Nanostructured Metal Oxide Anodes

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


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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
• A. Pesaran, NREL
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 = 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$ is presented here.)
MoO₃ 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.

Electrophoresis

Material slurry

Coin Cell

Previously Reported
Thin Film Electrodes by Novel Electrophoresis

- Porous thin film without binder or conductive additive obtained after electrophoresis.
- Improved durable capacity (~ 600 mAh/g) found when using the thin film as anode and cycling between 3.0-0.005 V.

- Slightly less reversible capacity initially reproduced in coin cell configuration with a ratio of 70:15:15 (active material: acetylene black: polyvinylidene fluoride).
- Better reversibility achieved by pre-heating the electrode at 250 °C:
  - ~ 600 mAh/g was observed at C/3;
  - ~ 400 mAh/g delivered at 2C.
Technical Accomplishments
Optimization by 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).
- Water desorption from the electrode observed at a high temperature (> 200 °C).
- CO\textsubscript{2} 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 MoO\textsubscript{3}.
Technical Accomplishments
Explanation of Pre-heat Requirements
Results confirmed by Infrared Spectroscopy (IR)

- $\text{H}_2\text{O}/\text{OH}$ 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.
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.
Technical Accomplishment
Nano-sized $\text{Li}_x\text{MoO}_3$ : Displacement redox reaction?

Displacement redox reaction* for $\text{MoO}_3$ 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 $\text{MoO}_3$
- $T = 600 \text{ K}$ (to speed up the MD simulations)
- VASP code

Small clusters of $\text{Mo}_n$ 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.
Technical Accomplishments

Full Cell Testing Using ANL Cathode

- 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).
- Cell contains 12 mg cathode material and 2.5 mg anode material.
- In the full cell MoO$_3$ has a reversible capacity of ~677 mAh/g
Technical Accomplishments

Full Cell Testing Using ANL Cathode

- Stable capacity of 140 mAh/g (commercial capacity: ~80 mAh/g) when cycling between 4.0-0.01 V at a constant capacity and coupled with lithium rich cathode (250mAh/g) obtained from M. Thackeray and S-H. Kang at Argonne.

- Cell contains 7.4 mg cathode material and 1.6 mg anode material.

- In the full cell MoO$_3$ has a reversible capacity of ~ 776 mAh/g.
Technical Accomplishments

HWCVD Production of Nano-MoO$_2$

XRD MoO$_2$

Voltage Profile

- Previously theoretical predictions indicated crystalline MoO$_2$ would have a lower lithium extraction potential.
- Nano-MoO$_2$ was produced by the modified HWCVD process.
- However, upon cycling a thin film of the MoO$_2$ material, the voltage profile was not significantly different from that of MoO$_3$.
- 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.
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.
• Oxygen vacancy creates defect states near the conduction band of transition metal oxides such as WO$_3$, MoO$_3$, and Fe$_2$O$_3$.
• For sub-stoichiometric amorphous WO$_{3-x}$ the conduction band is populated to a larger extent.
• The conduction band filling will lower the potential inserted Li.
• By creating oxygen vacancies and substoichimetric amorphous samples, we can reduce Li potentials of MoO$_3$ and Fe$_2$O$_3$ to make them more suitable anodes.
Recent Development
Atomic Layer Deposition (ALD) Improves Durability

Improved cyclability 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 oxides 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 ~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.

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


