High Capacity MoO$_3$ Nanoparticle Li-Ion Battery Anode

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Outline

• Purpose of work
• Barriers
• Approach
• Performance Measures and Accomplishments
• Technology Transfer
• Plans for Next Fiscal Year
• Summary
• Publications/Patents
**Purpose of Work:** Develop a high-energy Li-ion battery anode from an inexpensive, non-carbonaceous, benign material with improved rate capability. Techniques to fabricate the anode are low-cost and industrially scalable.

**Barriers:** Cost, Durability, Performance and Recyclability:

- **Cost**
  - Employing inexpensive metal oxide (MoO$_3$).
  - Production technique is a low energy, scalable process.

- **Durability**
  - High reversible capacity for nanostructured MoO$_3$ has been demonstrated.
  - Optimizing electrodes for vehicular applications.

- **Performance**
  - Rate capability is improved for nanoparticles.
  - Electrode fabrication must also be optimized.

- **Recyclability**
  - Mo is a non-toxic element.
Approach

- Bulk MoO$_3$ is a high-capacity Li-insertion compound but suffers from poor reversibility and slow kinetics.
- MoO$_3$ nanoparticles are made at high density with inexpensive hot wire chemical vapor deposition (HWCVD).
- Nanoparticle electrodes (2 µm thick) are shown to have high reversible capacity with good rate capability.
- Density functional theory (DFT) explains nanoscale phenomena.
- The HWCVD technique has been scaled-up such that properties in thicker electrodes may be optimized.
- Coin cell testing is employed for 100 µm thick films with MoO$_3$ nanoparticle active material revealing similar reversible capacity with diminished rate capability (further optimization required).
- In situ Raman spectroscopy has been employed to study structural degradation during cycling.
- Predictive DFT indicates MoO$_2$ nanoparticles will result in an anode with lower potential relative to Li/Li$^+$. 
Accomplishment/Status

Hot-Wire Chemical Vapor Deposition (HWCVD) for Metal Oxide Nanoparticle Synthesis

A.H. Mahan, P. A. Parilla, K.M. Jones and A.C. Dillon

The particles were initially made at a rate of ~ 200 mg/hr with inexpensive simple technique. Size and morphology are tailored by controlling reactor temperature or pressure, filament temperature and O\textsubscript{2} partial pressure in Ar.
Accomplishment/Status

New Lithium-ion Electrodes Using HWCVD Nanoparticles

MoO$_3$ nanoparticles

Electrophoresis

Porous nanoparticle film

A simple electrophoresis technique is employed to make high surface area porous electrodes with a thickness of ~2 µm. The density of the films is ~ 3.3 g/cm$^3$ compared to 4.7 g/cm$^3$ for the bulk. No binder required, hence all of the electrode is active material.

Accomplishment/Status

**MoO₃ Nanoparticle Anodes**

- Initial cycle is not fully reversible. Plateaus indicate structural change.
- Subsequent cycles show a capacity of 630 mAh/g with insignificant decay.

The thin film was cycled with cut off voltages between 3.0 - 0.005 V for 150 cycles with insignificant capacity fade. The potential at approximately 50% capacity is ~1.5 V.
Nanoparticles exhibit 630 mAh/g reversible capacity for 150 deep charge/discharge cycles at C/2 rate.

~500 mAh/g is delivered at 2C rate (corresponding to one complete charge or discharge in one-half hour).

The 5μm sized particles are shown to fail after several cycles even with conductive additive employed for electrode fabrication. However, nanoparticle films show a reversible capacity that is higher than graphite with excellent rate capabilities.
Accomplishment/Status

Mechanistic Understanding...

*From voltage composition trace*

\[ \text{MoO}_3 + 4.4 (\text{Li}^+ + \text{e}^-) \rightarrow \text{LiMoO}_3 + \]

Reversible

- X-ray diffraction reveals a broad peak consistent with ~10% lattice expansion that results in ~173% volume expansion.

The dominant XRD peak has a broad maximum between 0.41 and 0.45 nm d-spacing and has a significantly larger d-spacing than the stronger XRD peaks in \( \alpha \)-MoO\(_3\) (~0.33 and 0.38 nm), consistent with ~173% volume expansion.
Accomplishment/Status

Theoretical Capabilities Provide Insight

State-of-the-art First Principles Molecular Dynamics Calculations

• Capable of performing dynamic calculations with hundreds of atoms.

• Generation of molecular movement at the fs timescale is resolved.

• Energetics may be calculated at atomistic level within large systems.

(SIESTA code with norm-conserving pseudopotentials for first-principles molecular dynamics simulation and energetics [J. M. Soler et al, J. Phys.: Condens. Matter 14, 2745-2779 (2002)]; Simulation temperature is 400 K, for enhanced dynamics, controlled by the Nose thermostat; The minimal basis set (SZ) and Ceperley-Alder exchange-correlation energy functional were employed.)

Dr. Yong-Hyun Kim: in house theorist working side-by-side with experimentalists to both understand mechanisms and predict new promising electrode materials.
Accomplishment/Status

**Theoretical changes in Li-ion intercalated α-MoO$_3$**

- Four Li inserted in a theoretical nanoparticle.
- 9 ps of simulation
- Primarily the Li and O atoms are disordered with the heavier Mo atoms maintaining a stable framework, reminiscent of the initial α-phase.
- The Li-insertion causes significant expansion.

