Nanostructured Metal Oxide Anodes

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Project ID: ES064

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Overview

Timeline

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

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

Budget

- Total project funding

  FY08: $250K,

  FY09: $350K

  FY10: $350K

Project lead: Anne Dillon

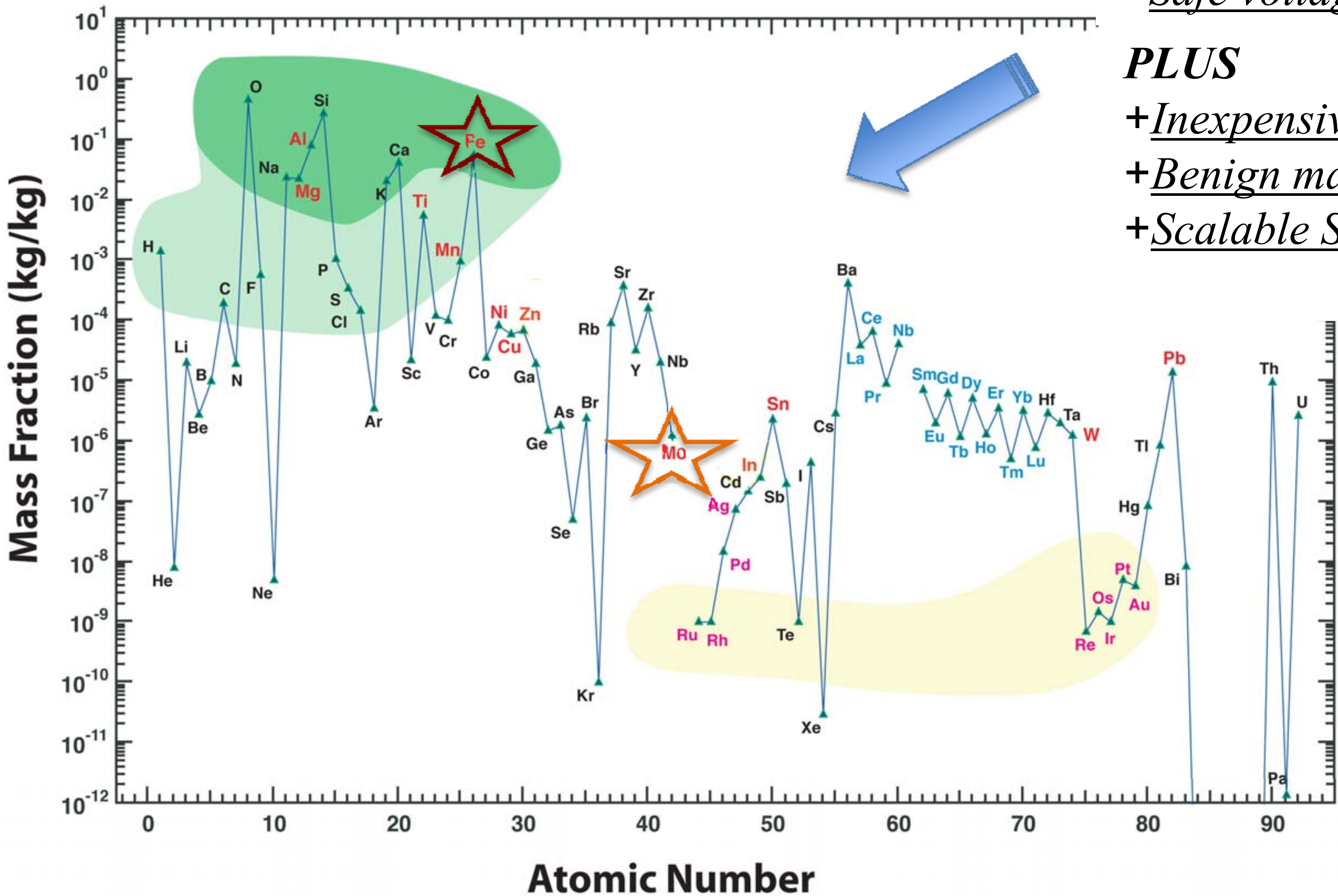
Collaborators

- 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_3O_4 anode

Transition metal oxides



✓*High capacity*

✓*Safe voltage window*

PLUS

+*Inexpensive*

+*Benign materials*

+*Scalable Synthesis*

◆ MoO_3

◆ Fe_3O_4

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.

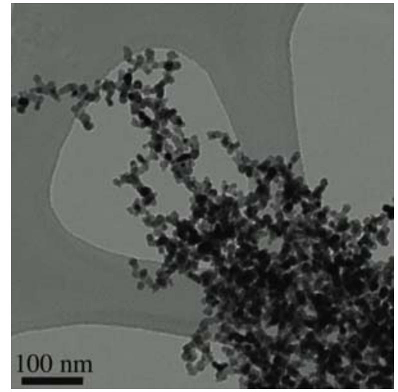
- Jan. 2010- Employed ALD-coated metal oxide (MoO_3) electrodes in full cells with lithium excess cathodes (LEC) supplied by ANL and demonstrated improved performance. (LEC = $0.5Li_2MnO_3 0.5Li(Mn_{0.31}Ni_{0.44}Co_{0.25})O_2$).

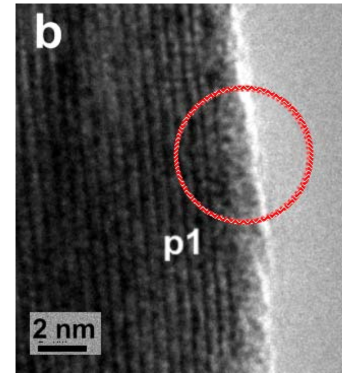
- March 2010- Showed high capacity and high rate capability of iron oxide in a conductive 3-D mesh without any binder and demonstrated durable cycling for a Li-ion anode.

- 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.

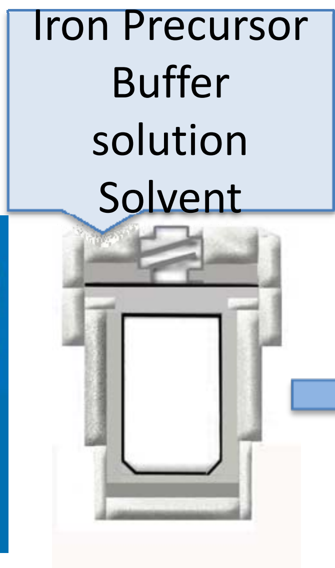
Approach: Improve Rate Capability of High Volume Expansion Materials

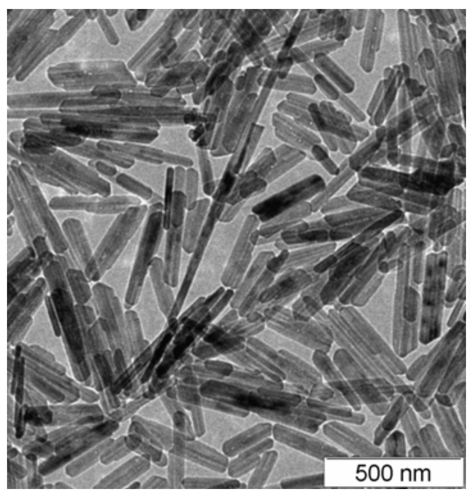
1. MoO_3 nanoparticles produced with economical hot-wire chemical vapor deposition (HWCVD). Atomic layer deposition (ALD) coatings enable durable rate capability.





