Nanostructured Metal Oxide Anodes

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Project ID: ES064
Overview

Timeline

- October 1, 2007
- September 30, 2010
- 90% complete

Budget

- Total project funding
  FY08: $250K
  FY09: $350K
  FY10: $350K

Project lead: Anne Dillon

Barriers

- Cost: developing metal oxide based anodes from abundant, inexpensive metals
- Capacity: improvements in both gravimetric and volumetric capacities have been demonstrated
- Rate capability: Durable rate capability has been achieved for high volume expansion materials with two separate methods.
- Life: Cycle life has also been improved with two different methods.
- Safety: Metal oxide anodes operate at higher potential relative to Li metal than graphite, eliminating the risk of Li plating

Collaborators

- V. Battaglia, LBL
- M.M. Thackeray and S-H. Kang, ANL
- M.S. Whittingham, SUNY-Binghamton
- E.A. Payzant and M.J. Kirkham, ORNL
- A. Greenshields, fortu
- S.M. George, Univ. of Colorado
- M. Groner, ALD nanosultions
Objectives

Develop high-capacity / rate, safe, MoO$_3$ and Fe$_3$O$_4$ anode

Transition metal oxides

- High capacity
- Safe voltage window

PLUS

- Inexpensive
- Benign materials
- Scalable Synthesis

![Graph of mass fraction vs. atomic number with Mo and Fe highlighted]
Milestones

• Sept. 2009-Develop methods and report on improvement of durable rate capability for high-capacity and high volume expansion metal oxide (>100 %) Li-ion anode materials.

• Jan. 2010- Employed ALD-coated metal oxide (MoO₃) electrodes in full cells with lithium excess cathodes (LEC) supplied by ANL and demonstrated improved performance. (LEC = 0.5Li₂MnO₃0.5Li(Mn₀.₃₁Ni₀.₄₄Co₀.₂₅)O₂).

• March 2010- Showed high capacity and high rate capability of iron oxide in a conductive 3-D mesh without any binder and demonstrated durable cycling for a Li-ion anode.

• July 2010-Report on optimization of molybdenum metal oxide anodes. Begin Go-No-Go process for molybdenum oxide anode materials for industrial electric vehicle applications.
Approach: Improve Rate Capability of High Volume Expansion Materials

1. MoO$_3$ nanoparticles produced with economical hot-wire chemical vapor deposition (HWCVD). Atomic layer deposition (ALD) coatings enable durable rate capability.

2. Iron oxide made with inexpensive hydrothermal process. 5 wt.% single wall carbon nanotubes (SWNTs) enable binder-free electrode with high-rate capability cycling.

Atomic Layer Deposition (ALD) Protective Coatings

Layer by layer conformal Al₂O₃ coatings with sequential surface reactions

A) Surface-OH + Al(CH₃)₃ → Surface-O-Al(CH₃)₂ + CH₄

B) Surface-O-Al(CH₃)₂ + 2 H₂O → Surface-O-Al(OH)₂ + 2 CH₄

- No solvent, no excessive amount of precursors, No post-heat-treatment at high-temperature
- Sequential & self-limiting surface reaction, Conformal coating & atomic thickness control

Accomplishment: ALD thin conformal coatings are employed to improve durable high-rate cycling performance of high-volume expansion materials.
ALD on nano-MoO$_3$ Particles

**BEFORE ALD**

**AFTER ALD**

New finding: Thin conformal coatings appropriate for nanoparticles are easily achieved with ALD. Thus the coating does not significantly contribute to the mass of the active material.
A thin ALD coating resulting from four ALD sequences (~8 Å) applied to the full electrode enables MoO₃ nanoparticles to cycle in a coin cell at high rate. The coating “knits or glues” the MoO₃ nanoparticles to the conductive additive and electrode preventing mechanical degradation due to volume expansion. Note: this does not occur when the coating is applied to the MoO₃ particles only.

Frequency Response Analysis Shows Importance of Full Electrode Coating

Similar frequency responses between bare and ALD coatings on electrode

Additional mid-and low-frequency signals found for ALD on particles attributed to loss of conductivity resulting from full particle coating.

