



... for a brighter future

Lithium Metal Anodes

Jack Vaughey, Carmen Lopez, Dennis Dees
Chemical Sciences and Engineering Division, Argonne

Annual Merit Review
DOE Vehicle Technologies Program

Washington, D.C.

May 19, 2009

*Project ID:
esp_17_vaughey*



U.S. Department
of Energy

UChicago ►
Argonne_{LLC}

A U.S. Department of Energy laboratory
managed by UChicago Argonne, LLC

Vehicle Technologies Program



This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Start date: October, 2008
- End date: September, 2014
- Percent complete: <8% complete

Budget

- Total project funding
 - 100% DOE
- FY08: \$300K
- FY09: \$300K

Barriers

- 40 mile range for PHEV
 - Meeting all of the goals of the PHEV program using a lithium electrode
 - Improving stability, safety, and cycling efficiency of the lithium metal electrode.

Partners

- Collaborations
 - Russell Cook, Rachel Kontala (National Electron Microscopy Center (ANL))
 - David Gosztola (Center for Nanoscale Materials (ANL))

Objectives

- To overcome the well known problems with the metallic lithium electrode - stability, safety, and cycling efficiency - that continue to block its implementation into advanced lithium batteries for PHEVs.
 - *Characterize the morphological evolution of the lithium electrode on cycling*
 - *Develop and characterize coating technologies that will withstand the lithium cell environment*

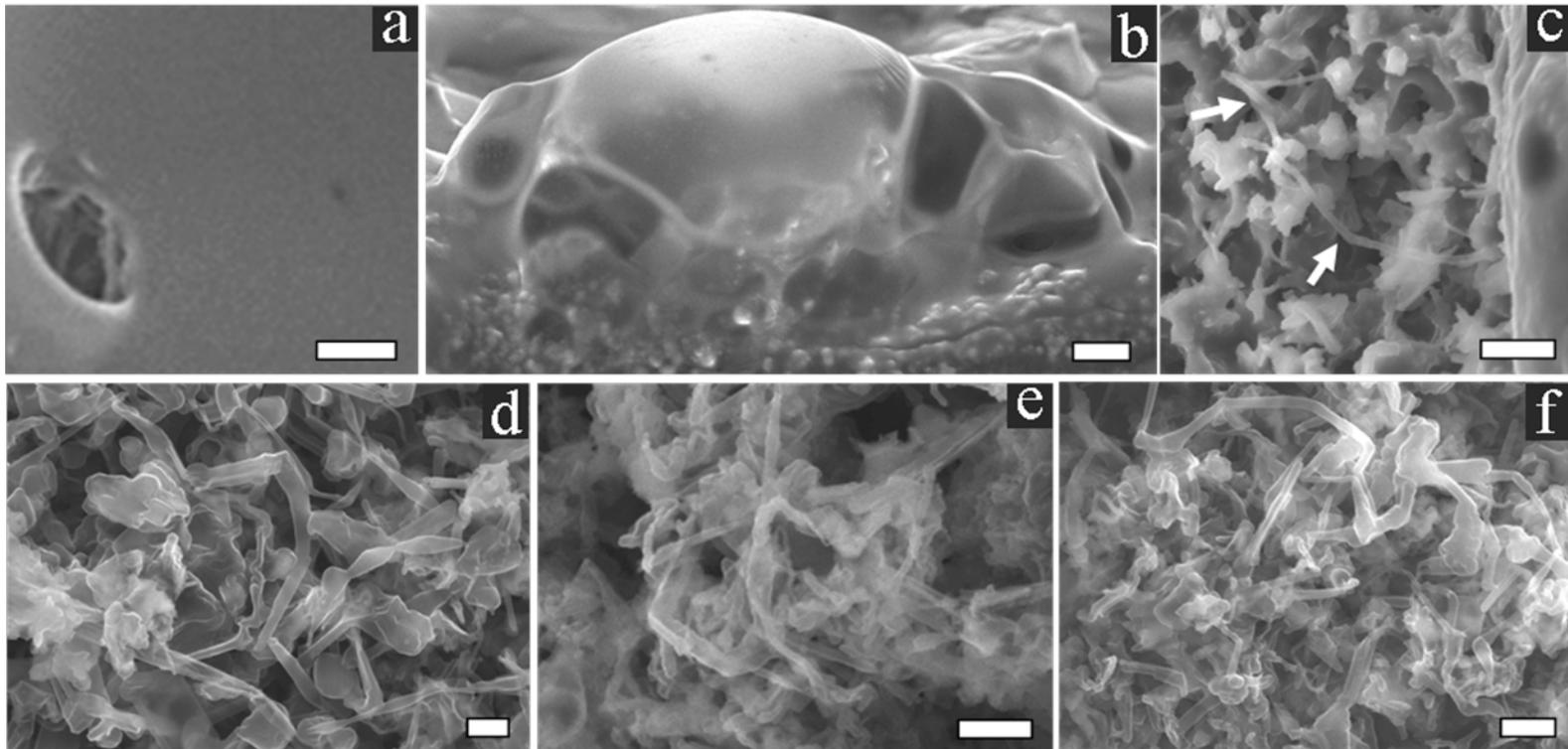
Milestones (FY08-09)

- Synthesize, design and characterize polymer-alloy composite films deposited on the surface of a lithium electrode – *ongoing*
- Utilize characterization tools available at the National Electron Microscopy Center and Center for Nanoscale Materials – *ongoing*
- Investigate new types of surface coatings with better surface adhesion – *ongoing*
- Synthesize, study, and determine failure mechanism for polymer and main group metal coatings – *completed*

Approach

- Establish a stable, dense, and uniform lithium/electrolyte interface exhibiting good electrochemical performance.
 - *Study and analyze the failure mechanism of various Li-metal electrode coatings. Develop conformal stable monolayer coatings using ALD (atomic layer deposition)-type chemistry.*
- Evaluate nanocomposite polymer/Li-ion conductor coatings and break the materials problem into its components.
- Use some of the latest microscopic and spectroscopic characterization equipment and develop methodologies to examine the lithium/electrolyte interface
 - *Established collaborations at the National Electron Microscopy Center and Center for Nanoscale Materials to gain access to required instrumentation.*

SEM Image of Cycled Lithium Electrode Surface



Lithium electrode surface - (a) with SEI (prior to cycling), (b) 2 cycles, (c) 10 cycles, (d) 50 cycles, (e) 100 cycles, (f) 250 cycles.

