentionally present or often intentionally added to alter IL properties including density, viscosity, friction, and electrochemical window. Ambient pressure X-ray photoelectron spectroscopy (AP-XPS) is sensitive to both the chemical and electrical states of materials, which makes it an ideal method for studying surface potentials in electrochemical devices. In this work we examine the IL-gas interface of 1-butyl-3-methylimidazolium acetate, [BMIM][OAc], deposited on an Au foil via AP-XPS as function of electrochemical potential and surrounding water vapor pressure. The electrochemically induced binding energy shifts ($\Delta BE/\Delta E$) of carbon, nitrogen, and oxygen species of the IL were analyzed. Results reveal that in the absence of water vapor there is an ohmic drop between the electrode-IL interface and the IL-vacuum interface, giving rise to a $\Delta BE/\Delta E$ value of less than one. Upon introducing water vapor, forming an IL/water mixture, the $\Delta BE/\Delta E$ approaches a value of one as a function of increasing pressure. We attribute this behavior to a decrease in the ohmic drop as the IL/water mixture becomes more conductive. These results suggest that the electrochemical potential of the IL-gas interface is influenced by both an external bias and by varying the surrounding relative humidity. The same is likely true for the IL-electrode interface where water is known to be present.

11:20am **PC+AS+BI+NS+PB+SS-TuM-11 Role of Air Gas at the Interface between Water and Graphite Surfaces, Ing-Shouh Hwang**, Institute of Physics, Academia Sinica, Taiwan, Republic of China; **C Yang, C Fang**, Institute of Physics, Academia Sinica, Taiwan, Republic of China, Taiwan, Republic of China; **Y Lu**, Institute of Physics, Academia Sinica, Taiwan, Republic of China; **H Ko**, Institute of Physics, Academia Sinica, Taiwan, Republic of China, Taiwan, Republic of China

The saturation concentrations of nitrogen and oxygen in water under ambient conditions are very small (~ 10 ppm), thus their roles have been largely ignored. Using advanced atomic force microscopy, we study the evolution of gas-containing structures at graphite/water interfaces at room temperature. Our study indicates that gas (mainly nitrogen and oxygen) molecules dissolved in water tend to adsorb onto hydrophobic/water interfaces [1]. In gas-undersaturated water, we observe gradual nucleation and growth of small two-dimensional (2D) ordered domains over time on graphite surfaces [2]. The ordered structures may eventually cover the entire interface. When water is gas-supersaturated or when fresh DI water is briefly heated, we observe cap-shaped fluid nanostructures in addition to the ordered domains [3]. The cap-shaped nanostructures are the so-called interfacial nanobubbles (INBs) or surface nanobubbles, whose nature, stability, and formation remain controversial. When water is slightly gas-supersaturated, we see evolution of the fluid-like structures. The fluid phase first appears as a circular wetting layer ~ 0.3 nm in thickness and is later transformed into a cap-shaped INB [4]. 2D ordered domains are nucleated and grow over time outside or at the perimeter of the fluid regions, eventually confining growth of the fluid regions to the vertical direction. We determined that INBs and the fluid layers have very similar mechanical properties, suggesting low interfacial tension with water and a liquid-like nature.

Our study suggests that, in gas-undersaturated water, dissolved gas molecules may mainly be in the dispersed monomer form. Their rearrangement with water molecules at hydrophobic/water interface may lead to gradual nucleation and growth of the ordered domains. In gas-supersaturated water, some dissolved gas molecules are well dispersed in water, but others may aggregate into clusters. Adsorption of gas clusters leads to the formation of circular fluid layers at the graphite/water

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interface. The work clearly shows the crucial role of gas molecules at hydrophobic/water interfaces and has broad implications in diverse research fields.

[1] H.-C. Ko, W.-H. Hsu, C.-W. Yang, C.-K. Fang, Y.-H. Lu, I.-S. Hwang, *Langmuir***32**, 11164 (2016)

[2] Y.-H. Lu, C.-W. Yang, and I.-S. Hwang, *Langmuir***28**, 12691 (2012).

[3] Y.-H. Lu, C.-W. Yang, C.-K. Fang, H.-C. Ko, I.-S. Hwang, *Sci. Rep.***4**, 7189 (2014).

[4] C.-K. Fang, H.-C. Ko, C.-W. Yang, Y.-H. Lu, I.-S. Hwang, *Sci. Rep.* **6**, 24651 (2016).

11:40am **PC+AS+BI+NS+PB+SS-TuM-12 Probing Cluster and Nanoparticle Growth Processes with X-Ray Spectroscopy and Mass Spectrometry**, *Musahid Ahmed*, *O Kostko*, Lawrence Berkeley National Laboratory
INVITED

Tunable synchrotron radiation (VUV and X-rays) provides a universal, yet selective scalpel to decipher molecular information in complex chemical systems when coupled to mass spectrometry and X-Ray spectroscopy. This provides profound insight into molecular growth mechanisms, solvation and electronic structure in clusters, complexes and nanoparticles. In the first part, I will describe how single photon ionization mass spectrometry may be applied to molecular beams to probe molecular growth that is mediated either by ion or neutral pathways. The association and dissociation pathways in acetylene clusters where bonding can change from van der Waals to covalent upon ionization leading to the formation of benzene will be described.¹ I will follow up with very recent results on association of water with “hydrophobic” naphthalene & “hydrophilic” glycerol where subtle non covalent interactions can lead to surprising results in electronic structure and its effect on the hydrogen bonding network of water.

X-ray spectroscopy provides a local probe of a sample’s electronic structure with elemental and site-specificity and is thus ideally suited for probing solvation. Since X-rays can probe surfaces, interfaces and bulk, and more important penetrate matter, it provides for interrogation of buried and confined spaces. Here I will describe a new approach, Velocity Map Imaging X-Ray Photoelectron Spectroscopy coupled to nanoparticle beams² that allows for the visualization of dynamic processes in solvation and molecular growth processes. I will describe its’ implementation on aqueous arginine aerosols, where by varying the pH of the constituent solution, evidence is provided that the guanidinium groups are protonated even in a very basic solution (pH 13).³ A molecular level picture of how charge and proton transport in aqueous solutions of arginine occur emerges by analyzing the energy shifts on the C and N X-ray photoelectron spectra. I will conclude by suggesting new approaches to probe gas liquid interactions and chemistry with X-Ray spectroscopy and microfluidic devices allowing access to liquids in vacuum.⁴

[1] T. Stein, B. Bandyopadhyay, T.P. Troy, Y. Fang, O. Kostko, M. Ahmed, M. Head-Gordon, *PNAS* (2017), DOI 10.1073/pnas.1616464114

[2] O. Kostko, B. Xu, M.I. Jacobs, M. Ahmed, *J. Chem. Phys.* DOI: 10.1063/1.4982822

[3] B. Xu, M.I. Jacobs, O. Kostko, M. Ahmed, *Chem. Phys. Chem.* DOI 10.1002/cphc.201700197

[4] J. Yao, D. Lao, X. Sui, Y. Zhou, S. K. Nune, X. Ma, T. P. Troy, M. Ahmed, Z. Zhu, D. J. Heldebrant, X.-Y. Yu, *Phys. Chem. Chem. Phys.* DOI: 10.1039/C7CP03754F

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