

Lithium Metal Anodes

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ES021*

Overview

- **Timeline**

- Start date: October, 2008
- End date: September, 2014
- Percent complete: < 33% complete

- **Budget**

- Total project funding
 - - 100% DOE
- FY09: \$300K
- FY10: \$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 (Electron Microscopy Center)
 - David Gosztola, Nancy Dietz-Rago (Center for Nanoscale Materials)
- John Zhang (ANL)
- Susi Nuehold, C. Grogger (TU Graz)



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

- Synthesize, design and characterize polymer-alloy composite films deposited on the surface of a lithium electrode – *ongoing*.
- Utilize characterization tools available within the Electrochemical Energy Group, at the National Electron Microscopy Center, and Center for Nanoscale Materials – *ongoing*
- Investigate new types of surface coatings with better surface adhesion – *ongoing*
- Evaluate stability of lithium-ion conducting ceramics in the system – *ongoing*.



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 and characterize conformal stable monolayer coatings.*
- 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.*



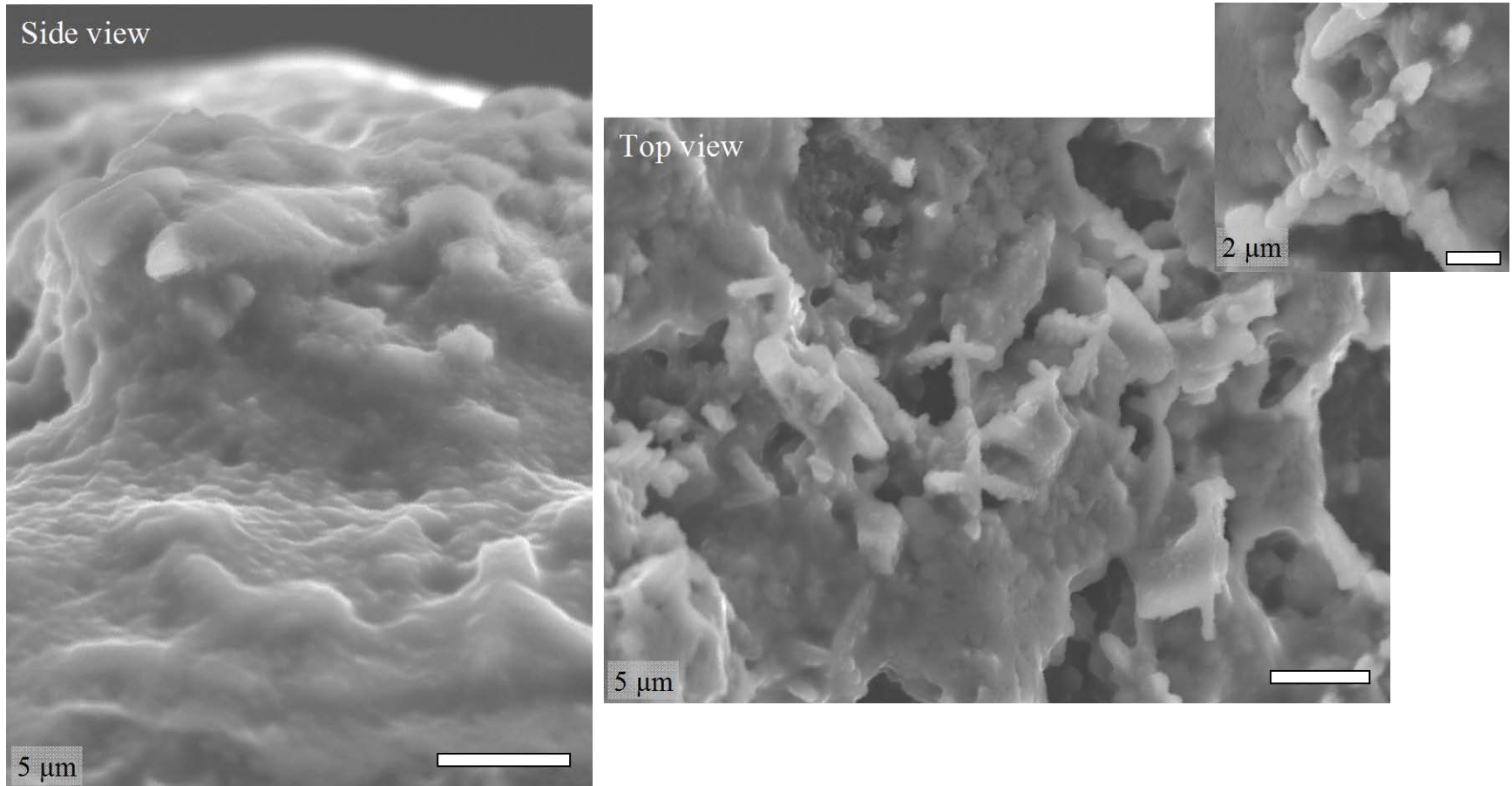
1. Morphological Studies

- *Studied effect of electrolyte exposure and cycling on Li metal anode*
- Examined opened cells by SEM, EDX at defined cycle numbers
- Standard Test Cell Materials –
 - $\text{Li}_4\text{Ti}_5\text{O}_{12}$ cathode
 - Flat 1.5 V insertion electrode, no SEI formation
 - Stable 160 mAh/g capacity
 - 1.2M LiPF_6 / (50/50 wt%) EC/EMC Electrolyte
 - **Lithium metal anode**
- Voltage window
 - 1-2 V (vs. Li)
 - C/2 – 3C rates



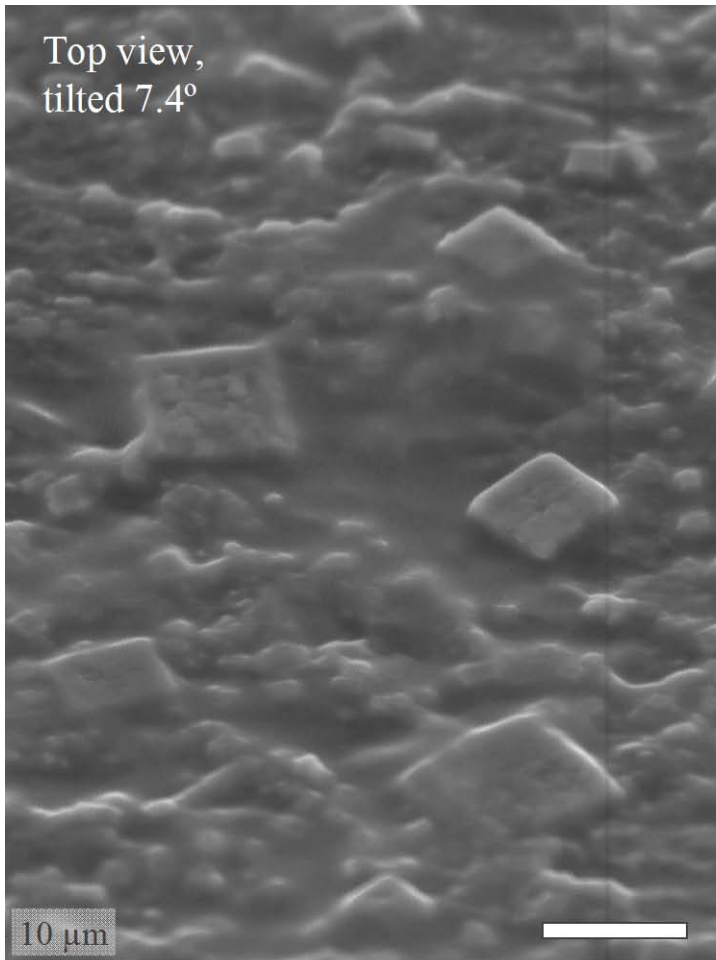
Short Contact Time: Initial SEI Formation

Static Cell: 20 second exposure of Li to electrolyte.

