Understanding and controlling reactions within electrochemical energy storage systems is a significant scientific and technical challenge. This is due to the complexity of these systems (e.g., for both the solids and electrolytes), as well as the extreme environments and significant structural and chemical changes that can take place as a function of applied potential. The behavior at the solid-electrolyte interface itself is especially poorly understood. I will review our recent work in which we seek to isolate and understand the role of interfacial reactivity in these systems through in-situ, real-time, observations of electrochemically driven reactions. This is achieved by observing well-defined model electrode-electrolyte interfaces using X-ray reflectivity. I will discuss two distinct types of electrochemical energy storage systems: 1) lithium ion battery chemistries in which energy is stored by lithium ion insertion into electrodes (e.g., Si, Si$_x$Cr, Ge, NiO). The goal of this work is to control the complex lithiation reaction path of these conversion reactions through the use of thin-film and multilayer electrode structures; and 2) super-capacitor systems, in which energy is stored by surface adsorption. For these systems, we are studying the static structures and dynamical response of room temperature ionic liquids at potential-controlled carbon interfaces which we find have inherently slow dynamics associated with the reorganization of the interfacial RTIL structure.

Acknowledgment: This work was supported as part of the Center for Electrochemical Energy Science (CEES) and the Fluid Interface Reactivity Structure and Transport Center (FIRST), which are Energy Frontier Research Centers funded by the U.S. Department of Energy, Office of Science, Basic Energy Sciences. The work was done in collaboration with T. Fister, S. S. Lee, A. Uysal, H. Zhou (ANL), J. Esbenshade, B. Long, A. Gewirth (UIUC), X. Chen, G. Evmenenko, M. Bedzyk (Northwestern), G. Feng, S. Li, P. Cummings (Vanderbilt), S. Dai (ORNL) and Y. Gogotsi (Drexel).