National Renewable Energy Laboratory

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Office of Energy Efficiency & Renewable Energy

Innovation for Our Energy Future

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:

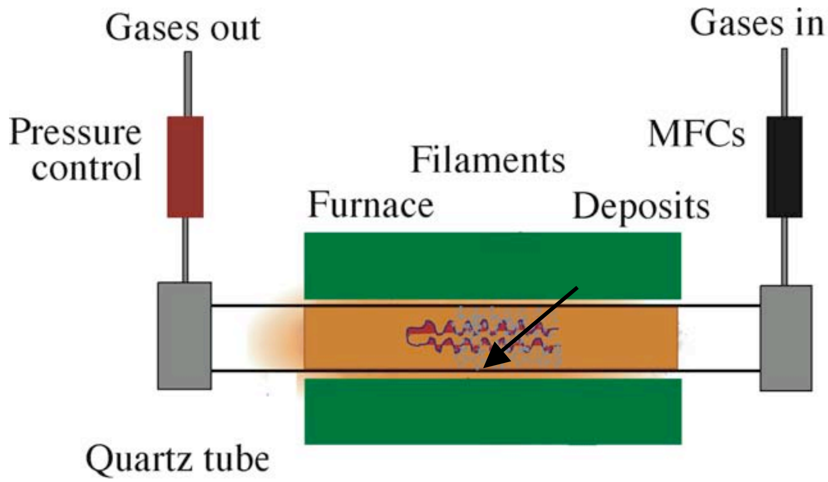
- Cost
  - Employing inexpensive metal oxide (MoO_3).
  - Production technique is a low energy, scalable process.
- Durability
  - High reversible capacity for nanostructured MoO_3 has been demonstrated.
  - Optimizing electrodes for vehicular applications.
- Performance
  - Rate capability is improved for nanoparticles.
  - Electrode fabrication must also be optimized.
- Recyclability
  - Mo is a non-toxic element.

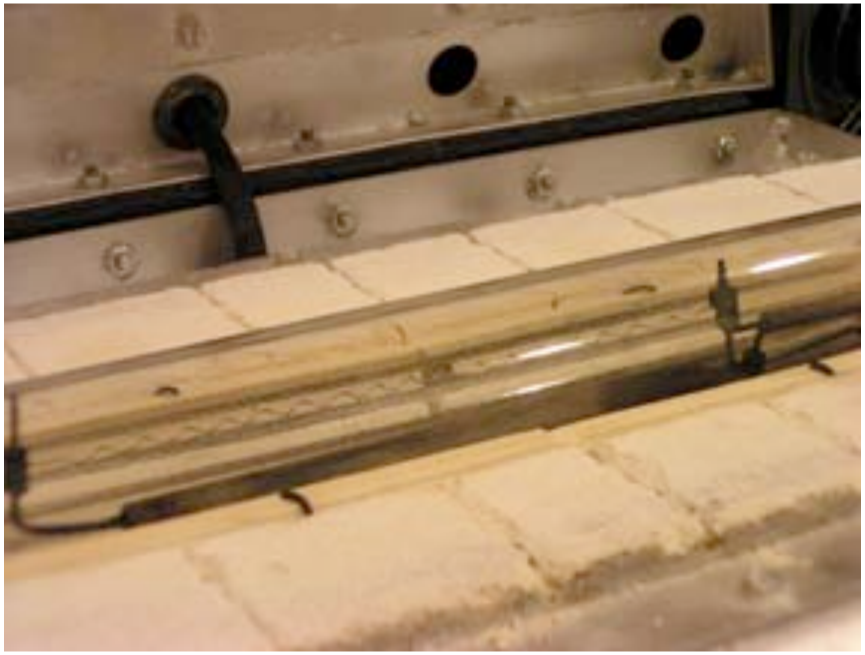
Approach

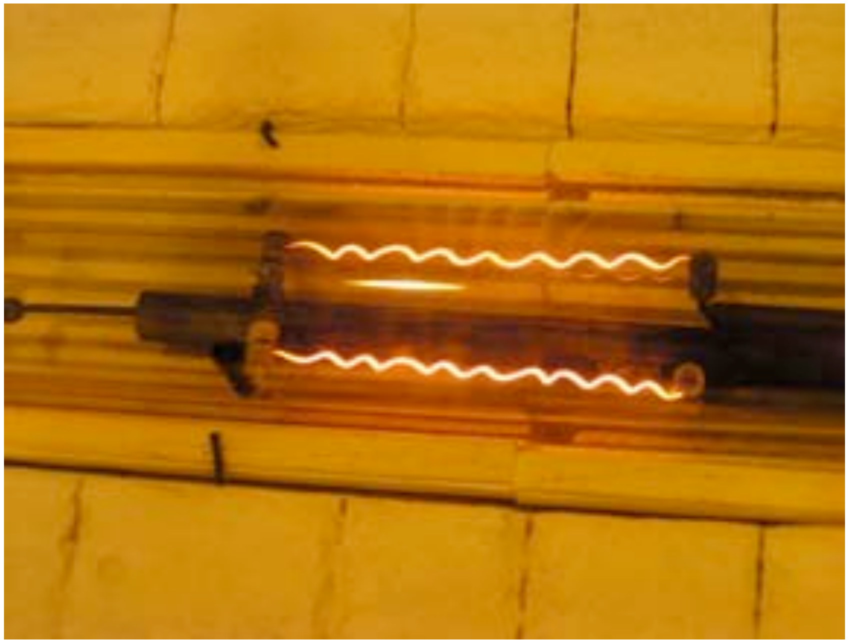
- Bulk MoO_3 is a high-capacity Li-insertion compound but suffers from poor reversibility and slow kinetics.
- MoO_3 nanoparticles are made at high density with inexpensive hot wire chemical vapor deposition (HWCVD).
- Nanoparticle electrodes (2 μm thick) are shown to have high reversible capacity with 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