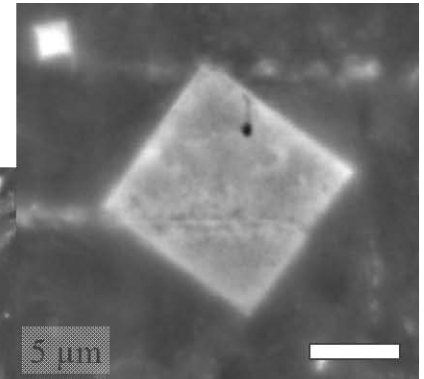
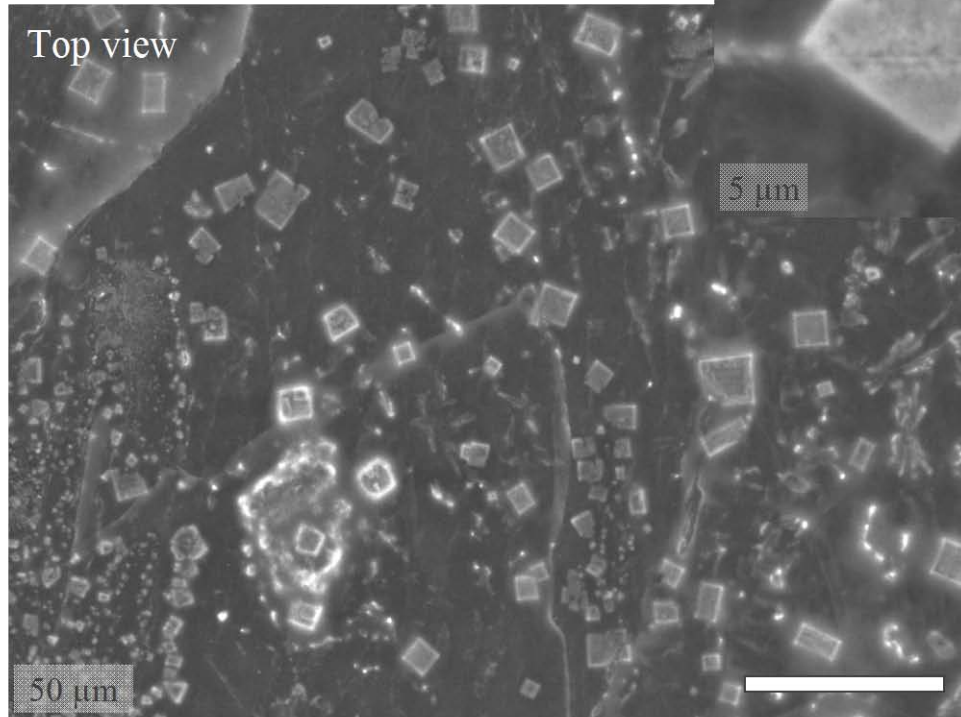


Short Contact Time: SEI Formation

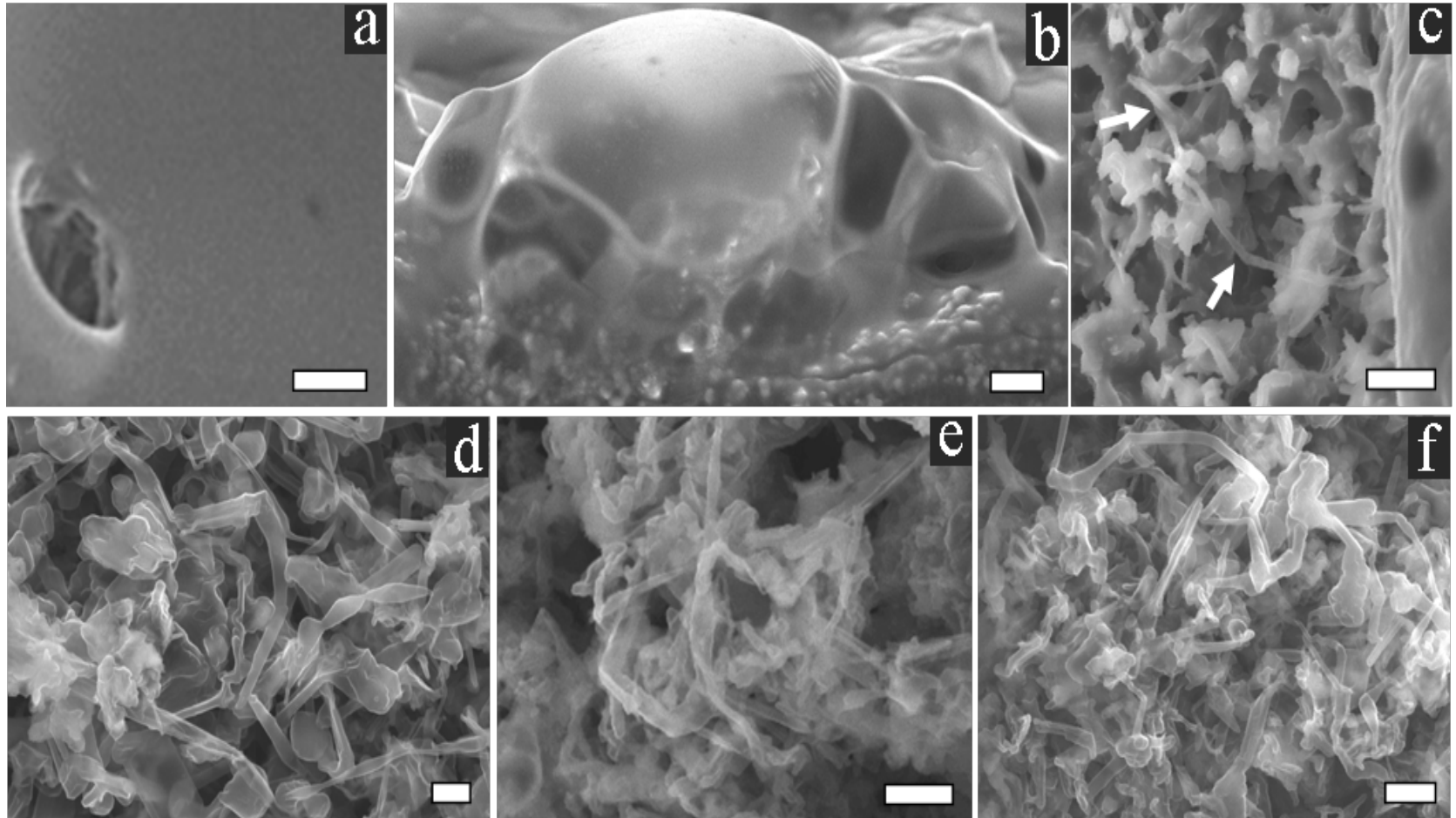
Static Cell: 5 minute exposure of Li to electrolyte.



■ Polymer and inorganic salts



Morphology Changes on Cycling: Top Down



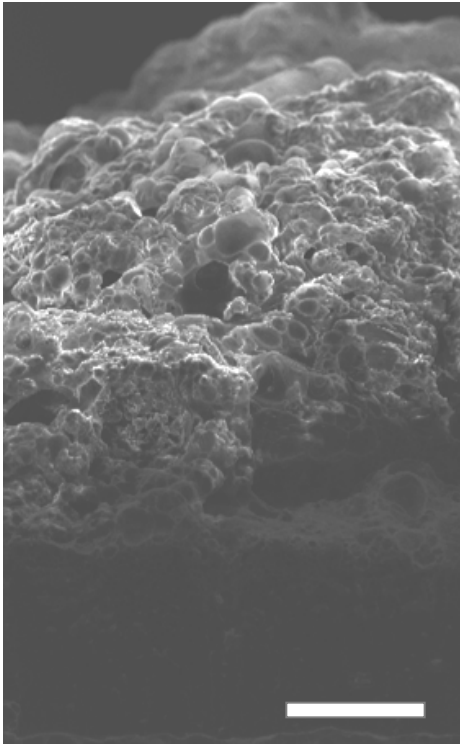
Evolution of the lithium metal surface in an electrochemical cell - (a) prior to cycling, (b) 2 cycles, (c) 10 cycles, (d) 50 cycles, (e) 100 cycles, (f) 250 cycles Scale bars: (a-b) 10 μm ; (c) 5 μm ; (d-f) 2 μm)

Characterization of Li electrode

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

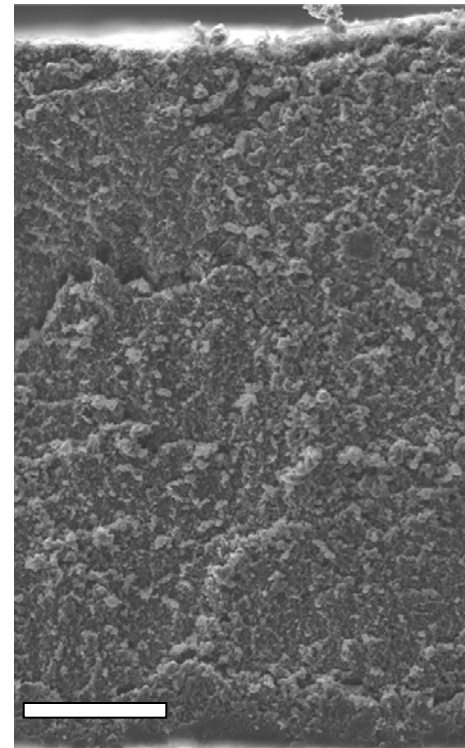
- **Region I: Significant gas evolution under polymeric layer**

