Layered Cathode Materials

presented by

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Overview

Timeline
• Start date: FY08
• End date: On-going
• Percent complete: - project on-going

Budget
• Total project funding
  - 100% DOE
• FY08: $300K
• FY09: $300K
• FY10: $400K

Barriers Addressed
• Low energy
• Cost
• Abuse tolerance limitations

Partners
• Co-investigators:
  - S.-H. Kang, C. Lopez Rivera, R. Benedek, C. Johnson (Argonne)
• Collaborators:
  - C. Grey, J. Cabana (SUNY – SB)
  - X.-Q. Yang (BNL)
  - C. Wolverton, D. Shin (NU)
  - Primet Precision Materials
Objectives

- Design high capacity, high-power and low cost cathodes for PHEVs and EVs
  - Improve the design, composition and performance of Mn-based cathodes
  - Use theoretical modeling as a guide to identify, design and understand the electrochemical properties of novel cathode structures
Milestones (FY08-09)

- Synthesize, evaluate and optimize high capacity Mn-based cathodes (>200 mAh/g, >3 V) – on going

- Enhance surface and cycling stability at high potentials (>4.2 V) – on going

- Model interfacial structures and dissolution phenomena – on going

- Determine electrochemical properties of blended xLi$_2$MnO$_3$$\bullet$(1-x)LiMO$_2$ and spinel electrodes – on going

- Explore new materials and processes, including phosphates – on going
Approach

- Exploit the concept and optimize the performance of structurally-integrated, high-capacity electrodes such as 'layered-layered' $x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2$ ($M=\text{Mn, Ni, Co}$) and 'layered-spinel' $y[\text{xLi}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2] \cdot (1-y)\text{Li}_{1+z}\text{Mn}_{2-z}\text{O}_4$ electrodes.

- Extend the concept of using integrated bulk electrode structures to surface structures that protect the underlying metal oxide particles from the electrolyte, when charged (delithiated) at high potentials.

- Use computational modeling to aid the design of bulk and surface cathode structures and to understand electrochemical properties.
xLi$_2$MnO$_3$•(1-x)LiMO$_2$ Electrodes (Recap)

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

- Keep Li$_2$MnO$_3$ content as low as possible to maximize capacity

- Li/0.3Li$_2$MnO$_3$•0.7LiMn$_{0.5}$Ni$_{0.5}$O$_2$

200-250 mAh/g achievable from high Mn-content electrodes at C/3 rate (50 °C)

**Disadvantage:** Lower capacity at RT

Large irreversible capacity loss on initial cycle (Li$_2$O removal from Li$_2$MnO$_3$)
The Challenge of Surface Stabilization

- Charging high-capacity $x\text{Li}_2\text{MnO}_3\bullet(1-x)\text{LiMO}_2$ electrodes to a high potential (>4.4 V) damages the electrode surface and reduces the rate capability of the electrode:
  
  \[
  \begin{align*}
  (1) \text{LiMO}_2 & \rightarrow \text{MO}_{2-\delta} + \text{Li}^+ + \frac{\delta}{2} \text{O}_2 + (1+2\delta)e \\
  (2) \text{Li}_2\text{MnO}_3 & \rightarrow \text{MnO}_2 + 2 \text{Li}^+ + \text{O}_2 + 2e 
  \end{align*}
  \]

- Oxygen loss, particularly through process (1), increases M cation concentration at the electrode surface that restricts Li diffusion and rate capability?
  \[
  \Rightarrow \text{Li}_x\text{Ni}_{1-x}\text{O} \text{ rock salt structure at surface of Li}_{1-x}\text{Ni}_{0.80}\text{Co}_{0.15}\text{Al}_{0.05}\text{O}_2
  \]

- **How does one prevent corrosion and cation disorder at the surface to allow high rate discharge and charge?**
Fluoride- vs. Phosphate Stabilized Surfaces

- Fluorination of layered LiMn$_{0.33}$Ni$_{0.33}$Co$_{0.33}$O$_2$ and xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrodes improves cycling stability and rate, notably at 50 °C (Sun, Amine)

- F$^-$ ions within the bulk or at the surface?

