Cathodes

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Annual Merit Review
DOE Vehicle Technologies Program

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Overview

Timeline
- Start date: FY09
- End date: On-going
- Percent complete: project on-going

Budget
- Total project funding
  - 100% DOE
- FY09: $300K
- FY10: $300K

Barriers Addressed
- Low energy
- Cost
- Abuse tolerance limitations

Partners
- Co-investigators:
- Collaborators:
  - Y. Shao-Horn, C. Carlton (MIT)
  - M. Balasubramanian (APS-ANL)
  - V. Battaglia (LBNL), Jose M. Calderon-Moreno (Romanian Academy)
Objectives

- Design high capacity, high-power and low cost cathodes for PHEVs and EVs
  - Improve the design, composition and electrochemical performance of Mn-based cathodes
  - Explore new processing routes to prepare advanced electrodes with new architectural designs
  - Use atomic-scale modeling as a guide to identify, design and understand the structural features and electrochemical properties of cathode materials
Milestones (FY09-10)

- Synthesize, evaluate and optimize high capacity Mn-based cathodes (>200 mAh/g, >3 V) – on going
- Engineer and evaluate the electrochemical effects of protective coatings on composite electrode structures with a high Mn content at high potentials (>4.2 V) – on going
- Model interfacial structures and dissolution phenomena – complete for LiMn$_2$O$_4$ electrodes
- Evaluate single-step, autogenic processes for synthesizing new (or improved) materials, cathode coatings and architectures – studies initiated
- Establish collaborative interactions with EFRC – Center for Electrical Energy Storage - Tailored Interfaces (Argonne-Northwestern University-University of Illinois (Urbana-Champaign) – collaborations initiated
Approach

- Exploit the concept and optimize the performance of structurally-integrated, high-capacity electrodes, particularly ‘layered-layered’ \( x\text{Li}_2\text{MnO}_3\bullet(1-x)\text{LiMO}_2 \) (\( M=\text{Mn, Ni, Co} \)) electrodes (Task 1)

- Design effective surface structures to protect the underlying metal oxide particles from the electrolyte and to improve their rate capability when charged (delithiated) at high potentials (Task 1)

- Explore autogenic (i.e., high pressure, solventless) reactions to synthesize advanced electrode materials and surface structures with new architectural designs (Task 2)

- Use first principles modeling to aid the design of bulk and surface cathode structures and to understand electrochemical phenomena (Task 3)
1. \( x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2 \) Electrodes

**Strategy:** Embed inactive \( \text{Li}_2\text{MnO}_3 \) component within \( \text{LiMO}_2 \) structure to stabilize the electrode at high potentials (reduce oxygen activity at surface)

Recap of typical performance:
- 200-250 mAh/g achieved at C/3 rate (50 °C)
- Lower capacity at RT
- Charging electrodes to high potential (>4.4 V) damages the electrode surface and reduces their rate capability
**Li-Ni-PO$_4$ Treatment**

*(0.5Li$_2$MnO$_3$•0.5LiNi$_{0.44}$Co$_{0.25}$Mn$_{0.31}$O$_2$ Electrodes)*

- **Concept**: Use Li-Ni-PO$_4$ as a solid electrolyte below 5.0 V to protect the xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrode surface at high potentials and to improve rate capability.

- **Sol-gel technique** (pH<4) used to etch and coat the electrode.

- **Theoretical modeling** discounts the possibility of a defect Li$_{3-2x}$Ni$_x$PO$_4$ (Li$_3$PO$_4$-type) surface structure (EFRC interaction – Shin, Wolverton, Northwestern University).

![Li-Ni-PO$_4$ Treatment](image)
Thermal Stability of Untreated and Li-Ni-PO$_4$ Treated $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ Electrodes

- DSC data show that surface-protected electrodes, charged to 4.6 V, are more tolerant to temperature excursions in the electrolyte (1.2 M LiPF$_6$ in EC:EMC)

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Scan rate: 10°C/min
Charged to 4.6 V

<table>
<thead>
<tr>
<th></th>
<th>Heat Flow (W/g)</th>
<th>Temperature (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pristine powder</td>
<td>- - -</td>
<td>- - -</td>
</tr>
<tr>
<td>Enthalpy</td>
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<tr>
<td>Coated powder</td>
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<tr>
<td>Enthalpy</td>
<td>1205 J/g</td>
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</tbody>
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The rate capability increases as a function with increasing Ni content, x
- Li$_3$PO$_4$ (x=0) provides the most resistive layer at 150 mA/g (~C/1 rate)
- All Li$_{3-2x}$Ni$_x$PO$_4$-treated electrodes cycle with near 100% cycling efficiency, unlike the parent, untreated electrode (98.7%)
- Electrodes (x=1) meet the 200 mAh/g, C/1 rate, 3.5 V average, capacity/power yardstick for a 20-40 mile range PHEV at room temperature
$x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMO}_2$ Electrodes

