Nanostructured Metal Oxide Anodes

A. C. Dillon (P.I.)
Ahmad Pesaran (Task Leader)
National Renewable Energy Laboratory, Golden
*University of Colorado, Boulder

Project ID:
es_35_dillon
Overview

Timeline

• October 1, 2007
• September 30, 2010
• 50% complete

Budget

• Total project funding
  FY08: $250K, FY09: $350K
Project lead: Anne Dillon

Barriers

– Cost: developing metal oxide based anodes from abundant, inexpensive metals
– Energy density: improvements in both gravimetric and volumetric energy densities have been demonstrated
– Safety: Anodes operate at higher potential relative to Li metal than graphite, eliminating the risk of Li plating
– Lifetime: Durable and reversible cycling has been achieved

Partners

• M.M. Thackeray and S-H. Kang, Argonne
• M.S. Whittingham, SUNY-Binghamton
• A. Greenshields, fortu
• S-H. Lee, Univ. of Colorado
• S.M. George, Univ. of Colorado
Objectives

The ultimate goal of this activity is to develop optimized metal oxide nanostructured electrode materials to enable high-performance, durable, and affordable Li-ion batteries for power-assist HEVs and PHEVs that meet the DOE/FreedomCAR targets.

- Optimize MoO$_3$ nanoparticle electrodes in coin cell configuration and compare to previous results for electrophoresis deposited thin film MoO$_3$ electrodes.
- Demonstrate a full cell with an MoO$_3$ anode and state-of-the-art cathode with a high energy density and stable cycling performance.
- Employ first principles calculations to obtain better understanding of Li-insertion processes and for the prediction of new materials.
- Synthesize MoO$_2$ nanoparticles to test theoretical prediction that Li will be extracted at a lower potential (~1 V).
- Explore possibility of other metal oxide nanostructures made from even less expensive starting materials.
Milestones

• Sept 2008-report on optimization of MoO$_3$ thick electrodes tested in a coin cell configuration, complete. (In this report a reversible capacity of ~ 1050 mAh/g was demonstrated with good cycling and rate capability. This high capacity represents a 60% improvement compared to the thin film MoO$_3$ electrodes, 630 mAh/g)

• July 2009-report on optimization of MoO$_3$ anodes in a full cell with cathodes supplied by ANL. (Full cell data for the MoO$_3$ anodes coupled with both Li$_{1.05}$M$_{0.95}$O$_2$, $M = \text{Ni}_{1/3}, \text{Co}_{1/3}, \text{Mn}_{1/3}$ and the state-of-the-art lithium rich cathode 0.5Li$_2$MnO$_3$0.5Li(Mn$_{0.31}$Ni$_{0.44}$Co$_{0.25}$)O$_2$ is presented here.)
Approach

- MoO$_3$ nanoparticles (nano-rods and nanospheroides) are produced using hot-wire chemical vapor deposition (HWCVD) at different reactor pressures.

- Thin film battery electrodes (2-3 µm) have been fabricated with novel electrophoresis.

- Thick film electrodes (~35 µm) for coin cell testing have been optimized versus a Li counter electrode by varying: binder/conductive additive composition and electrode pretreatment.

- Full cell has been also optimized with ANL cathodes.

Previously Reported
Thin Film Electrodes by Novel Electrophoresis

- Porous thin film without binder or conductive additive obtained after electrophoresis.
- Improved durable capacity (~ 630 mAh/g) found when using the thin film as anode and cycling between 3.0- 0.005 V.

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Technical Accomplishments
Varying the Ratio of AB : PVDF

- Polymer rich electrodes provide continuous adhesion through the film.
- Maximum cycling capacity of ~1050 mAh/g (theoretical 1170 mAh/g) achieved at a ratio of 70:10:20 (MoO$_3$;AB: PVDF).
Technical Accomplishments

Variation in Pre-heat Treatment

- Highly improved capacity of 1050 mAh/g is achieved by using a ratio of 70:10:20 and pre-heating at 250 °C.
- Electrical resistance steadily decreases with increase of temperature.
- Decreased capacity at 300 °C likely due to the binder breakdown and isolation of certain particle clusters.
Water desorption from the electrode observed at a high temperature (> 200 °C).