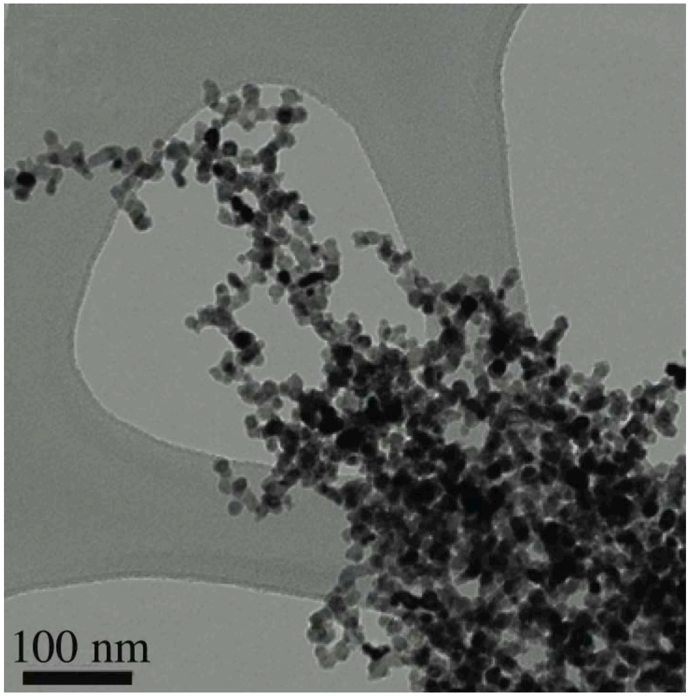
A.H. Mahan, P. A. Parilla, K.M. Jones and A.C. Dillon *Chem. Phys. Lett.* 413 (2005) 88.

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_2 partial pressure in Ar.