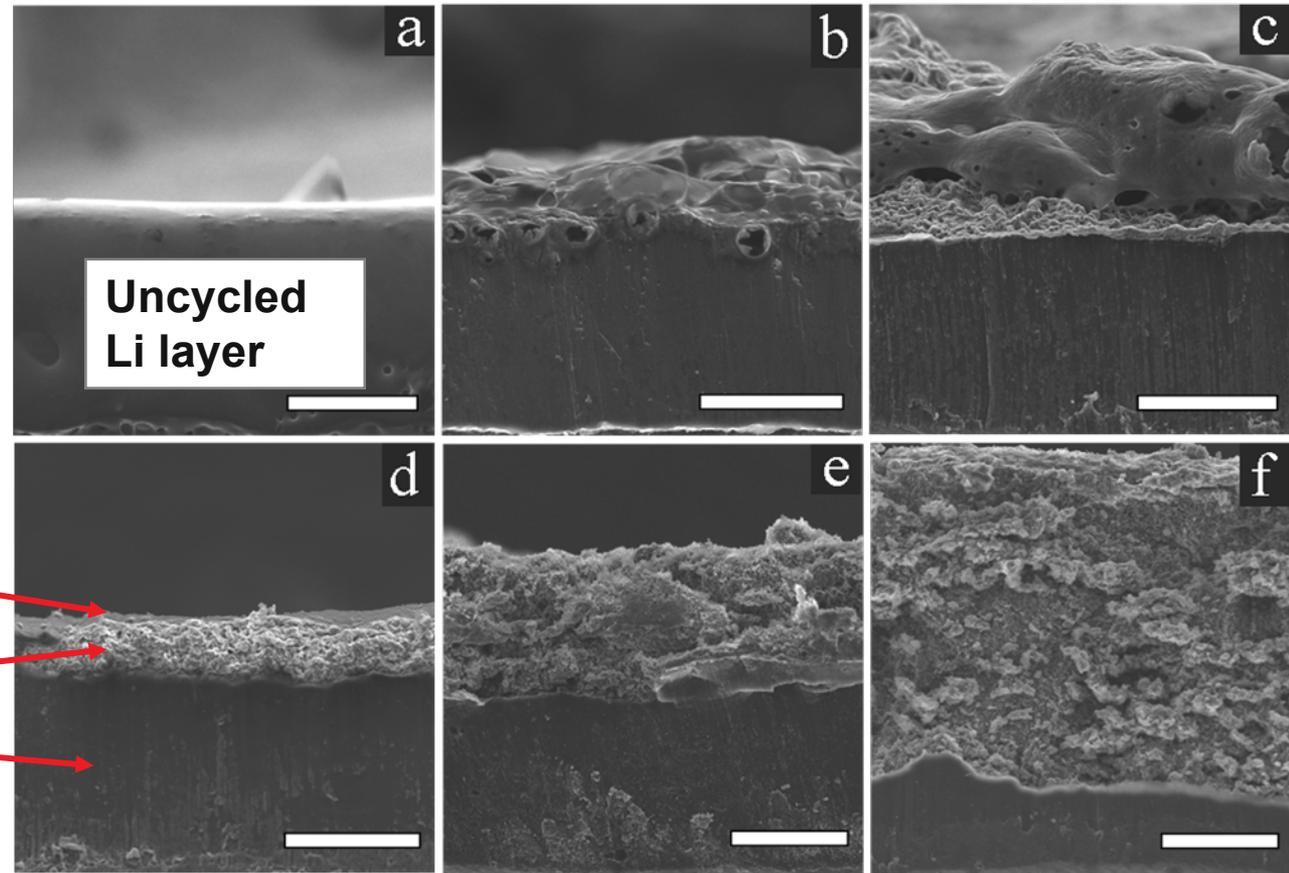
Scale bars: (a-b) 10 μm ; (c) 5 μm ; (d-f) 2 μm)

- Evidence for sub-SEI gas evolution leading to surface de-stabilization,
- Re-deposition creates higher porosity and supports formation of a surface dendritic layer.

Cross Sectional Analysis of the Lithium Electrode

SEM images (a) before cycling (with SEI layer), and (b) 2 cycles, (c) 10 cycles, (d) 50 cycles, (e) 125 cycles and, (f) 250 cycles. *The scale bars represent 100 microns.*

Dendritic layer →
Porous layer →
Dense layer →



- Cross sectional analysis highlights non-uniform growth of SEI.
- Typical cell cycles until initial lithium is 'used up'. Growth of central porous layer uses up available electrolyte ⇒ cell runs dry.
- Dendritic layer is only on top and has a relatively constant depth (15 μm).

Characterization of Li electrode w/ Cycling Current

■ Changes in cycling current produce different morphologies in different current regions.

