Nanostructured Metal Oxide Anodes

A. C. Dillon (P.I.)
L. A. Riley, S-H. Lee*, Y-H. Kim, C. Ban, D. T. Gillaspie and
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

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

Budget

- Total project funding

  FY08: $250K, FY09: $350K

Project lead: Anne Dillon

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.

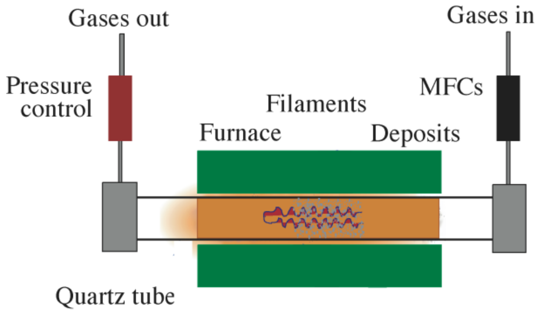
Milestones

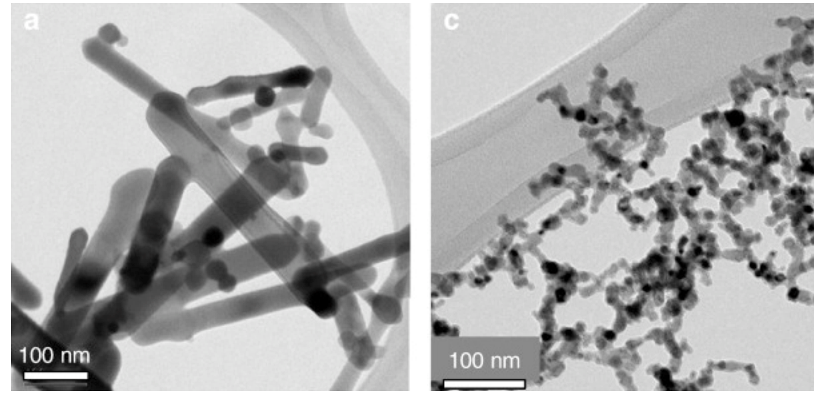
- Sept 2008-report on optimization of MoO_3 thick electrodes tested in a coin cell configuration, complete. (In this report a reversible capacity of ~ 1050 mAh/g was demonstrated with good cycling and rate capability. This high capacity represents a 60% improvement compared to the thin film MoO_3 electrodes, 630 mAh/g)

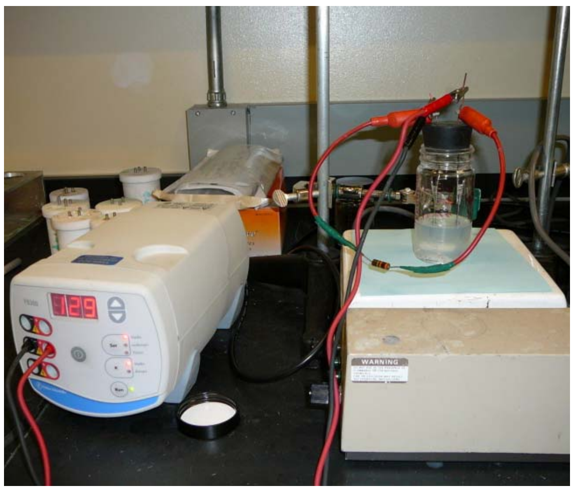
- July 2009-report on optimization of MoO_3 anodes in a full cell with cathodes supplied by ANL. (Full cell data for the MoO_3 anodes coupled with both $Li_{1.05}M_{0.95}O_2$, M = $Ni_{1/3}$, $Co_{1/3}$, $Mn_{1/3}$ and the state-of-the-art lithium rich cathode $0.5Li_2MnO_3 0.5Li(Mn_{0.31}Ni_{0.44}Co_{0.25})O_2$ is presented here.)

Approach

- MoO_3 nanoparticles (nano-rods and nanospheroides) are produced using hot-wire chemical vapor deposition (HWCVD) at different reactor pressures.







Electrophoresis

Material slurry

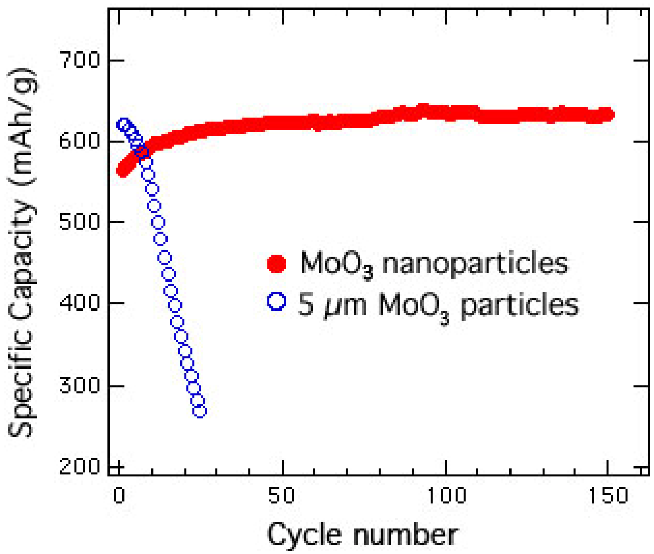
Coin Cell

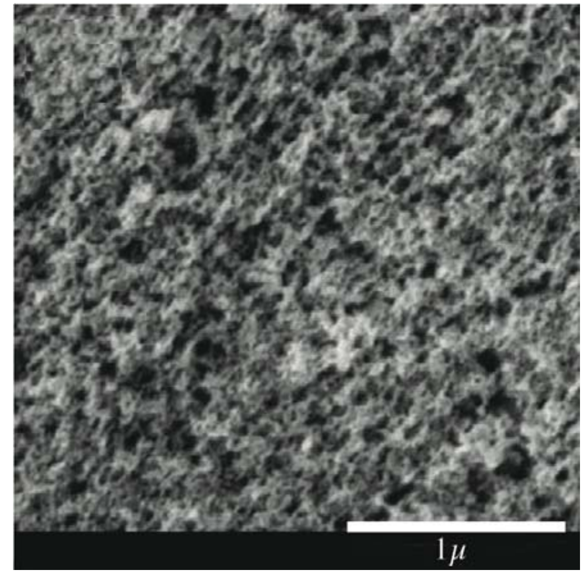
- Thin film battery electrodes (2-3 µm) have been fabricated with novel electrophoresis.
- Thick film electrodes (~35 µm) for coin cell testing have been optimized versus a Li counter electrode by varying: binder/conductive additive composition and electrode pretreatment.
- Full cell has been also optimized with ANL cathodes.

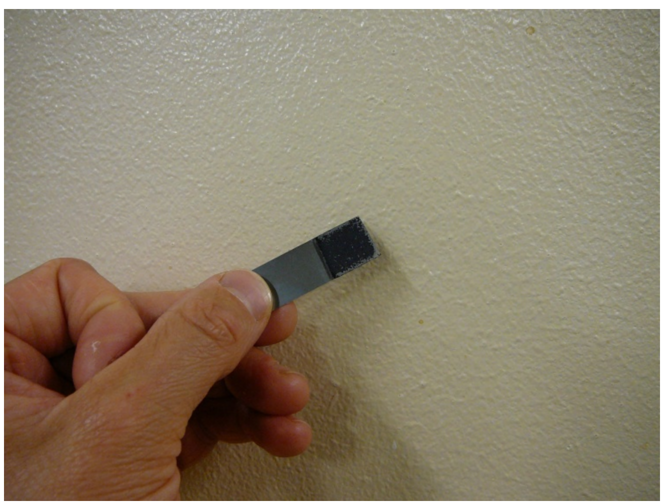
A.C. Dillon, A.H. Mahan, S-H. Lee, R. Deshpande, P.A. Parilla, K.M. Jones, *Thin Solid Films* 516 (2008) 794.