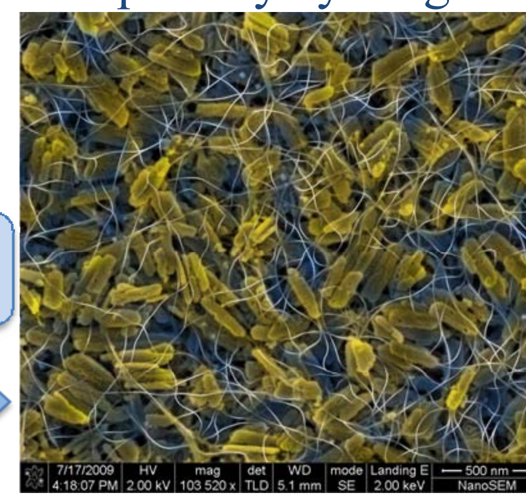
2. Iron oxide made with inexpensive hydrothermal process. 5 wt.% single wall carbon nanotubes (SWNTs) enable binder-free electrode with high-rate capability cycling.





TEM of as-synthesized product

Annealing w/ SWNT



Fe_3O_4/ SWNT electrode

L.A. Riley, A.S. Cavenagh, S.M. George, Y. S. Jung Y. Yan S-H. Lee and A.C. Dillon *ChemPhysChem* (in press).
C. Ban, Z. Wu, D. T. Gillaspie, L. Chen, Y. Yan, J. L. Blackburn, and A.C. Dillon , *Advanced Materials* (in press).

Atomic Layer Deposition (ALD) Protective Coatings

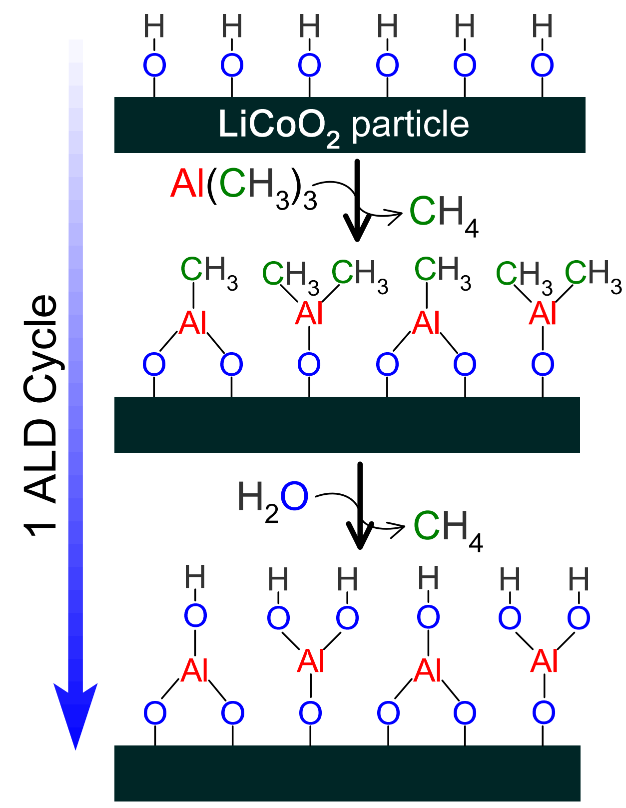
Layer by layer conformal Al_2O_3 coatings with sequential surface reactions

A) Surface-OH + $Al(CH_3)_3$

→ Surface-O-$Al(CH_3)_2$ + CH_4

B) Surface-O-$Al(CH_3)_2$ + 2 H_2O

→ Surface-O-$Al(OH)_2$ + 2 CH_4



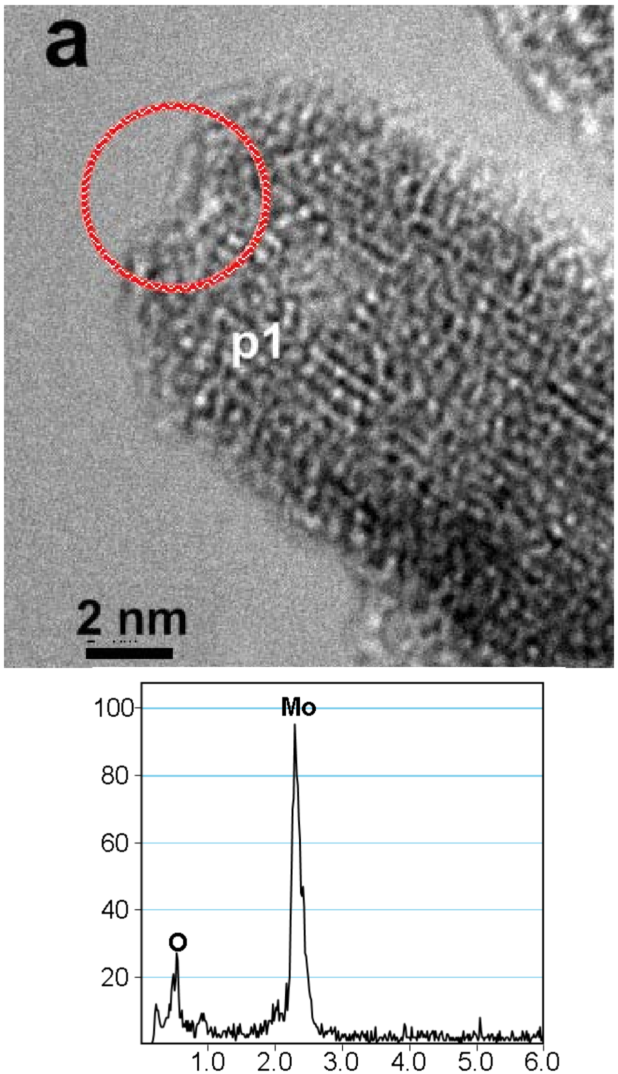
A.C. Dillon, A.W. Ott, J.D. Way and S.M. George *Surface Sci*. 322 (1995) 230.

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

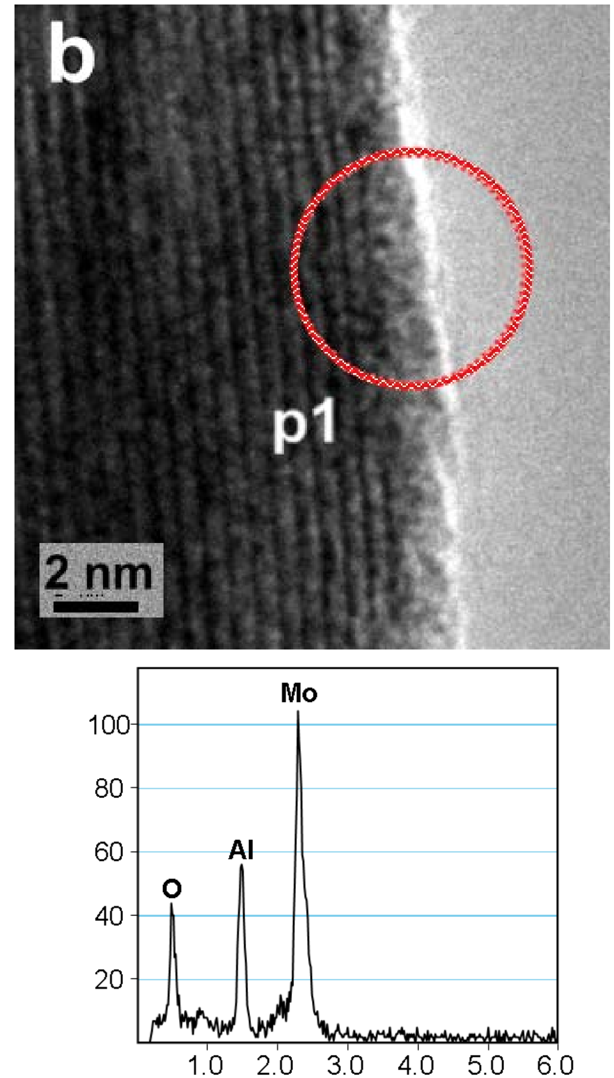
Accomplishment: ALD thin conformal coatings are employed to improve durable high-rate cycling performance of high-volume expansion materials.