■ Region I: Significant gas evolution under polymeric layer

■ Region II & III: Three-layer morphology

■ Region IV: No apparent changes

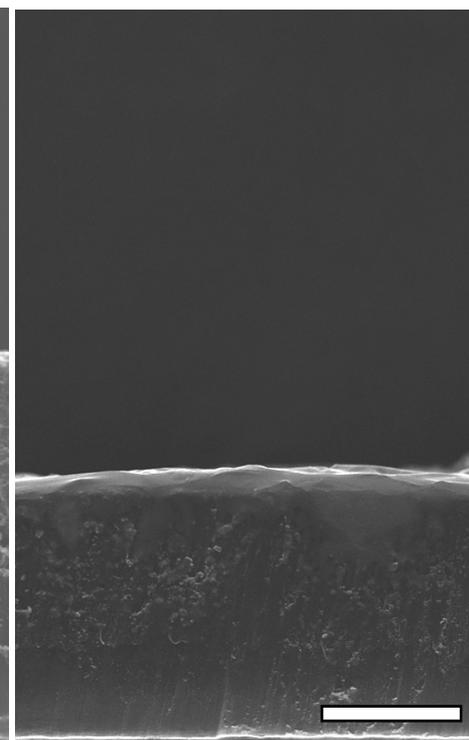
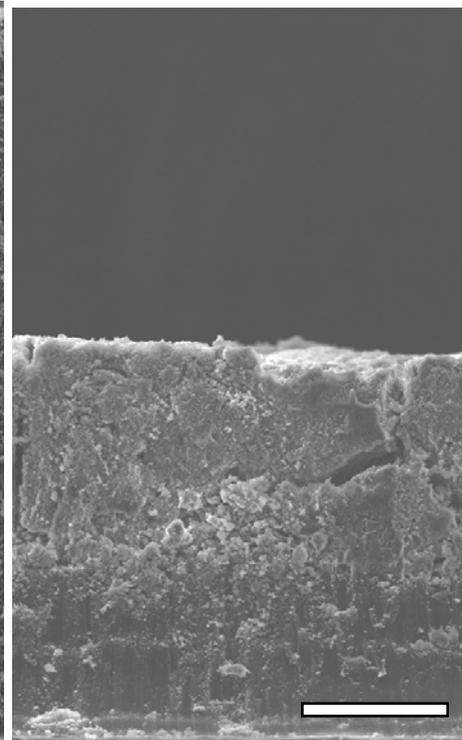
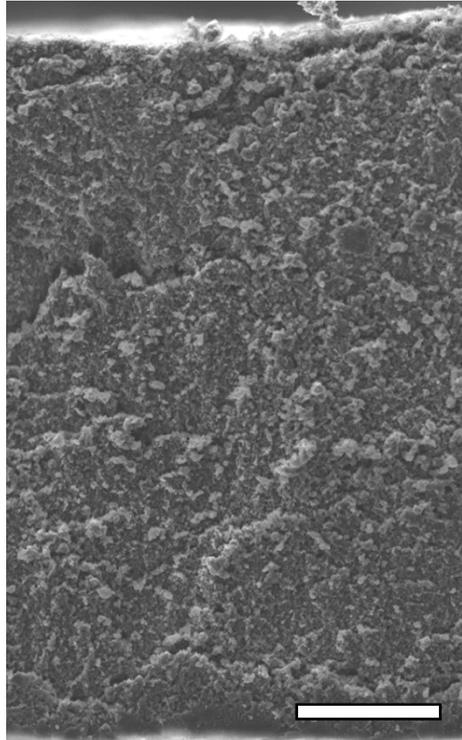
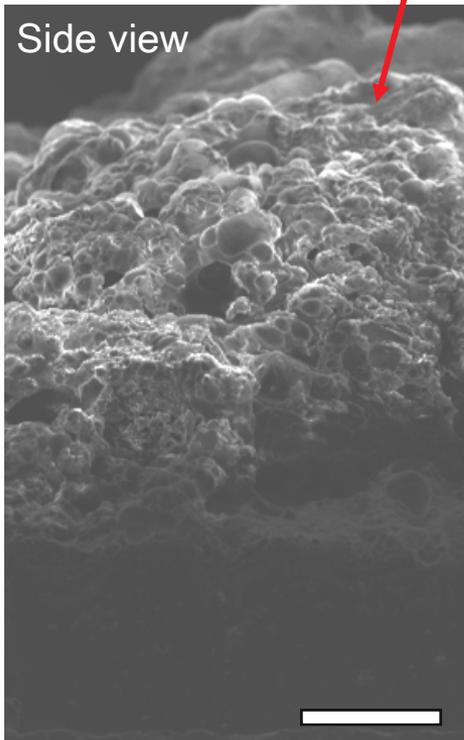
I: 0.1-0.125 mA/cm²