Accomplishment: ALD allows for protective coating to be applied to full electrode instead of just particles. With conventional sol-gel techniques this is not possible. **Full electrode coating results in improved performance.**
Hypothesis for Mechanism of ALD Protection for High Volume Expansion (High Capacity) Materials

Accomplishment: Although cracking of the $\text{Al}_2\text{O}_3$ ALD coating likely occurs upon volume expansion / contraction, it still provides an adhesive layer that delays the onset of mechanical degradation due to volume expansion. Development of more flexible ALD coatings is possible.
Evidence that ALD “Glues” MoO₃ to Conductive Additive

BARE MoO₃
Carbothermal reduction through annealing

ALD-coated MoO₃
Annealing effects

Accomplishment: Carbothermal reduction upon heat treatment for ALD coated electrode confirms that MoO₃ particles remain in excellent contact with conductive additive.
ALD MoO$_3$ Improves Full Cell with ANL Cathode

High capacity (~160 mAh/g), high efficiency (>99%) full cell with no pre-lithiation of the electrodes. *MoO$_3$ electrode coated with 4-sequences Al$_2$O$_3$ by ALD.*

Reversible Capacities: Full: ~160 mAh/g, ANL lithium excess cathode (LEC) : ~185 mAh/g, MoO$_3$: ~1000 mAh/g. Full cell capacity exceeds capacity of graphite/LiCoO$_2$

Accomplishment: By coating MoO$_3$ with ALD the full cell performance when coupled with ANL state-of-the-art cathode is improved.
Synthesis of Inexpensive Iron Oxide Binder-free Electrodes

FeOOH nanorods are prepared by a simple hydrothermal technique.

For optimal results the FeOOH nanorods are suspended with 5 wt.% carbon single-wall nanotubes (SWNTs). The suspension is subjected to vacuum filtration.

The film is transferred to a copper current collector and heated to 450 °C.

Accomplishment: Abundant / inexpensive and light iron oxide precursors are made by potentially scalable economical hydrothermal technique.
SEM Images of Binder-free Fe$_3$O$_4$ / SWNT Anodes that Contain 95 wt.% Active Material and 5 wt.% SWNTs

Fe$_3$O$_4$ nanorods in a SWNT net

C. Ban, Z. Wu, L. Chen, Y. Yan and A.C. Dillon
*Advanced Materials.*, (in press).

Accomplishment: A binder-free electrode containing 95 wt.% active material and 5 wt.% SWNTs as conductive additive and flexible net is created with a simple process.

Color-enhanced cross sectional image with Fe$_3$O$_4$ (yellow/blue) and 5 wt.% SWNTs (white).
Cycling stability of Binder-free Fe$_3$O$_4$ / SWNT Anodes

- Voltage profiles and cycling performance of Fe$_3$O$_4$/SWNT (nano) compared to µm-sized Fe$_3$O$_4$/SWNT (micro2) and µm-sized Fe$_3$O$_4$ with PVDF binder / acetylene black (micro1).

- This suggests that this process could be employed for any high-volume expansion material.

- Gravimetric capacity is 1000 mAh/g, and volumetric capacity at 1C is 2000 mAh/cm$^3$ (3 x graphite).

Accomplishment: Both high gravimetric and high volumetric capacities are obtained for high volume expansion iron oxide with deep charge/discharge cycles at 1C rate without holding the voltage between cycles.
**Durable Rate Capability Fe₃O₄ / SWNT Anodes**

Stable capacity of over 600 mAh/g is observed at 10C (one charge/discharge in 6 minutes) and with only 5 wt.% SWNTs.

Fe₃O₄ nanorods in an SWNT net (5 wt.%) cycled at 5C (one charge/discharge in 12 minutes).

Accomplishment: By suspending high-volume expansion metal oxide materials in a conductive flexible net, it is possible to achieve durable high-rate capability: over 100 deep charge/discharge cycles at 5C with a capacity of 800 mAh/g, and 95 wt.% active material.
Initial particles change from tetragonal $\alpha$-FeOOH (a) to a mixture of $\text{Fe}_2\text{O}_3$ (hematite) and $\text{Fe}_3\text{O}_4$ (magnetite) when heated at 450 °C in Ar but are completely reduced to $\text{Fe}_3\text{O}_4$ when heated with SWNTs.

Finding: Simple annealing process converts hydrothermal precursor to $\text{Fe}_3\text{O}_4$. 
Raman Spectroscopy of Fe$_3$O$_4$ / SWNT Anodes

Raman tangential vibrational (~1500-1600 cm$^{-1}$) modes and disorder band (~1350 cm$^{-1}$) for SWNTs in the binder-free electrode.