Accomplishment/Status

New Lithium-ion Electrodes Using HWCVD Nanoparticles

MoO_3 nanoparticles

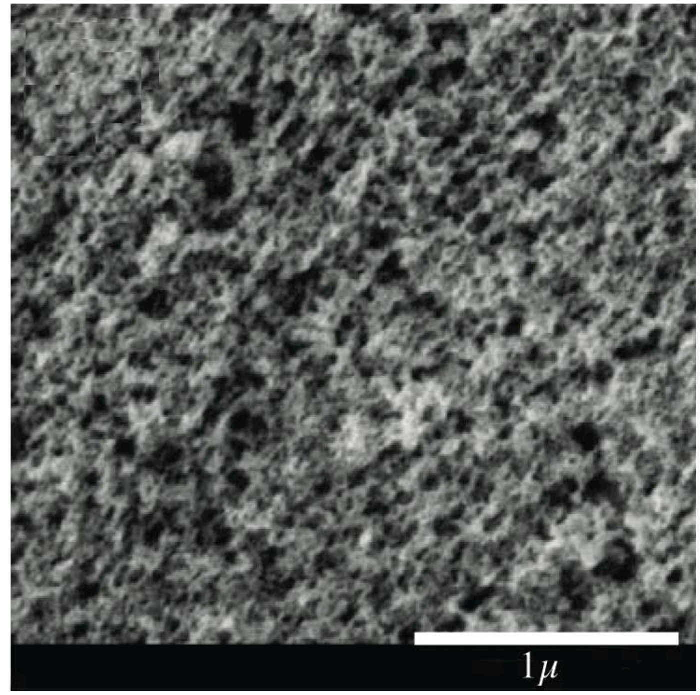


TEM

Electrophoresis

Electrode

Porous nanoparticle film



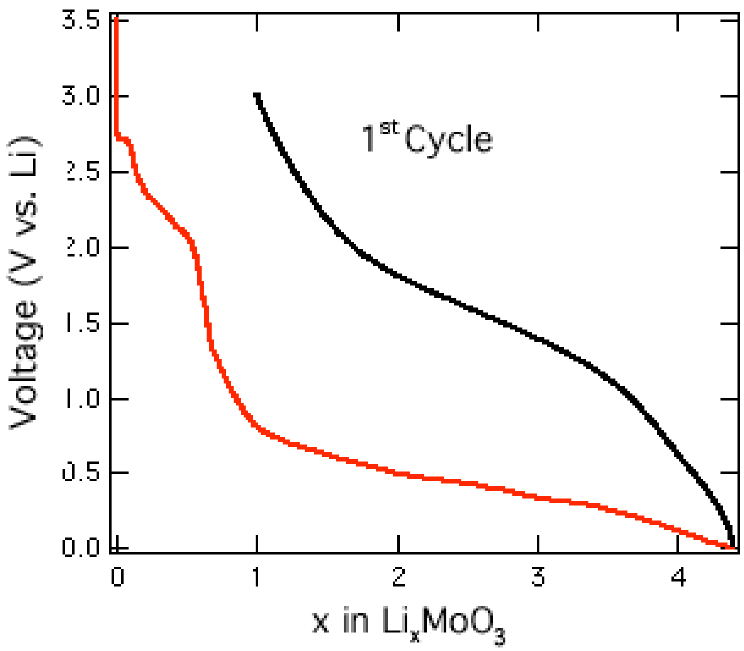
SEM

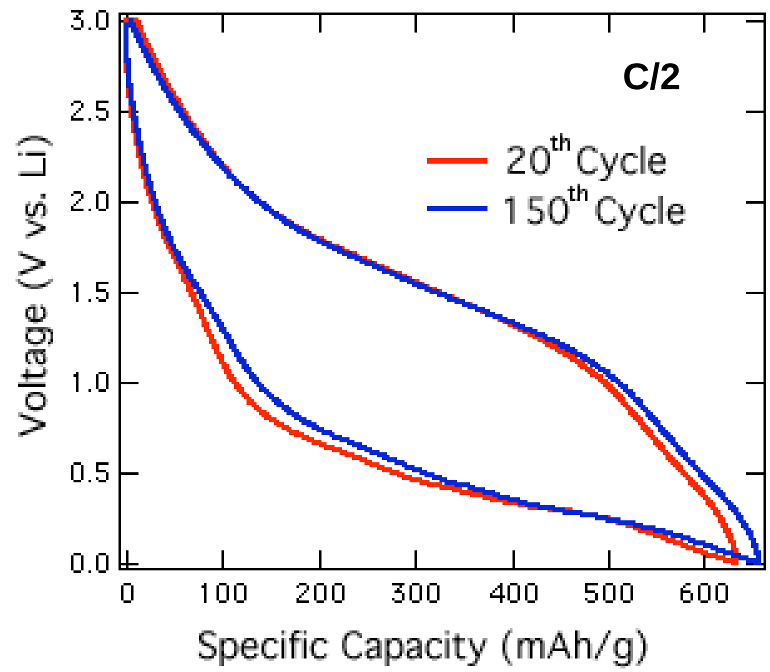
A simple electrophoresis technique is employed to make high surface area porous electrodes with a thickness of ~2 μm. The density of the films is ~ 3.3 g/cm^3 compared to 4.7 g/cm^3 for the bulk. No binder required, hence all of the electrode is active material.

S-H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, B.To, A.H. Mahan, A.C. Dillon, *Advanced Materials* 18 (2006) 763.

Accomplishment/Status

MoO_3 Nanoparticle Anodes





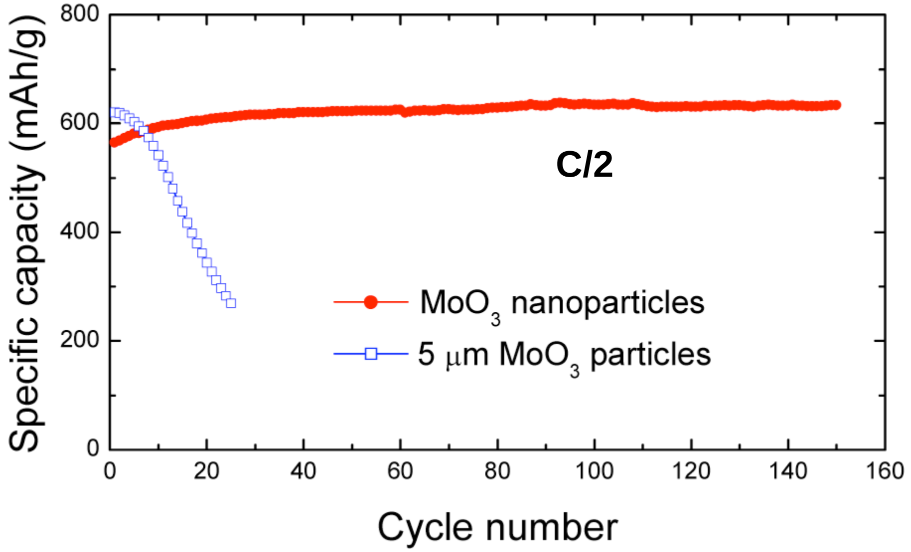
- **Initial cycle is not fully reversible. Plateaus indicate structural change.**

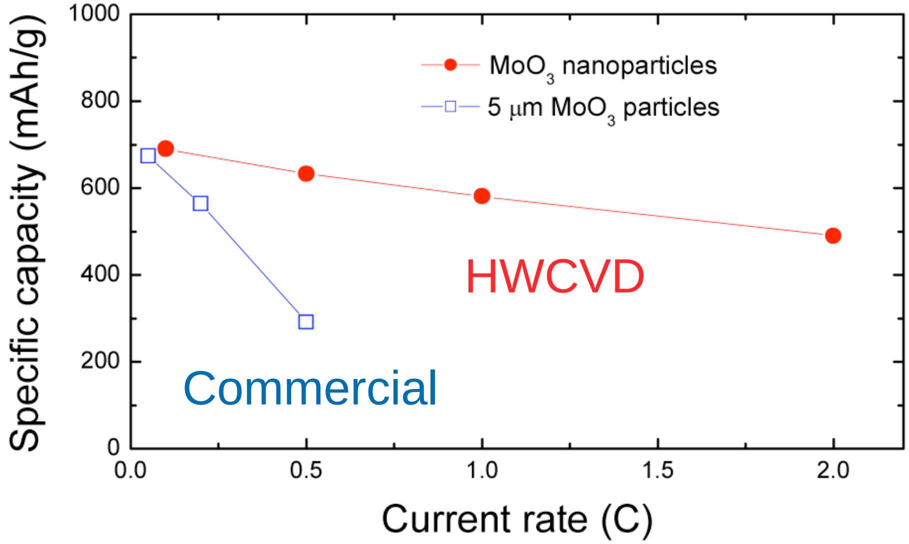
- **Subsequent cycles show a capacity of 630 mAh/g with insignificant decay.**

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.

Accomplishment/Status

Improved Durable Capacity and Rate





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.

