Fluid Interface Reactions, Structures and Transport (FIRST) Center
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Lead Institution: Oak Ridge National Laboratory

The FIRST Center will integrate novel synthesis, experimental and computational approaches to develop predictive models relating the nanoscale structures, dynamics and reactivities of fluid-solid interfaces encountered in electrical energy storage and heterogeneous catalysis. The ultimate goal of this research is to provide predictive insights into the design, synthesis and function of the next generation of materials with superior performance to address our Nation's Future Energy Needs.

The overarching goal of the FIRST Energy Frontier Research Center is to address the fundamental gaps in our current understanding of interfacial systems of high importance to future energy technologies, including electrical energy storage (batteries, supercapacitors) and heterogeneous catalysis for solar energy and solar fuels production. The FIRST Center will address three key questions:

- How does the interfacial region differ in structure, dynamics and reactivity from the bulk properties of the fluid and solid phases?
- How do these altered properties couple with complex interfacial textures and potential gradients (electrical and/or chemical) to influence chemical reactions, ionic and molecular transport and charge transfer within and across the interface?
- How can we control and predict interfacial phenomena by informed design of fluid- and solid-phase components, interfacial geometries, field gradients and environmental parameters?

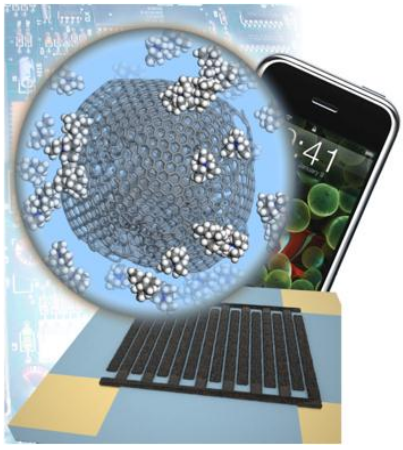

Figure 1. Microsupercapacitors developed with novel carbon nano-onion electrodes exhibit extremely high power density (Pech, Gogotsi, et al., *Nature Nanotechnology* **5**, 641, 2010). We are now investigating the origins of this behavior using X-ray and neutron scattering, electrochemical and molecular modeling approaches.

The interaction of fluids with solid substrates controls many chemical processes encountered in nature and industry. However, the atomic-nanoscale structures, reactivities and transport properties of the fluid-solid interface (FSI) are poorly understood for the vast majority of fluid-substrate combinations. This lack of fundamental molecular-level understanding of interfacial phenomena has often lead to Edisonian approaches to the resolution of challenges related to advanced energy technologies, including solar energy utilization, energy storage (batteries and capacitors), heterogeneous catalysis, and chemical separations. The First Center will bring together a multidisciplinary, multi-institutional team of scientists, postdoctoral associates and students to redefine the FSI and enable predictive understanding and control of interfacial processes.

Unique FSI properties emerge from a complex interplay of short- and long-range forces and reactions among the molecular fluid components, solutes and substrates. Potential gradients (chemical, electrical, etc.) can be highly non-linear at the angstrom-nanometer scale. The finite size, shape, directional bonding, charge distribution and polarizability of solvent and solute components are convoluted with their ability to reorient, 'unmix' and react with one another and the substrate. The truncated solid surface exposes under-bonded atoms that drive dynamic interactions with the adjacent fluid by local bond relaxation, charge redistribution, dissolution, precipitation,

sorption and porosity development and destruction. To achieve true predictive understanding of such systems, our strategy is hierarchical and highly-integrated, coupling unique experimental, chemical imaging, materials synthesis and computational approaches to probe FSI structures, reactions, and transport phenomena. In Thrust 1, we investigate organic and inorganic electrolyte interactions with charged and uncharged carbon surfaces in a planar or unconfined geometry. This enables coupling of advanced neutron, X-ray, NMR and nonlinear optical probes of interfacial structure and dynamics with multiscale computational models that capture the chemical realism of interfaces. In Thrust 2, we extend these approaches to determine how nanoscale confinement, surface roughness, functionalization and alteration due to chemical reactions with the fluid influence solvent/solute transport at uniquely-tailored carbon surfaces and with novel electrolyte structures and chemistries (Figure 1). In Thrust 3, we seek to identify the unique properties of interfacial fluids that control reaction pathways, selectivity, and energetics of proton-coupled electron transfer reactions involving CO_2 and O_2. The goal of these thrusts is to develop predictive FSI models that capture the actual structures, compositions and solute-solvent-substrate interactions that control interfacial properties, reactivity and transport.

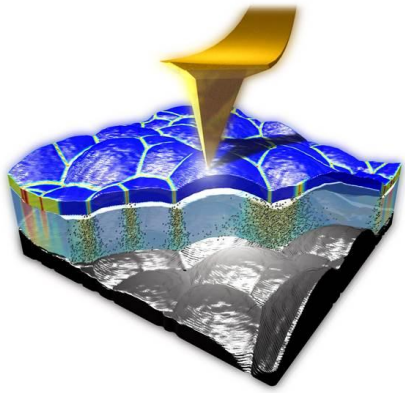

Figure 2. Electrochemical Strain Microscopy, being developed jointly by the FIRST Center and ORNL's user-driven Center for Nanophase Materials Sciences, reveals the diffusional dynamics of lithium ions in working battery electrodes with nanometer resolution (Balke et al, *Nano Letters* **10**, 3420, 2010).

The research is mainly conducted at Oak Ridge National Laboratory (ORNL), with extensive activities at our partner institutions - Vanderbilt, Drexel and Northwestern Universities, Argonne National Laboratory (ANL) and the University of Virginia. Much of the key research is conducted through peer-reviewed proposals to major DOE/BES user facilities, including ORNL's Spallation Neutron Source/High Flux Isotope Reactor (SNS/HFIR), National Center for Computational Sciences (NCCS), and Center for Nanophase Materials Sciences (CNMS), as well as ANL's Advanced Photon Source (APS). The Center currently supports 20 students and postdoctoral fellows at ORNL and our partner institutions.

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