II: 0.25-3.12 mA/cm²

III: 6.25-12.5 mA/cm²

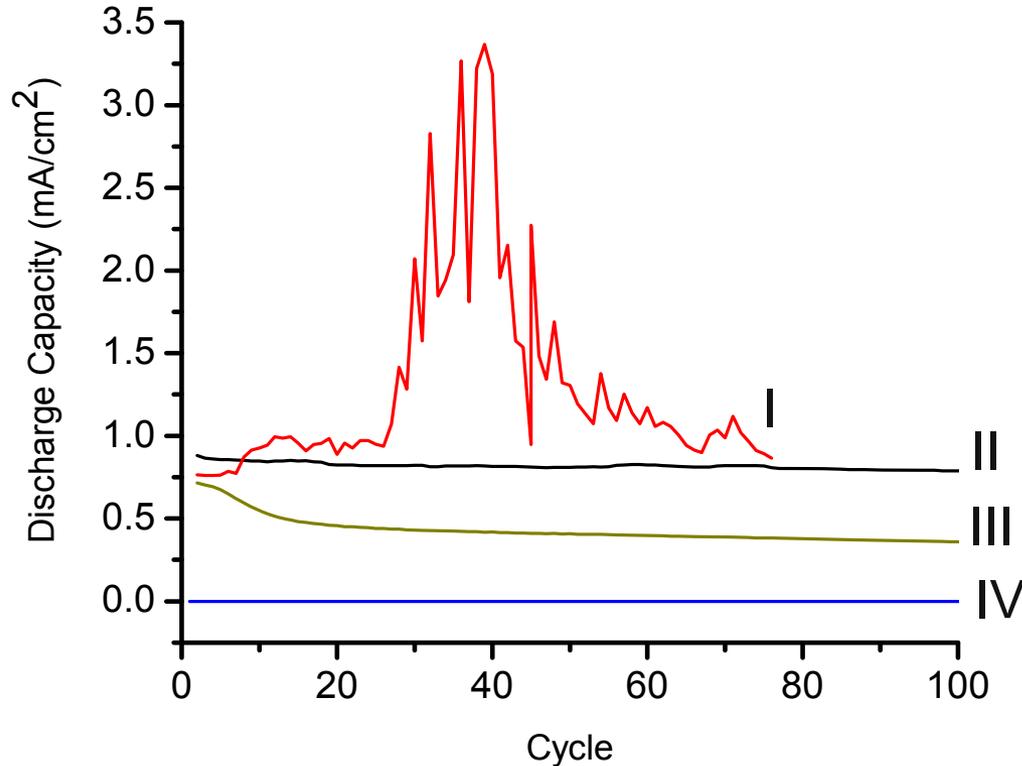
IV: ~ 25 mA/cm²

Side view

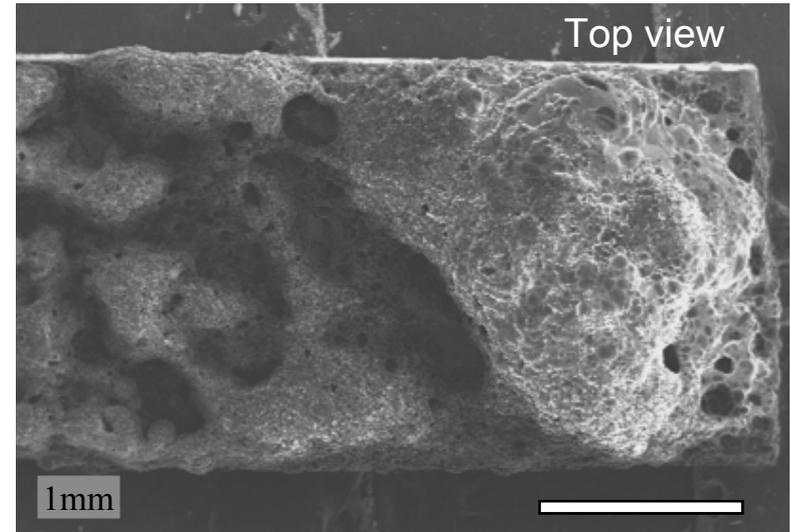


Scale bar: 100 μ m

Characterization of Li Electrode (cycling current)



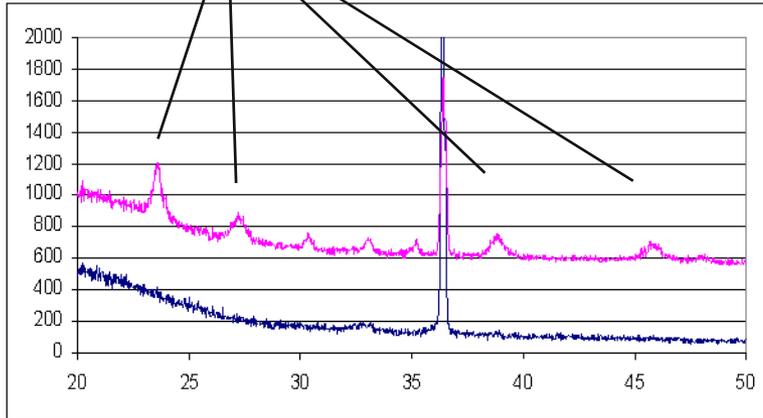
Region I



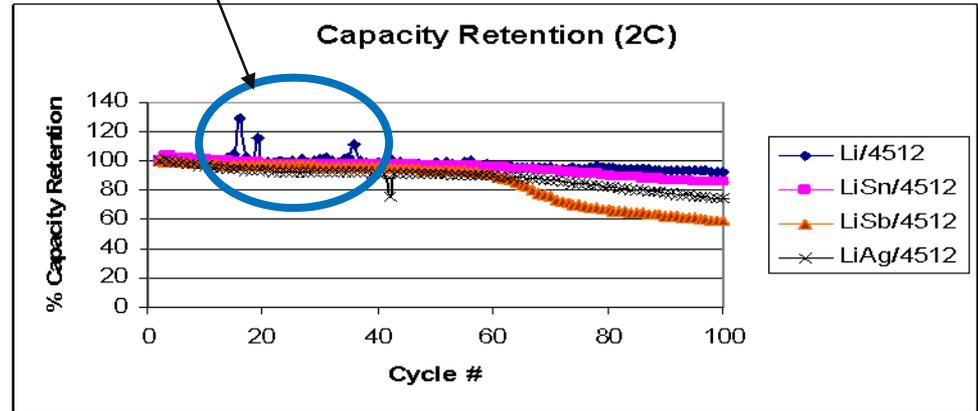
- Evidence of cell failure by short circuit (red line) only on current region I, where macroscopically rough morphology develops.
- Cell failure by shorting only occurs in lithium cells run at $< 0.25 \text{ mA/cm}^2$.