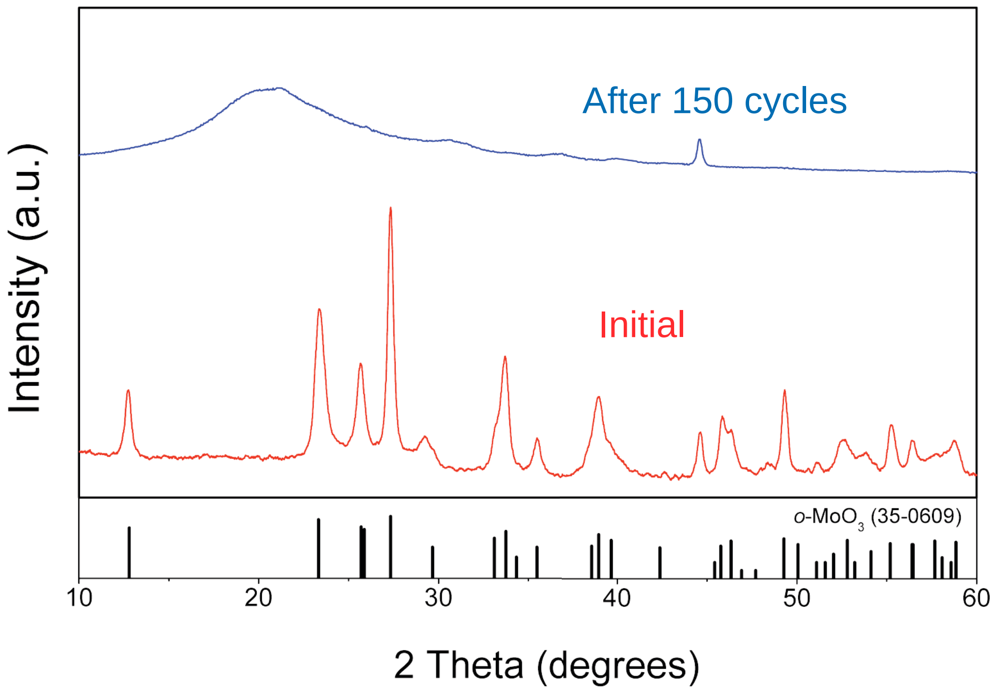
Accomplishment/Status

Mechanistic Understanding…

From voltage composition trace

$$MoO_3 + 4.4\ (Li^+ + e^-) \longrightarrow LiMoO_3 + \bigcirc$$

Reversible



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

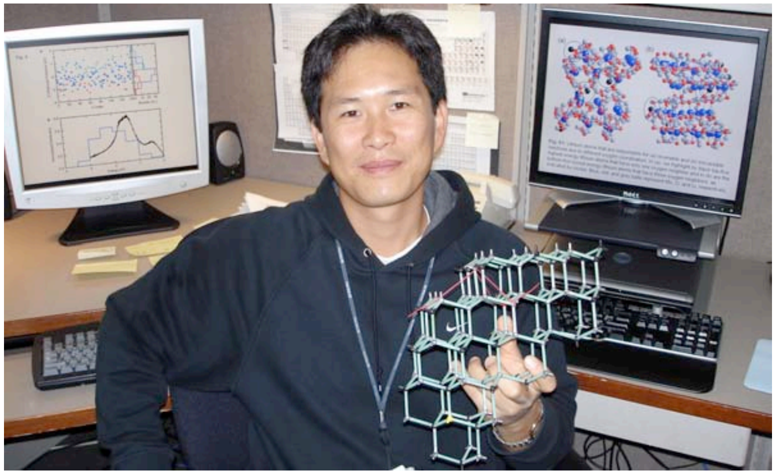
The dominant XRD peak has a broad maximum between 0.41 and 0.45 nm d-spacing and has a significantly larger d-spacing than the stronger XRD peaks in α-MoO_3 (~0.33 and 0.38 nm), consistent with ~ 173% volume expansion.

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.**

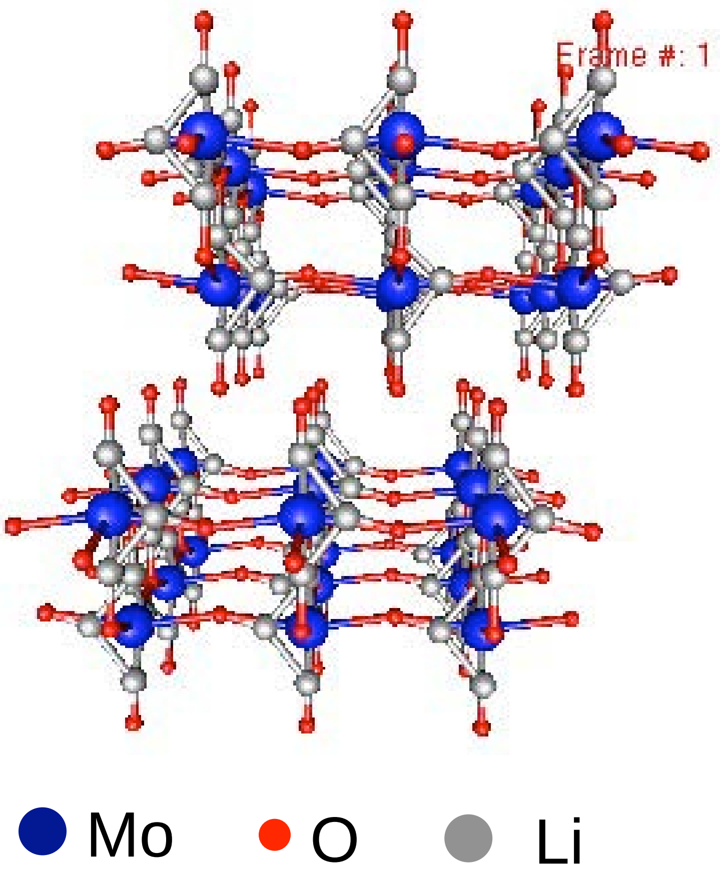


Dr.Yong-Hyun Kim: in house theorist working side-by-side with experimentalists to both understand mechanisms and predict new promising electrode materials.