Previously Reported

Thin Film Electrodes by Novel Electrophoresis





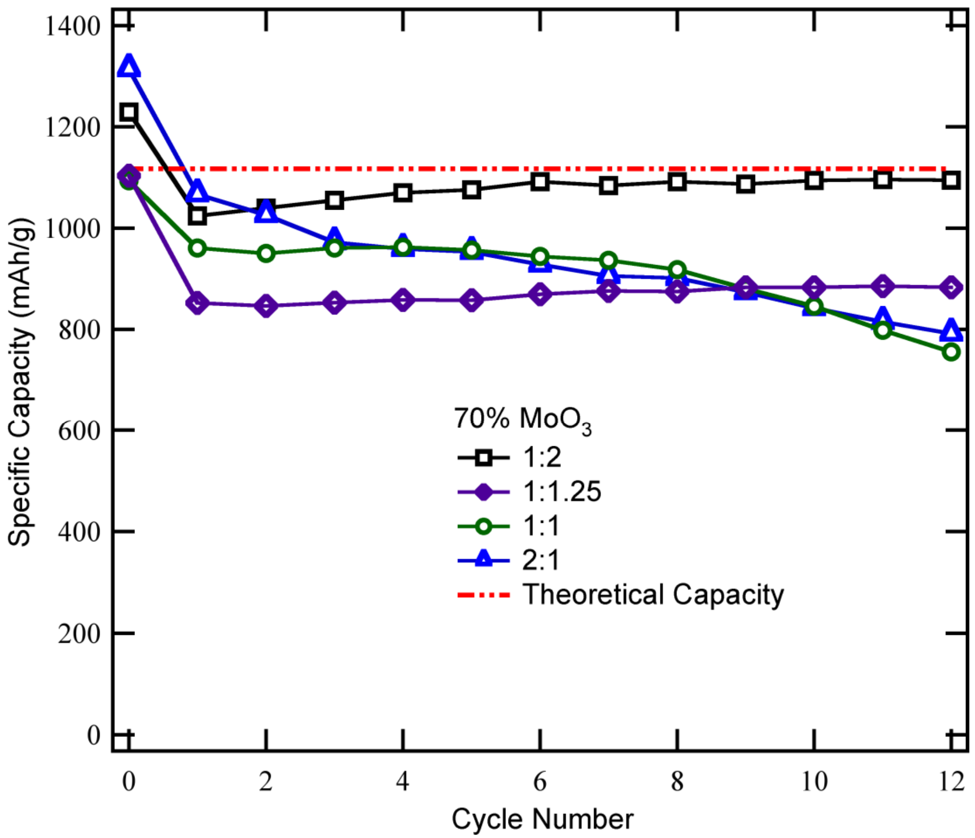


- Porous thin film without binder or conductive additive obtained after electrophoresis.
- Improved durable capacity (~ 630 mAh/g) found when using the thin film as anode and cycling between 3.0- 0.005 V.

S-H. Lee, Y-H. Kim, R. Deshpande, P.A. Parilla, E. Whitney, D. T. Gillaspie, K.M. Jones, A.H. Mahan, S. Zhang, and A.C. Dillon, *Advanced Materials* 20 (2008) 3627

Technical Accomplishments

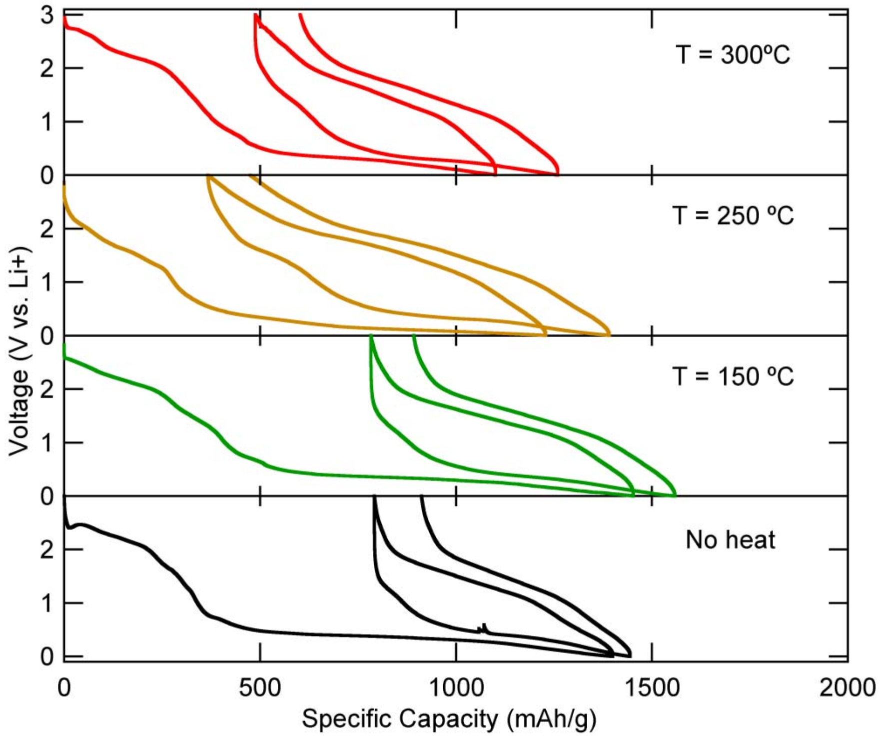
Varying the Ratio of AB : PVDF

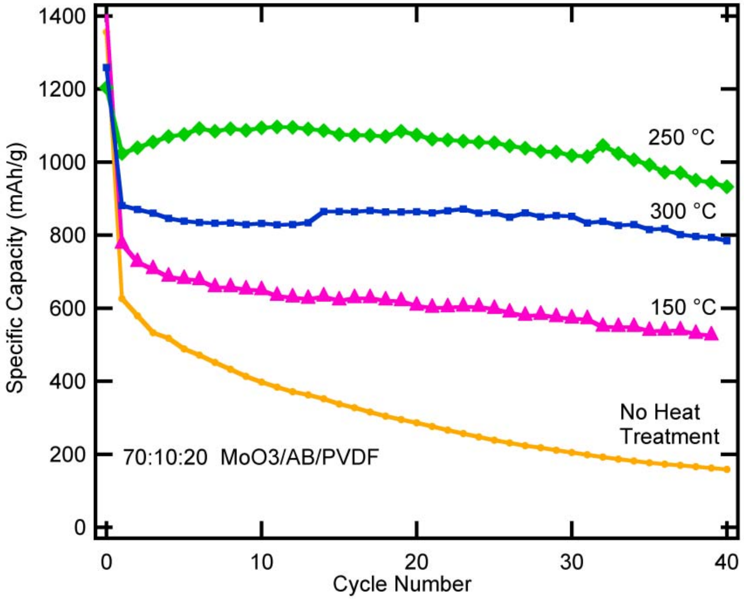


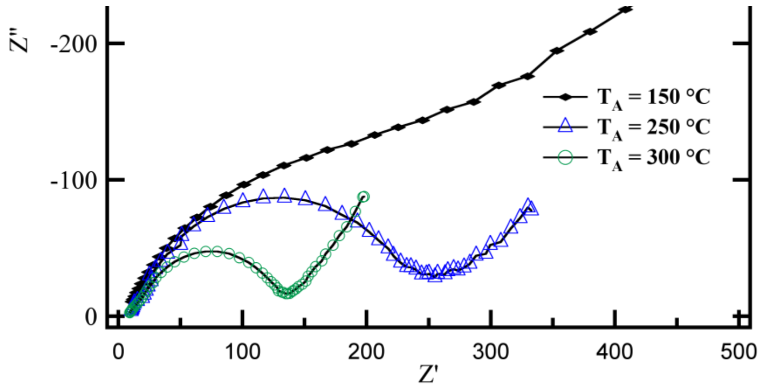
- Polymer rich electrodes provide continuous adhesion through the film.
- Maximum cycling capacity of ~1050 mAh/g (theoretical 1170 mAh/g) achieved at a ratio of 70:10:20 (MoO_3:AB: PVDF).