ALD on nano-MoO_3 Particles

BEFORE ALD

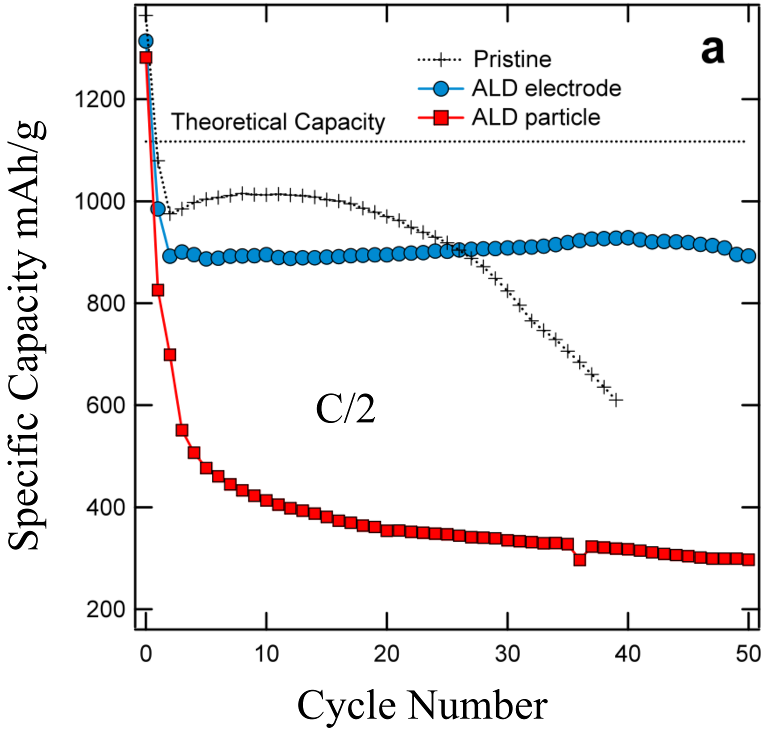


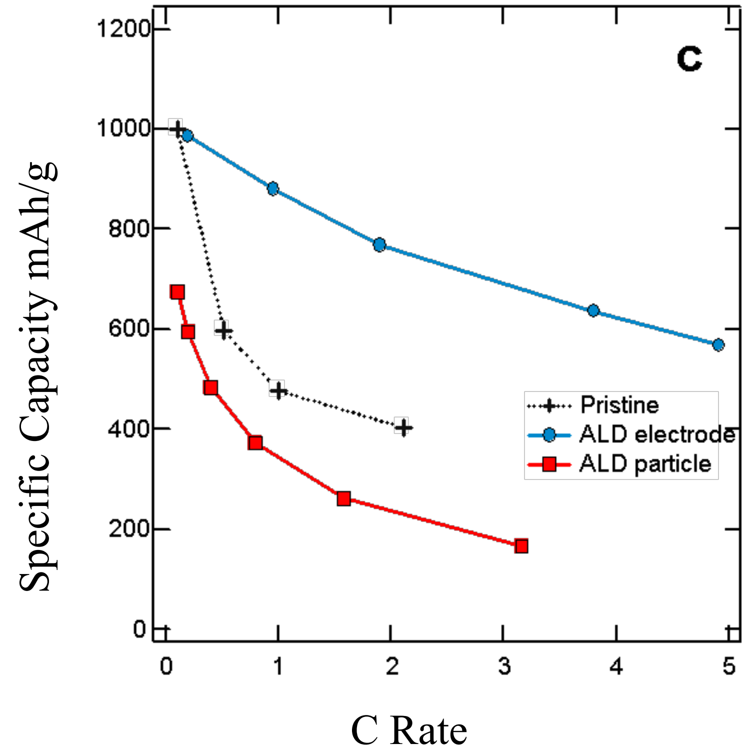
AFTER ALD



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.

Improved Rate Capability for MoO_3 Coin Cell

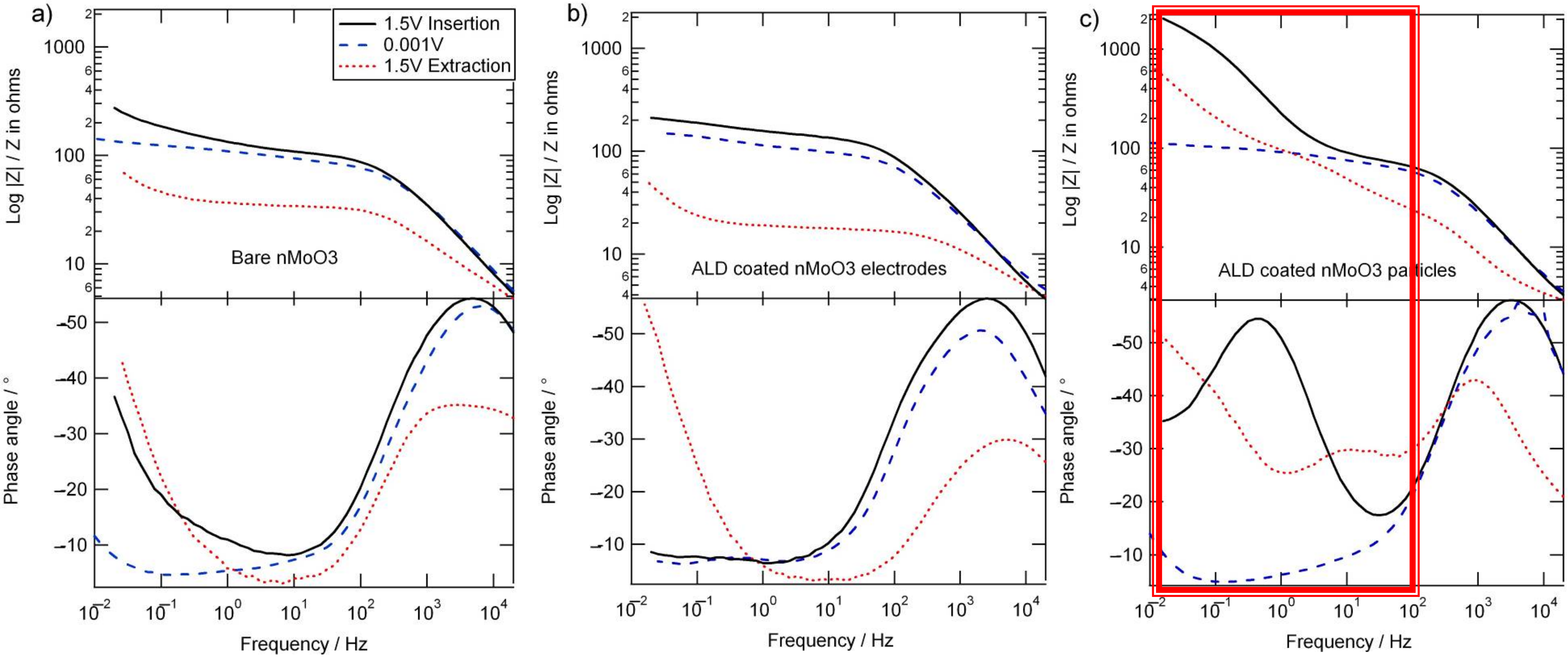




A thin ALD coating resulting from four ALD sequences (~8 Å) applied to the full electrode enables MoO_3 nanoparticles to cycle in a coin cell at high rate. The coating "knits or glues" the MoO_3 nanoparticles to the conductive additive and electrode preventing mechanical degradation due to volume expansion. Note: this does not occur when the coating is applied to the MoO_3 particles only.

L.A. Riley, A.S. Cavanagh, S.M. George, Y.S Jung, Y..Yan, S.-H. Lee and A.C. Dillon ChemPhysChem (in press).