CD < 0.125 mA/cm²



- **Region II Three-layer morphology**

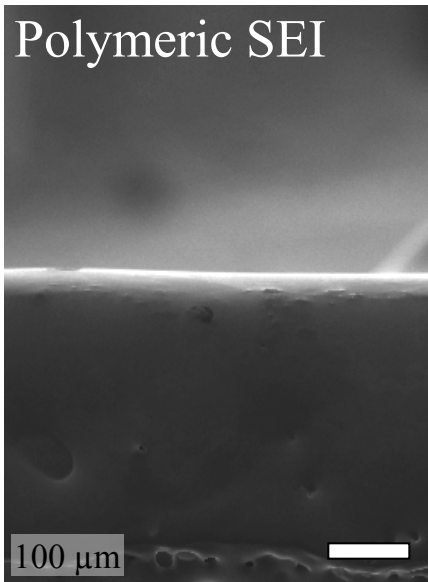
CD > 0.25 mA/cm²



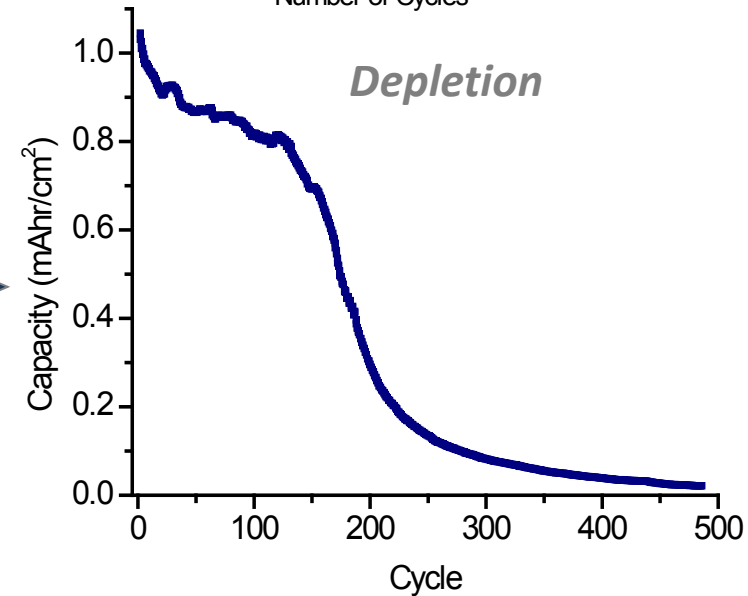
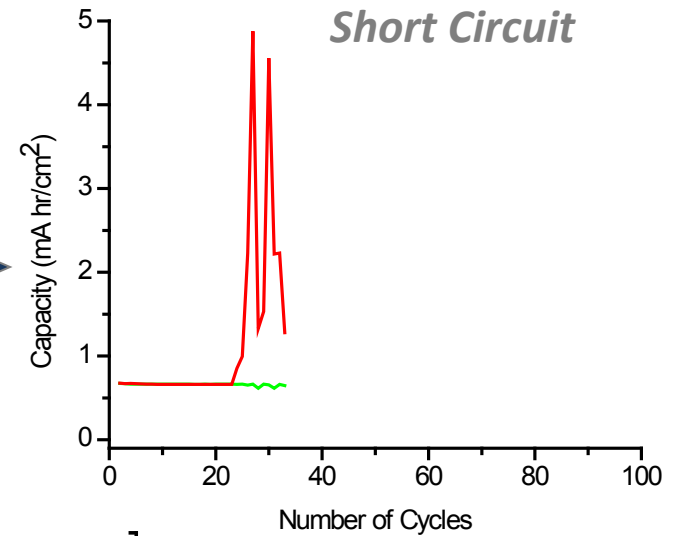
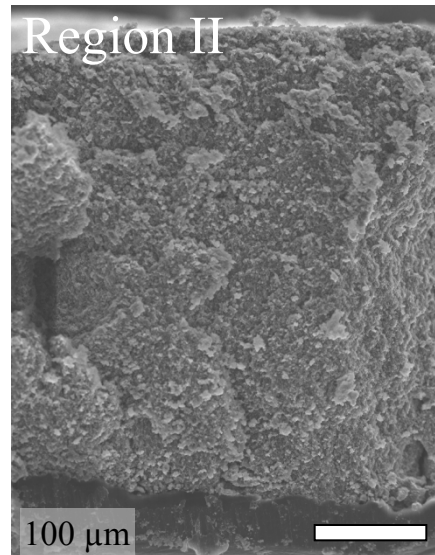
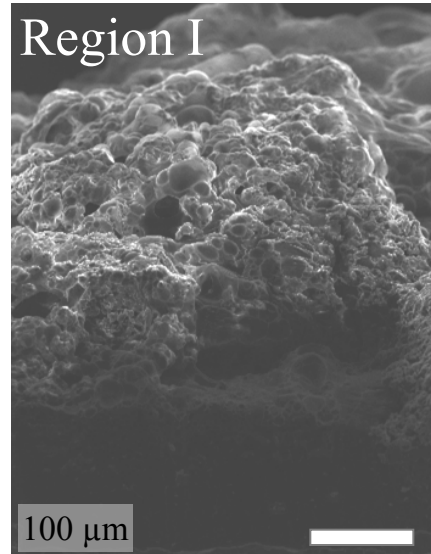
Scale bar: 100 μm

Mechanism of Failure vs. Cycling Current

- Changes in SEI with cycling



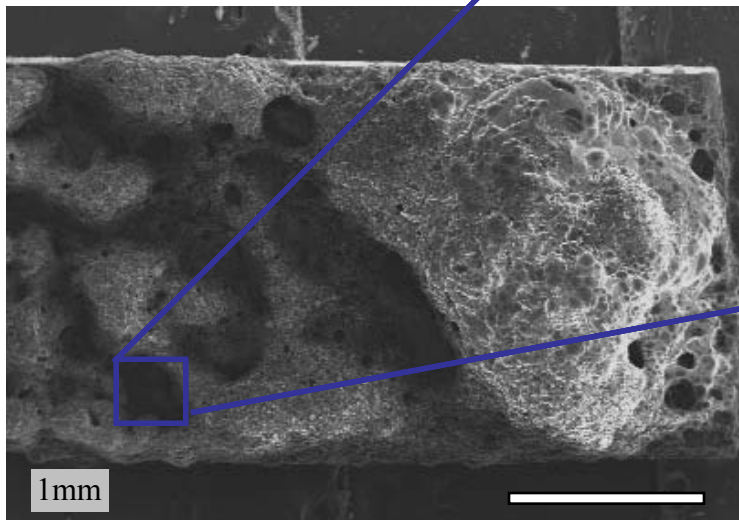
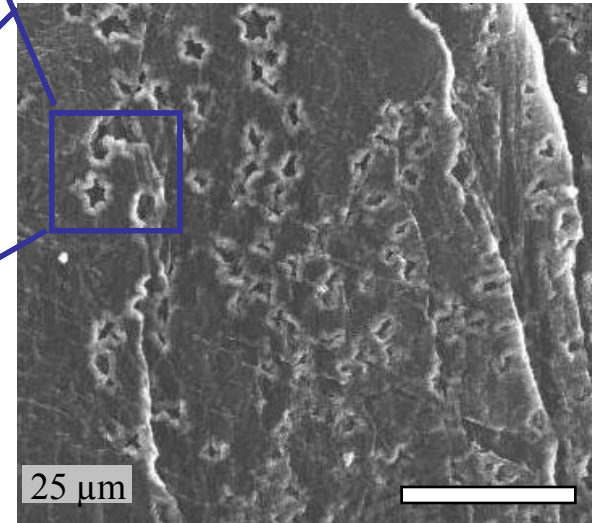
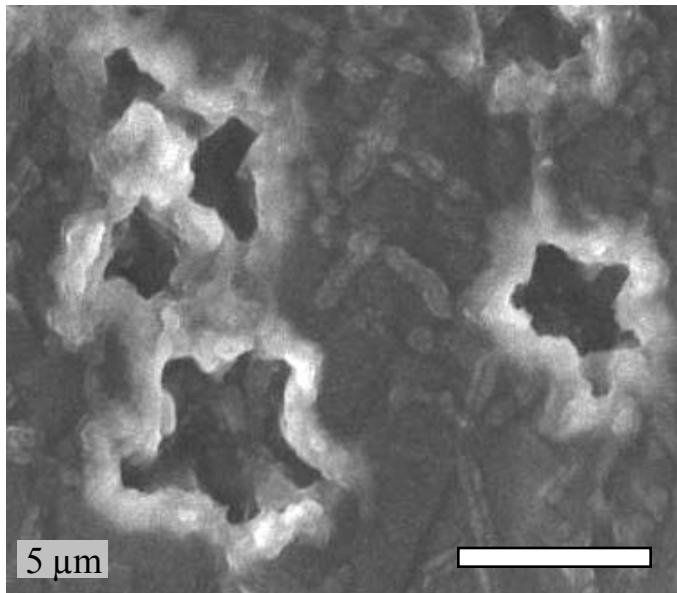
- Direct relationship between mechanism of failure and morphology



