Northeast Center for Chemical Energy Storage (NECCES)
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Mission Statement*: To develop an understanding of how key electrode reactions occur, and how they can be controlled to improve electrochemical performance, from the atomistic level to the macroscopic level through the life-time of the operating battery.*

The design of the next generation of rechargeable batteries requires both the development of new chemistries and the fundamental understanding of the physical and chemical processes that occur in these complex systems. Although some significant advances have been made to prepare and utilize new materials, efforts towards the understanding of mechanisms have waned. This will eventually choke efforts to efficiently develop new materials if this issue is not addressed now. Batteries are inherently complex and dynamic systems, their electrochemistry, phase transformations, and transport processes often varying throughout their lifetime. Although often viewed as simple to use by the customer, their successful operation relies heavily on a series of complex mechanisms, involving thermodynamic instability in many parts of the charge-discharge cycle and the formation of metastable phases. The requirements for long-term stability are extremely stringent and necessitate control of the chemistry at a wide variety of temporal and structural length scales. This in turn necessitates the development and use of new characterization tools to monitor these processes. The overall goal is to understand the transformations (and their rates) that occur in an electrode composite structure, from the atomistic level to the macroscopic level, throughout the lifetime of the functioning battery. The scientific research goals are to:

1. Close the gap between the theoretical and practical energy density for intercalation compounds.
2. Attain reversible multi-electron transfer in a cathode material using lithium and sodium.
3. Understand performance limiting transport in positive electrode structures from the local through the meso to the macroscale.
4. *Enable new chemistries* involving electrode systems that were previously considered intractable for use in batteries, including the understanding of the role of anion redox in intercalation cathodes.

These research goals will be achieved by dividing our research effort into three closely connected and integrated thrusts; the theory effort is integrated into thrusts 1 and 2.

Thrust 1: Intercalation Materials Chemistry. This thrust will identify the key parameters that are required to optimize intercalation reactions in the active material in the electrodes. We will determine:

(i) The structural parameters required for rapid ionic (Li^+) motion (and thus high rate), particularly at close to full lithium removal.
(ii) The minimal electronic (and ionic conductivity), required to completely extract Li from materials for different crystal structures and particle sizes.
(iii) How to control (minimize) structural changes so as to enable redox processes involving more than one electron.
(iv) What determines the contribution of anion redox in intercalation reactions, and how it could be optimized.
(v) The key structural parameters required to enable battery chemistries involving ions other than Li^+.

Thrust 2. Transport - Establishing the Local-Meso-Macro Scale Continuum. This thrust will establish a comprehensive understanding of the ionic and electronic transport in model electrode materials and establish a direct link to electrochemical performance through the correlation of physical phenomena in the increasingly complex hierarchy of a model battery electrode. We will determine:

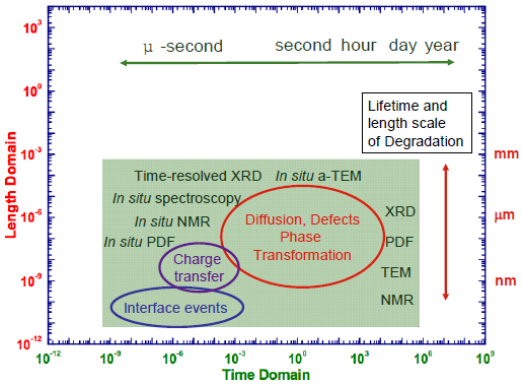
(i) Definitive links of local ionic and electronic transport to correlated physical phenomena occurring across and within phase transformations.

(ii) The complex ionic and electronic pathways at the meso to microscale to develop a working theory of composite electrode design.

Thrust 3: Cross-cutting research: Developing the characterization and diagnostic tools to investigate battery function. This thrust involves the development of novel *operando* and *ex-situ* experimental approaches aimed at probing electrical energy storage materials at the atom, single crystal/particle, and across the electrode heterostructure. Emphasis is placed on *in-situ* methods that use multiple experimental tools simultaneously or that combine imaging with spectroscopy. *In-situ* spectroscopy is crucial as the materials are exceptionally dynamic over all levels of material structure during the operation of a battery and can be highly sensitive to ambient contamination if *ex-situ* techniques are employed. Metastable phases, including key reaction intermediates can relax to form different phases if probed by ex-situ techniques. Several major developments are proposed:

(i) *Atomic level structure*: operando XAS, diffraction, PDF, SAXS, and NMR, annular dark/bright field STEM imaging of both heavy and light elements.

(ii) *Single crystal/particle level imaging:* Strain mapping with CXDI, high energy resolution STEM-EELS; and Nano-scale mapping at the nm-level (at the Debye length) across interfaces – including oxidation state mapping, operando TEM, high energy resolution STEM-EELS.



(iii) *Imaging reactions across the electrodes hetero-structures*: Imaging the whole electrode intact ideally under operando conditions, through development of high-resolution PDF/SAXS tomography and compatible operando electrochemical cells; structural insights with NMR experiments of studies of transport connected with MRI, PFG and SIMS studies of structure and tortuosity.

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