Lithium Main Group Metal Coatings (Recap)

Li_3Sb (10 nm particle size)



Shorting seen in uncoated Li-cell



- Baseline Cell \Rightarrow $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathode, 1.2M LiPF_6 EC/EMC electrolyte
 - *very stable cell chemistry allows assignment of cell changes to the lithium anode.*
- Lithium-Metal (Zintl) coatings on the lithium surface suppressed dendrite formation with minimal impact on cell impedance, notably at low coating thicknesses.
- Insulating or semiconducting intermetallics were found to be very stable in the cell environment with very high Li-ion diffusivities $\sim 3 \times 10^{-7} \text{ cm}^2/\text{s}$

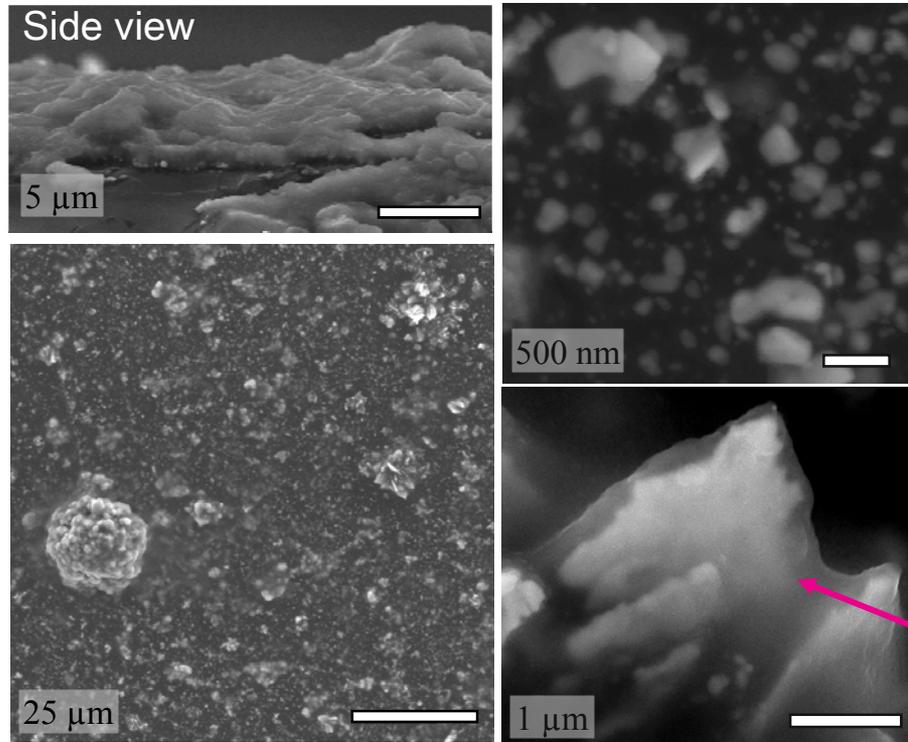
Intermetallic coatings suppressed dendrite formation but brittleness limits cell lifetimes.

Morphology of Coatings

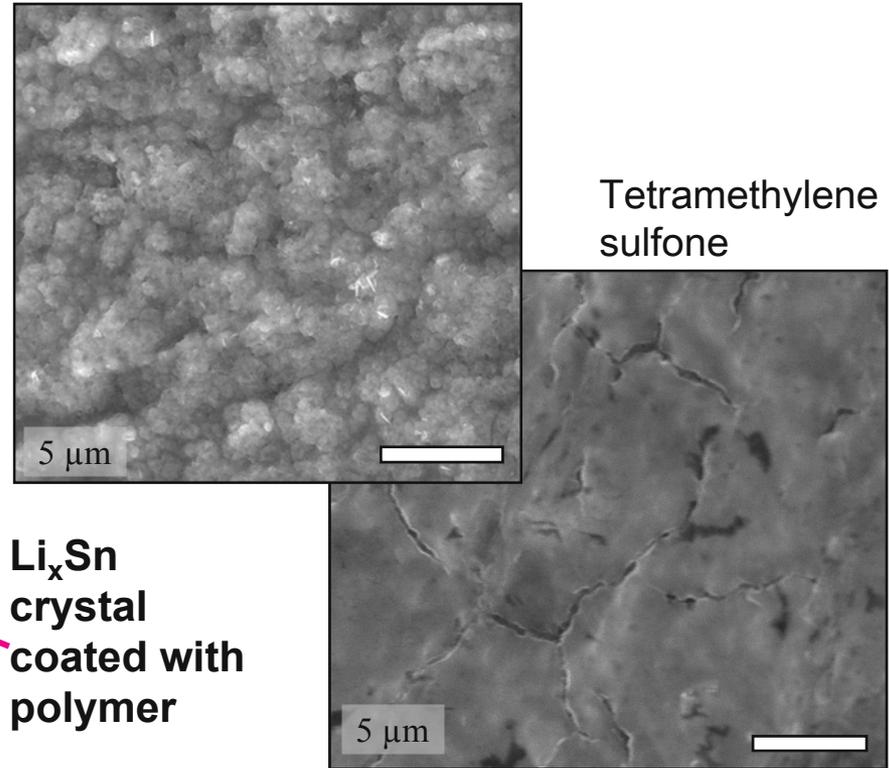
- Organic-Inorganic Nano-composites: nanoparticles/nanocrystals embedded on a polymeric matrix (VEC-derived)

- Organic-Organic composites: polymers formed on the surface of Li metal by solvent reduction and organic additives.

