Optimization of Ion Transport in High Energy Composite Electrodes

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University of California San Diego
June 2015

Project ID ES216

Overview

Timeline

- April 1st, 2013
- March 31st, 2017
- Percent complete: 50%

Barriers

- Barriers addressed
  - Low rate
  - Poor voltage stability
  - First cycle inefficiency

Budget

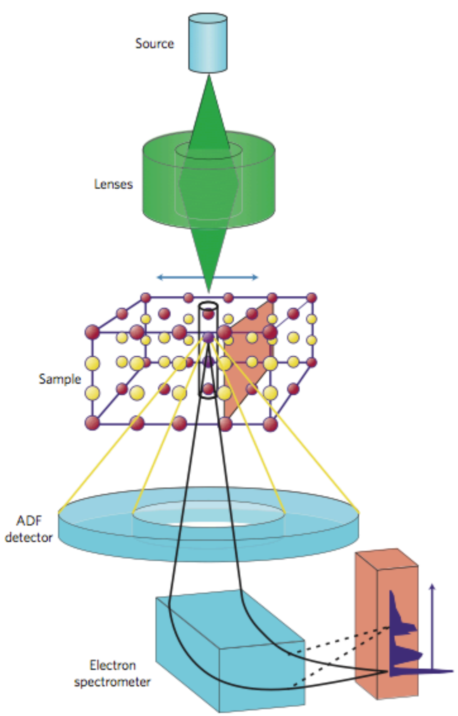
- Total project funding
  - US$ 899,999
- Funding received in FY13
  - US$ 225,000
- Funding for FY14
  - US$ 225,000

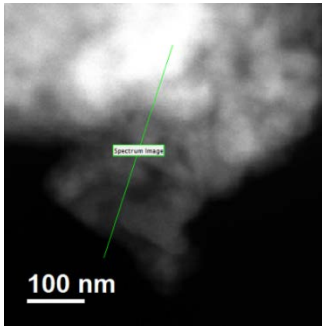
Partners

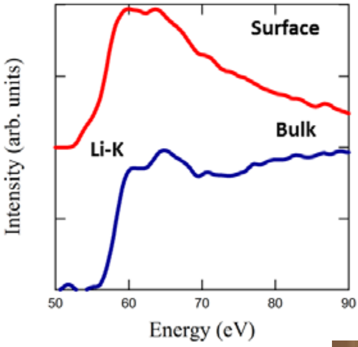
- Interactions/ collaborations
  - Envia Systems
  - Oak Ridge National Lab
  - University of Texas at Austin
  - National Renewable Energy Laboratory
  - Ningbo Institute of Materials Technology & Engineering

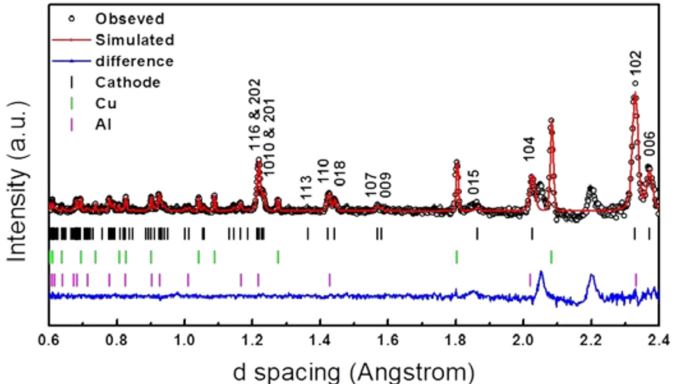
Relevance and Project Objectives

- ❑ Probe and control the atomic-level kinetic process that govern the rate and stability in high energy (high voltage) composite electrodes
- ❑ Establish quantitative diagnosis methods to determine the optimum bulk composition and surface characteristics for high rate and long life
- ❑ Extend the suite of surface-sensitive tools to diagnose the silicon

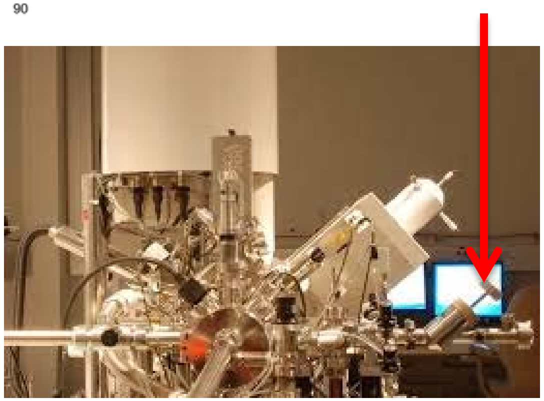








Anoxic transfer capsule for XPS and TOF-SIMS



Milestones

- Identify ways to extend the STEM/EELS and XPS techniques for anode materials, such as silicon anode. (09/30/14) **On Track**
- Identify at least two high voltage cathode materials that deliver 200mAh/g reversible capacity when charged to high voltages (12/31/14) **Complete**
- Obtain the optimum surface coating and substitution compositions in lithium rich layered oxides when charged up to 4.8V (or 5.0 V) (3/31/15) **Complete**
- Identify the appropriate SEI characteristics and microstructure for improving first cycle irreversible capacity of silicon anode. (Improve to 85-95%) (6/30/15) **On Track**
- Identify the mechanisms of ALD and MLD coated silicon anode for their improved chemical stability upon long cycling. (9/30/15) **On Track**