CO₂ species are also observed at a higher temperature perhaps due to oxidation of the acetylene black.

Polymer decomposition observed at a surprising low temperature (300°C).

Early decomposition may be catalyzed by nanostructured MoO₃.
H₂O/OH originated from acetylene black, PVDF and NMP solvent.
Weakly bound water removed by pre-heat treatment.
Presence of bound water is one reason for irreversibility in cycling without pre-heating treatment.

Results confirmed by Infrared Spectroscopy (IR)

Technical Accomplishments
Explanation of Pre-heat Requirements
Technical Accomplishment
Nano-sized Li$_x$MoO$_3$ : Displacement redox reaction?

Displacement redox reaction* for MoO$_3$ nanoparticles:

$$\text{MoO}_3 + 6\text{Li}^+ + 6\text{e} \leftrightarrow 3\text{Li}_2\text{O} + \text{Mo}$$

$$6\text{Li} \leftrightarrow 6\text{Li}^+ + 6\text{e}$$

$$\text{MoO}_3 + 6\text{Li} \leftrightarrow 3\text{Li}_2\text{O} + \text{Mo}$$

What is size distribution of Mo clusters?

First-principles molecular dynamics (FPMD)

- $(\text{Li}_4\text{MoO}_3)_{36}$ & $(\text{Li}_6\text{MoO}_3)_{36}$
- Start from uniformly lithiated alpha phase of MoO$_3$
- $T = 600$ K (to speed up the MD simulations)
- VASP code

Technical Accomplishments
FPMD simulations for Li$_x$MoO$_3$ nanoparticles ($x = 4, 6$)

<table>
<thead>
<tr>
<th>Mo$_n$</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
<th>6</th>
<th>7</th>
<th>8</th>
<th>9</th>
</tr>
</thead>
<tbody>
<tr>
<td>(Li$_4$MoO$<em>3$)$</em>{36}$</td>
<td>4</td>
<td>1</td>
<td>3</td>
<td>4</td>
<td>1</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>(Li$_6$MoO$<em>3$)$</em>{36}$</td>
<td>-</td>
<td>6</td>
<td>-</td>
<td>2</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
<td>1</td>
</tr>
</tbody>
</table>

Small clusters of Mo$_n$ are easily formed within the nanoparticle.

The size $n$ of the Mo cluster ranges from 2 to 9. The Mo nanoclusters are small enough to enable reversible Li insertion/desertion.

Our theoretical results support a displacement redox reaction which involves the formation and decomposition of metal nanoclusters.
Technical Accomplishments

*In Situ* Raman Showing Disordered Structure after Cycles

*In situ* Raman confirms significant loss in structural order in first insertion cycle consistent with molecular dynamics simulations.
• Full cell capacity of ~80 mAh/g achieved when cycling between 4.0-1.0 V by coupling with Gen 2 cathode obtained from M. Thackeray and S-H. Kang (ANL).
• The coin cell contains 13 mg cathode material and 1.7 mg anode material.
• In the full cell MoO$_3$ has a reversible capacity of ~677 mAh/g and the cathode capacity is 90 mAh/g.
Technical Accomplishments
Full Cell Testing Using ANL Cathode

- Stable capacity of 140 mAh/g (commercial capacity: ~80 mAh/g) when cycling the coin cell between 4.0-0.01 V by coupling with lithium rich cathode, 0.5Li₂MnO₃0.5Li(Mnₐ.₃1Ni₀.₄₄Co₀.₃₅)O₂ from M. Thackeray and S-H. Kang at Argonne.
- Cell contains 7.4 mg cathode material and 1.6 mg anode material.
- MoO₃ has a reversible capacity of ~ 776 mAh/g and cathode capacity is 170 mAh/g.¹⁵
• Previously theoretical predictions indicated crystalline MoO₂ would have a lower lithium extraction potential.
• Nano-MoO₂ was produced by the modified HWCVD process.
• However, upon cycling a thin film of the MoO₂ material, the voltage profile was not significantly different from that of MoO₃.
• The discrepancy with the theory may be attributed to the fact that the nanoparticles become highly disordered upon cycling, with the calculations performed for crystals.
Technical Accomplishments
Durable Cycling at High Rate of C/2