(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.)*

Accomplishment/Status

Theoretical changes in Li-ion intercalated α-MoO_3

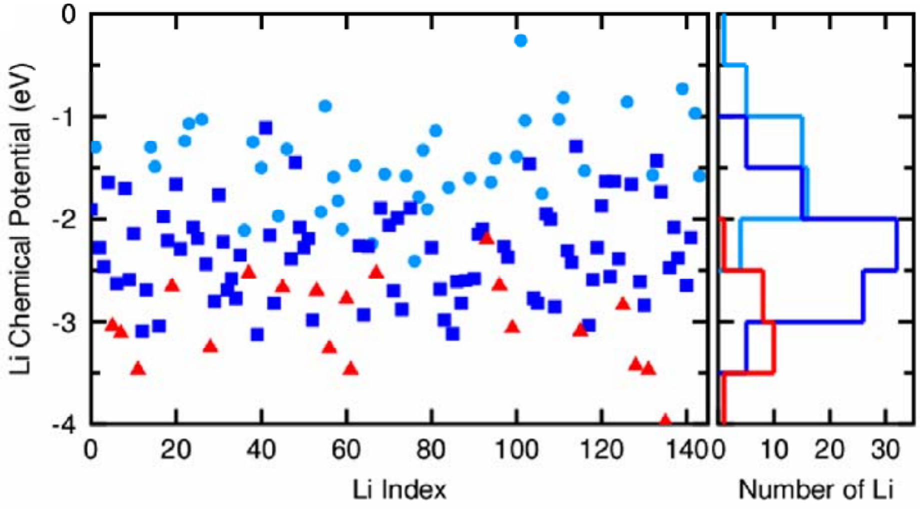


- Four Li inserted in a theoretical nanoparticle.
- 9 ps of simulation
- Primarily the Li and O atoms are disordered with the heavier Mo atoms maintaining a stable framework, reminiscent of the initial α-phase.
- The Li-insertion causes significant expansion.

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.

Accomplishment/Status

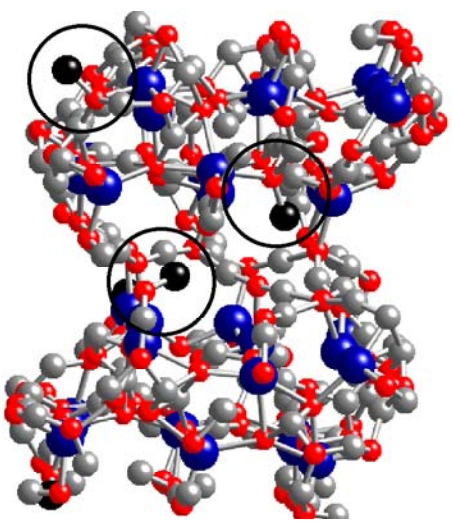
Theoretical Atomistic Energetics



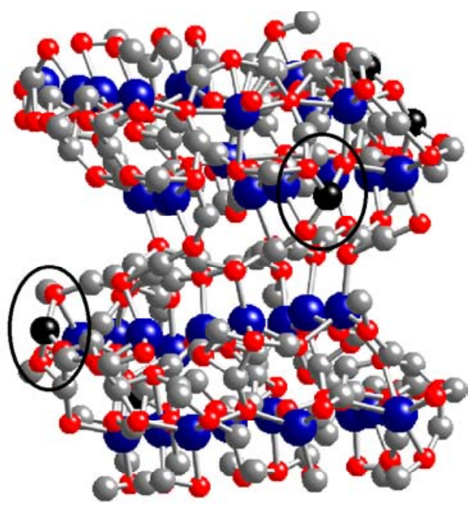
● Loosely bound Li

■ Intermediately bound Li

▲ Li inserted irreversibly



Li /one oxygen



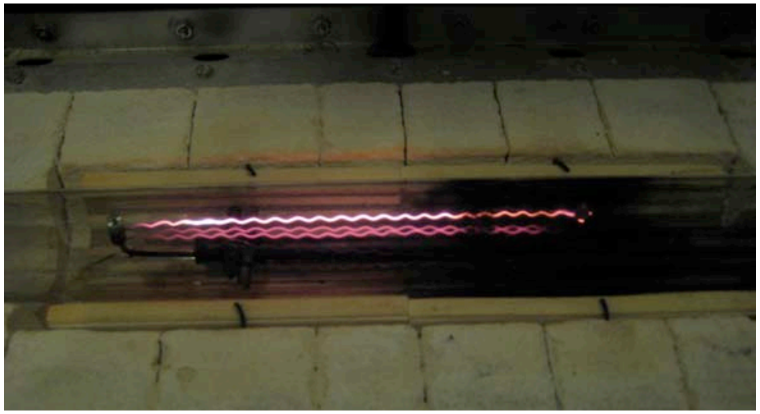
Li / three oxygen

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.