Approaches/Strategies

Combines atomistic modeling, scanning transmission electron microscopy (a-STEM) & Electron energy loss spectroscopy (EELS), X-ray photoelectron spectroscopy (XPS), Neutron Diffraction (ND) to elucidate the dynamic changes of the bulk and surfaces.

EELS/TEY/XPS(Mn3p)

$Mn^{2/3+}$ during charge

$Mn^{\sim 3.5+}$ discharge

EELS/XAS

Mn^{3+} during charge

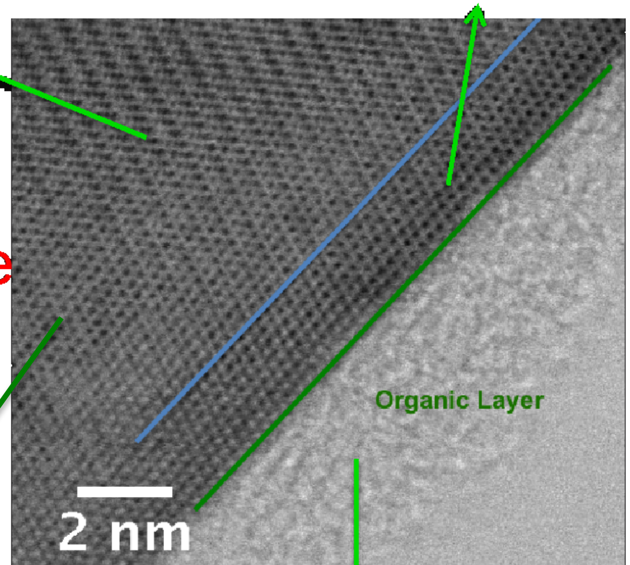
Mn^{4+} discharge

$Ni^{2+} \rightarrow Ni^{4+}$ charge

$Ni^{4+} \rightarrow Ni^{2+}$ discharge

Neutron Diffraction

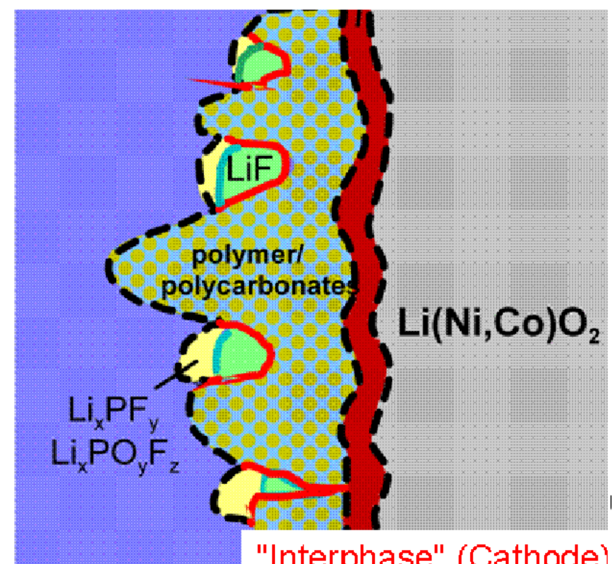
Oxygen Vacancy



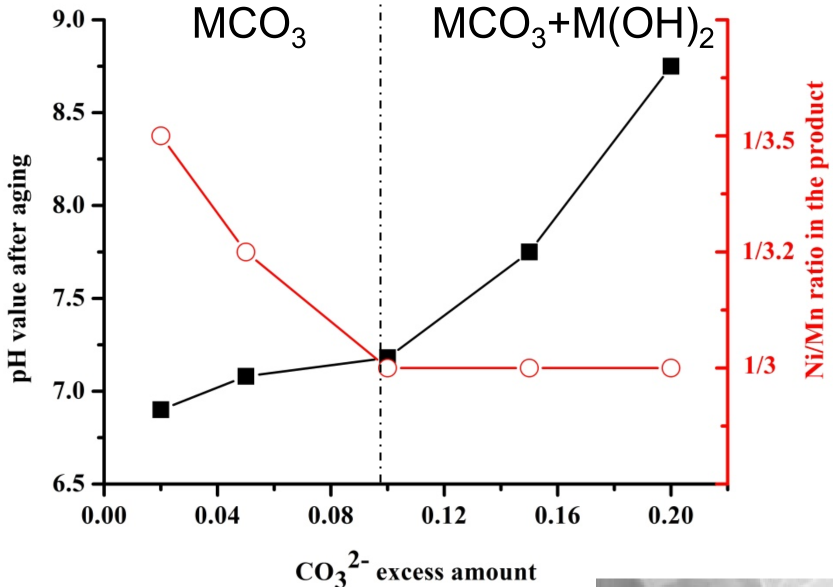
XPS(Mn2p)

