

Center for Electrochemical Energy Science (CEES)
EFRC Director: Paul Fenter
Lead Institution: Argonne National Laboratory
Class: 2009 – 2020

Mission Statement: *To create a robust fundamental understanding of the phenomena that control the reactivity of electrified oxide interfaces, films and materials relevant to lithium-ion battery chemistries.*

The Center for Electrochemical Energy Science (CEES) EFRC seeks to enable significant advances in energy storage technology through a concerted and broad-based science research program. This program is designed to create a foundational understanding of the structures and electrochemical processes that limit the technological properties and advantages of lithium ion battery (LIB) systems with a central focus on the behavior of metal oxide cathode materials used in today's LIB cathode systems. The CEES program addresses two important challenges that confront LIBs: 1) LIB lifetime and safety are strongly influenced by secondary reactions that occur primarily at the electrode-electrolyte interface. The inability to completely control electrochemical reactivity and associated side reactions is reflected by capacity loss through electrolyte decomposition, active materials dissolution and structural decay, and oxygen evolution with the possibility of fire and/or explosion. 2) The energy density of current LIB systems is limited predominantly by the inherent electrochemical capacity of lithium-intercalated metal oxide cathodes. Various "beyond Li-ion insertion" chemistries can, in principle, exceed the cathode capacity and energy density of current LIBs, but these reactions generally involve phase transitions that are kinetically challenging and suffer from poor reversibility and significant over-potentials. Within this context, CEES research efforts are designed to: develop a robust understanding of the electrochemical reactivity of metal oxide cathode materials relevant to lithium ion battery technology; leverage this understanding to control the associated lithiation/delithiation processes; and, explore new conceptual approaches and materials that may be used to advance present-day LIB systems.

CEES focuses on the structure and reactivity of the electrode-electrolyte interface. One set of objectives is to understand the molecular-scale structure and reactivity of simple oxide-electrolyte interfaces, including both primary reactivity of reversible lithiation, and secondary reactivity associated with capacity loss and electrode decomposition. This activity will develop a mechanistic understanding of how interfacial coatings and surface modifications alter the reactivity of $\text{Li}_x\text{Mn}_2\text{O}_4$ ("LMO"). This work will build on

the foundational understanding of the reactivity of model LMO(111) thin-film cathodes that we have explored both computationally and experimentally, through the use of model systems and state of the art experimental and computational approaches with an emphasis on developing conceptual advances. Parallel to this effort will be studies to understand the elementary steps in the modification of LMO electrode surfaces with atomic layer deposition, such as in ongoing work with alumina coatings. These studies will leverage the CEES capabilities to directly and independently probe both stress and strain evolution in LMO electrodes enabling new insights into the thermodynamic and kinetic controls over

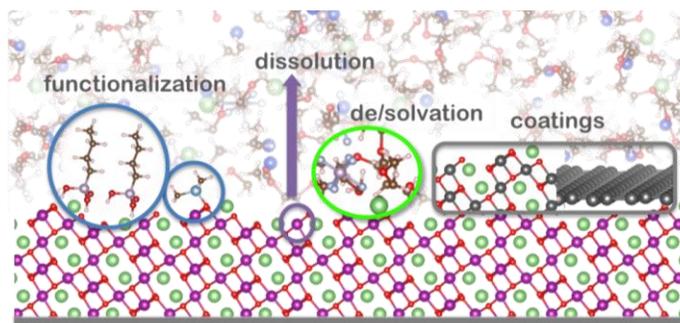


Figure 1: Interfacial coatings and modifications to control the reactivity of LMO-electrolyte interfaces.

these processes and the development of a new concept, “electrochemical stiffness” with ongoing work exploring how coatings influence stress/strain development. These insights compliment ongoing studies of model LMO thin-film reactivity in which preliminary results suggest that strain modifies the lithiation pathway for laterally constrained (i.e., epitaxial) LMO thin films.

A second theme seeks to define and implement strategies for robust interfacial modification that can control secondary reactivity at elevated potentials. This effort focuses on the development of structure-function relationships with respect to the surface modification of LMO interfaces to control its reactivity. We will extend these capabilities to stabilize the cathode-solid electrolyte interface. This work builds on earlier CEES work on the active functionalization of model LMO surfaces and related interfaces. Our hypothesis in these studies is that the interface separating solid-electrolytes from an electrode is a key weak-link whose structure and reactivity is largely unknown. It is postulated that: 1) the atomistic interfacial structure controls the rate limiting steps for lithium ion transfer; 2) evolution of these interfaces is due to intrinsic chemical/electrochemical instabilities associated with chemical and physical disequilibria; and 3) interface stabilization requires the development of new materials and design strategies that provide stability while retaining functionality. Based on these postulates we will identify the atomistic structures and instabilities at the interfaces through the study of selected solid electrolytes with LMO and their relationship to mechanisms that control ion transfer. These insights will be used to guide the creation of interlayers that achieve stability and functionality at solid electrolyte interfaces in the presence of disequilibria.

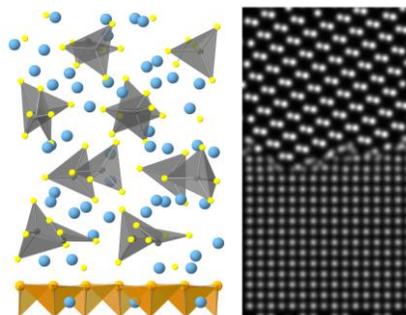


Figure 2: A model interface between a solid-electrolyte and a solid electrode, and a simulated transmission electron microscopy image.

Center for Electrochemical Energy Science (CEES)	
Argonne National Laboratory	Paul Fenter (Director), Larry Curtiss (Deputy Director), Timothy Fister, Maria Chan, Jeffrey Elam, Michael Thackeray
University of Illinois, Urbana-Champaign	Andrew Gewirth, Nancy Sottos, Ralph Nuzzo
Northwestern University	Mark Hersam, Chris Wolverton, Michael Bedzyk, Vinayak Dravid
Purdue University	Jeffrey Greeley

Contact: Paul Fenter, Director, fenter@anl.gov
630-252-7053, <http://www.cees.anl.gov>