

*Thrust 1: Structure and Dynamics of Simple Fluid-Solid Interfaces (Peter T. Cummings, Vanderbilt University, Thrust Leader).* This thrust integrate multiscale computational modeling and novel experimental probes of interfacial fluid properties at ‘simple’ interfaces, such as planar, cylindrical, and spherical surfaces, parallel slit and cylindrical pores, etc. which can be rigorously modeled with the minimum incorporation of simplifying approximations and assumptions. Such simple interfaces are also inherently suited to atomic-nanoscale experimental probes of interfacial fluid structures and molecular/ionic distributions, diffusional, rotational and vibrational dynamics, and interfacial reaction properties, and have the highest potential to be directly linked with, and often predicted by, atomistic/molecular modeling approaches. However, synthesizing truly simple interfaces in order to validate our models is a challenge that is a significant part of the activity in this Thrust. The primary focus of Thrust 1 is thus to achieve fundamental understanding of interfacial structures, dynamics, and reactivity through the development of predictive conceptual and computational models, guided and validated by experimental studies of highly controlled, simple FSIs.

*Thrust 2: Structure and Dynamics of Complex Fluid-Solid Interfaces (Sheng Dai, ORNL, Thrust Leader).* Here we use the insights and predictive capabilities obtained in Thrust 1 to guide the synthesis and characterization of complex interfacial materials, including both nanotextured and nanoporous solids and mixed electrolytes, designed to validate our conceptual and computational predictions of interfacial system performance in capacitive electrical energy storage and electrocatalysis. Such complex interfaces often involve multiple parameters that must be approximated (e.g., surface geometries, chemistries, defects and terminations; emergent nanoconfined fluid effects; and dynamic properties of the nanoporous substrates themselves) and then refined, using multiscale models to extract the underlying atomic/molecular causal relationships controlling the overall system response. A significant challenge for complex interfaces is quantitatively characterizing the synthesized substrate, in terms of pore size and shape distributions, surface geometries, roughness and defectiveness, conductivity, local functionality, and other variables that require novel combinations of experimental and modeling approaches for unambiguous quantification. The primary focus of this Thrust is to demonstrate Model-Integrated Synthesis, Characterization and Experiment (*MISCE*) in the guided design of transformative functional materials for energy storage/delivery and chemical transformations, involving FSIs that are complex in terms of surface and pore architectures, chemistries and electrolyte compositions.

*Cross-Cut 1: Interfacial Transport (Yury Gogotsi, Drexel University, Coordinator).* The transport of ions to and from charged surfaces in a supercapacitor, and of reactant and product molecules to and from an electrocatalyst surface, ultimately control power density and catalytic throughput of the interfacial systems targeted in this Center. Independently of maximum capacitance or specific reaction rates and mechanisms, properties such as fluid viscosity, solvation/desolvation at interfaces, volume exclusion effects under ultraconfinement, and the connectivity and hierarchical distribution of nano- to macro-pores often dictate the limits of performance of such functional interfaces. These properties, often obtainable from fundamental modeling and experimental probes of simple interfaces, are complexly convoluted in more complex FSIs, and must be decoupled in order to achieve predictive design of novel materials. Electrochemical flow capacitor behavior (dynamic electrochemical interface) and the tailoring of electrolyte ion size/charge distributions to match substrate pore distributions are efforts that epitomize the need to fully understand transport of ions, electrolytes and even electrons and suspended particles, in order to effectively design functional devices for capacitive energy storage and delivery.

*Cross-Cut 2: Interfacial Reactivity (Steven H. Overbury, Coordinator).* Pseudocapacitive electrical energy storage involves fast and highly reversible Faradaic redox reactions of covalently bonded or adsorbed species exactly at the FSI. Such surface redox reactions can enhance the energy density of high power supercapacitor electrode/electrolyte systems, including flow capacitors, making them approach the performance of battery systems, while retaining the long lifetimes and high power densities of pure EDLCs. Achieving fundamental and predictive understanding of the FSI controls on surface redox

processes must be built up from detailed computational and experimental probes of simple interfaces, and then the determination of how these reactions are altered at non-planar nanoparticle surfaces and within complex nanopores. Similarly, electrocatalysis involves catalytically-promoted fast reactions at charged interfaces that take place within a dense fluid medium, and which often involve desolvation and concerted rearrangements of ions and molecules at the interface, as well as concerted ion and electron transfer processes. Fundamental insights into the specific reaction rates and mechanisms controlling such reactions can only be obtained by the controlled synthesis and integrated molecular modeling of simple interfaces. However, effective electrocatalysts must be nanotextured, since like supercapacitors, their performance is fundamentally limited by reactive surface area, and subject to emergent nanoconfinement effects.