The Center for Electrochemical Energy Science (CEES)

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A Lithium Ion Battery:

Charged: 3.6 V

Anode: (e.g., Carbon, Silicon...)
Electrolyte: (e.g., LiPF₆ in EC/DMC)
Cathode: (e.g., LiMn₂O₄, LiCoO₂, LiFePO₄, ...)

Secondary reactions: Solid electrolyte interphase ("SEI")

Electrolyte decomposition: barrier for Li insertion, stabilization of carbon anode
CEES Mission and Team:

**Mission:** To understand and control the molecular-scale reactivity of electrified oxide interfaces and materials that limit the performance of lithium-ion battery systems.

**Goal:** Enable transformative breakthroughs in energy storage technology that address societal needs (e.g., transportation, personal electronic devices, grid storage for wind/solar).

**Organization:**

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<th>CEES Directorate:</th>
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<tr>
<td>Paul Fenter, Director (ANL)</td>
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<td>Michael Thackeray, Deputy Director (ANL)</td>
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<td>Andrew Gewirth (UIUC), Institutional and Task Lead</td>
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<td>Mark Hersam (NU), Institutional and Task Lead</td>
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<td>Larry Curtiss (ANL), Task Lead</td>
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<td>Jeffrey Elam (ANL), Task Lead</td>
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**Task 1: The Oxide-Electrolyte Interface:**

**Task 1A: Structure and Reactivity**
Gewirth, Curtiss (Task Leads)
Fenter, Sottos, Greeley, Barnett, Marks, Nuzzo

**Task 1B: Control of Reactivity by Interfacial Modification**
Hersam, Elam (Task Leads)
Nuzzo, White, Johnson, Wolverton

**Task 2: Oxide Solid-Phase Electrochemical Reactivity:**

**Task 2A: Interfacial Control of Conversion Reactions**
Fenter, Fister (Task Leads)
Dravid, Bedzyk, Greeley

**Task 2B: Hybrid (Li-ion/Li-O2) Chemistries**
Thackeray, Chan (Task Leads)
Amine, Wolverton, Dravid

**External Advisory Committee:**
Daniel Scherson, Chair (CWRU)
Héctor Abreuña (Cornell)
Marc Anderson (Wisconsin)
Michael Andrew (Johnson Controls)
David Cahill (UIUC)
Sossina Haile (Northwestern)
J. Woods Halley (Minnesota)
Michael F. Toney (SLAC)
M. Stanley Whittingham (Binghamton)

**Management Council:**
Paul Kearns (ANL)
Harry Weerts (ANL)
Cynthia Jenks (ANL)
Jay Walsh (NU)
Sossina Haile (NU)
Peter Schiffer (UIUC)
David Cahill (UIUC)
Suresh V. Garimella (Purdue)

http://www.anl.gov/cees
CEES: Science Challenges of Electrochemical Energy Storage:

Task 1: Structure and Reactivity of the Oxide-Electrolyte Interface
- Understand and control electrochemical reactivity at well-defined electrode-electrolyte interfaces relevant to lithium ion insertion chemistries
  - Electrolyte and Electrode instabilities: decomposition, solid-electrolyte interphases, cation dissolution, oxygen loss, fires
  - Observing and controlling interfacial reactivity through interfacial modification

Task 2: Beyond Li-ion insertion
- Can we direct electrochemical reactivity to enable advances in the energy storage capacity of oxide cathodes?
  - Understand and control the challenges to achieve significant increases in stored energy
  - More complex structural transformations
**Novel CEES Approach: “Electrochemical Stiffness”**

Combined *in situ* stress and strain measurements are used to calculate the “electrochemical stiffness”, a newly defined property of electrodes.

Electrochemical stiffness: the ratio of the stress change to strain change of an electrode.

Measurement obtained during the lithiation of a composite graphite electrode reveal:

- Stress and strain develop asynchronously during lithiation reactions:
  - stress varies proportional to the charging rate
  - strain varies with capacity (and inversely with rate).
- Dramatic changes in electrochemical stiffness occur due to the formation of different graphite-lithium intercalation compounds during cycling.