Technical Accomplishments

Variation in Pre-heat Treatment





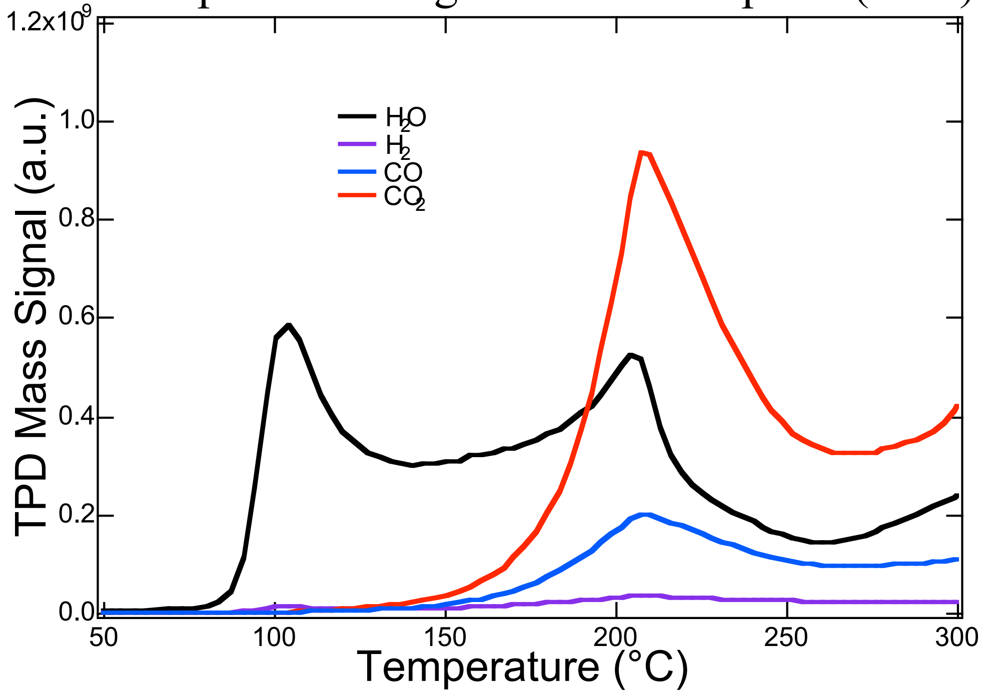


- Highly improved capacity of 1050 mAh/g is achieved by using a ratio of 70:10:20 and pre-heating at 250 ˚C.
- Electrical resistance steadily decreases with increase of temperature.
- Decreased capacity at 300 ˚C likely due to the binder breakdown and isolation of certain particle clusters.

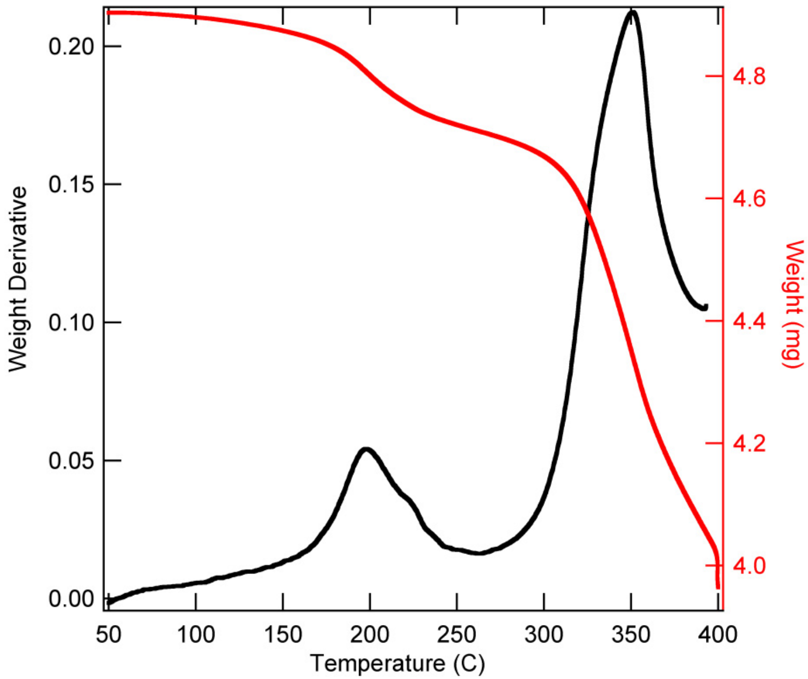
Technical Accomplishments

Explanation of Pre-heat Requirements

Temperature Programmed Desorption (TPD)



Thermalgravimetric Analysis (TGA)