- Fluorination with mildly acidic solutions (~2.5 x 10$^{-3}$ M; pH ≈ 6.0 - 6.5) stabilizes electrode surface at 4.6 V and improves rate capability (BATT Review 2008).

- AlPO$_4$ coatings improve cycling stability of LiCoO$_2$ and xLi$_2$MnO$_3$•(1-x)LiMO$_2$ electrodes (Cho, Manthiram)

- Improvement in the rate capability of xLi$_2$MnO$_3$•(1-x)LiMO$_2$ high-capacity electrodes particularly at room temperature is still required to meet the 40-mile range battery requirement for PHEVs.

Integrated Olivine-Spinel Structures/Surfaces?

- Olivine (LiFePO_4) and Spinel (LiMn_2O_4) both have AB_2O_4 formulae with the A cations in tetrahedral sites and the B cations in octahedral sites.
- In LiFePO_4, the P cations are in tetrahedral sites.
- In LiMn_2O_4, the Li cations are in tetrahedral sites.
- Olivine has a hexagonally close packed structure.
- Spinel has a cubic close packed structure.
- Relatively small difference in the d-spacings of the close-packed layers in LiFePO_4 and LiMn_2O_4.
  - Can we synthesize ‘olivine-spinel’ composite structures, ‘olivine-layered’ structures or other close-packed phosphate structures to stabilize spinel and layered metal oxide bulk structures and/or surfaces?
Hypothetical LiNiVO$_4$ Spinel – LiNiPO$_4$ Olivine Intergrowth

In principle, a spinel-olivine intergrowth structure seems possible.

- Experiment shows otherwise: CBED patterns and EDS signals (Ni/V or Ni/P) suggest that discrete olivine and spinel phases exist.
- Can Li-M-PO$_4$ films provide effective surface protection on metal oxides?
Li-M-PO$_4$ surface treatment (e.g., M=Ni)

(0.5Li$_2$MnO$_3$$\bullet$0.5LiNi$_{0.44}$Co$_{0.25}$Mn$_{0.31}$O$_2$ electrodes in Li half cells)

- Concept: Use Li-Ni-PO$_4$ as a solid electrolyte below 5.0 V to protect surface of xLi$_2$MnO$_3$$\bullet$(1-x)LiMO$_2$ electrode at high potentials
- Sol-gel treatment technique used
- Olivine LiNiPO$_4$ or defect Li$_3$PO$_4$, e.g., Li$_{3-2x}$Ni$_x$PO$_4$?
- Theoretical modeling of surface structures initiated (Shin, Wolverton)

Treated electrodes meet the 200 mAh/g, C/1 rate, 3.5 V average, capacity/power yardstick for a 40-mile range PHEV at room temperature
Cycling Stability at Various C Rates (mA/cm²)
(0.5Li₂MnO₃•0.5LiNi₀.44Co₀.25Mn₀.31O₂ electrodes in Li half cells)

- Li-Ni-PO₄-treated electrodes show stable cycling at various rates
- Surface-treated electrodes show superior cycling efficiency
  ⇒ suppression of electrode-electrolyte reactions at 4.6 V?
Cycling stability of a Li$^+$-ion cell
(Li-Ni-PO$_4$ treated 0.5Li$_2$MnO$_3$$\bullet$0.5LiNi$_{0.44}$Co$_{0.25}$Mn$_{0.31}$O$_2$ electrode)

- Li-ion cell data (MAG-10 anode) validate the half-cell data
- The electrodes deliver 225 mAh/g at a C/2 rate at RT
- Compositional and electrochemical performance optimization in progress
Other Applications: $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMnO}_2$ Electrodes

- The utility of $x\text{Li}_2\text{MnO}_3 \bullet (1-x)\text{LiMnO}_2$ cathodes was demonstrated in other Li-ion cell configurations:
  - blended with spinel to compensate for rate limitations (Commercialized; U.S. Pat. 7,303,840 (2007)).
  - with $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anodes in 3.0-2.0 V cells

\[ \text{Li}_4\text{Ti}_5\text{O}_{12}/\text{Li}_{1.05}(\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3})_{0.95}\text{O}_2 \] Cell