Sn_xLi coatings

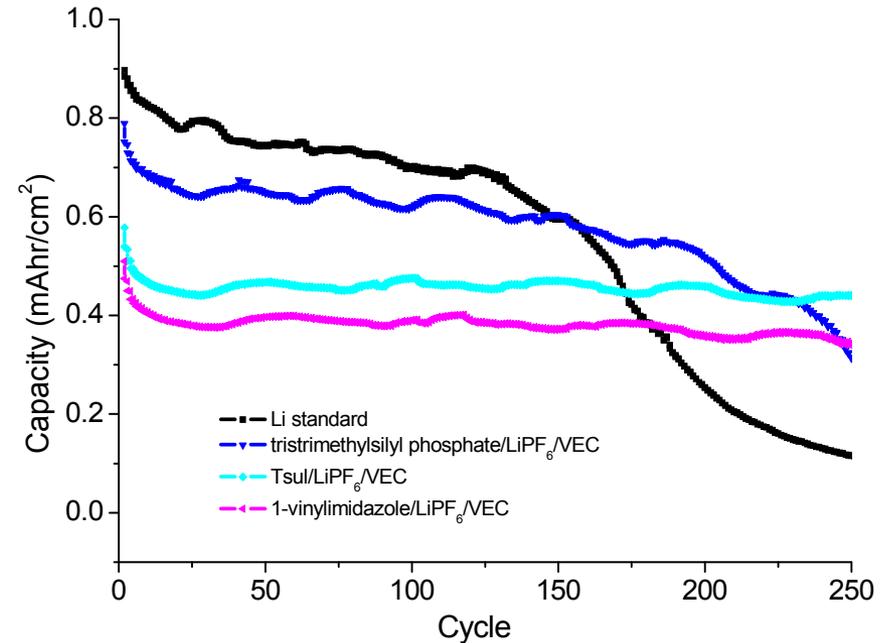
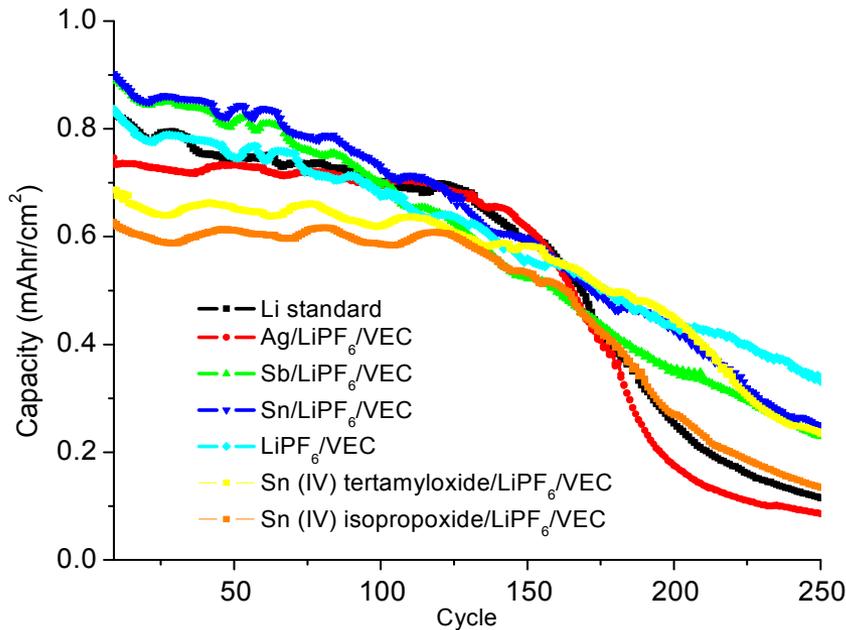


1-vinylimidazole



Electrochemical Performance of Coated Li

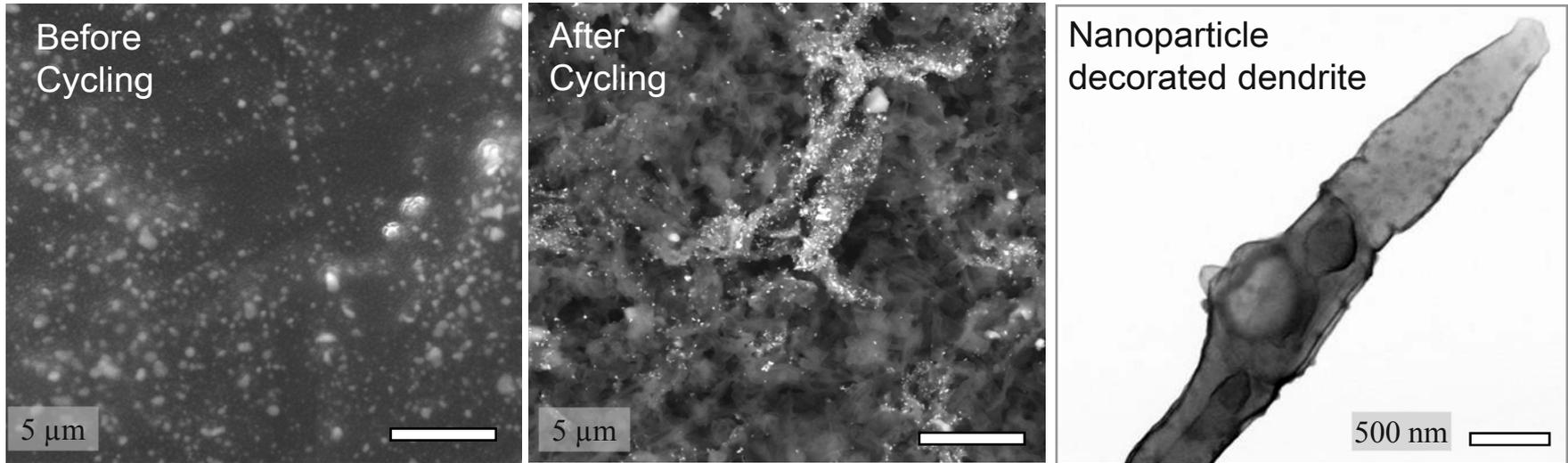
- Various solvent mixtures and composites have been tested:



- Organic-Inorganic nanocomposites inhibit dendrite-driven cell failure but confer only minimal improvements in cycle life.