Frequency Response Analysis Shows Importance of Full Electrode Coating

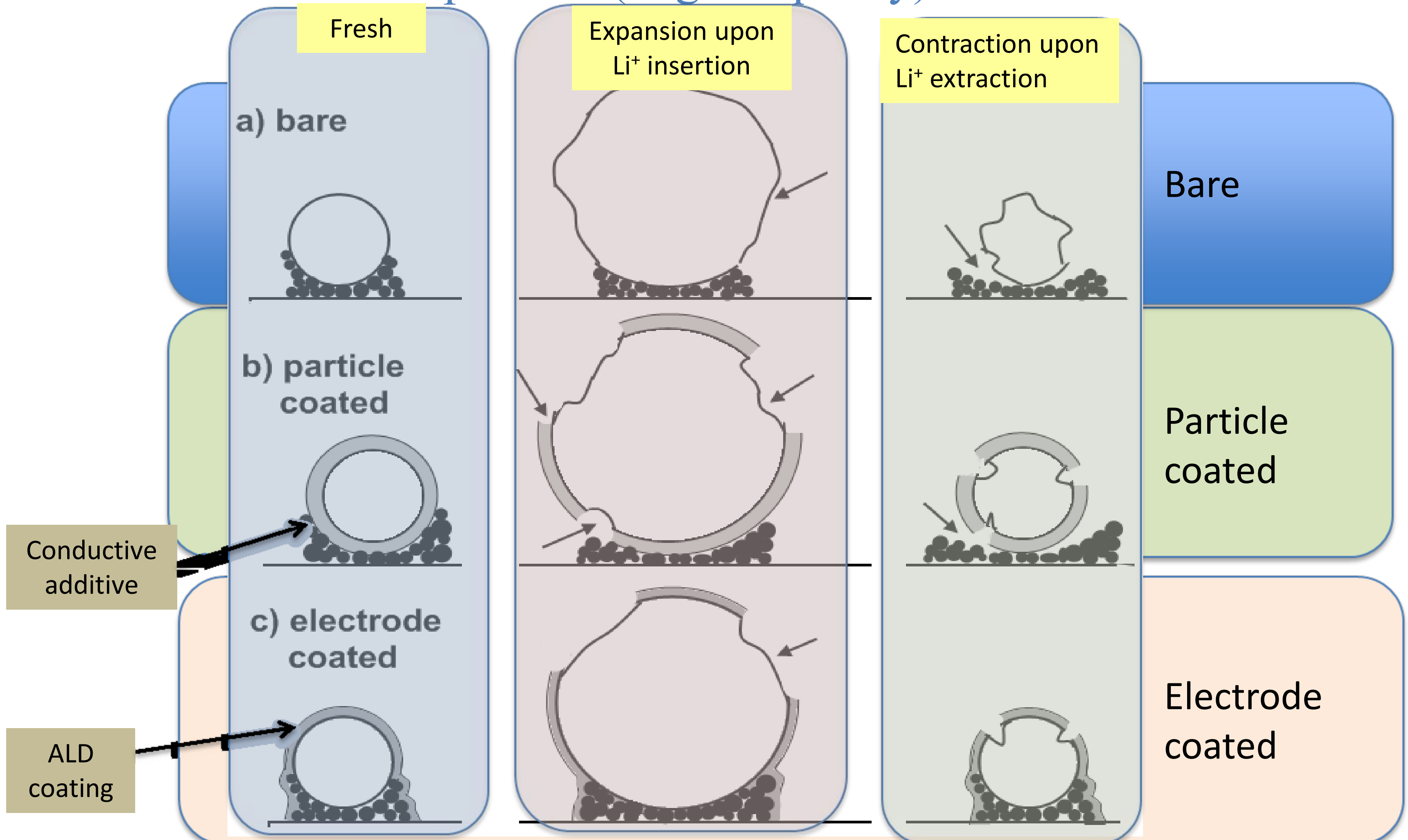


Similar frequency responses between bare and ALD coatings on electrode

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

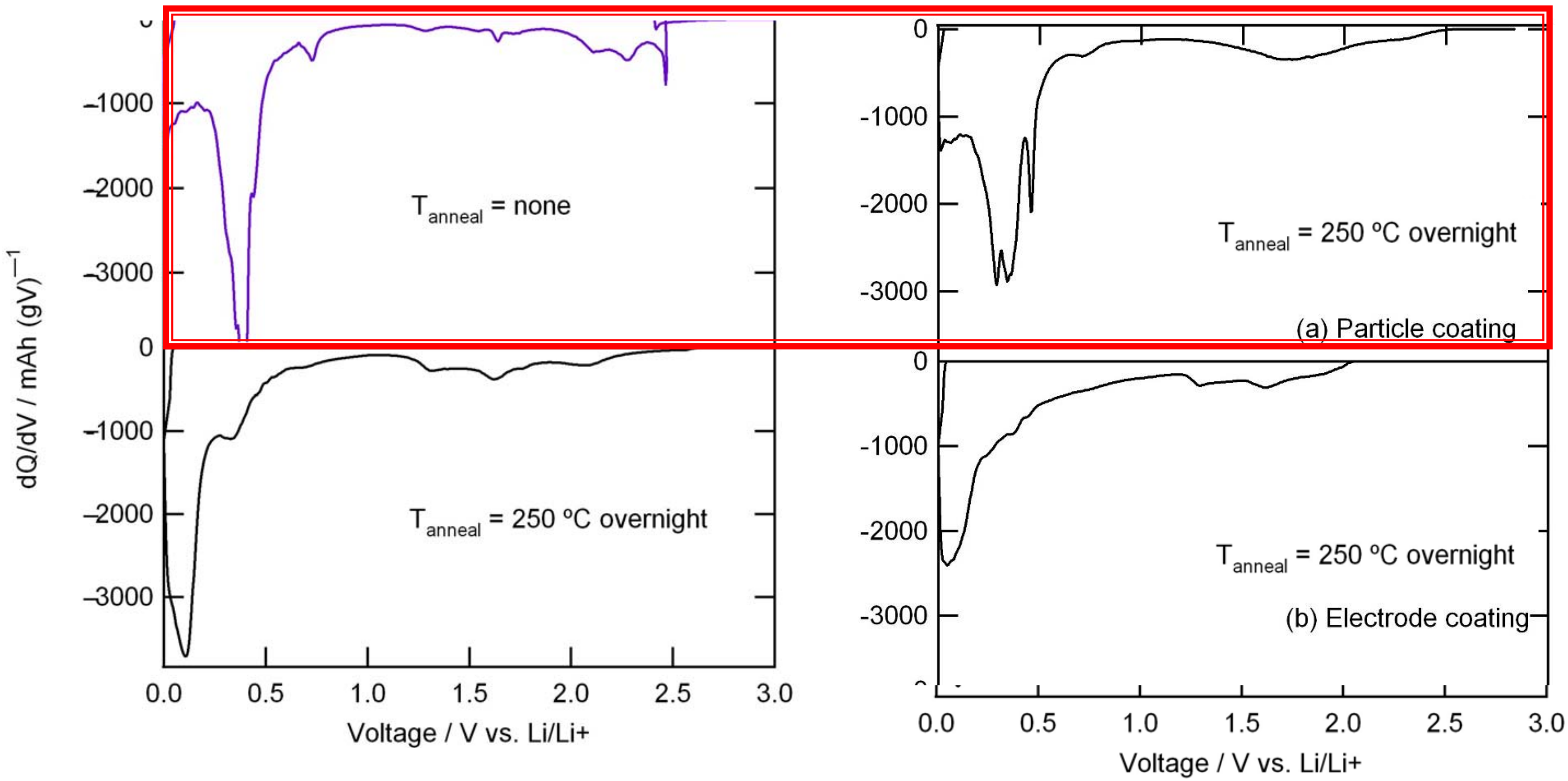


Accomplishment: Although cracking of the Al_2O_3 ALD coating likely occurs upon volume expansion / contraction, it still provides an adhesive layer that delays the onset of mechanical degradation due to volume expansion. Development of more flexible ALD coatings is possible.

