Northeastern Center for Chemical Energy Storage (NECCES)
EFRC Director: M. Stanley Whittingham
Lead Institution: Stony Brook University

Mission Statement*: To understand how fundamental chemical reactions occur at electrodes and to use this knowledge to design new chemical energy storage systems.*

The design of the next generation of lithium-ion batteries (LIBs) requires both the development of new chemistries and significant improvements in our fundamental understanding of the physical and chemical processes that occur in these systems. The mechanisms by which LIBs operate are often extremely complex and interconnected, occurring over timescales that vary from femto-seconds to years, and over equally broad spatial scales. Progress in this area requires a multidisciplinary approach involving both experiment and theory, making use of existing methodologies, while developing new tools specifically designed to investigate electrode processes in real time. The specific goals of this center are to develop a fundamental understanding of how electrode reactions occur, what phases are formed, and how the reaction path can be tailored and controlled by appropriate electrode design (doping, particle size, shape, composite structure); identify critical structural and physical properties that are vital to improving battery performance; and use this information to design new battery systems. The role of reaction overpotential will be a unifying theme for all materials. Examples of electrode materials chosen for investigation include doped olivines and conversion chemistries based on the FeF_3-FeOF system. An emphasis is being placed on the development of *in situ* characterization methods that use multiple experimental tools simultaneously or that combine imaging with spectroscopy. Theoretical predictions are being used to determine the most likely reaction routes, and how overpotential and diffusion might control the route and reversibility. To achieve these goals we have established four closely coupled thrusts that enable the necessary synergy and focus on areas of critical relevance to improving energy storage:

Thrust 1: Intercalation chemistry. Experimental studies closely coupled to computational modeling is being used to understand the fundamental ultimate limitations of structure-retention reactions, of both single phase and multi-phase type. Theoretical models have been developed to explain the very high rate of the olivine cathodes, and experiments are underway to determine why partial substitution of the iron has a marked effect on the rate. Cross-over reactions where the initial reaction is intercalation, such as those of lithium with SnCo, FeF_3 and FeOF, and the subsequent conversion are also being studied, thus building a synergistic bridge between thrusts 1 and 2. These studies will, where possible, be performed in-situ so as to study the dynamic system, rather than after relaxation. This will allow the elucidation of the ultimate limits of intercalation reactions, both energy and power, and lead to the key materials criteria for the discovery of the next generation battery materials that have significantly higher energy densities, yet maintain today's highest reaction rates, and maintain or self-heal their structures over thousands of redox cycles.

Thrust 2. Conversion chemistries. Conversion chemistries offer a potential path to high energy density electrodes and also new ways to form materials on a very fine nm scale. As opposed to most present day intercalation systems, which operate through a single or at most two phase process, conversion materials operate with at least three phases being present, sometimes four. All of these phases are in a dynamic state and are electrochemically formed and reformed on a scale of 1-10nm. The goal of this thrust is to establish an understanding of the phase development, redox, and ionic and electronic transport involved at such scales, which allow these systems to operate and to identify kinetically limiting processes. The emphasis is being placed on the Fe-F-O system, and studies to date have shown

the criticality of the nanophases formed, both composition and morphology. A good understanding of the phases formed has been obtained. Emphasis is now being placed in two areas. First determining the origin of the high overpotential on cycling, and finding ways to control it. A highly synergistic theory and experimental effort is in place. The second challenge being addressed is how to control the nanostructures formed and in particular their high reactivity.

Thrust 3: **Cross-cutting research: Developing the characterization and diagnostic tools to investigate battery function.** The development of novel characterization tools and methodologies with increased spatial, energy and temporal resolution will provide the fundamental understanding of electrochemical energy storage systems. The major tool effort is being focused on in-situ studies to specifically address challenges related to understanding the materials in thrusts 1 and 2, and this effort is highly synergistic with the materials and the modeling efforts. These tools are being used to reveal the complex and interdependent processes in electrodes, electrolyte and at their interface. Four major developments are underway: (i) *in situ* NMR studies of battery materials, (ii) *in situ* imaging and spectroscopy of surface and bulk processes in composite electrodes and model single particle nano- and micro-electrodes, (iii) *in situ* analytical TEM and Electron Energy Loss Spectrometry (EELS) investigations of the electrochemical reactions at the nanometer scale, and (iv) *in situ* pair distribution function (PDF) analysis of local and intermediate range structure in functional nano-crystalline or disordered materials. These studies are utilizing the BES major facilities, including the synchrotrons and nanolabs, available at the Brookhaven, Argonne, Berkeley and Oak Ridge National Laboratories (e.g., for *in* and *ex-situ* PDF, X-ray diffraction, X-ray absorption spectroscopy, TEM and nanofabrication). One example is the development of unique *in situ* transmission electron microscopy/scanning tunneling microscopy that showed, in real-time, the formation of iron nanoparticles, < 5 nm, on reaction of lithium with FeF_2.

Thrust 4. Cross-cutting research: Theory and computational modeling to understand and predict kinetic phenomena in electrode materials. Computational modeling is being used to develop models that predict the rate behavior and reaction paths of electrode materials. A model has been developed that explains the high rate for nano-sized olivine particles, based on a single-phase reaction mechanism. This model identified overpotential as controlling the reaction path, and experiments are underway to test the model. This overpotential model will be broadened beyond structure retention materials such as the olivine and $CuTi_2S_4$ and applied to a range of electrode materials, including the FeF_y conversion materials. The development of this model will also help to guide the discovery of new battery materials with higher power and energy density.

Northeastern Center for Chemical Energy Storage (NECCES)	
Stony Brook University	M.S. Whittingham (Director), C. P. Grey (Assoc. Director, Thrust 1 leader), P. Khalifah
Rutgers University	G. Amatucci (Assoc. Director, Thrust 2 leader) S. Garofalini, F. Cosandey, R. Bartynski
Binghamton University	M.S. Whittingham
University of Cambridge	C. P. Grey
Massachusetts Institute of Technology	G. Ceder (Thrust 4 leader)
Lawrence Berkeley National Laboratory	R. Kostecki (Thrust 3 leader), J. Cabana
Argonne National Laboratory	P. Chupas
Brookhaven National Laboratory	J. Graetz and X.-Q. Yang
University of California, San Diego	Y. S. Meng
University of Michigan	A. Van Der Ven and K. Thornton

Contact: M. Stanley Whittingham; stanwhit@gmail.com; 631.632.5724; http://necces.chem.sunysb.edu/