The theoretical nanoparticle containing the irreversibly inserted Li$^+$ has dimensions of 19.2x15.7x17.1 Å$^3$, corresponding to ~174 % volume expansion, compared to pristine MoO$_3$ nanoparticles. 15.1x14.4x13.6 Å.
Theoretical Atomistic Energetics

Loosely bound Li

Intermediately bound Li

Li inserted irreversibly

The Li that is inserted irreversibly interacts with three oxygen atoms. The reversible Li interact with either one (loosely bound) or two (intermediately bound) oxygen atoms.
Accomplishment/Status

Scale-up of MoO$_3$ Production

Multiple Filaments Running Simultaneously

Uniform Particle Size Distribution Not Achieved

Optimized Temperature Occurs with < 100 W

To ensure small particles it is best to operate a single filament in the small 2” diameter chamber. At an optimized filament temperature corresponding to < 100 W for power output, uniform nanoparticles are made at ~1 g / hr. By scaling the size of the chamber, a high throughput inexpensive process may be achieved.
Accomplishment/Status

Coin Cell Testing at University of Colorado

Slurry

Active material: acetylene black: PVDF 70:15:15

Mechanical spreader

~100 µm thick films

Press
Accomplishment/Status

Coin Cell Data, 100 µm film

Reversibility capacity similar to thin film.

High reversible capacity is reproduced for the 100 µm thick films in coin cell testing. The rate capability is slightly less the thick electrodes indicating electrode fabrication is not optimized.

Rate capability is ~ 400 mAh/g at 2C.
Accomplishment/Status

New *In situ* Raman Capabilities

*In situ* Raman confirms significant loss in structural order in first insertion cycle consistent with both experimental data and molecular dynamics simulations.

*In situ* Raman has been set-up to analyze structural changes to electrode materials during electrochemical cycling.
Predictive Theory Employed to Identify a MoO$_2$ Nanoparticle with a Lower Discharge Potential

LiMoO$_3$ (α-phase)
Li Chem. Potential = 2.3 V
Volume expansion: 0%

LiMoO$_3$ (β-phase)
Li Chem. Potential = 2.4 V
Volume expansion: 3%

LiMoO$_2$ (rutile)
Li Chem. Potential: 1.1 V
Volume expansion: 12%

<table>
<thead>
<tr>
<th>Anode Properties</th>
<th>MoO$_3$</th>
<th>MoO$_2$</th>
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</thead>
<tbody>
<tr>
<td>Theoretical maximum</td>
<td>6Li (1120 mAh/g)</td>
<td>4Li (840 mAh/g)</td>
</tr>
<tr>
<td>Experimental capacity</td>
<td>3.4Li (630 mAh/g)</td>
<td>3Li (630 mAh/g), 2Li(420 mAh/g)</td>
</tr>
<tr>
<td>Average voltage</td>
<td>1.5 V</td>
<td>&lt; 1 V</td>
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Density functional theory indicates that MoO$_2$ nanoparticles are promising for an anode material with a lower potential relative to Li/Li$^+$. 
Technology Transfer

• NDA with commercial Li-ion battery is in place.
• Large batch of MoO$_3$ nanoparticles has been sent.
• The MoO$_3$ nanoparticles will be tested with a commercial cathode.
FY08 Future Work

- Optimize electrode for coin cell testing
  - Employ different ratios of active material, conductive additive and binder.
  - Employ different conductive additives and pretreatment processes.
  - Employ *insitu* spectroscopy to monitor breakdown mechanisms.
- Assemble and optimize an MoO$_3$ anode cell with a state-of-the-art cathode.
- Work with industrial partner interested in testing our MoO$_3$ anode.
- Continue molecular dynamics studies
  - Employ predictive theory to explore failure modes
  - Continue to predict new optimized materials.
- Employ HWCVD to generate MoO$_2$ nanoparticles.
  - MoO$_2$ species have already been detected under certain synthesis conditions. The synthesis process may be tailored to generate nanoparticle enriched with MoO$_2$ species.
  - Electrochemical properties of these species will be explored.
- NREL funding has been obtained to purchase a glovebox combination sputter evaporator system that will be used for pre-lithiation.
Summary

• MoO$_3$ nanoparticle electrodes fabricated with electrophoresis are shown to have a reversible capacity of 630 mAh/g, delivering ~ 500 mAh/g at 2C rate (2 µm thick).
• Density functional theory (DFT) explains the atomistic nanoscale mechanism and confirms experimental structural changes.
• The nanoparticles are made with an inexpensive HWCVD technique has been scaled-up such that properties in thicker electrodes may be optimized.
• Coin cell testing has been performed through collaboration with the University of Colorado.
• Coin cell testing, employed for 100 µm thick films with 70% MoO$_3$ nanoparticle active material, reveals the same high reversible capacity as the thin film electrodes with only slightly diminished rate capability. (Further optimization required).
• In situ Raman spectroscopy has been demonstrated to study structural degradation during cycling.
• Predictive DFT indicates MoO$_2$ nanoparticles will result in an anode with lower potential relative to Li/Li$^+$. 
• By modifying the HWCVD synthesis conditions it may be possible to produce MoO$_2$ nanoparticles.
Publications, Patents, Visibility

• **Publications**

• **Patents**

• **Visibility**

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