Evidence that ALD "Glues" MoO_3 to Conductive Additive

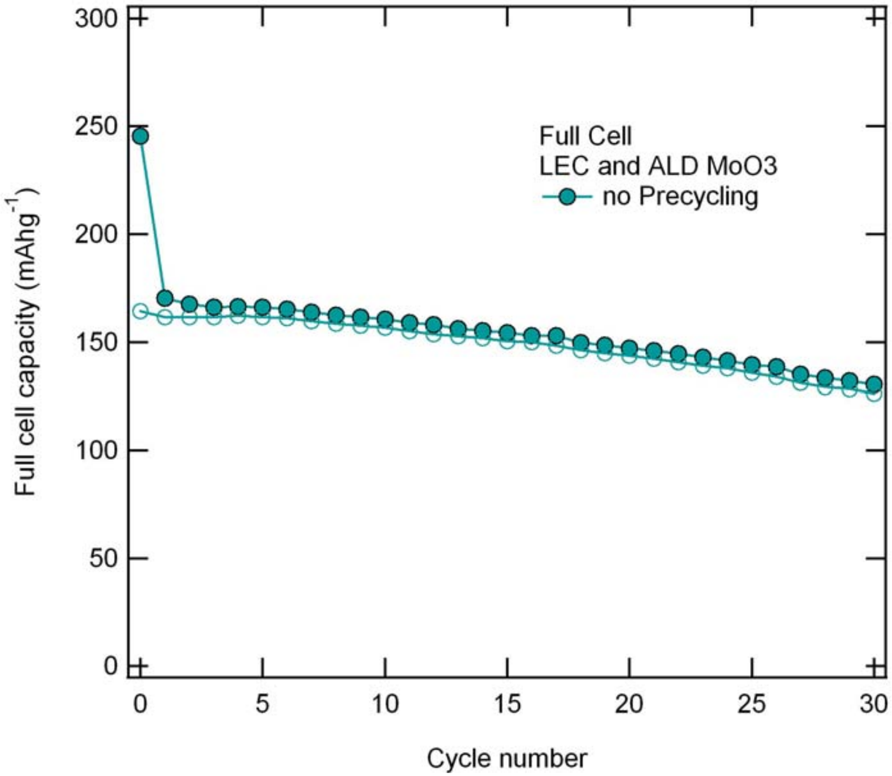
BARE MoO_3
Carbothermal reduction through annealing

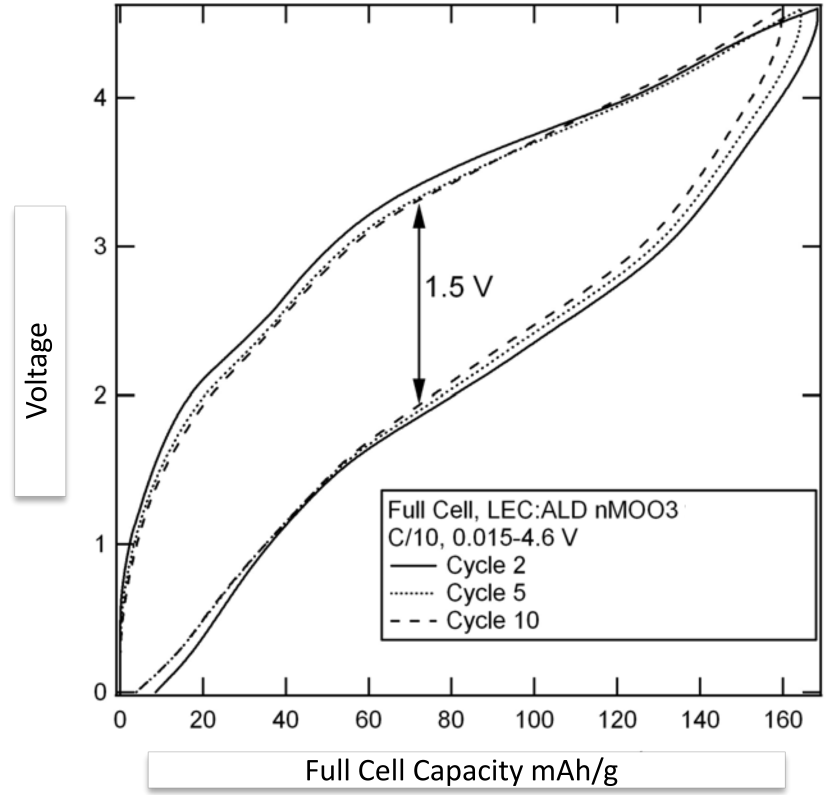
ALD-coated MoO_3
Annealing effects



Accomplishment: Carbothermal reduction upon heat treatment for ALD coated electrode confirms that MoO_3 particles remain in excellent contact with conductive additive.

ALD MoO_3 Improves Full Cell with ANL Cathode





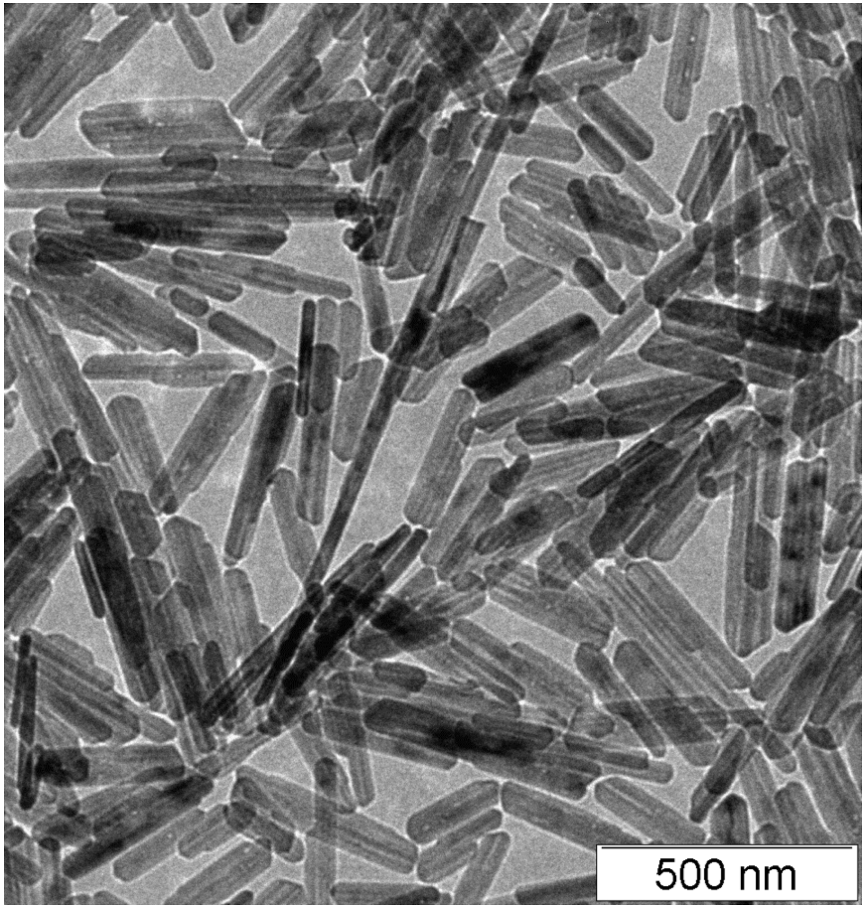
High capacity (~160 mAh/g), high efficiency (>99%) full cell with no pre-lithiation of the electrodes. *MoO_3 electrode coated with 4-secquences Al_2O_3 by ALD.*

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/$LiCoO_2$

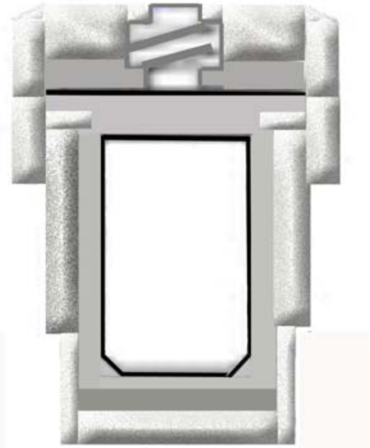
Accomplishment: By coating MoO_3 with ALD the full cell performance when coupled with ANL state-of-the-art cathode is improved.