● Mo ● O ● Li

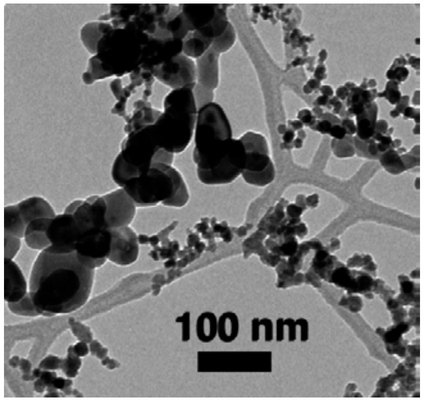
Accomplishment/Status

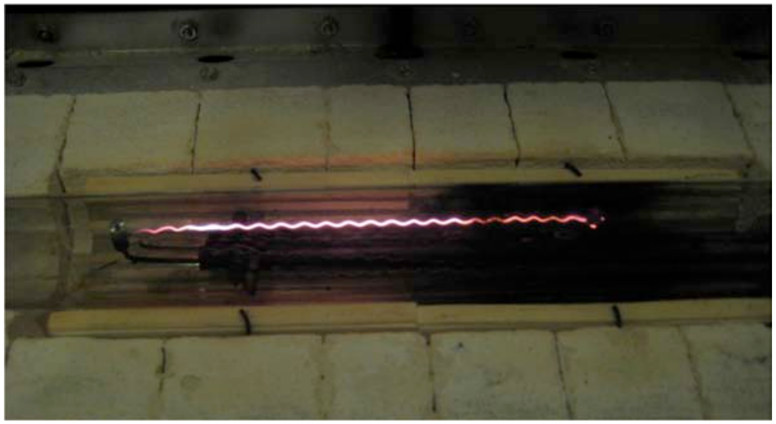
Scale-up of MoO_3 Production



Multiple Filaments Running Simultaneously

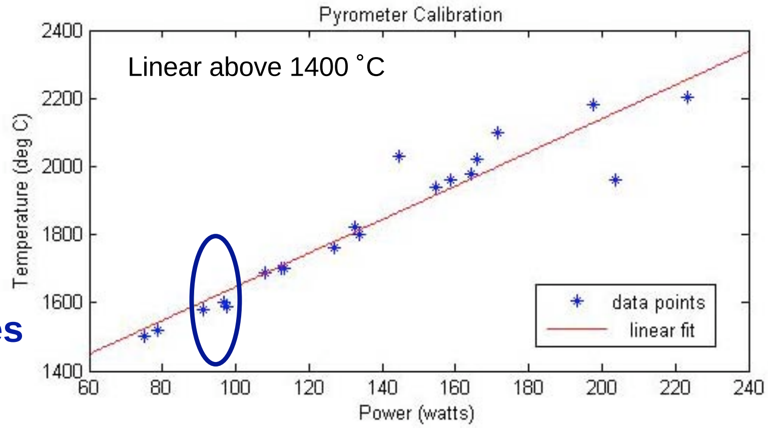
Uniform Particle Size Distribution Not Achieved





Optimized T

High Yield Uniform Particles



Optimal Temperature Occurs with < 100 W

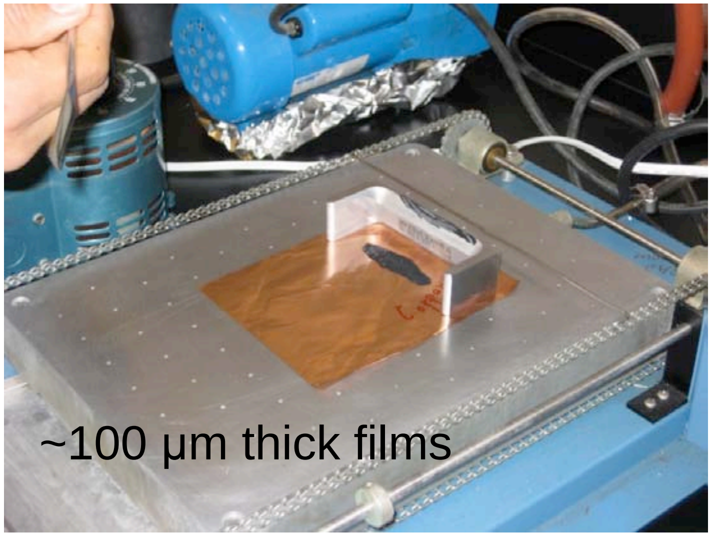
To ensure small particles it is best to operate a single filament in the small 2" diameter chamber. At an optimized filament temperature corresponding to < 100 W for power out put, uniform nanoparticles are made at ~1 g / hr. By scaling the size of the chamber, a high throughput inexpensive process may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

