

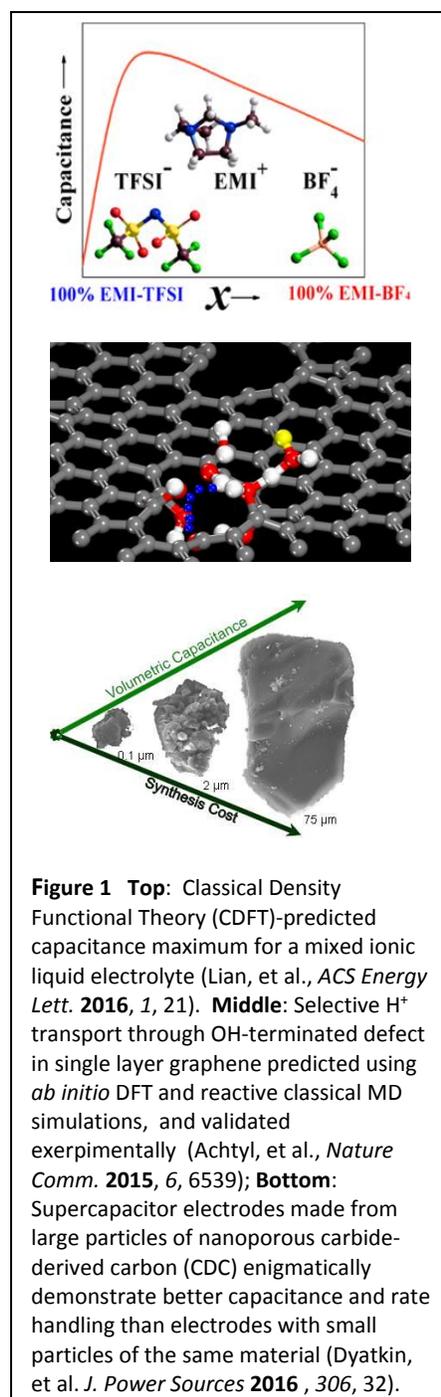
**Fluid Interface Reactions, Structures and Transport (FIRST)**  
**EFRC Director: David J. Wesolowski**  
**Lead Institution: Oak Ridge National Laboratory**  
**Start Date: August 2009**

**Mission Statement:** *To develop fundamental understanding and validated, predictive models of the unique nanoscale environment at fluid-solid interfaces that will enable transformative advances in electrical energy storage and electrocatalysis.*

Fluid-Solid Interfaces (FSIs) share a common characteristic – the juxtaposition of dense fluids (e.g. aqueous, polar organic, ionic liquid), with charged and reactive surfaces (e.g. electrodes, catalyst substrates). Transport of ions and molecular reactants through the fluid (typically nanoconfined) to the surface (typically nanotextured) results in charge storage in the so-called electrical double layer (EDL) and/or surface reactions that result in pseudocapacitance or electrocatalytic conversions. The unique structural and dynamic properties of the FSI emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes and substrates. The finite size, shape, directional bonding, charge distribution and polarizability of solvents and solutes are convoluted with their ability to reorient, ‘un-mix’, and react with one another and the substrate. The truncated surface exposes under-coordinated atoms, defects, dopants and active sites that drive interactions with the fluid by bond relaxation, charge redistribution, sorption and intercalation. The FIRST Center addresses fundamental gaps in our current understanding of FSIs to answer these questions of high importance to future energy technologies:

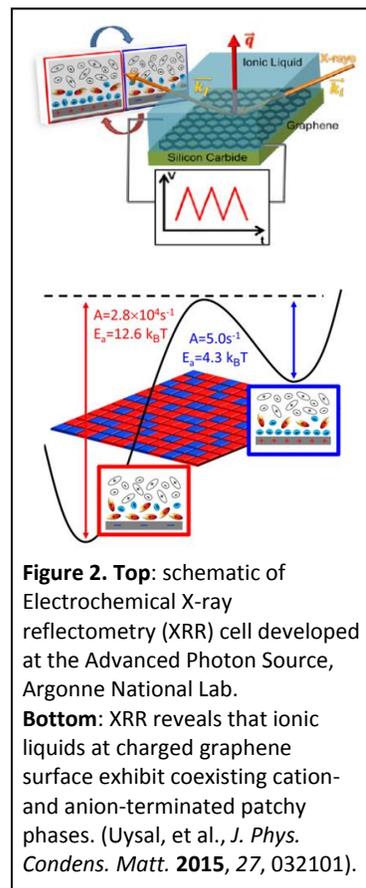
- *How does the interfacial region differ in structure, dynamics and reactivity from the bulk properties of the juxtaposed fluid and solid phases?*
- *How do altered interfacial fluid properties couple with complex substrate nanogeometries and functionalities to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?*
- *Can we achieve a quantitative, atomic-nanoscale understanding of FSI phenomena that will enable informed selection and design of fluid and solid components, chemistries and interfacial geometries to attain desired FSI functionality?*

Our goal is to unleash the ever-increasing power of computer simulations to illuminate the atomistic origins of FSI phenomena and guide the creation of new systems for energy storage and chemical conversion. However, because of current limitations in computational approaches, modeling efforts must be integrated



with atomic/nanoscale and macroscopic experimental studies of real FSIs. We synthesize and probe very simple interfaces, such as single graphene sheets, atomically-flat single crystal surfaces, etc., in contact with simple electrolyte solutions, to validate computational models of such interfaces, and in turn to use these models to better interpret the experimental results. We then use insights and inferences from these models, applied to more complex interfaces such as slit pores, nanoscale surface curvature, multimodal porosity distributions, surface defects and functional groups, etc. to predict their interfacial structures and transport properties, which can then be tested in real functional interfaces such as supercapacitor electrodes and catalytic substrates.

A range of multiscale models will be needed in order to fully understand and predict the properties of complex interfaces. A FIRST goal is to determine how simple our interfacial models can be, and still capture the essential behavior of the interfaces of interest, such as our classical density functional theory models applied to supercapacitors (**Fig. 1**, top). Such coarser-grained models are generally far less computationally-intensive than first-principles approaches, enabling us to simulate larger systems over longer time scales than can be addressed using even the currently-available petaflop computers. Another foundational aspect of the FIRST Center is our ability to synthesize and characterize novel substrates (including various forms of carbon and transition metal carbonitrides) and electrolytes (including room temperature ionic liquids) with highly controlled properties and unique functionality (**Fig. 1**, middle). In order to probe the atomic/nanoscale properties of interfacial systems, we apply a sophisticated array of neutron and X-ray scattering methodologies (**Fig. 2**), and we have developed entirely new analytical approaches, such as electrochemical strain microscopy (*e.g.* Come, et al., *Nano Energy* **2015**, *17*, 27).



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