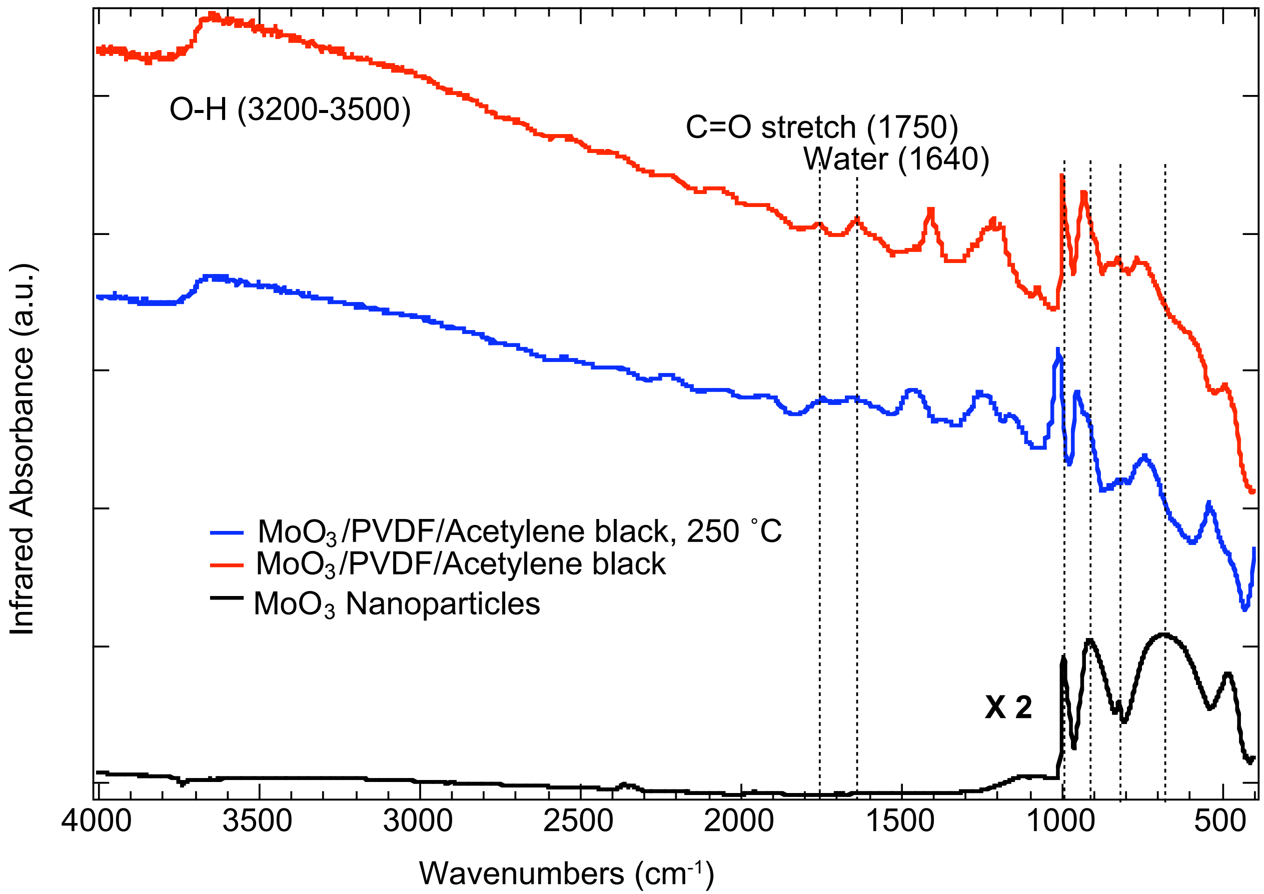


- Water desorption from the electrode observed at a high temperature (> 200 ˚C).
- CO_2 species are also observed at a higher temperature perhaps due to oxidation of the acetylene black.
- Polymer decomposition observed at a surprising low temperature (300˚C).
- Early decomposition may be catalyzed by nanostructured MoO_3

Technical Accomplishments

Explanation of Pre-heat Requirements

Results confirmed by Infrared Spectroscopy (IR)



- H_2O/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.

Technical Accomplishment

Nano-sized Li_xMoO_3 : Displacement redox reaction?

Displacement redox reaction* for MoO_3 nanoparticles :

$$MoO_3 + 6Li^+ + 6e \leftrightarrow 3Li_2O + Mo$$

$$6Li \leftrightarrow 6Li^+ + 6e$$

$$\overline{MoO_3 + 6Li \leftrightarrow 3Li_2O + Mo}$$

What is size distribution of Mo clusters?

First-principles molecular dynamics (FPMD)

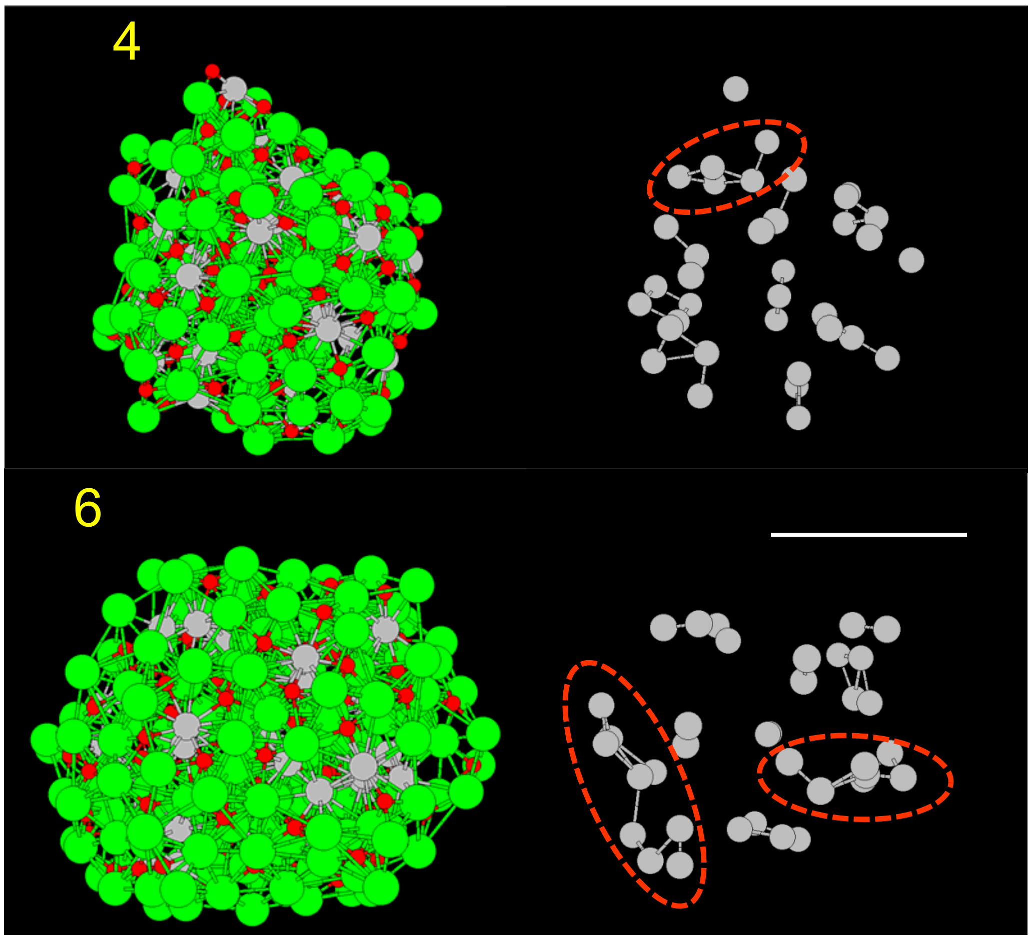
- $(Li_4MoO_3)_{36}$ & $(Li_6MoO_3)_{36}$
- Start from uniformly lithiated alpha phase of MoO_3
- T = 600 K (to speed up the MD simulations)
- VASP code

*P. Poizot et al., Nature 407, 496 (2000)

Technical Accomplishments

FPMD simulations for Li_xMoO_3 nanoparticles (x = 4, 6)

Mo_n	1	2	3	4	5	6	7	8	9
$(Li_4MoO_3)_{36}$	4	1	3	4	**1**	-	-	-	-
$(Li_6MoO_3)_{36}$	-	6	-	2	-	-	1	-	**1**