Tangential modes indicate presence of both semiconducting and metallic SWNTs.

- Decrease in D-band upon heat treatment is consistent with oxidation of carbon impurities.
- Large shift in G-band indicates charge transfer / perhaps binding.
- Quenching is consistent with irreversible Li-ion intercalation.

Finding: Raman suggests it may be possible to bind high volume expansion materials to a flexible carbon conductive matrix and improve mechanical integrity.
Collaborative Efforts

**LBL:** We sent Vince Battaglia ALD coated MoO$_3$ electrodes, and the durable high capacity was confirmed at LBL.

**ANL:** Michael M. Thackeray and Sun-Ho Kang supplied us with Li-excess cathode materials. Full cells containing the ALD coated MoO$_3$ and Li-excess cathode had a stable capacity of $\sim 160$ mAh/g without any pre-lithiation. This capacity is approximately twice that of graphite/LiCoO$_2$ cells.

**SUNY, Binghamton:** M. Stanley Whittingham provided us with a new cathode material, and we have demonstrated improved rate performance with this material by using our recently developed binder-free electrode fabrication process.

**ORNL / HTML:** E.A. Payzant and M.J. Kirkham allowed and assisted us with high temperature XRD measurements that enabled mechanistic understanding.

**fortu Holding AG:** fortu has tested our MoO$_3$ nanoparticles with their inorganic high-voltage electrolyte and is interested in more collaborative efforts as they plan manufacturing in Michigan.

**University of Colorado:** Through a collaborative effort with Steven M. George, we have demonstrated thin ALD coatings for improved rate capability of high volume expansion MoO$_3$.

**ALD Nanosolutions:** We are working with ALD nanosolutions to demonstrate ALD electrode coatings for economical roll-to-roll processing.
Future Directions

- Full cells with the ANL cathode continue to be optimized, and a paper on this joint work is in preparation.

- The binder-free SUNY, Binghamton cathode also continues to be tested and a joint publication is in preparation.

- SWNTs have shown us that a 3-D mesh matrix is a way to effectively deal with high volume expansion materials, we understand the concerns about its cost so we will explore alternate low cost approaches.

- We are presently investigating the viability of SiO$_x$ as an anode material and will make a Go / No-Go recommendation with DOE / BATT for metal oxide anode materials.

- We have submitted two proposals to the BATT anode call and will continue working on the development of high capacity, high-rate, long life, safe and inexpensive anode materials for next generation electric vehicles in FY11-FY13.
Summary

• Thin conformal Al₂O₃ atomic layer deposition (ALD) deposited coatings on fully fabricated MoO₃ electrodes with conductive additive and binder enabled capacity of 900 mAh/g at C/2 for more than 50 cycles and 600 mAh/g at 5C.

• An ALD coated MoO₃ anode was successfully paired with ANL’s state-of-the-art lithium excess cathode 0.5Li₂MnO₃0.5Li(Mn₀.₃₁Ni₀.₄₄Co₀.₂₅)O₂ and a capacity of 160 mAh/g was achieved without pre-lithiation.

• A binder-free electrode containing 95 wt.% Fe₃O₄ active material suspended in a “flexible single-wall carbon nanotube net” had a capacity of 1000 mAh/g (2000 mAh/cm³) at 1C and 800 mAh/g at 5C for deep charge / discharge cycles without a voltage hold for over 100 cycles.

• We believe that a flexible matrix can enable high volume expansion materials with good rate capability to be achieved.

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<thead>
<tr>
<th></th>
<th>Gravimetric Capacity (mAh/g)</th>
<th>Volumetric Capacity (mAh/cm³)</th>
<th>Full Cell Capacity (mAh/g)</th>
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</thead>
<tbody>
<tr>
<td>MoO₃</td>
<td>900 (C/2)</td>
<td>~800</td>
<td>160</td>
</tr>
<tr>
<td>Fe₃O₄</td>
<td>1000 (C)</td>
<td>~2000</td>
<td>N/A (to be measured later)</td>
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<tr>
<td>Commercial</td>
<td>350 (graphite)</td>
<td>770 (graphite)</td>
<td>80 (graphite/LiCoO₂)</td>
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