Accomplishment/Status

Coin Cell Testing at University of Colorado

Slurry

Mechanical spreader

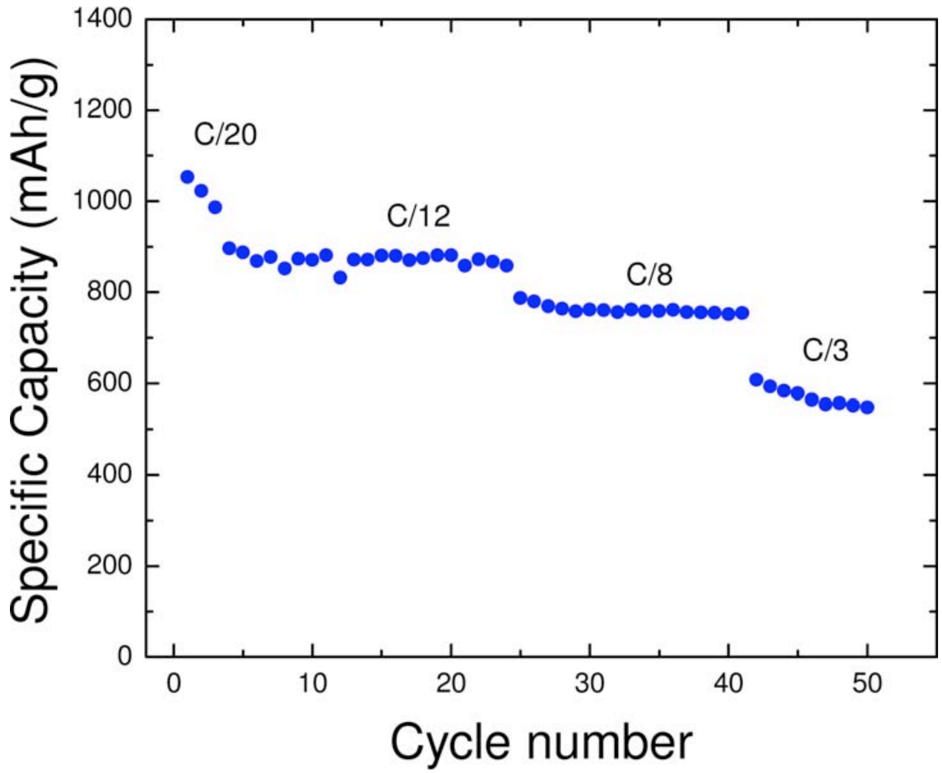


Active material:acetylene black:PVDF 70:15:15

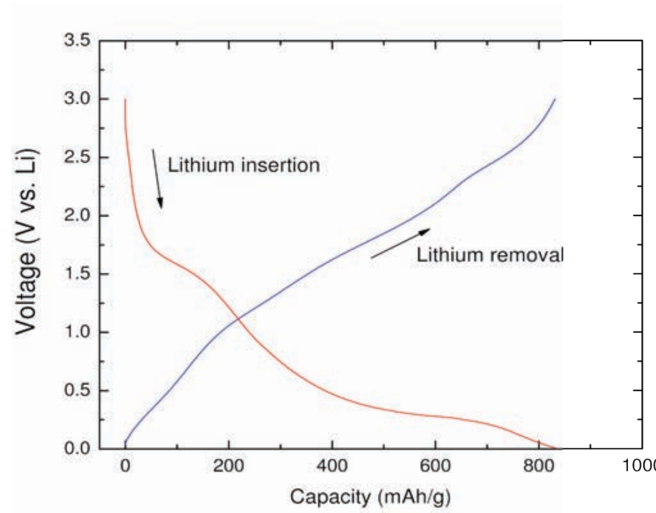
Press

Accomplishment/Status

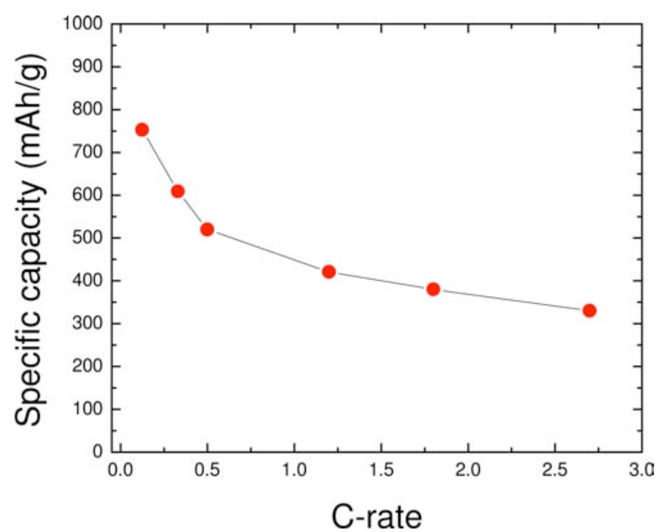
Coin Cell Data, 100 µm film



Reversible capacity similar to thin film.



Charge discharge similar to thin film.

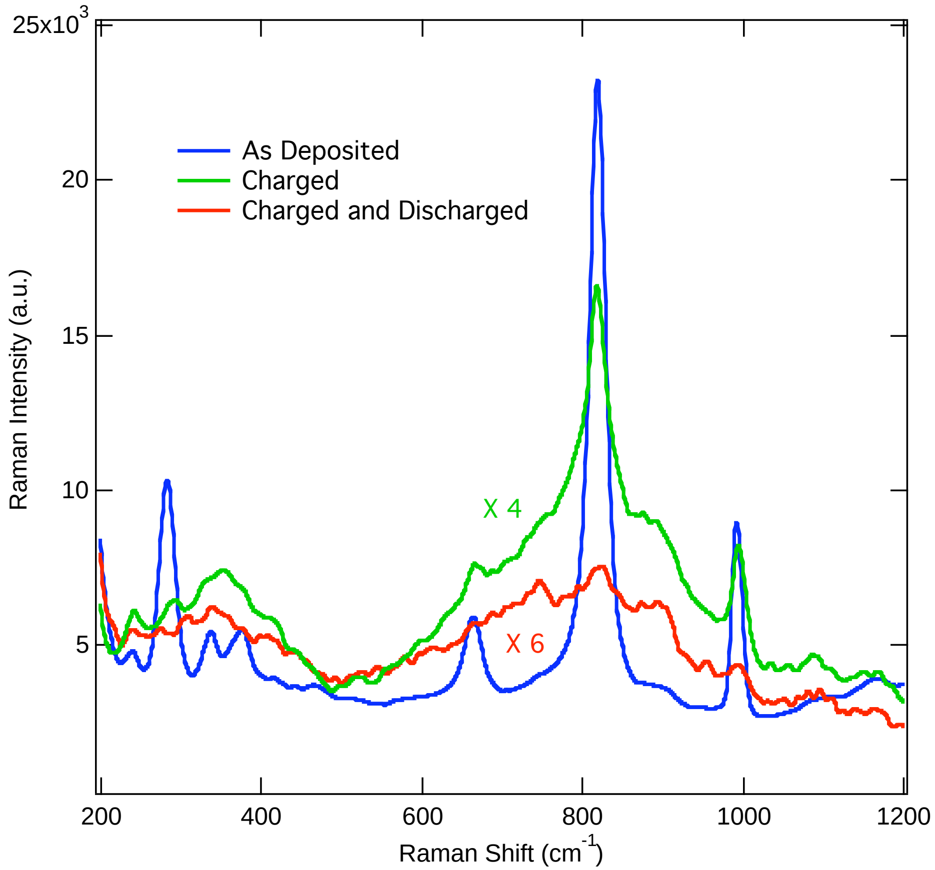


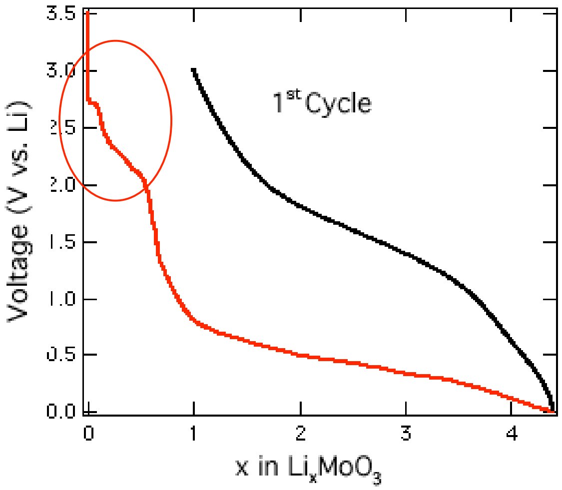
Rate capability is ~ 400 mAhr/g at 2C.