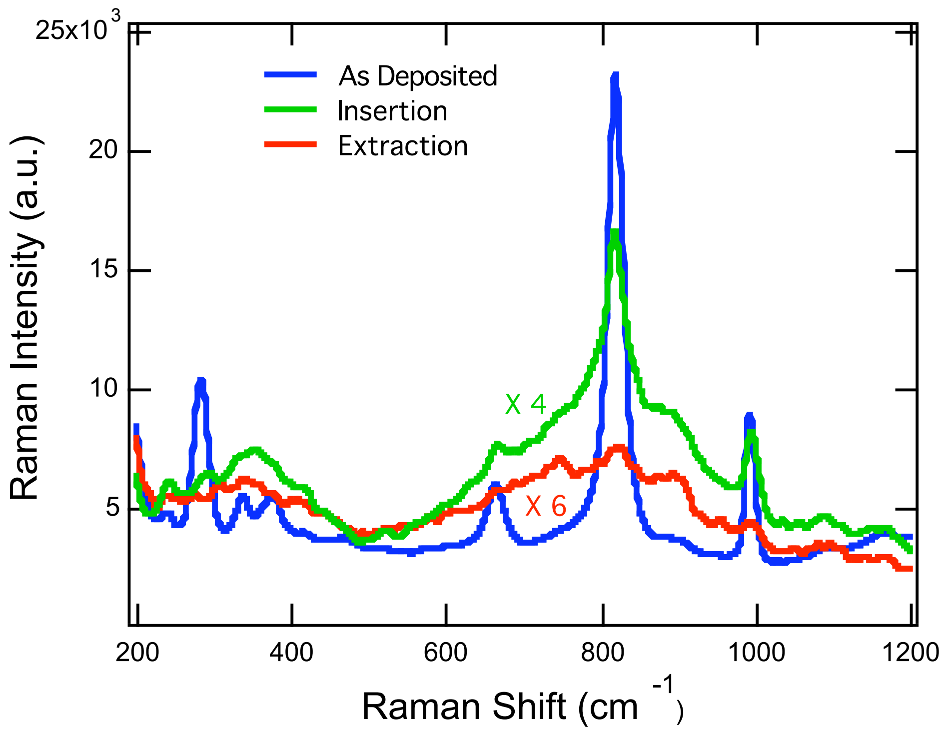
Small clusters of Mo_n are easily formed within the nanoparticle.

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.

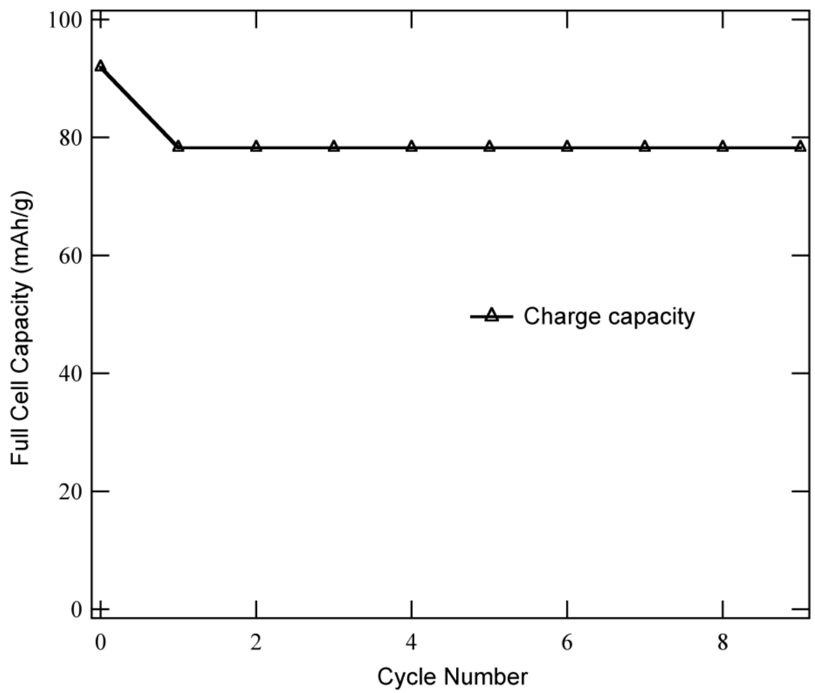
Technical Accomplishments

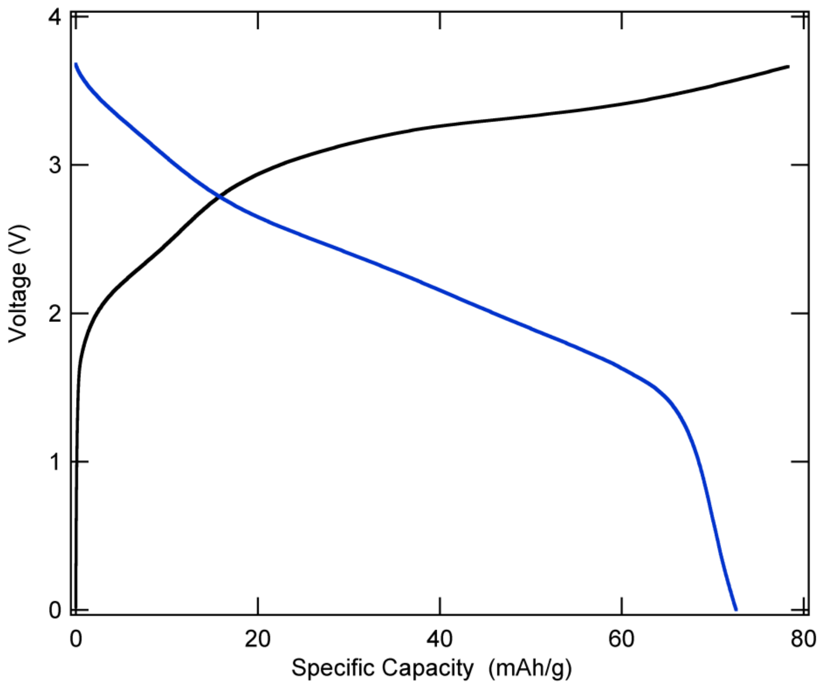
In Situ Raman Showing Disordered Structure after Cycles



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

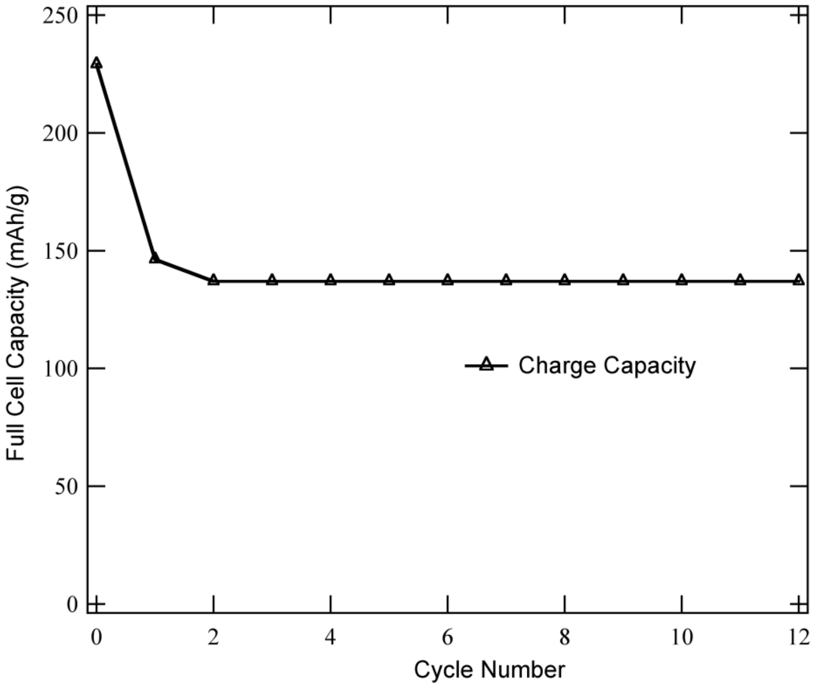
Technical Accomplishments
Full Cell Testing Using ANL Cathode