Synthesis of Inexpensive Iron Oxide Binder-free Electrodes

Patent Application Filed



As prepared FeOOH nanorods



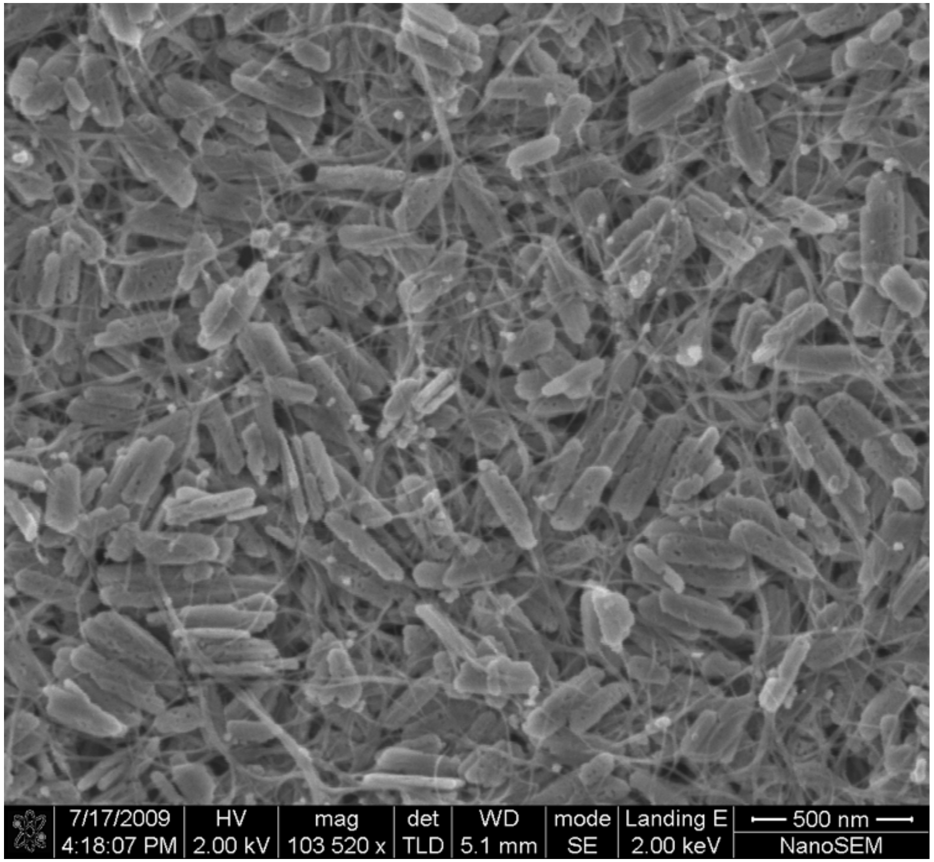
• FeOOH nanorods are prepared by a simple hydrothermal technique.

• 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

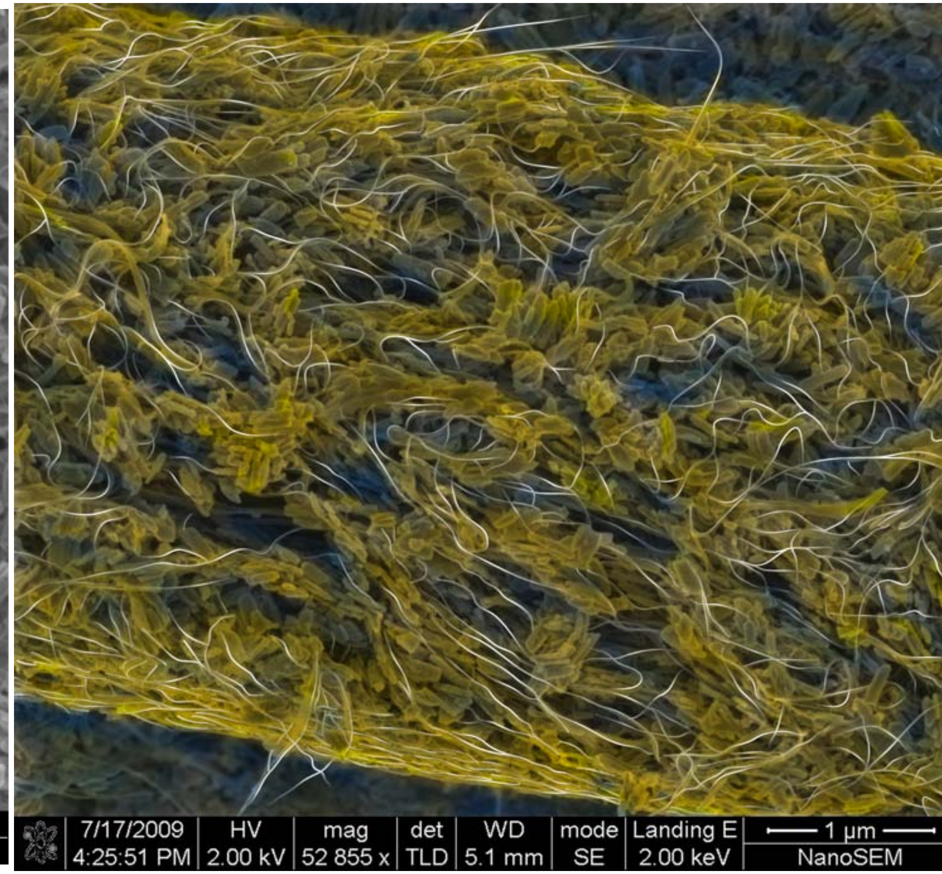
Accomplishment: Abundant / inexpensive and light iron oxide precursors are made by potentially scalable economical hydrothermal technique.

SEM Images of Binder-free Fe_3O_4 / SWNT Anodes that Contain 95 wt.% Active Material and 5 wt.% SWNTs



Fe_3O_4 nanorods in a SWNT net

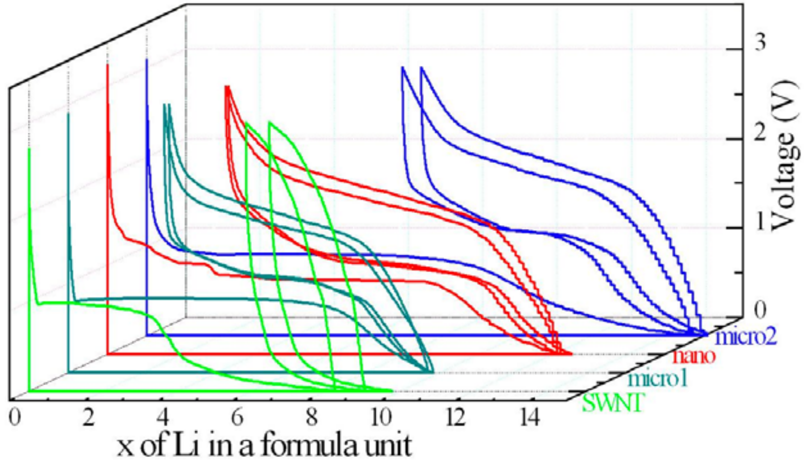
C. Ban, Z. Wu, LChen, Y. Yan and A.C. Dillon *Advanced. Materials.*, (in press).