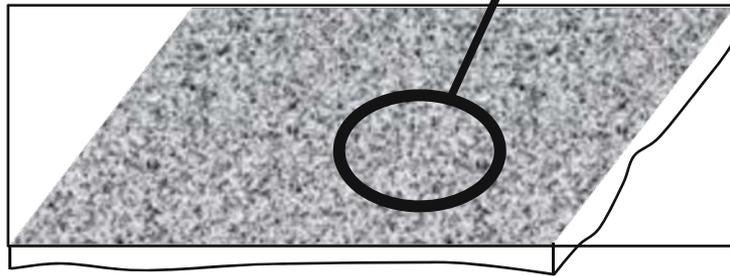
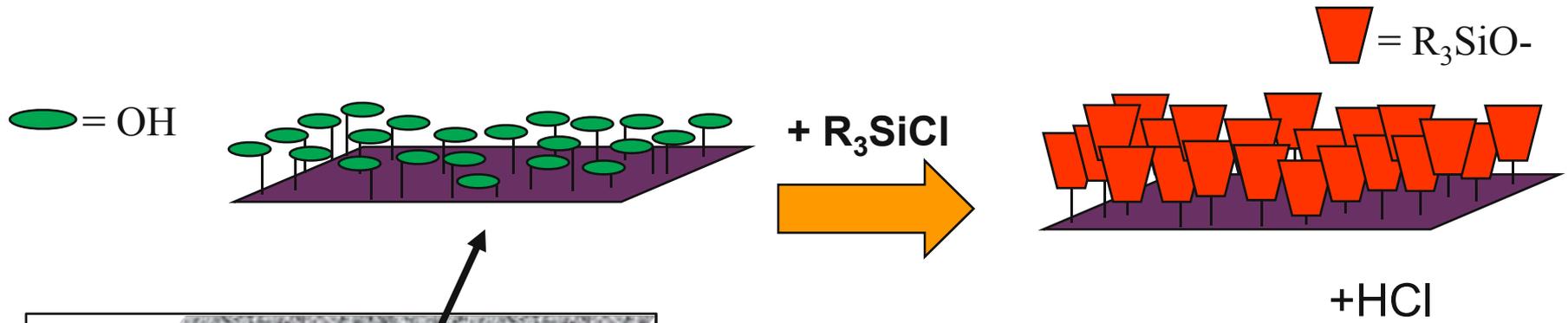
- Organic-additive derived polymer coatings exhibit lower capacity fade but with lower capacity due to an increase in cell impedance.

Composite Coatings: Li_xSn / VEC



- Polymeric component of the coating decomposes during cycling.
 - Nanoparticles remain localized on the dendritic layer
 - No evidence of nanoparticles migration into the porous layer
 - Nanoparticle *decorated* dendrites are produced instead of smooth wall dendrites
 - Further studies are required to determine stability/reactivity of these type of dendrites
- ⇒ *Nanoparticle coatings appear to alter dendrite formation and growth.*

Conformal Coatings- Synthesis



- *Li metal surface is hydroxy-terminated.* Kanamura, et al., *JES*, **141**, 2379 (1994); Naudin, et al., *JPS*, **124**, 518 (2003).
- *Chlorosilanes react with surface OH to form a siloxane bond.* Hair, et. al., *Colloids Surf A* **105**, 95 (1995).

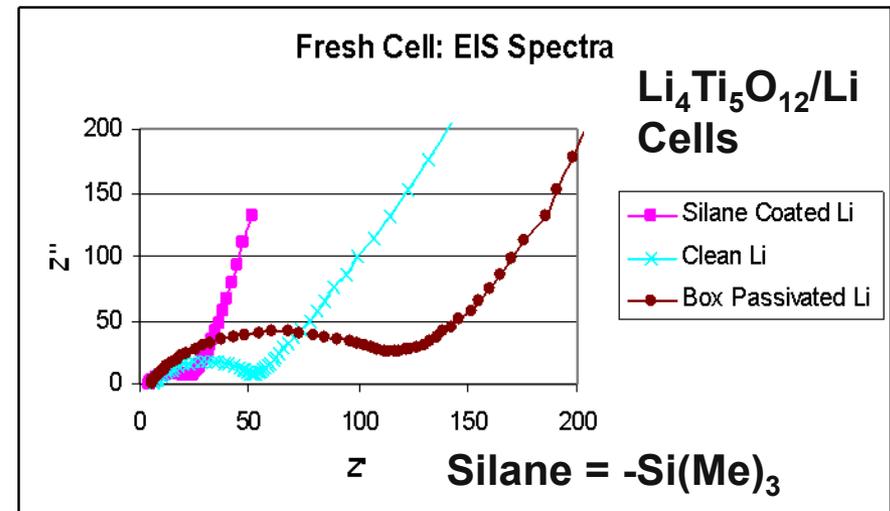
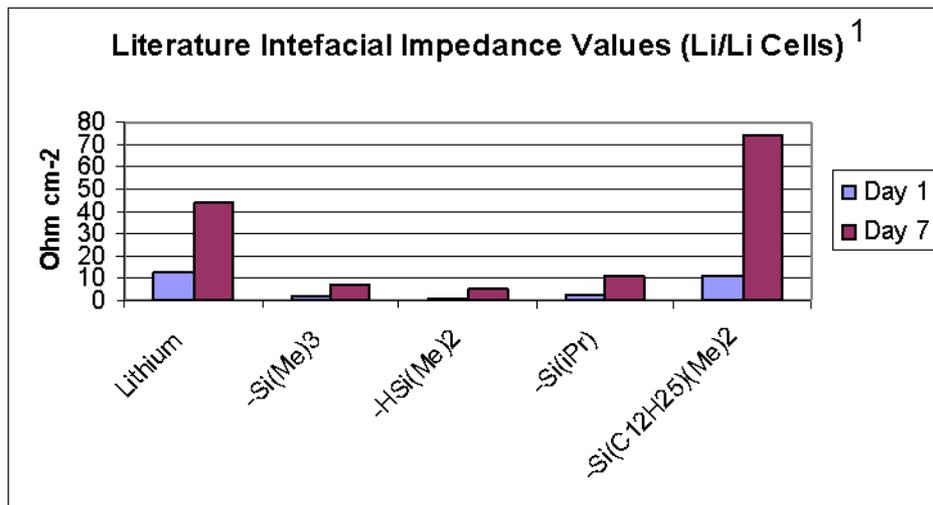
■ ALD (*atomic layer deposition*)-type chemistry – self terminating surface reactions. Reactive group on silane displaces surface protons forming stable direct Si-O connection to the lithium surface.