Evaluation against $\text{Li}_4\text{Ti}_5\text{O}_{12}$ and TiO$_2$ Anodes for Safe Li-Ion Cells

Opportunity:
TiO$_2$ electrodes offer a significantly higher theoretical capacity (335 mAh/g) compared to $\text{Li}_4\text{Ti}_5\text{O}_{12}$ (175 mAh/g)

$\text{Li}_4\text{Ti}_5\text{O}_{12}$ (LTO) Cells

- Two sets of $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiNi}_{0.44}\text{Co}_{0.25}\text{Mn}_{0.31}\text{O}_2$ electrodes with loadings of 2.1 and 3.1 mg/cm$^2$ were prepared with 100-µm and 125-µm blades (ANLCC100 and ANLCC125, respectively).
- LTO/ANLCC125 – anode limited
- LTO/ANLCC100 – cathode limited

Carbon-coated TiO$_2$ (TiO$_2$-C) Cells

- Carbon-encapsulated anatase (TiO$_2$-C) product synthesized by an autogenic process (EFRC interaction)
- TiO$_2$-C product evaluated against ANLCC100 and ANLCC125, as above
- TiO$_2$-C/ANLCC125 – anode limited; TiO$_2$-C/ANLCC100 – cathode limited
Li$_4$Ti$_5$O$_{12}$/xLi$_2$MnO$_3$•(1-x)LiMO$_2$ Cells

### Anode-limited

- Two formation cycles used to activate cathodes (C/11-C/16).
- Cells cycled 100 times at 8 to 16 times the formation rate.
- Anode-limited cells showed superior cycling stability. When discharged at ~C/1, the cathodes delivered ~175 mAh/g in anode-limited cells and >200 mAh/g in cathode-limited cells.

### Cathode-limited

- The data bode well for developing higher energy Li-ion cells than those offered by the Li$_4$Ti$_5$O$_{12}$/Li$_{1+x}$Mn$_{2-x}$O$_4$ ‘spinel-spinel’ system, without compromising too heavily on power.
**TiO\textsubscript{2}-C/xLi\textsubscript{2}MnO\textsubscript{3} \bullet (1-x)LiMO\textsubscript{2} Cells**

- Voltage profiles of TiO\textsubscript{2}-C/ANL-NMC cells are similar to Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12}/ANL-NMC cells.
- TiO\textsubscript{2}-C/ANL-NMC cells operate at slightly lower voltage because the TiO\textsubscript{2}-C anode has a higher redox potential (~1.8 V vs. Li\textsuperscript{0}) than Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} (~1.55 V vs. Li\textsuperscript{0}).
- Nanoparticulate TiO\textsubscript{2}-C anodes offer a higher rechargeable anode capacity (~200 mAh/g) compared to Li\textsubscript{4}Ti\textsubscript{5}O\textsubscript{12} cells.
- TiO\textsubscript{2}-C/xLi\textsubscript{2}MnO\textsubscript{3} \bullet (1-x)LiMO\textsubscript{2} cells show a steady capacity fade, attributed to the instability of the lithiated Li\textsubscript{x}TiO\textsubscript{2} (anatase) electrode structure at high lithium loadings (x>0.5). **Goal:** Design improved TiO\textsubscript{2}-based anode structures/architectures.
2. Autogenic Reactions

Autogenic Reactions: Self-generating reactions that occur within an enclosed vessel, typically at high pressure and temperature.

Product highly dependent on precursor and reaction conditions.

- Allyl triphenyltin \([\text{C}_{21}\text{H}_{20}\text{Sn}]\) at 700 °C and 450 psi (3 MPa) produces
  \[
  \text{Sn} (s) + \text{C} (s) + \text{H}_2 (g)
  \]
Synthesis and Properties of LiFePO₄

1) FeC₂O₄ precursor

LiH₂PO₄ + FeC₂O₄ $\xrightarrow{700 \, ^\circ\text{C}}$ 3h LiFePO₄ + C + gaseous product

- Despite apparent single-phase, spherical character of a nano-sized LiFePO₄ product (containing some carbon) from a FeC₂O₄ precursor, the olivine electrode displays very poor electrochemical behavior (<20 mAh/g) at a 0.08 mA/g rate.
**Synthesis and Properties of LiFePO₄**