Film Formation and Dissolution: Pitting

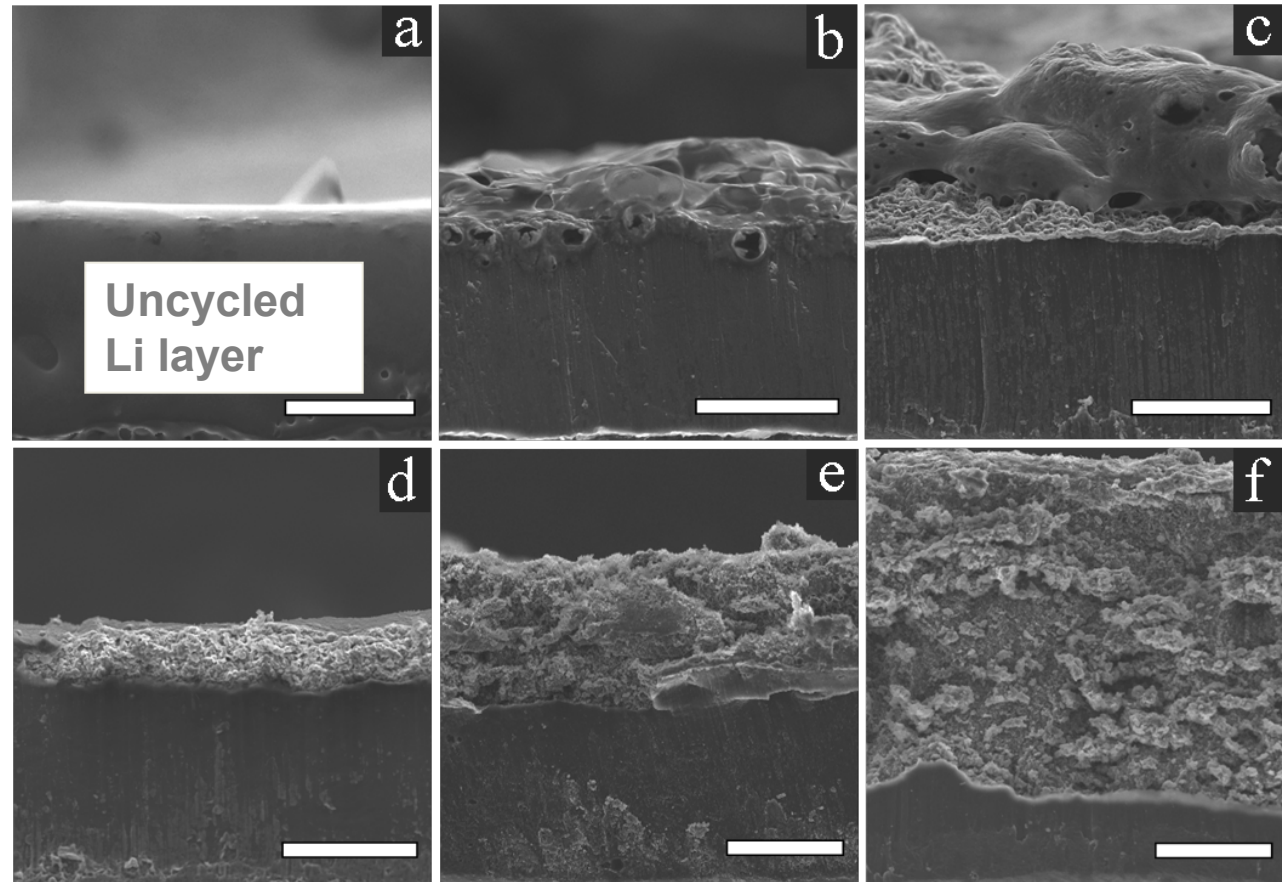
Morphology vs. Cycling Current: Region I

- Pitting



Changes on Cycling: Cross Sectional Analysis - Region II

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.*

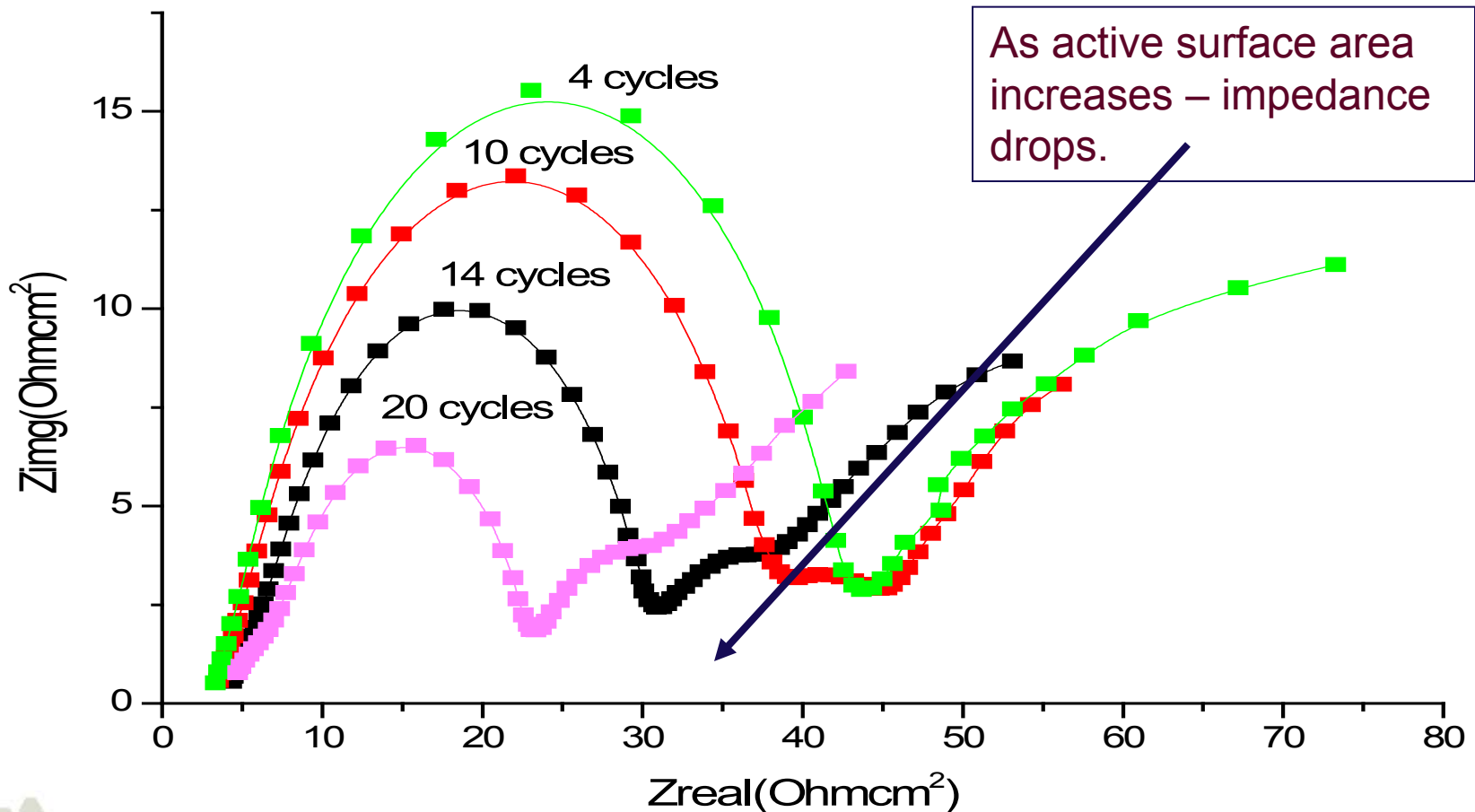


- Cross sectional analysis highlights non-uniform growth of SEI.
- Typical cell cycles until initial lithium is 'used up'. Growth of central porous layer uses up available electrolyte $\Rightarrow$ cell runs dry.
- Dendritic layer is only on top and has a relatively constant depth ($15\text{ }\mu\text{m}$).

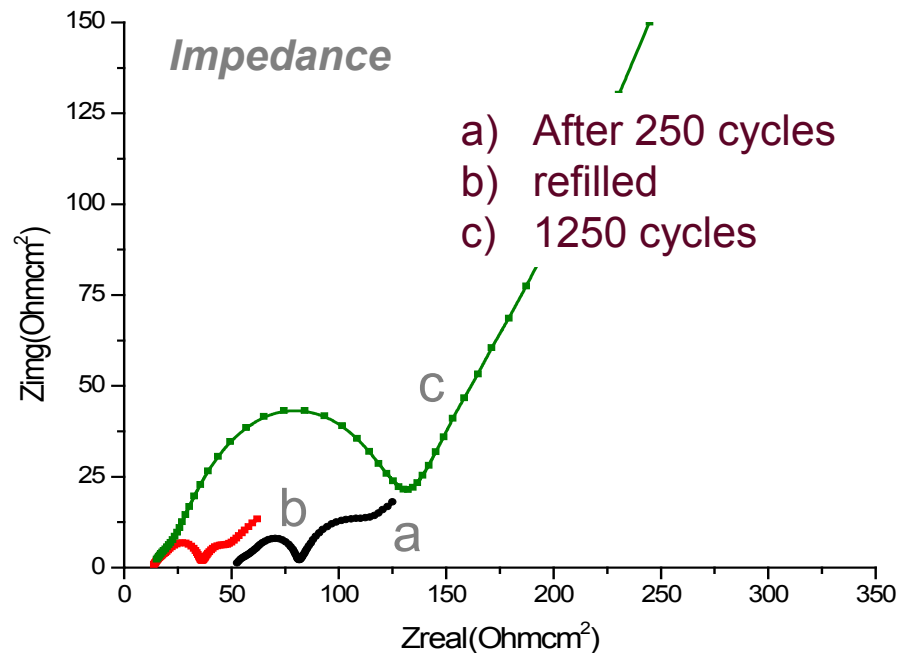
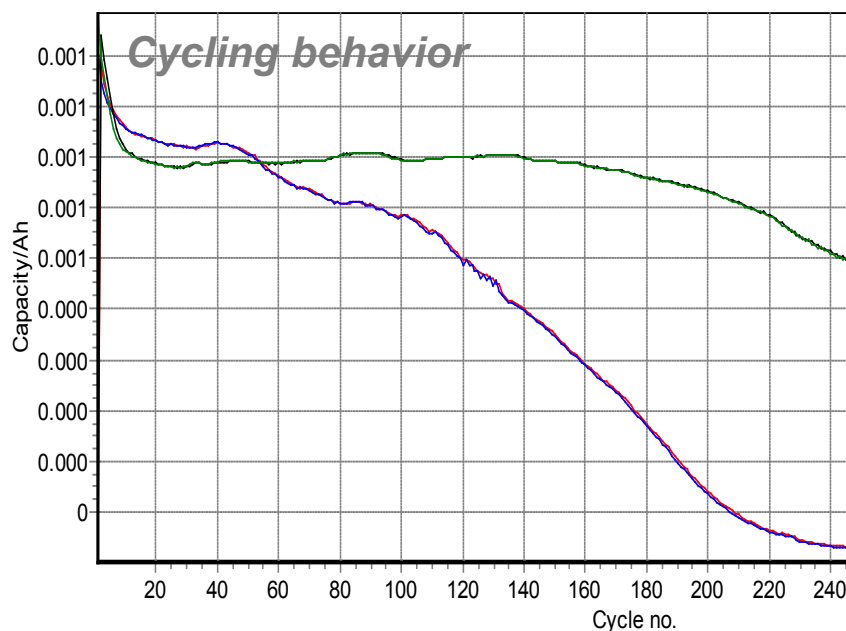
Impedance vs. Cycle (Region II - Establishing the Porous Layer)