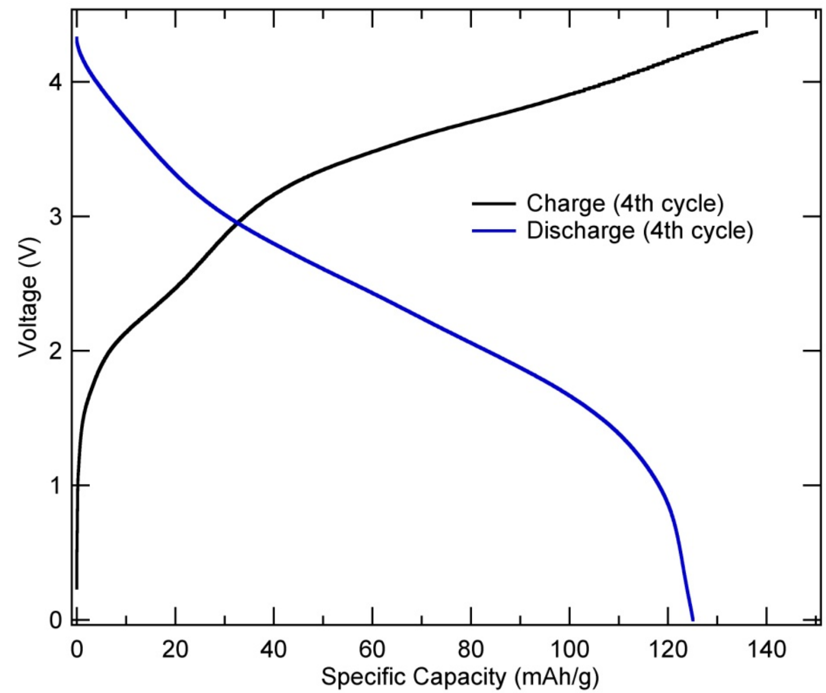




- Full cell capacity of ~80 mAh/g achieved when cycling between 4.0-1.0 V by coupling with Gen 2 cathode obtained from M. Thackeray and S-H. Kang (ANL).
- The coin cell contains 13 mg cathode material and 1.7 mg anode material.
- In the full cell MoO_3 has a reversible capacity of ~677 mAh/g and the 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, $0.5Li_2MnO_3 0.5Li(Mn_{0.31}Ni_{0.44}Co_{0.25})O_2$ from M. Thackeray and S-H. Kang at Argonne.

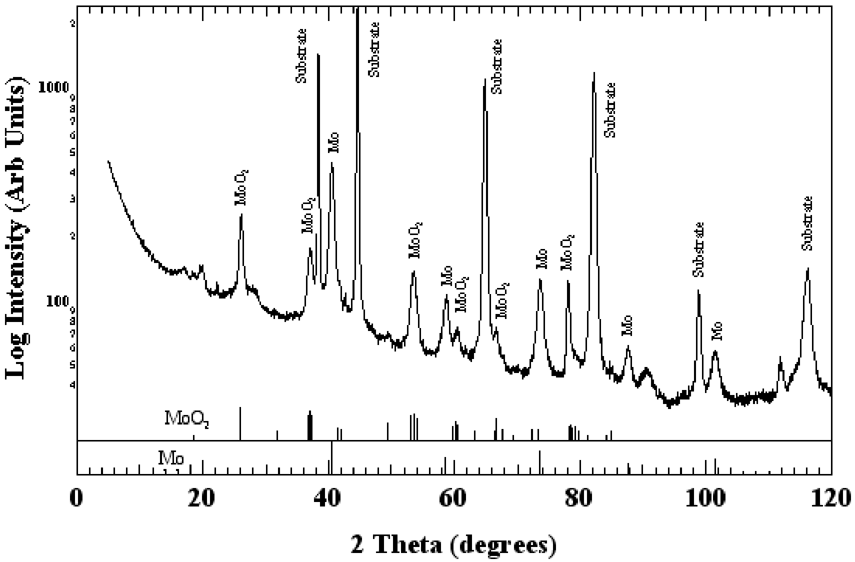
•Cell contains 7.4 mg cathode material and 1.6 mg anode material.

•MoO_3 has a reversible capacity of ~ 776 mAh/g and cathode capacity is 170 mAh/g.