■ Variety of R-groups are possible opening up possibility of tuning this surface layer to optimize electrochemical properties.

Conformal Coatings - Protection

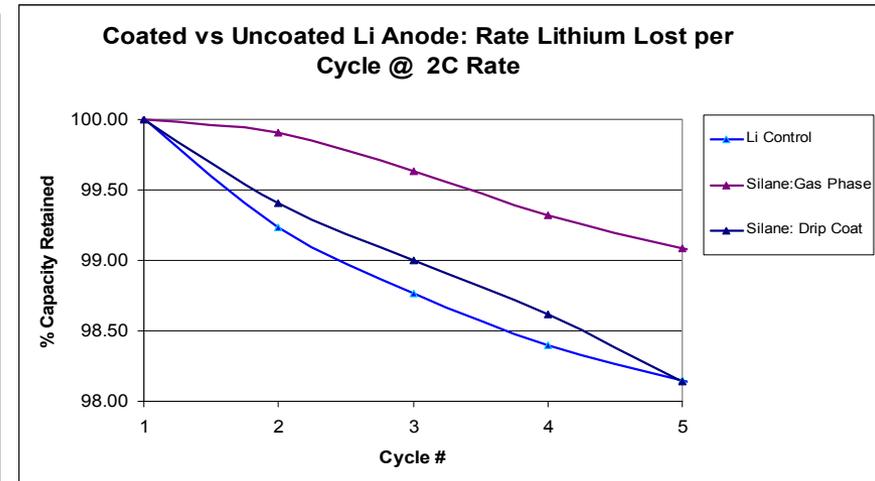
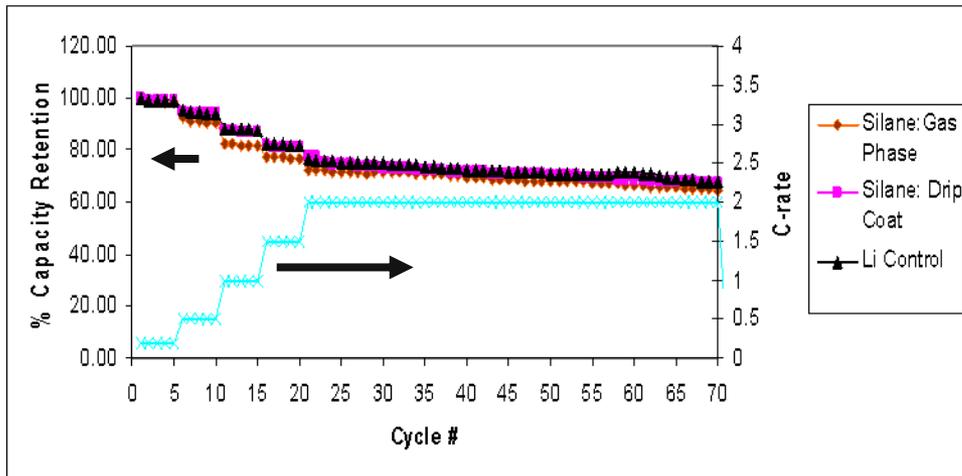
FY08 Coatings study (polymer, Zintl salts) fail to protect the lithium surface for a variety of reasons - including mechanical failure (Li_xM salts) and chemical instability (polymers).

Numerous studies have shown that an increase in impedance of Li anode cells can be attributed to film growth on the surface. Controlling the growth of this layer should give some control over the impedance rise. A recent study of silane-coated lithium surfaces concluded that “short chain silanes ... form a dense layer (on lithium) giving rise to much slower growth of the SEI layer and a smaller impedance rise over time.”¹



¹ Marchioni, et al., *Langmuir*, **23**, (2007) 11597.

Coated vs Uncoated on Cycled Li Metal Anodes



- Rate capability (to 2C) for lithium metal versus trimethylsilane-coated lithium metal is similar (using $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathodes)
- Method of coating the trimethylsilane has little effect on performance of coating – consistent with the formation of an ALD-type monolayer.
- Trimethylsilane-coated lithium metal anodes lose less lithium per cycle than uncoated anodes at 2C rate.

Future Work - FY2009/FY2010

- Continue studies of silane and related materials coatings on lithium metal surface. Assess thermal stability of coatings.
- Extend studies to other ALD-type coatings with higher oxygen content in R-group to increase Li^+ conductivity.
- Continue studies of polymer/lithium-ion conductor nanocomposites and assess the relationship between their composition and cell lifetimes.
- Relate changes in cell impedance to changes in morphology.

Summary

- Zintl metal coatings (Li_xM) are effective in suppressing dendrites by changing their growth mechanism, however the layers lack mechanical stability on cycling. In-situ formed polymer coatings extend cycle life but an associated impedance rise significantly reduces rate capability.
- Cycled lithium metal anodes have a complex morphology that lies at the heart of the lifetime problems. Dendritic lithium tends to form as a surface layer ($\sim 15 \mu\text{m}$) on top of the metal anode on cycling with a porous lithium bulk.
- Changes in the surface chemistry of the porous lithium anode result in a large impedance rise and eventual cell failure.
- ALD-type silane coatings on the surface of lithium reduce the rate of lithium loss (to side reactions) when compared to uncoated lithium metals at rates of up to 2C – future work.

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged
- David Howell