Use impedance spectra to follow morphology evolution.

Current Region II: Three layer morphology



Countering Solvent Loss Due to Porous Layer Formation



- Refilling the cell produced the same initial resistance
- Second arch shows reduced intensity indicative of some (minimal) electrochemical activity within the porous layer
- Additional cycling shows increases in charge transfer resistance – increase reactions at electrode/electrolyte interface and degradation of particle - particle contacts.



Morphology Results

- **Cross sectional analysis of cycled lithium anodes shows subsurface evolution**
 - Dendritic layer has constant depth of about 15 microns.
 - Growth of porous mid-layer accounts for most of volume expansion observed.
 - Dense Li at base with good CC contact preferentially cycles.
- **Effect of cycling rate on re-deposition**
 - Low rate cycling - denser SEI layer formation with gas formed on cycling trapped below surface.
 - Mid-rate cycling - more porous SEI formed with predominant effect being formation of large porous Li layer.
- **Impedance Studies**
 - Impedance of cell drops (Region II) as porous layers forms due to increase in active surface area.
 - Porous layer grows till electrolyte solvent or bulk Li used up. Addition of electrolyte to 'dry cell' shows recovery of initial resistances.



2. Coatings

- Coating lithium metal has mixed results.
 - Polymeric materials formed by electrolyte components don't have enough stability to prevent break down on cycling (volume changes).
 - Polymer coatings formed externally tend to break down over time on exposure to the lithium surface and dissolve into the electrolyte.
 - Zintl-based coatings have high ionic conductivity and are stable but are too brittle (volume changes)
 - Composite coatings (e.g. Li_3As in poly DN) are good at low rates.
- Covering the lithium
 - Coatings based on Li_3PO_4 (e.g. LiPON) or other solid electrolytes have been studied → stable to lithium but has low conductivity.
 - Use of ceramic coatings with a high Li conducting interlayer (e.g. Li_3N) that forms a stable interface between the Li and the ceramic.



Simple Coatings - Top Down

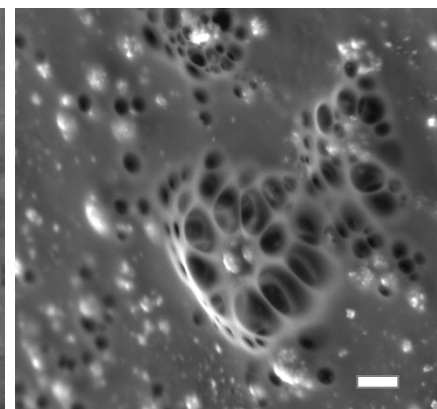
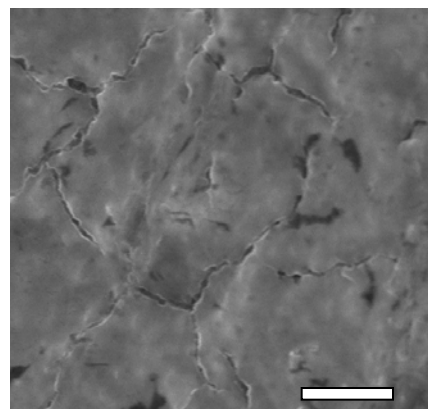
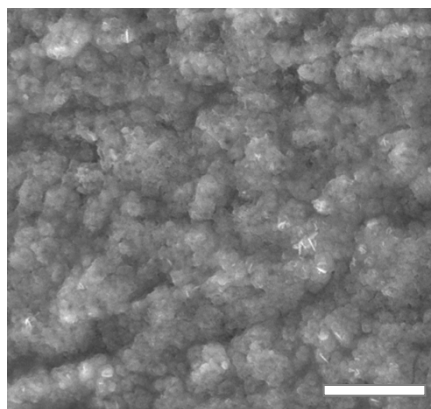
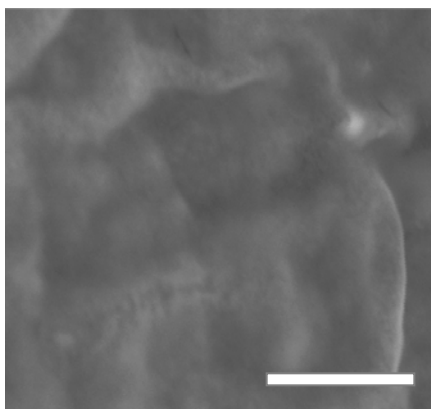
VEC/LiPF₆

1-vinylimidazole

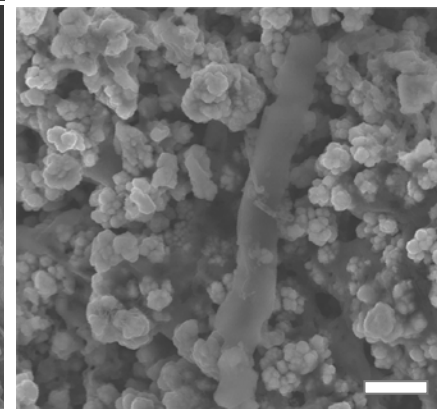
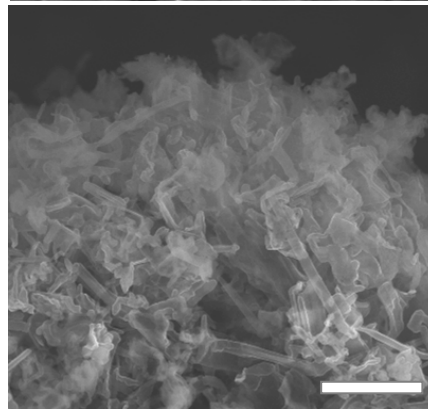
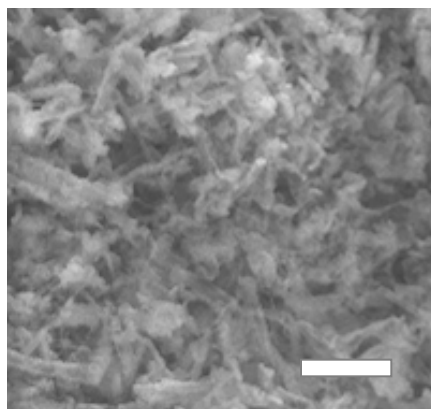
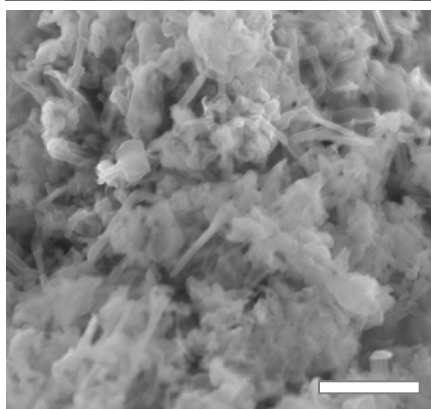
Tetramethylene
Sulfone