These results reveal a sharp increase in stiffness that is associated with stress development prior to strain development (i.e., the active materials have yet to expand significantly).

→ *In operando* measurements of electrochemical stiffness provide insights into the origin of rate-dependent chemo-mechanical degradation of battery electrodes.

Task 1: The Oxide Electrolyte Interface

Insertion reactions allows a primary focus on interfacial reactivity in the context of lithium ion electrodes: Li$^+ + e^- + \text{Mn}_2\text{O}_4 \leftrightarrow \text{Li Mn}_2\text{O}_4$

- The spinel LiM$_2$O$_4$ ("LMO") was chosen as the materials focus of activities.
  - LMO crystal habit is amenable to molecular level interfacial characterization and modification.

- Known technological challenge: Mn dissolution
  - Mn(III) disproportionation: Mn(III) $\rightarrow$ Mn(II) + Mn(IV)
  - Dissolved Mn(II) deposits at the anode and disrupts the anode SEI.
Task 1: LMO Interfacial Structure and Reactivity

Computational Studies of LMO stability:
- Electrochemical Stiffness of LMO:
  - Warburton (ACS-AMI, 2016)

Stabilization of LMO by Coatings:
- Au@LMO
- Surface Doping of LMO
  - Esbeshade (JEchemSoc, 2015)
  - Lu (NatComm, 2014)

Graphene Coated LMO:
- Jaber-Ansari (AdvEnergyMat, 2015)

Graphene-LMO Composite Electrodes:
- Chen (NanoLetters, 2017)

Graphene-LMO Composite Electrodes:
Task 2A: Interfacial Control of Conversion Reactions

\[ 2xLi^+ + 2xe^- + MO_x \leftrightarrow M + xLi_2O \]

Compared with insertion cathodes:

- Lithium capacity is ~5 fold higher
- Lithiation voltages are ~2-fold lower

→ Potential for ~2 fold increase in stored energy
  (e.g., capacity × voltage)

However there are many challenges:

- reactions tend to be largely irreversible
- observed voltages are ~2-3-fold lower than thermodynamically predicted (~0.6 V vs. 1.8 V).

→ Use nanostructured electrodes to guide reactivity and understand limitations.
Task 2A: Interfacial Control of Conversion Reactions

Structure and Reactivity of Ni/NiO\textsubscript{x} Multilayer Electrodes

X-ray Reflectivity (XR) During Lithiation:

- TEM of PLD-Grown Electrodes:

  - Spatially Resolved Lithiation Profiles from XR:

  - Defining and controlling fundamental challenges in conversion reactions

Evmenenko (ACS Appl. Mater. Interfaces, 2016)

CEES Presentations:

**ORAL Presentations:**

Tuesday 9:10-9:30 am (D-II-3):
Atomistic Studies of Nucleation and Growth in Conversion Reactions for Lithium-Ion Batteries, Jeffrey P. Greeley

Team Science: Tuesday 10:40-11 am (D-III-1) [plus Poster Monday Evening 5-6:30]
Understanding and Controlling the Reactivity of LiMn$_2$O$_4$-Electrolyte Interfaces,
Robert Warburton, Bruno Nicolau, Kendra Letchworth-Weaver

Tuesday, 11:40-12 pm: (D-III-4)
Interfacial Properties of Graphene/Lithium Manganese Oxide Spinel Cathodes for Lithium-Ion Batteries, Kan-Sheng Chen

Tuesday, 2:50-3:10 (D-IV-5)
Characterization and Modeling of Oxygen Reactivity and Structural Evolution During Electrochemical Charging of Li-rich Li$_5$FeO$_4$, Maria Chan

**Posters:**

Monday, 5-6:30 pm
The Role of Interfaces in Lithium Battery Conversion Reactions
Jae Jin Kim

Oxygen Redox Activity in Lithium-Rich Cathode Materials
Fernando C. Castro

Tuesday, 3:30-5:00 pm
Asynchronous Stress and Strain in Li-ion Composite Cathodes
Kimberly E. Lundberg

Photo-Accelerated Fast Charging of Lithium-Ion Batteries
(Wesley M. Dose) Christopher S. Johnson