- 190-200 mAh/g from $0.1\text{Li}_2\text{MnO}_3 \bullet 0.9\text{LiMn}_{0.256}\text{Ni}_{0.372}\text{Co}_{0.372}\text{O}_2$
- 240 mAh/g from $0.5\text{Li}_2\text{MnO}_3 \bullet 0.5\text{LiMn}_{0.31}\text{Ni}_{0.44}\text{Co}_{0.25}\text{O}_2$ (fluorinated)
Theoretical Modeling of Surface Structures and Electrochemical Phenomena

- Studies motivated by the necessity to understand solubility of metal oxide cathodes and their instability at high potentials
- Initial studies on H\(^+\)-Li\(^+\) ion exchange phenomena in LiCoO\(_2\) (BATT Review 2008)
- Current studies on solubility and surface structure of LiMn\(_2\)O\(_4\)
- \(2 \text{LiMn}_2\text{O}_4 + 4 \text{H}^+ \rightarrow 3\lambda\text{MnO}_2 + \text{Mn}^{2+} + 2 \text{Li}^+ + 2 \text{H}_2\text{O}\) (Hunter, 1981)
  - Calculate *Hunter-dissolution-reaction* free energy
    - \(\Rightarrow\) Pourbaix-like phase diagram
  - Disproportionation reaction - *No bulk Mn\(^{2+}\), anion neglected*
  - Model LiMn\(_2\)O\(_4\) - (111) free surface atomic structure
  - Model LiMn\(_2\)O\(_4\) - (111)/H\(_2\)O interface structure (in progress)
Calculation of $\Delta G$ (Dissolution) for LiMn$_2$O$_4$

**Solids - GGA+U (VASP)**

$$G(T) = G_{static}(T = 0) + G_{vibrational}(T)$$

**Aqueous Ions**

$$G_{aq} = G_{atom}^{GGA} + G_{ionization}^{EXPT} + G_{hydration}^{EXPT}$$

- Calculated phase diagram consistent with experimentally observed solubility trends of Mn$^{3+}$ in acidic electrolytes (disproportionation) and in Zn/MnO$_2$ alkaline cells.
Modeling LiMn$_2$O$_4$ Surfaces

- Layers pure for (111) orientation:
  ... | 3Mn | 4O | Li | Mn | Li | 4O | ...

- Treat Mn-terminated slab (84 atoms)

- Slab dimensions ~ 12 x 10 x 25 Å

- Model surface reconstruction:
  Mn site occupancy = 0.5 on termination layers
Preliminary Conclusions:

- O atoms rearrange to encapsulate under-coordinated Mn ions
- Li atoms drawn in wake of O to maintain neutrality
  \[ \Rightarrow \] 3 top layers form “mixed” Li-Mn-O at free surface
- Mn coordination no. \(~4\) at Mn-terminated (111) free surface
- Mn coordination no. \(~5\) at (111) \(\text{LiMn}_2\text{O}_4 / \text{H}_2\text{O}\) interface
- Mn oxidation state \(~3+\) at free surface or \(\text{H}_2\text{O}\) interface
Future Work - FY2009/FY2010

- 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: fluorides, phosphates – use both experimental techniques and theoretical modeling that will lead to an improved stability and rate capability of metal oxide electrodes at high potentials – continue existing, unfinished thrusts in projects (surface structure analysis, modeling and prediction).

- Explore synthesis routes to fabricate novel cathode materials and architectures or improve existing ones. (New, proprietary technique shows promise).
Summary

- Progress was made in stabilizing the surface, and improving the rate capability of high-capacity \(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2\) electrodes (M=Mn, Ni, Co) when charged to a high potential (4.6 V).
- Rechargeable 200 mAh/g obtained at C/1 rate
- \(x\text{Li}_2\text{MnO}_3 \cdot (1-x)\text{LiMO}_2\) electrode materials are now also under investigation in the ABRT program and have the attention of industry
- The approach adopted opens the door to new stabilizing surface structures and for further performance improvements – future work.
- Theoretical modeling was used to complement experiment to understand, and provide direction for designing, stabilized surfaces – future work.
- Preliminary results show that a new (proprietary) synthesis technique shows promise for fabricating electrode materials with modified morphologies and electrochemical properties – future work.

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