SnCl₂

As coated



After cycling



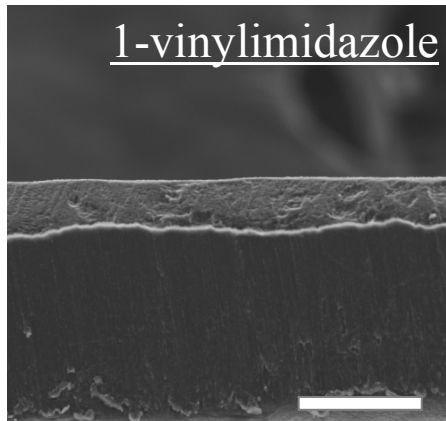
Scale bar: 5 μ m



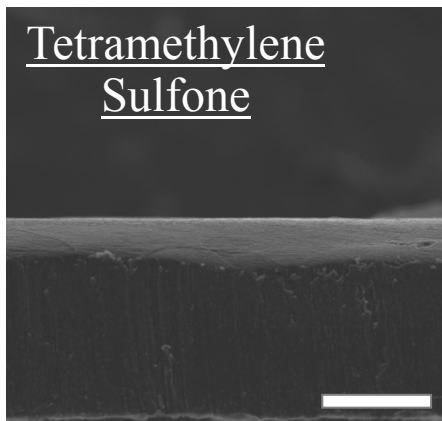
Simple Coatings - Edge On

As coated

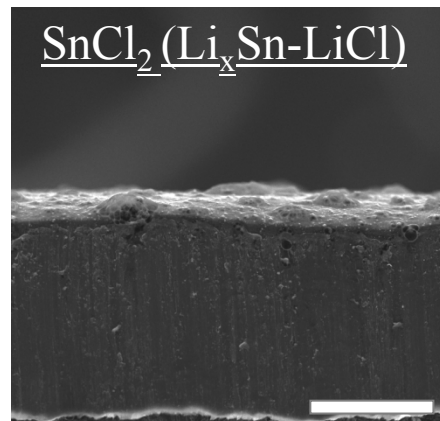
1-vinylimidazole



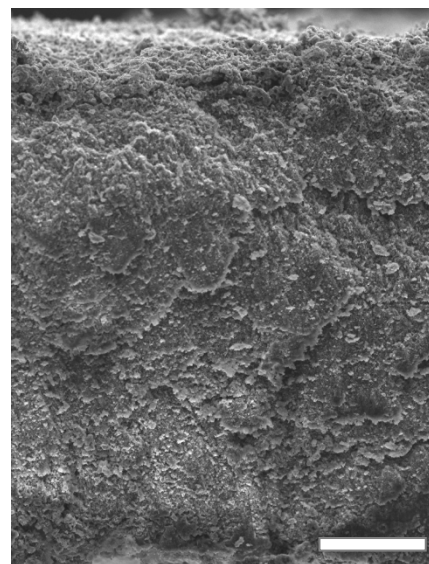
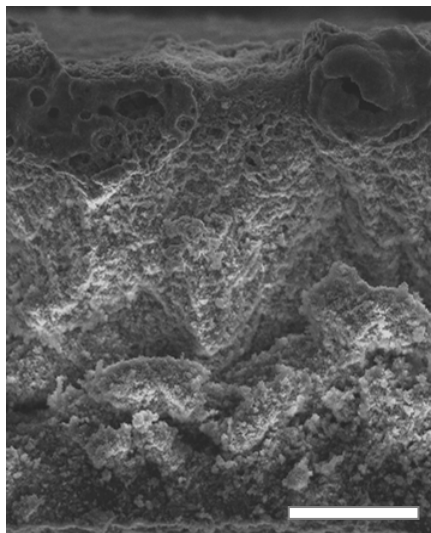
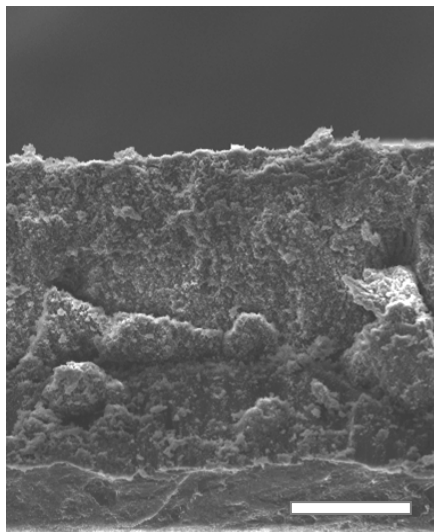
Tetramethylene
Sulfone



SnCl₂ (Li_xSn-LiCl)



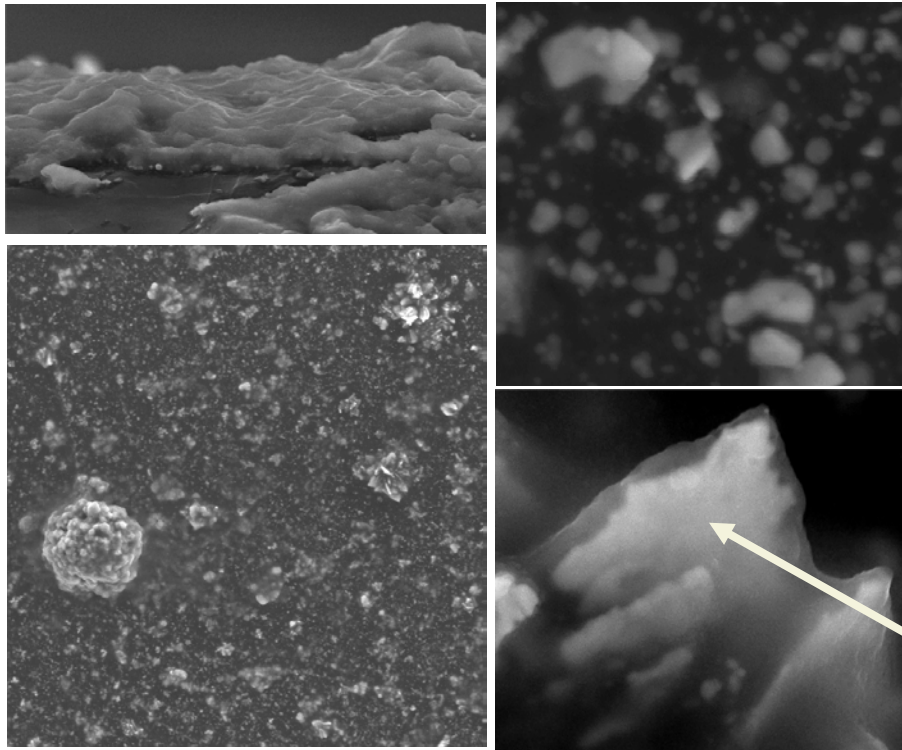
After cycling



Scale bar:
100 μ m

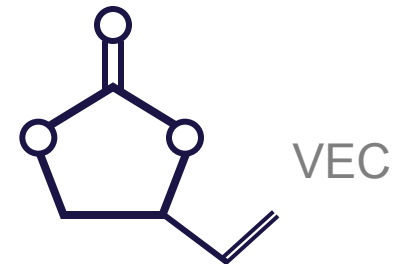
Lithium Zintl Phase / Polymer Composite Coatings

Organic-Inorganic Nano-composites: nanoparticles embedded in a polymeric matrix (VEC-derived).

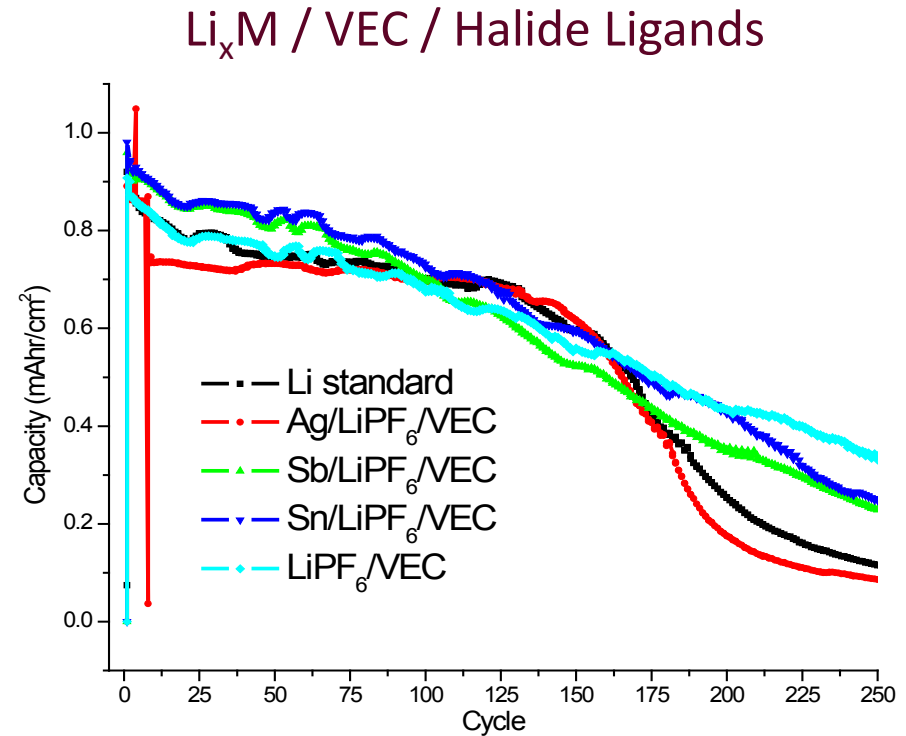
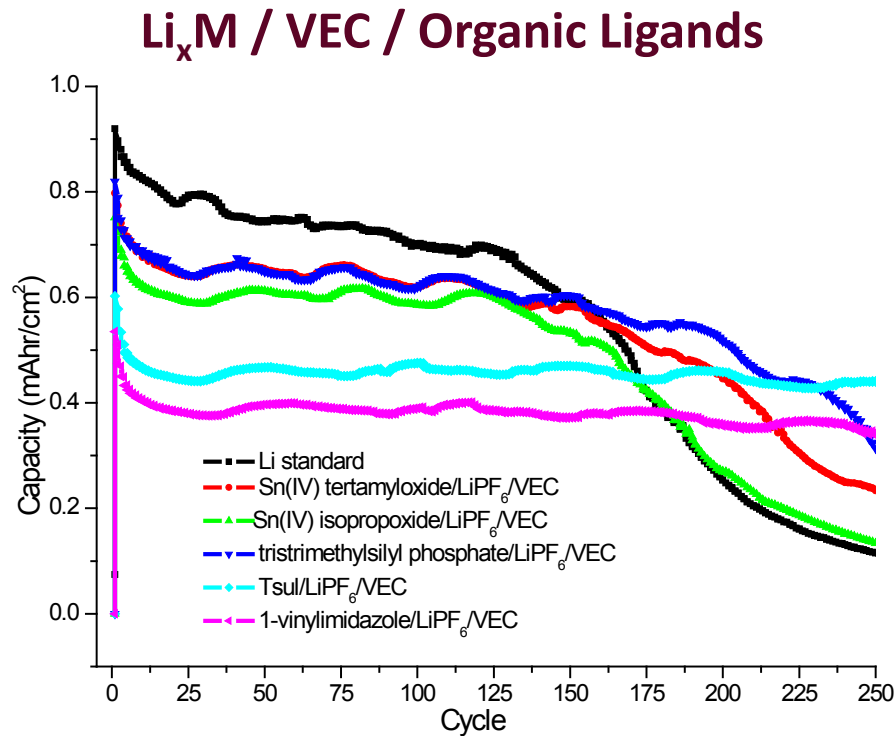


