EFRC: FLUID INTERFACE REACTIONS, STRUCTURES AND TRANSPORT (FIRST)

UPDATED: AUGUST 2016

AWARDS: $19.3M (August 2009 – July 2014); $15.2M (August 2014 – July 2018)

WEBSITES: http://science.energy.gov/bes/efrc/centers/EFRC/; http://web.ornl.gov/sci/first/

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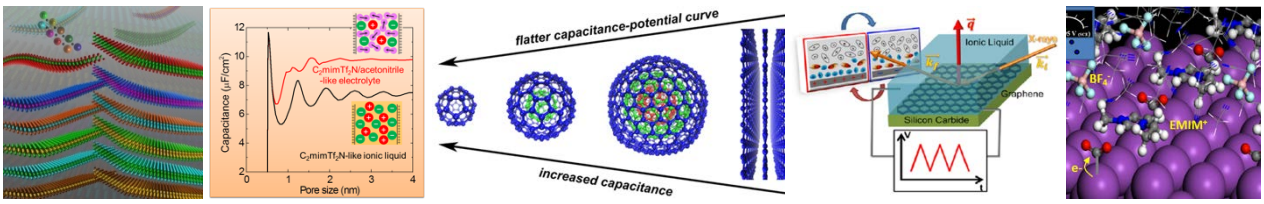
SCIENTIFIC MISSION AND APPROACH

The overarching goal of the FIRST Center is 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. FIRST's primary emphasis is on capacitive and pseudocapacitive energy storage controlled by ion sorption and surface redox reactions that occur within the so-called electrical double layer (EDL) at electrode/electrolyte interfaces. The center studies aqueous, organic and room temperature ionic liquid (RTIL) electrolyte solutions and electrode materials including various forms of nanoporous carbon, the novel 2D MXene transition metal carbonitrides and metals. Such interfaces also facilitate electrocatalytic reactions and FIRST seeks to understand the interfacial structures and dynamics that control the mechanisms and efficiency of selected energy-relevant redox reactions. The center consists of two highly interactive Thrusts:

1) **Structure and Dynamics of Simple Fluid-Solid Interfaces:** Develop predictive conceptual and multiscale computational models and validate them using advanced nanoscale probes of electrolyte structures, dynamics and reactivity at well-understood interfaces.
2) **Structure and Dynamics of Complex Fluid-Solid Interfaces:** Use these models to guide the synthesis of novel materials and functional interfacial systems that address current technological barriers in (pseudo)capacitive electrical energy storage and electrocatalysis.

SELECTED SCIENTIFIC ACCOMPLISHMENTS

- Developed a deep body of integrated synthesis, computation and nanoscale characterization studies of the structure, dynamics and capacitive energy storage potential of RTILs that is enabling predictive design of supercapacitors that operate at extremes of temperature and electrochemical potential.
- Developed and patented novel electrode materials including onion-like carbons (OLC) with superior rate-handling and sorptive properties for micro- and pseudo-capacitors, and hierarchical ordered mesoporous carbons using a 'bricks and mortar' synthesis approach that enables incorporation of additives like few-layers graphene and OLC to enhance energy and power density and conductivity.
- Used Density Functional Theory (DFT) approaches to predict the stabilities of an entirely new class of conducting 2D mixed-transition-metal carbonitrides (MXenes) and then successfully synthesized several such materials that show great promise for psuedocapacitors and electrocatalysts.
- Combined DFT and reactive classical molecular dynamics simulations to reveal the detailed mechanisms controlling the reduction of CO_2 to CO (a liquid fuel precursor) co-catalyzed by RTIL cations at post-transition metal electrodes, in quantitative agreement with FIRST experiments.



FIRST research, from left: Novel 2D double-transition-metal carbonitrides (MXenes) synthesized based on computational predictions; Classical MD and classical DFT prediction of the oscillatory capacitance of nanoporous electrodes as a function of ion size versus pore size; CMD-predicted effect of surface curvature on nanoparticulate electrode capacitance; novel synchrotron X-ray and neutron scattering and spectroscopic approaches developed to validate computationally-predicted interfacial structures and dynamics; mechanism revealed that controls highly efficient and selective reduction of CO_2 to CO co-catalyzed by imidazolium RTIL cations at a cheap and nontoxic bismuth electrode surface in acetonitrile electrolyte.

IMPACT

- In a series of high impact publications FIRST demonstrated how a new scanning-probe microscopic approach, termed Electrochemical Strain Microscopy (ESM), enables real time monitoring of the rates of ion and electrolyte transport into and out of battery and capacitor electrodes. It works by measuring the local volumetric responses (with submicron lateral resolution) to ion intercalation and pore pressure changes associated with electrode charging/discharging. ESM was licensed to **Asylum Research** and is now available to general users of ORNL's Center for Nanophase Materials Science (CNMS) where it is heavily subscribed. https://www.asylumresearch.com/
- FIRST developed and patented the Electrochemical Flow Capacitor (EFC) concept that involves a slurry of micron-sized or larger conducting particles suspended in an aqueous or polar organic electrolyte. The particles become charged by collisions with the current collectors and one another when the slurry is pumped through electrode compartments, storing electrical energy in the EDLs developed in the nanoporous particles and in redox-active sorbed organic molecules. FIRST laid extensive groundwork for establishing the roles of particle size/shape/loading, collector channel size and pseudocapacitive enhancement in controlling performance, and is now developing multiscale computational models to accelerate predictive design. EFC's combine the high power handling and cycle life of supercapacitors with scalable energy storage for grid-scale applications.

PUBLICATIONS AND INTELLECTUAL PROPERTY

As of May 2016, FIRST had published 242 peer-reviewed publications cited over 10,400 times and filed 8 disclosures, 7 US patent applications, and 5 foreign patent applications. 3 patents have been issued and 1 patent application licensed. The following is a selection of impactful papers:

- Balke, N. *et al*. Nanoscale Mapping of Ion Diffusion in a Lithium-Ion Battery Cathode. *Nature Nanotechnology* **5**, 749-754, doi: 10.1038/nnano.2010.174 (2010). [**204 citations**]
- Feng, G. *et al*. Supercapacitor Capacitance Exhibits Oscillatory Behavior as a Function of Nanopore Size. *J. Physical Chemistry Letters* **2**, 2859-2864, doi: 10.1021/jz201312e (2011). [**125 citations**]
- Mochalin, V. *et al.* The Properties and Applications of Nanodiamonds. *Nature Nanotechnology* **7**, 11-23, doi: 10.1038/NNANO.2011.209 (2012). [**667 citations**]
- Pech, D. *et al*. Ultrahigh-Power Micrometre-Sized Supercapacitors Based on Onion-Like Carbon. *Nature Nanotechnology* **5**, 651-654, doi: 10.1038/nnano.2010.162 (2010). [**921 citations**].
- Simon, P., Gogotsi, Y., Dunn, B. Where do Batteries End and Supercapacitors Begin? *Science* **343**, 1210-1211, doi: 10.1126/science.1249625 (2014). [**526 citations**]
- Xie, Y. *et al.* Prediction and Characterization of MXene Nanosheet Anodes for Non-Lithium-Ion Batteries. *ACS Nano* **8**, 9606-9615, doi: 10.1021/nn503921j (2014). [**94 citations**]
- Zhai, Y. *et al.* Carbon Materials for Chemical Capacitive Energy Storage. *Advanced Materials* **23**, 4828-4850, doi: 10.1002/adma.201100984 (2011). [**943 citations**]