2) **FePO₄ precursor**

\[ \text{Li}_2\text{CO}_3 + \text{FePO}_4\cdot\text{H}_2\text{O} + \text{C}_6\text{H}_{12}\text{O}_6 \; \text{(glucose)} \rightarrow \text{LiFePO}_4/\text{C} + \text{gaseous product} \]

- Significantly improved electrochemical behavior obtained from single-phase, nano-sized LiFePO₄ particles from a FePO₄ and glucose precursors, the carbon-coated product delivering 100-120 mAh/g at a 0.08 mA/g rate.
- Autogenic reactions to be pursued further in the search for advanced electrode materials and architectures.
3. Simulation of Atomic Structure and Properties of LiMn$_2$O$_4$ Surfaces

- Study motivated by the necessity to understand the surface stability of metal oxide cathodes at high potentials and implications for solubility
- Chemical and electrochemical reactions are sensitive to surface atomic structure, particularly coordination
- Focus on simulation of surface structure of LiMn$_2$O$_4$ ('GGA + U' level of density functional theory using VASP code)
- Consideration given to Mn- and MnO-terminated surfaces
- Classical-potential simulations of MgAl$_2$O$_4$ spinel have shown that the (001) surface is lowest in energy, followed by (110) and (111)
- Radical reconstruction is predicted for Mn-terminated (111) surface, in which the top layers mix to form a stoichiometric Li-Mn-O termination layer
- Surface reconstruction of (111) minimizes under-coordination of surface Mn, O
- Surface Mn ions are reduced
- Despite under-coordination of flat surfaces (terraces), dissolution may require additional defects, such as non-bridging O
Unreconstructed and Reconstructed (111) Surfaces
Features of Reconstructed LiMn$_2$O$_4$ Surfaces

- Under-coordination results in reduction of surface Mn ions, relative to bulk (see figure for reconstructed (111) slab)
- 3-fold coordinated Mn divalent at (110) surfaces
The presence of non-bridging oxygen greatly increases driving force for dissolution, i.e., energy gain for acid promoted dissolution reactions:

\[
\text{LiMn}_2\text{O}_4 + 2H^+ \rightarrow \{\text{LiMn}_2\text{O}_4-[\text{MnO}]\} + \text{Mn}^{2+} + \text{H}_2\text{O} \quad (1)
\]

\[
\{\text{LiMn}_2\text{O}_4-[\text{MnO}]\} + 2H^+ \rightarrow \{\text{LiMn}_2\text{O}_4-[\text{MnO, Li}_2\text{O}]\} + 2\text{Li}^+ + \text{H}_2\text{O} \quad (2)
\]
Future Work - FY2010/FY2011

- Continue to exploit and optimize $x\text{Li}_2\text{MnO}_3\bullet(1-x)\text{LiMO}_2$ electrodes (composition and performance) with the particular goal of reaching or exceeding the energy and power goals required for 40-mile PHEVs and EVs.
- Focus on surface studies: phosphates and fluorides – use complementary experimental and theoretical approaches to improve the surface stability, rate capability and cycle life of high capacity Mn-rich oxide electrodes at high potentials.
- Exploit highly versatile, autogenic synthesis technique to fabricate and evaluate novel electrode materials and coating architectures, e.g., high capacity TiO$_2$ anodes coupled to high capacity Mn-based cathodes for safe Li-ion cells.
- Pursue interactions with energy storage EFRCs.
Further progress was made to stabilize the surface, and improve the rate capability and cycle life of high-capacity $x\text{Li}_2\text{MnO}_3\bullet(1-x)\text{LiMO}_2$ electrodes ($M=$Mn, Ni, Co) when charged to high potentials (>4.5 V).

$x\text{Li}_2\text{MnO}_3\bullet(1-x)\text{LiMO}_2$ electrode materials have the attention of industry – collaborations are in place with materials manufacturers worldwide.

$\text{Li}_{3-2x}\text{Ni}_x\text{PO}_4$ coatings ($0<x\leq1$) improve the rate capability (200 mAh/g at C/1) and cycling efficiency ($\sim100\%$) at room temperature; charged, coated electrodes generate less heat when reacted with electrolyte at elevated temperature.

Autogenic reactions have been used to prepare carbon-coated electrodes in a single step – this versatile technique holds promise for fabricating electrode advanced materials (cathodes and anodes) with modified morphologies and electrochemical properties.

Simulation of Mn- and MnO terminated surface structures of LiMn$_2$O$_4$ has provided insight into atomic coordination and Mn oxidation state that impact solubility.

Acknowledgment
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