VEC polymerizes around 0.9 V to coat the anode with a dense film. The film grows on cycling (e.g. filling surface cracks) and gradually isolates the anode causing an impedance rise.

Li_xSn
crystal
coated with
polymer



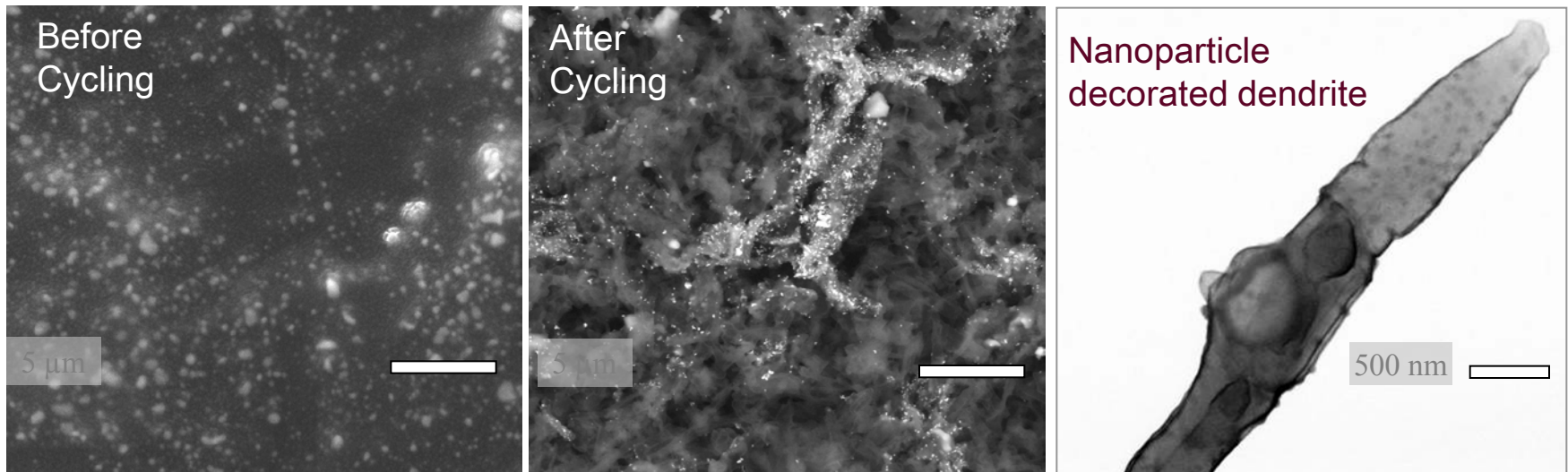
Lithium Zintl Phase / Polymer Composite Coatings



- Li_xM (Zintl) containing coatings suppress dendrite formation. Cells tended to fail by solvent depletion.
- Coating/lithium interphase is rate determining and the porous layer always forms.



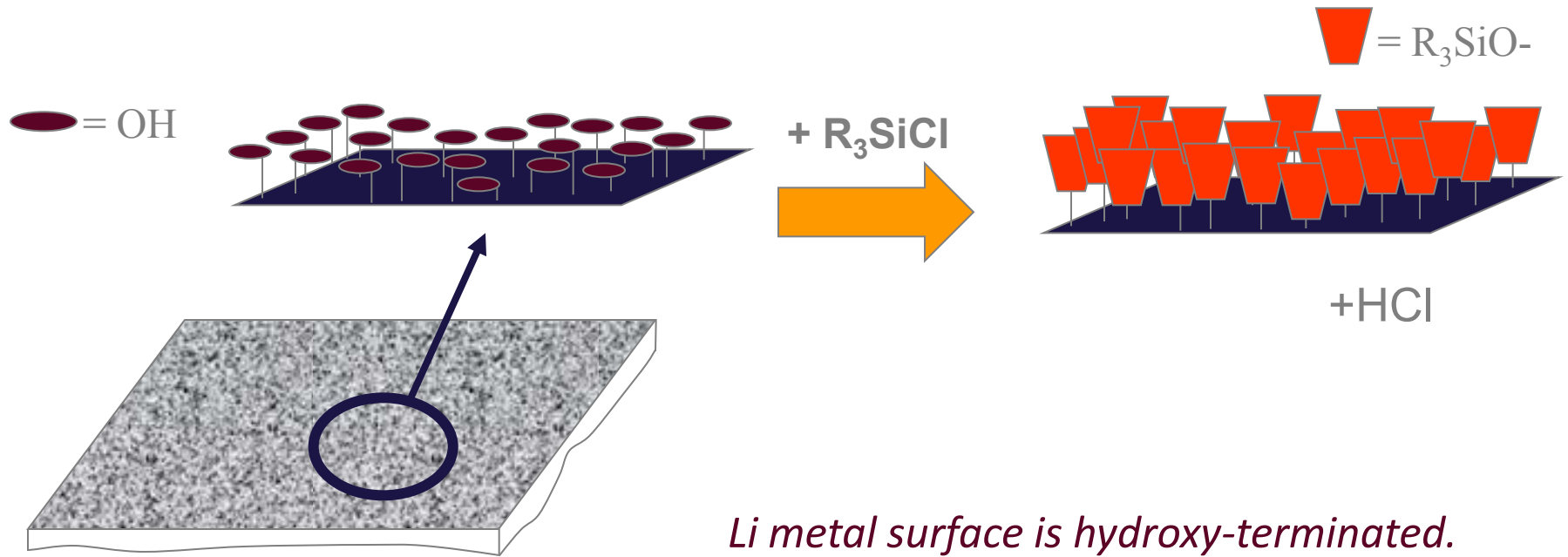
Composite Coatings: Li_xSn / VEC



- 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.***

Silane-based Coatings- Synthesis



Li metal surface is hydroxy-terminated.

- Kanamura, et al., *JES*, **141**, 2379 (1994)
- Naudin, et al., *JPS*, **124**, 518 (2003).

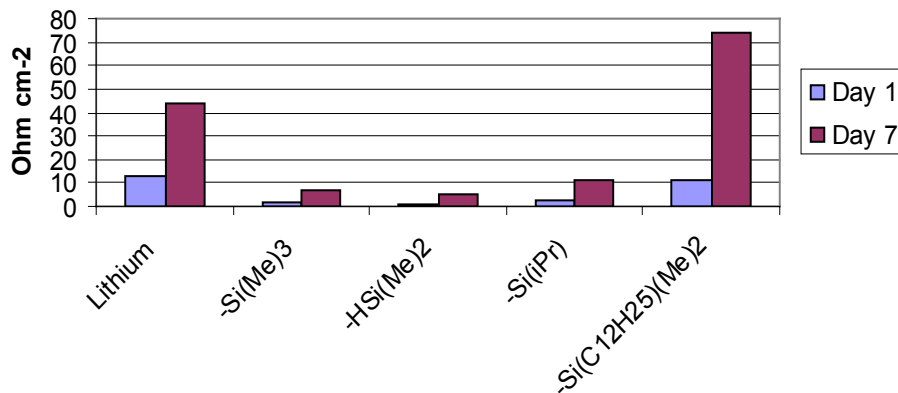
Self terminating surface reactions limit thickness to one layer. Chloride group on silane displaces surface protons forming stable direct Si-O connection to the lithium surface.