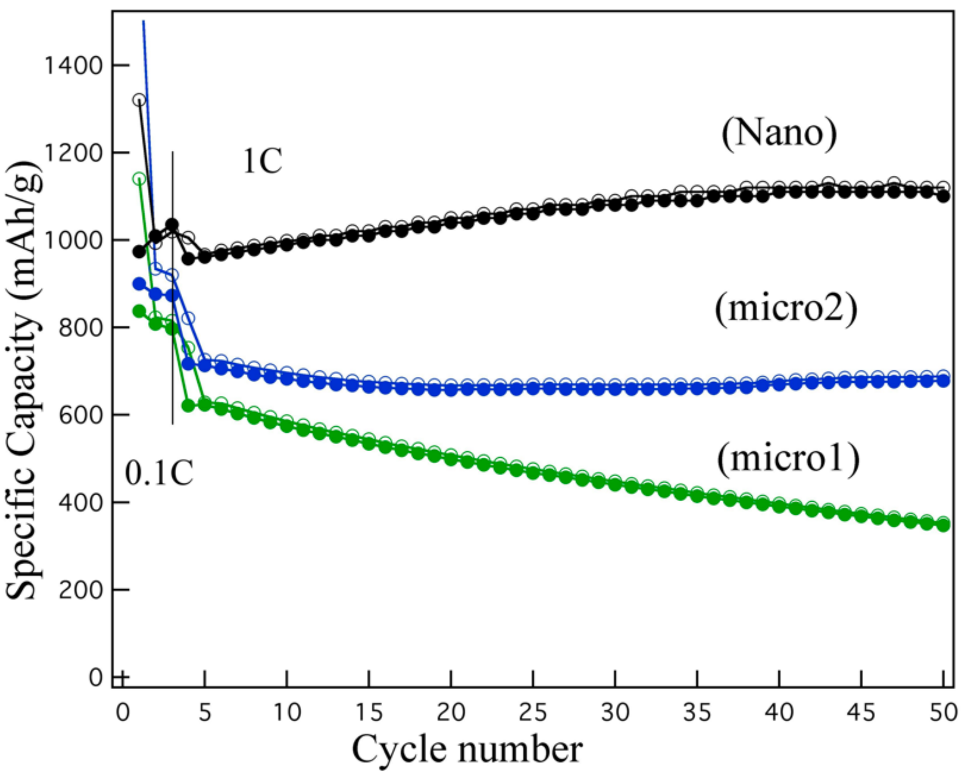


Color-enhanced cross sectional image with Fe_3O_4 (yellow/blue) and 5 wt.% SWNTs (white).

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.

Cycling stability of Binder-free Fe_3O_4 / SWNT Anodes





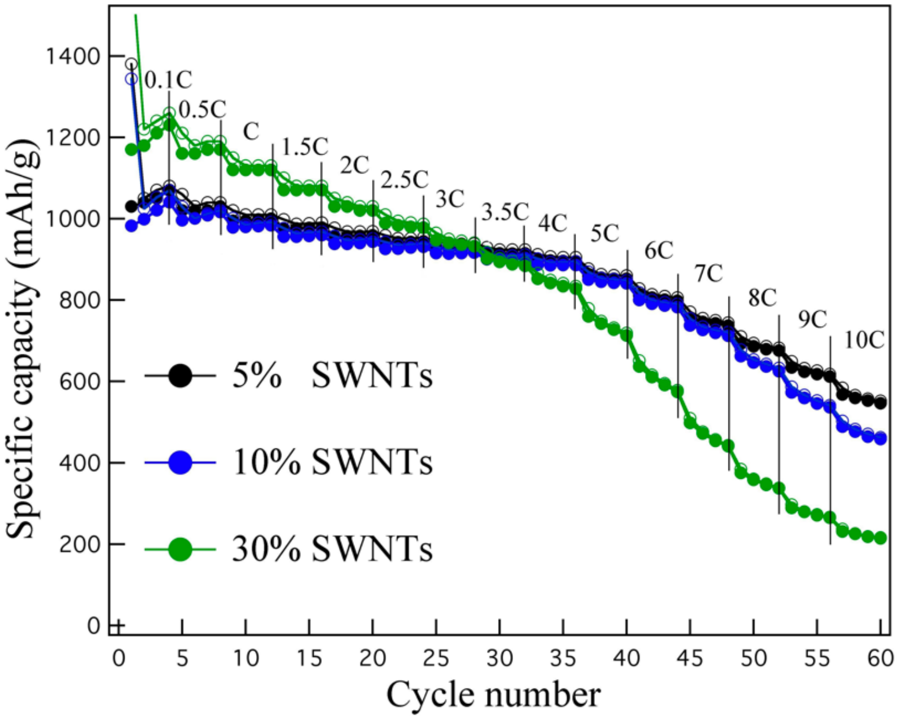
• Voltage profiles and cycling performance of Fe_3O_4/SWNT (nano) compared to μm-sized Fe_3O_4/SWNT (micro2) and μm-sized Fe_3O_4 with PVDF binder / acetylene black (micro1).

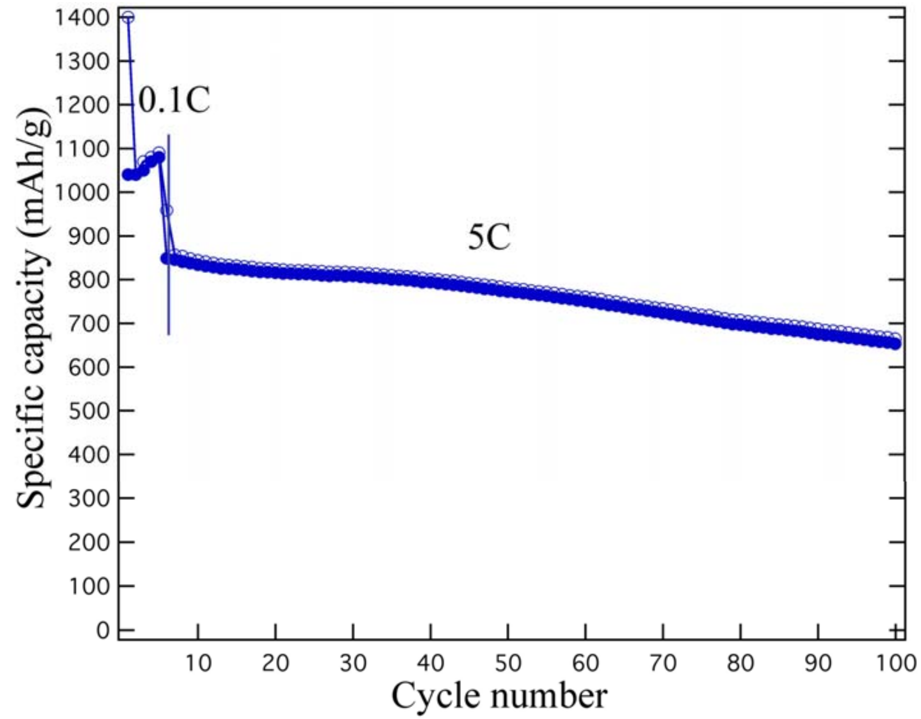
• This suggests that this process could be employed for any high-volume expansion material.