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.

Accomplishment/Status

New *In situ* Raman Capabilities

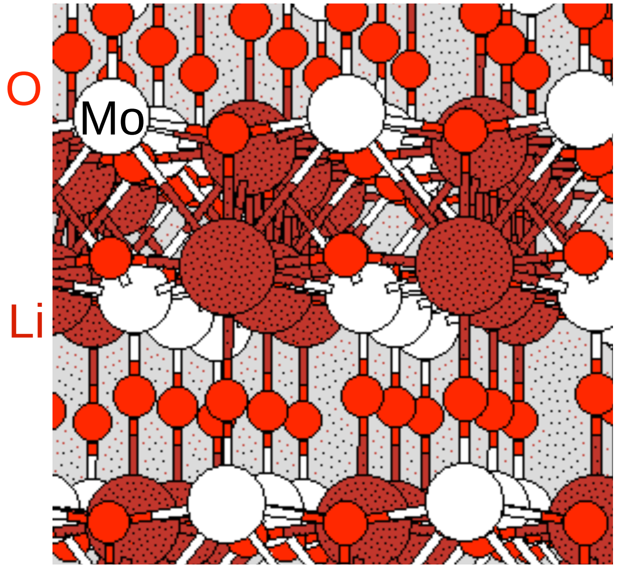




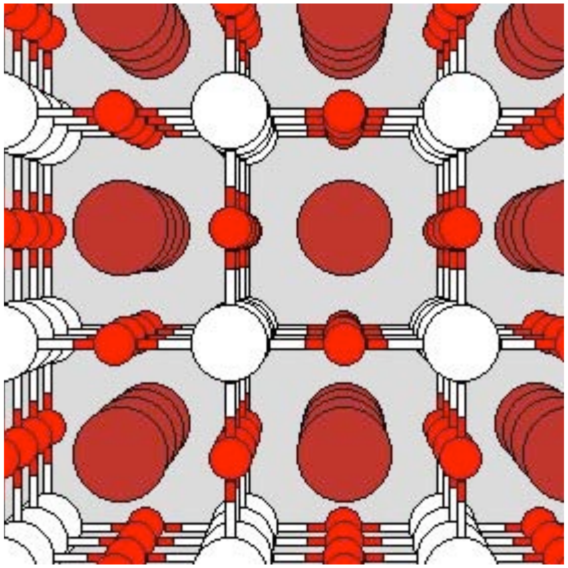
In situ Raman confirms significant loss in structural order in first insertion cycle consistent with both experimental data and molecular dynamics simulations.

***In situ* Raman has been set-up to analyze structural changes to electrode materials during electrochemical cycling.**

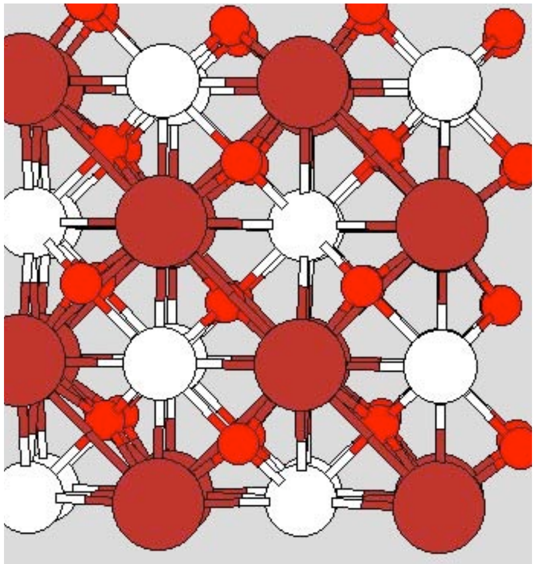
Predictive Theory Employed to Identify a MoO_2 Nanoparticle with a Lower Discharge Potential



$LiMoO_3$ (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%

Anode Properties	MoO_3	MoO_2
Theoretical maximum	6Li (1120 mAh/g)	4Li (840 mAh/g)
Experimental capacity	3.4Li (630 mAh/g)	3Li (630 mAh/g), 2Li(420 mAh/g)
Average voltage	1.5 V	< 1 V

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**

  S-H. Lee, Y-H. Kim, R. Deshpande, P. A. Parilla, K. M. Jones, B. To, H. Mahan, S. B. Zhang, and A. C. Dillon, “Anomalous Reversible Lithium-Ion Intercalation in Molybdenum Oxide Nanoparticles,” Nature Materials, (under review).

- **Patents**

  A.C. Dillon, R. Deshpande, S-H. Lee and H. Mahan “MoO_3 Nanoparticles for High-Performance Li-Ion Battery Electrodes” Patent Application.

- **Visibility**

  S-H. Lee gave an invited presentation entitled “MoO_3 Nanoparticles for Improved Li-Ion Battery Electrodes” at the Materials Research Society Fall Meeting, Boston Massachusetts, Dec. 2007.

  A.C. Dillon was a co-organizer of a symposium entitled “Life-Cycle Analysis for New Energy Conversion and Storage Systems” at the Materials Research Society Fall Meeting, Boston Massachusetts, Dec. 2007.

Acknowledgments

- DOE OVTP Support
  - Tien Duong
- NREL Program/Project Guidance
  - Ahmad Pesaran
  - Terry Penney