Conformal Coatings - Protection

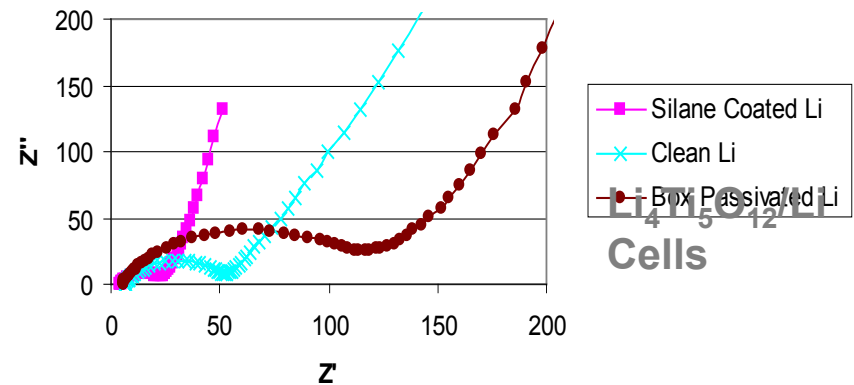
Studies have shown that an increase in impedance of Li anode cells can be attributed to film growth on the surface. Controlling the film growth at this interface layer should offer some control over the impedance rise.

¹
A study of silane-coated surfaces showed that short chain silanes can form a dense layer on lithium.

Literature Intefacial Impedance Values (Li/Li Cells)



Fresh Cell: EIS Spectra

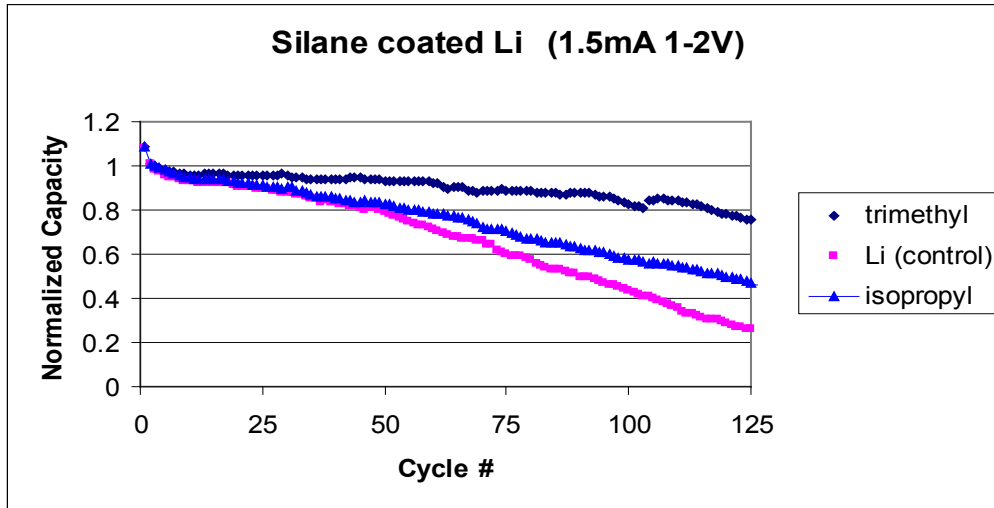


Silane = -Si(Me)₃

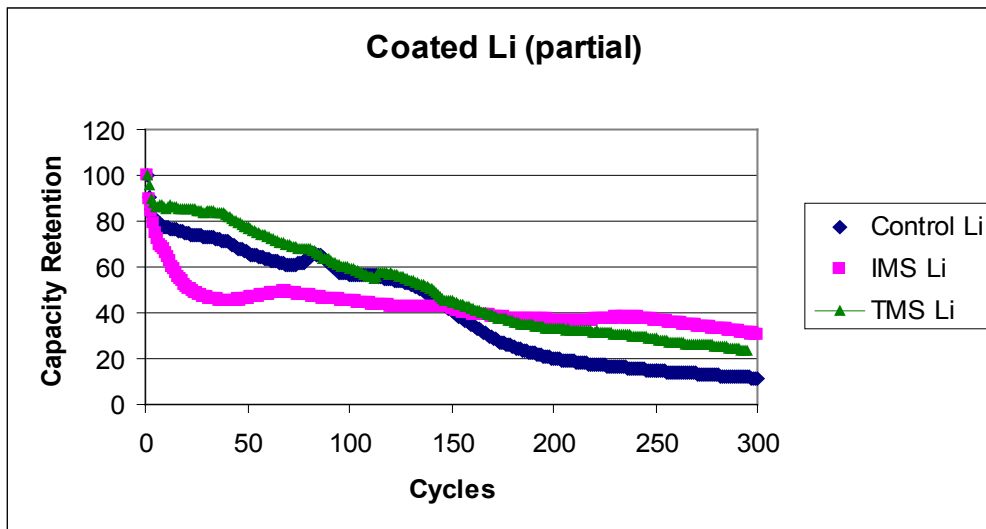
¹ Marchioni, et al., *Langmuir*, **23**, (2007) 11597.



Silane-based Coatings - Cycling



Consistent with those results the TMS-coated Li shows lower fade than the control or the isopropyl silane coated sample.

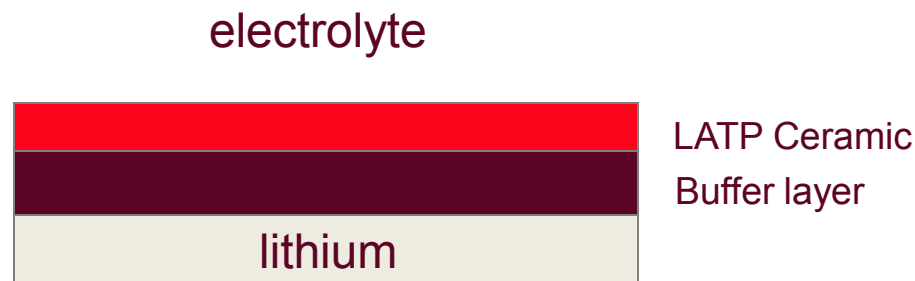


Coating a *partially* cleaned Li surface with silanes shows minor differences.



Preliminary Studies of Li-ion Conducting Ceramics

- Recent advances in lithium metal protection by Polyplus et al., using $\text{Li(Al,Ti)}_2(\text{PO}_4)_3$ (LATP) ceramics have highlighted this as a new direction.
 - By virtue of its conduction mechanism it desolvates the Li as it passes thru the membrane.
- Recent papers have shown that as a membrane it may have stability issues in aqueous systems depending on the pH.



Chemical Stability

- GITT Studies of LATP indicate that it inserts Li (to form $\text{Li}_{1+x}((\text{Al},\text{Ti})_2(\text{PO}_4)_3)$ around 1.2V (reduction of Ti (IV) $\rightarrow$ Ti(III))
 - Similar value has been observed for $(\text{Li},\text{La})_{1-x}\text{TiO}_3$ (Chen, et al., SSI, 2004)
- A long plateau around 720 mV corresponds to material decomposition and formation of Li_3PO_4 , $\text{Li}_x(\text{Ti},\text{Al})\text{O}_2$.
- Reaction studies
 - Plates of LATP were gradually heated up while in contact with Li metal.
 - Between 260-300 °C the lithium reacted with the LATP to form Li_3PO_4 , $\text{Li}_4\text{P}_2\text{O}_7$, and $\text{Li}_x(\text{Al},\text{Ti})\text{O}_2$. (XRD analysis)



Collaboration and Coordination with Other Institutions

- **Within Argonne**
 - National User Facilities:
 - Russell Cook (Electron Microscopy Center)
 - David Gosztola (Center for Nanoscale Materials, CNM)
 - Nancy Dietz-Rago (CNM)
 - John Zhang – Organic Chemistry
 - Wenquan Lu – Diagnostics and Evaluation
 - Lynn Trahey – Electrodeposition
 - Christopher Johnson – High capacity cathodes, charged cathodes.
- **Outside of Argonne**
 - Lawrence Berkeley National Lab
 - Models, diagnostics, useful discussions.
 - S. Neuhold, C. Grogger (TU Graz)
 - Silane chemistry, surface treatments



Proposed Future Work

- Investigate the surface layer created on the lithium surface as coatings, cycling rate, and other additives are evaluated.
 - How do the silane coatings change over time?
 - What is the effect of solvent on the protective nature of the silanes?
- Continue to study the morphology of the lithium metal surface as a function of various coatings and protective layers.
- Continue to study stability of ceramic lithium ion conductor in the cell environment
 - As the electrolyte composition changes over time the stability of the ceramic may be effected.
- Investigate interactions between buffer layer and ceramic layer.
 - What range of compounds exist at the interface that effect the cycling and stability of the electrochemical cell?



Conclusions

- We have examined the lithium metal electrode as a function of cycling using various tools.
 - SEM studies show that reactions of the lithium with its environment set the cell on particular path.
 - EIS studies have shown that impedance initially drops as surface area increases, stabilizes, then rises depending on depletion rate of available lithium within cycling window.
- Various coating studies indicate that controlling the ability of the electrolyte solvent to reach the lithium surface while maintaining ionic conductivity is a key synthetic variable for designing new systems.
 - Zintl coatings – too brittle
 - Polymeric coatings – growth, SEI penetration, gradual dissolution/break up
 - Composite Zintl/VEC Polymer Coatings – VEC failure mechanism prevails.
 - Silane-based coatings – controls surface better but SEI still will permeate causing capacity fade (solvent loss).



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