• 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 Fe_3O_4 / SWNT Anodes



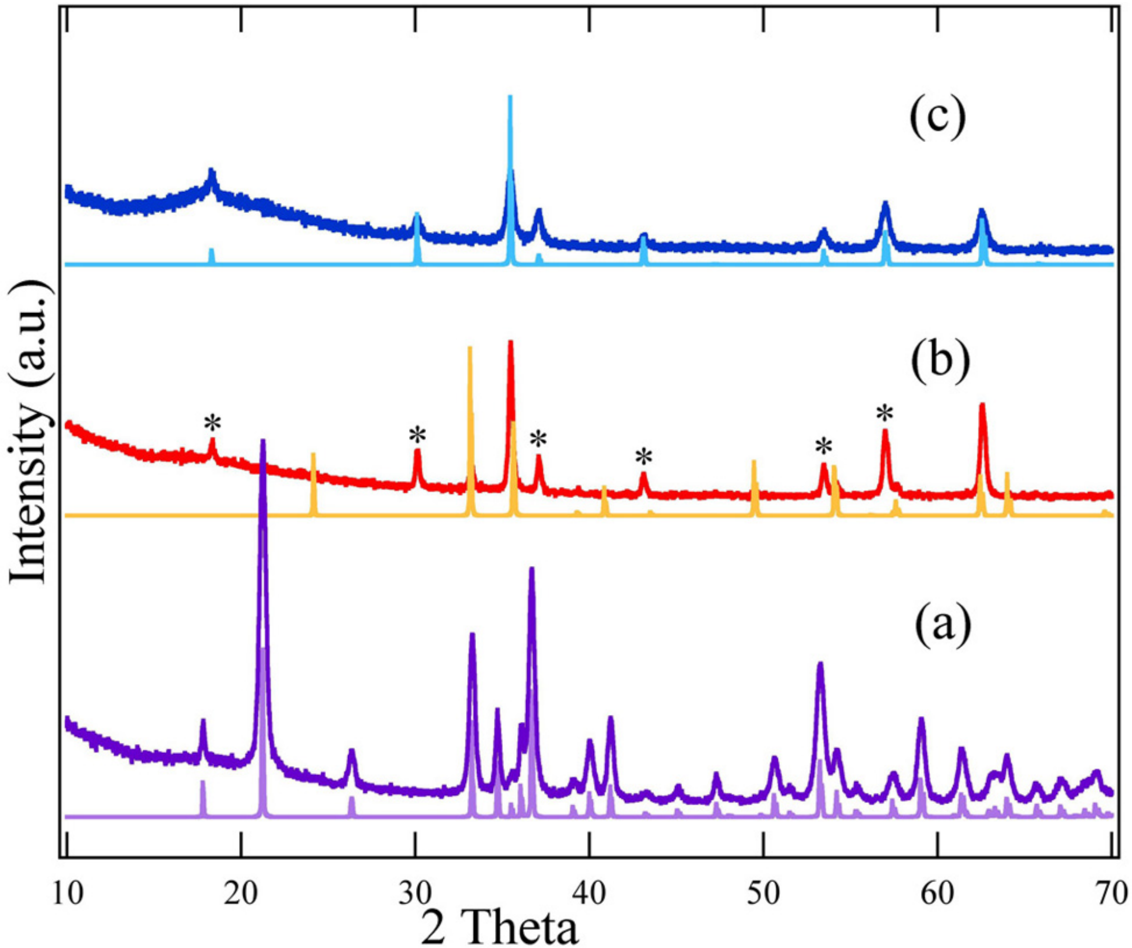


Stable capacity of over 600 mAh/g is observed at 10C (one charge/discharge in 6 minutes) and with only 5 wt.% SWNTs.

Fe_3O_4 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.**

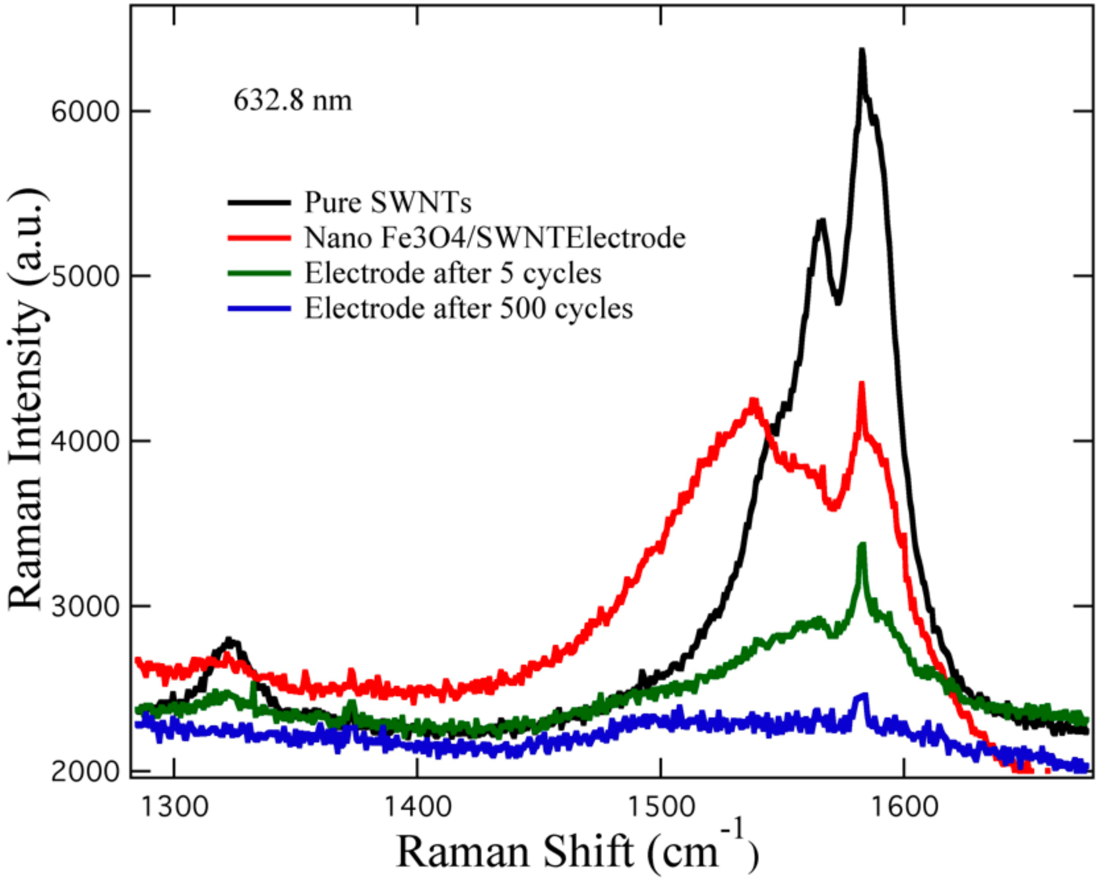
Mechanistic Understanding with X-ray diffraction (XRD)



Initial particles change from tetragonal α-FeOOH (a) to a mixture of Fe_2O_3 (hematite) and Fe_3O_4 (magnetite) when heated at 450 ˚C in Ar but are completely reduced to Fe_3O_4 when heated with SWNTs.

Finding: Simple annealing process converts hydrothermal precursor to Fe_3O_4.

Raman Spectroscopy of Fe_3O_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 ~ 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 Al_2O_3 atomic layer deposition (ALD) deposited coatings on fully fabricated MoO_3 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 MoO_3 anode was successfully paired with ANL's state-of-the-art lithium excess cathode $0.5Li_2MnO_3 0.5Li(Mn_{0.31}Ni_{0.44}Co_{0.25})O_2$ and a capacity of 160 mAh/g was achieved *without pre-lithiation*.
- A binder-free electrode containing 95 wt.% Fe_3O_4 active material suspended in a "flexible single-wall carbon nanotube net" had a capacity of 1000 mAh/g (2000 mAh/cm^3) 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.

	Gravimetric Capacity (mAh/g)	Volumetric Capacity (mAh/cm^3)	Full Cell Capacity (mAh/g)
MoO_3	900 (C/2)	~ 800	160
Fe_3O_4	1000 (C)	~2000	N/A (to be measured later)
Commercial	350 (graphite)	770 (graphite)	80 (graphite/$LiCoO_2$) (J.Power Sources 88, p.237, 2000)

Acknowledgments

- DOE Vehicle Technologies Office, BATT
  - Tien Duong
  - David Howell

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