• Improved cycling stability achieved by applying a thin atomic layer deposition (ALD) coating.
• ALD coating enables reversible capacity of ~910 mAh/g when cycled at C/2.
• Fe$_2$O$_3$ nanofibers (40-50 nm width) has been produced using hydrothermal process followed by post-heat at 300 °C.
• Fe$_3$O$_4$ nanoparticles (10-20 nm) obtained by using reducing agent in hydrothermal process.
• Iron oxides allow for a more economical system.
Recent Development
Oxygen Vacancy: WO₃, MoO₃, and Fe₂O₃

- Oxygen vacancy creates defect states near the conduction band of transition metal oxides such as WO₃, MoO₃, and Fe₂O₃.
- For sub-stoichiometric amorphous WO₃-x the conduction band is populated to a larger extent.
- The conduction band filling will lower the potential inserted Li.
- By creating oxygen vacancies and substoichiametric amorphous samples, we can reduce Li potentials of MoO₃ and Fe₂O₃ to make them more suitable anodes.
Recent Development
Atomic Layer Deposition (ALD) Improves Durability

ALD on LiCoO₂

ALD on Natural Graphite

Improved cycling stability achieved for both cathode and anode by applying a thin ALD coating. ALD coatings eliminate SEI and surface reactions that cause degradation.
Proposed FY 09 Future Work

• Optimize full cells with ANL cathodes to improve durable capacity and rate capability (July 2009 Milestone).

• Work with fortu (Switzerland) to develop high-voltage cell.

• Perform theoretical calculations to understand the hysteresis of the charge/discharge for the MoO₃ nanoparticles. Use theoretical calculations to predict composition and orientation of economical oxide nanoparticles with more desirable voltage profiles.

• Synthesis of alternative nanostructures made from abundant elements, such as Fe₂O₃, Fe₃O₄, and MnO₂ will be explored. Inexpensive synthesis routes—including HWCVD, hydrothermal techniques, and electrodeposition—will be employed.

• Apply a protective ALD coating on graphite nanoparticles to eliminate surface degradation mechanisms and improve rate capability.
Conclusions

- Capacity of MoO$_3$ anode has been increased to $\sim$ 1050 mAh/g by optimizing the coin cell configuration. TPD, TGA, and IR employed to facilitate these optimizations.
- Theoretical calculations were performed to explain the mechanism for the increased Li-insertion observed in the coin cell testing.
- The MoO$_3$ anode has been successfully paired with two Argonne cathodes: Li$_{1.05}$M$_{0.95}$O$_2$, M = Ni$_{1/3}$, Co$_{1/3}$, Mn$_{1/3}$ and the state-of-the-art lithium rich cathode 0.5Li$_2$MnO$_3$0.5Li(Mn$_{0.31}$Ni$_{0.44}$Co$_{0.25}$)O$_2$
- In-situ Raman capabilities, established this year, show that MoO$_3$ nanoparticles become highly disordered in the initial cycle.

<table>
<thead>
<tr>
<th></th>
<th>Gravimetric Capacity (mAh/g)</th>
<th>Volumetric Capacity (mAh/cm$^3$)</th>
<th>Full Cell Capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FY08</td>
<td>630</td>
<td>2200</td>
<td>--</td>
</tr>
<tr>
<td>FY09</td>
<td>1050</td>
<td>800</td>
<td>140</td>
</tr>
<tr>
<td>Commercial</td>
<td>350 (graphite)</td>
<td>770 (graphite)</td>
<td>80 (graphite/LiCoO$_2$)</td>
</tr>
</tbody>
</table>

(J.Power Sources 88, p.237, 2000)
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