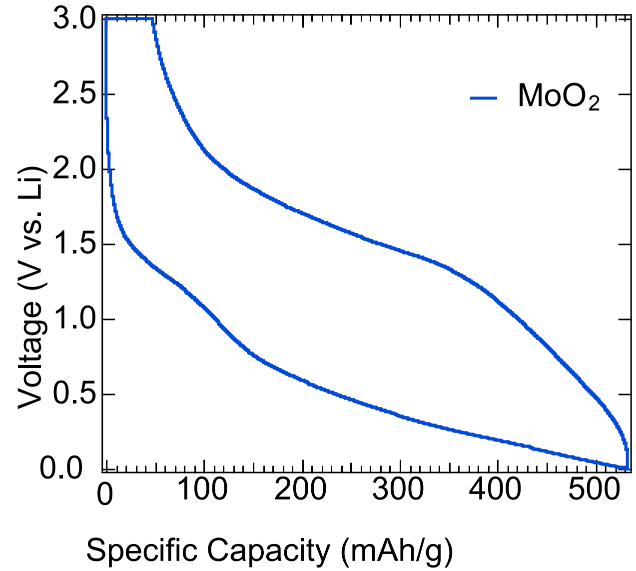
Technical Accomplishments

HWCVD Production of Nano-MoO_2

XRD MoO_2



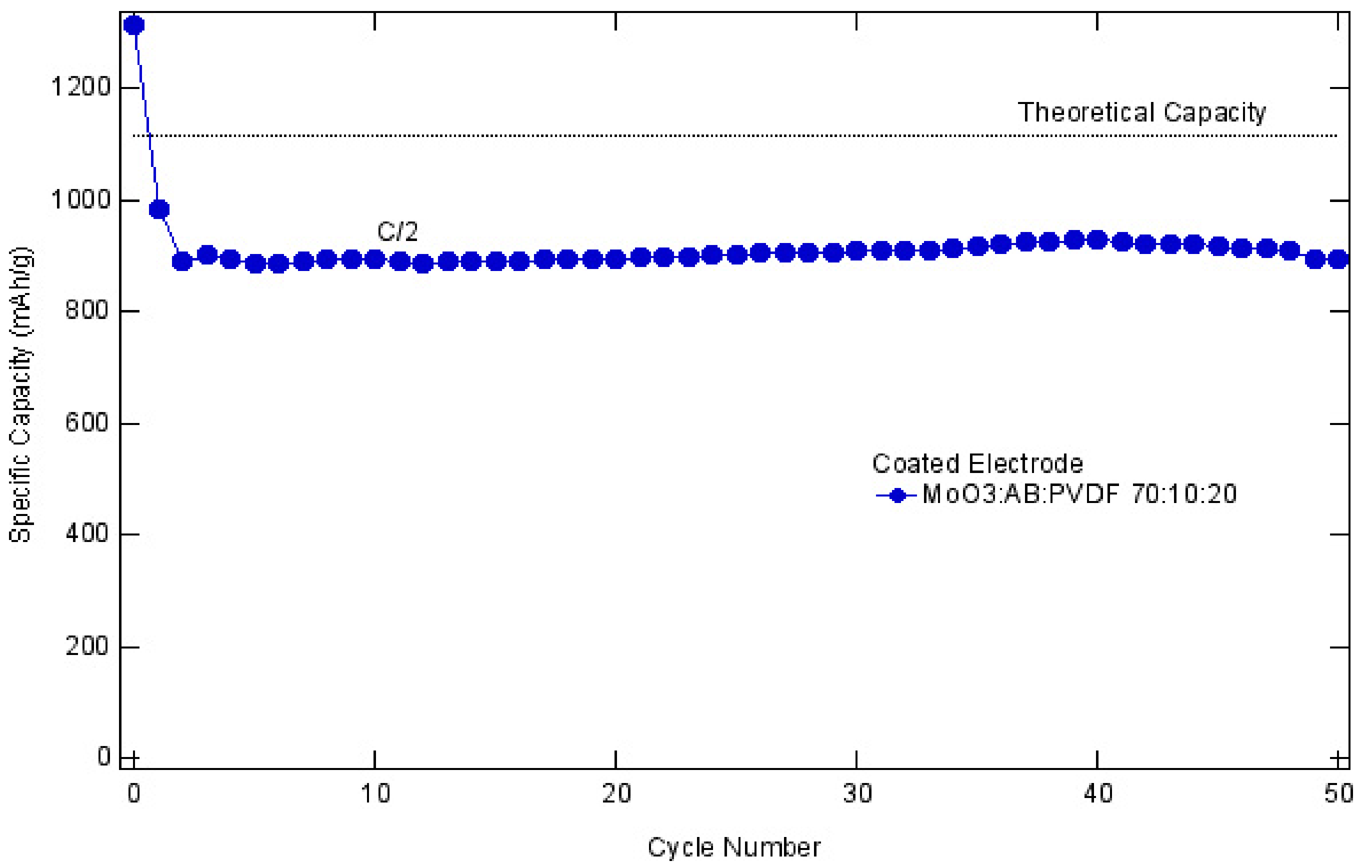
Voltage Profile



- 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.

Technical Accomplishments

Durable Cycling at High Rate of C/2

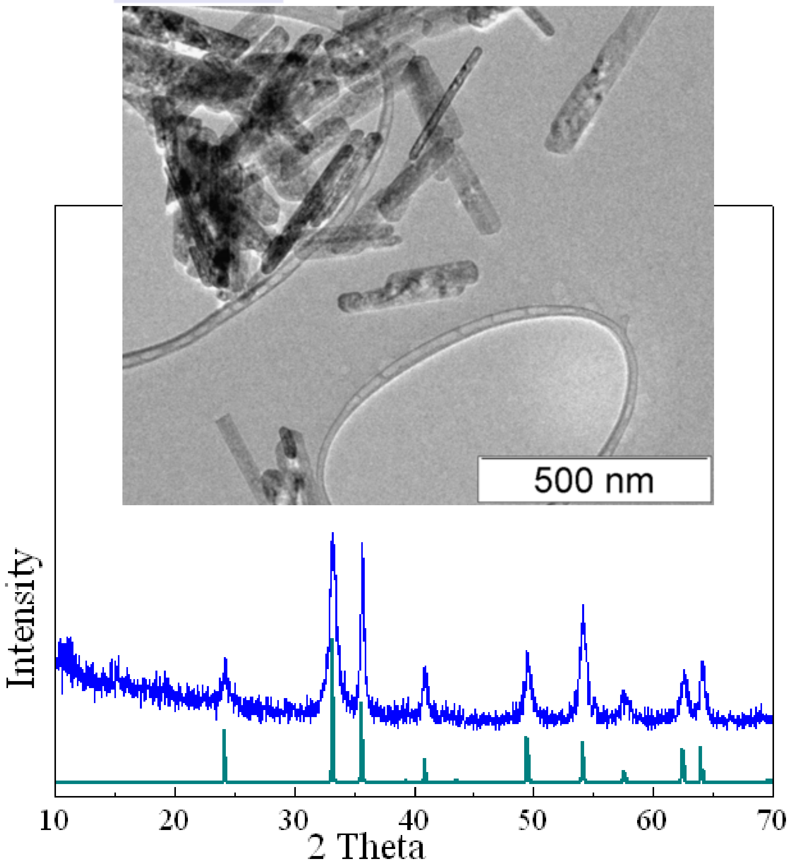


- Improved cycling stability achieved by applying a thin atomic layer deposition (ALD) coating.
- ALD coating enables reversible capacity of ~910 mAh/g when cycled at C/2.

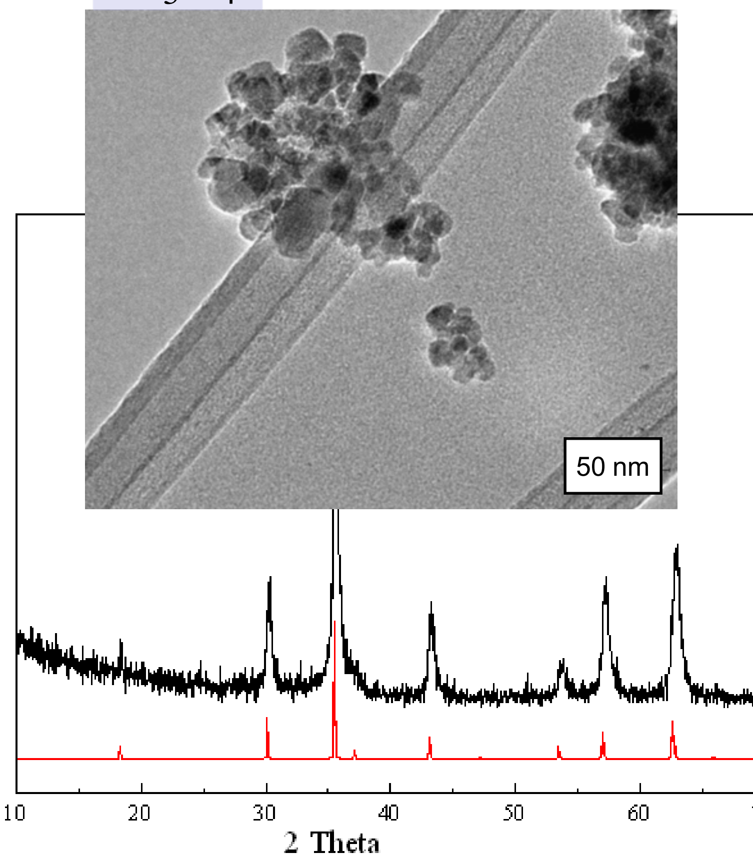
Recent Development

Synthesis of Iron Oxide by Hydrothermal Technique

Fe_2O_3



Fe_3O_4

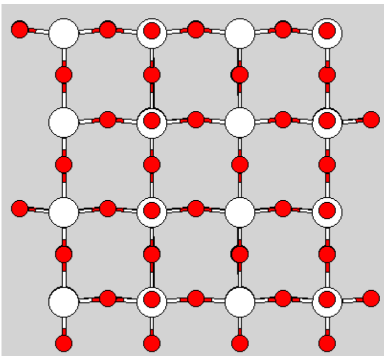


- Fe_2O_3 nanofibers (40-50 nm width) has been produced using hydrothermal process followed by post-heat at 300 °C.
- Fe_3O_4 nanoparticles (10-20 nm) obtained by using reducing agent in hydrothermal process.
- Iron oxides allow for a more economical system.

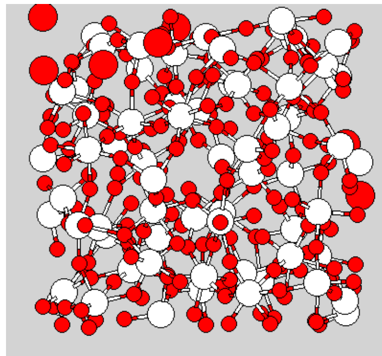
Recent Development

Oxygen Vacancy: WO_3, MoO_3, and Fe_2O_3

Atomic structure

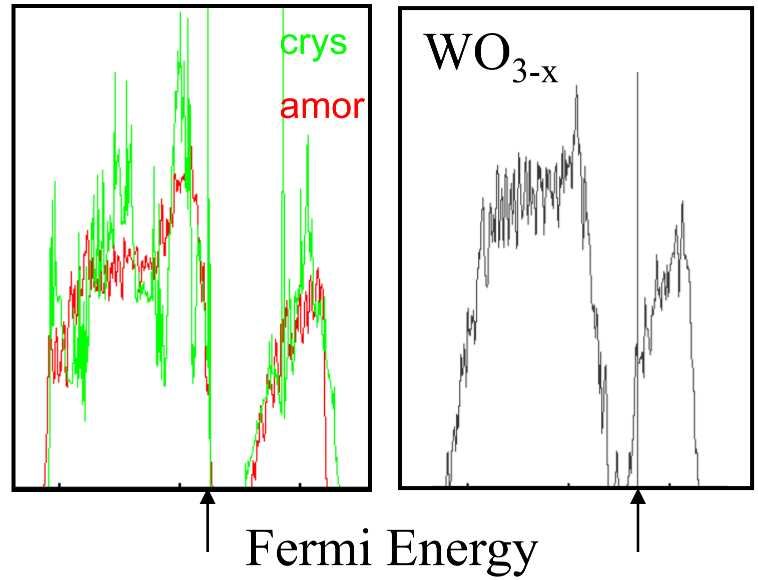


Crystalline WO_3



Amorphous WO_3

Electronic structure

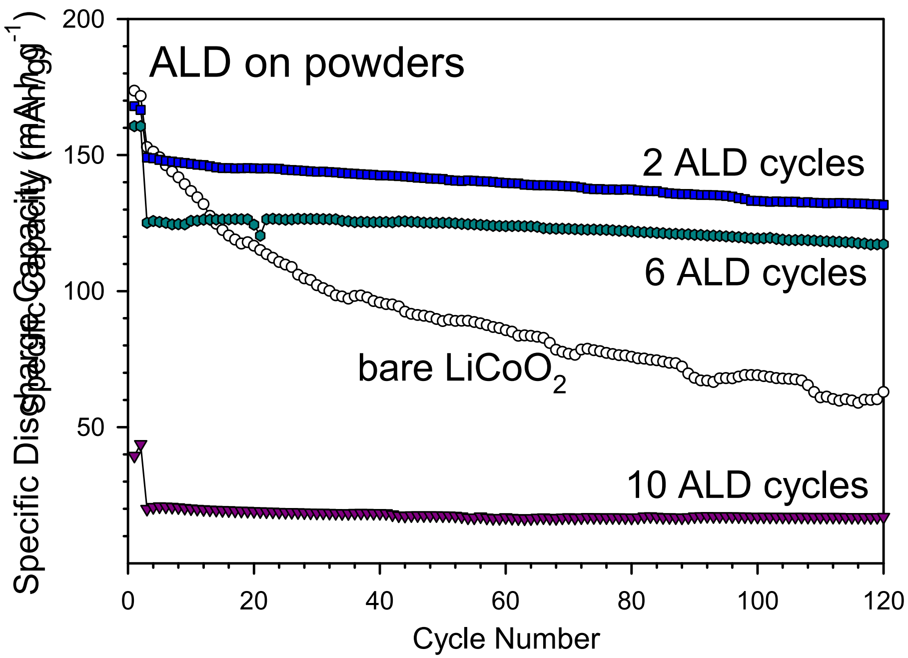


- Oxygen vacancy creates defect states near the conduction band of transition metal oxides such as WO_3, MoO_3, and Fe_2O_3.
- For sub-stoichiometric amorphous WO_{3-x} the conduction band is populated to a larger extent.
- The conduction band filling will lower the potential inserted Li.
- By creating oxygen vacancies and substoichiametric amorphous samples, we can reduce Li potentials of MoO_3 and Fe_2O_3 to make them more suitable anodes.

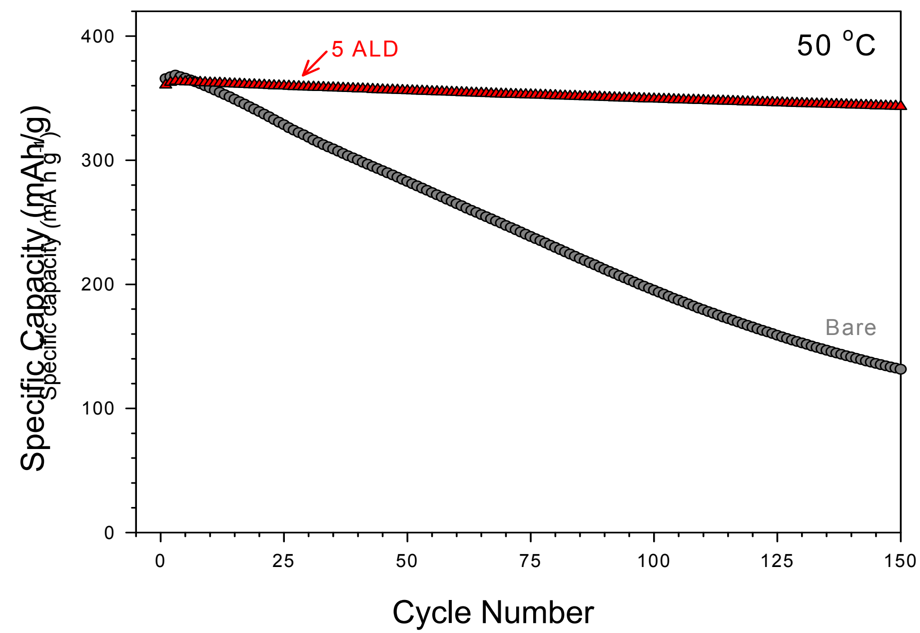
Recent Development

Atomic Layer Deposition (ALD) Improves Durability

ALD on $LiCoO_2$



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 MoO_3 nanoparticles. Use theoretical calculations to predict composition and orientation of economical oxide nanopaticles with more desirable voltage profiles.
- Synthesis of alternative nanostructures made from abundant elements, such as Fe_2O_3, Fe_3O_4, and MnO_2 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 $0.5Li_2MnO_3 0.5Li(Mn_{0.31}Ni_{0.44}Co_{0.25})O_2$
- In-situ Raman capabilities, established this year, show that MoO_3 nanoparticles become highly disordered in the initial cycle.

	Gravimetric Capacity (mAh/g)	Volumetric Capacity (mAh/cm^3)	Full Cell Capacity (mAh/g)
FY08	630	2200	--
FY09	1050	800	140
Commercial	350 (graphite)	770 (graphite)	80 (graphite/$LiCoO_2$) (J.Power Sources 88, p.237, 2000)

Acknowledgments

- DOE OVTP Support
  - David Howell

- NREL Program/Project Guidance
  - Ahmad Pesaran
  - Terry Penney