Higher Oxidation

Mn after Charge



Accomplishment to Date FY15
Controlled Parameters in Synthesis

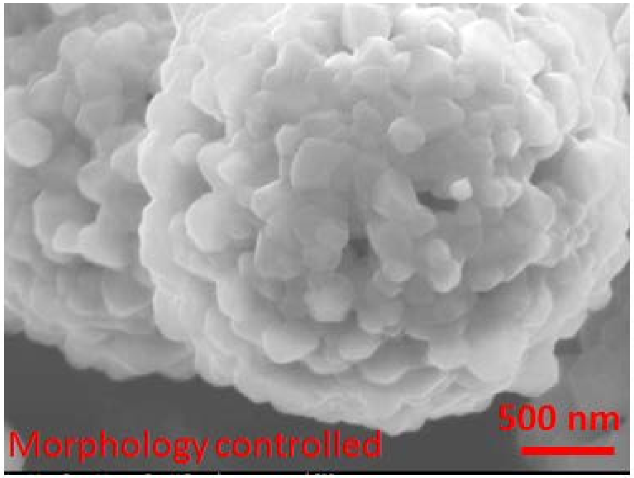


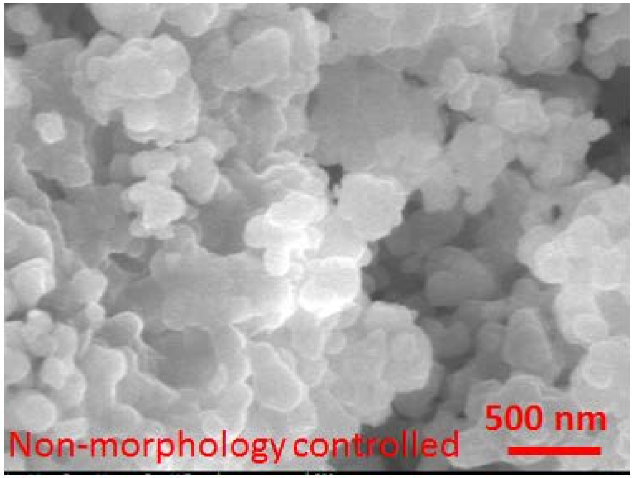
- **Mixed metal ion solution (Mn/Ni=3) concentration: 1 M; precipitant dropping speed: 6 ml/min; Stirring speed 700 rpm**
- **pH value is controlled by the excess amount of precipitant (CO_3^{2-})**

Surface area by BET method (m^2/g)

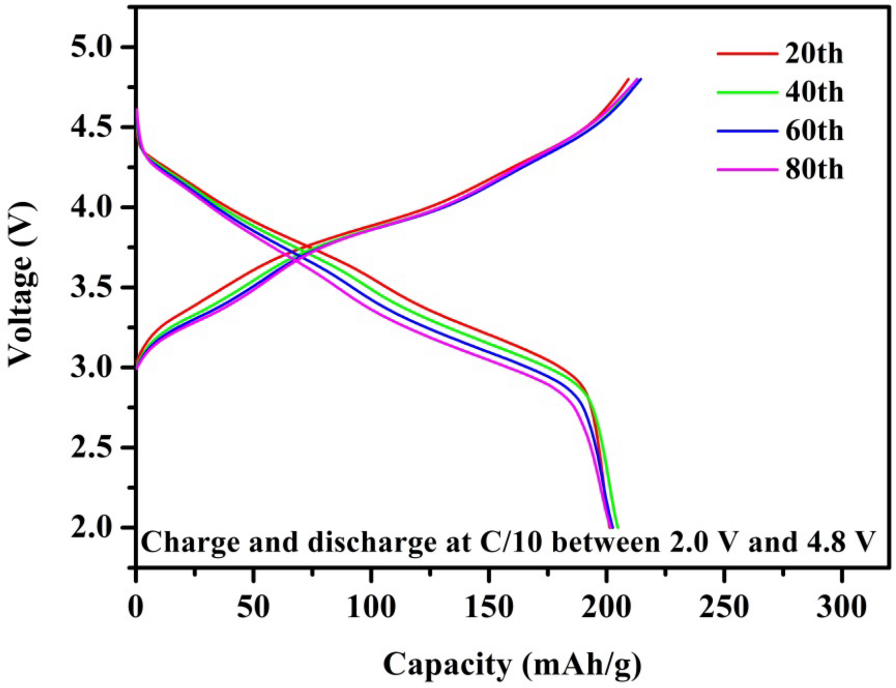
Morphology controlled sample: 2.0

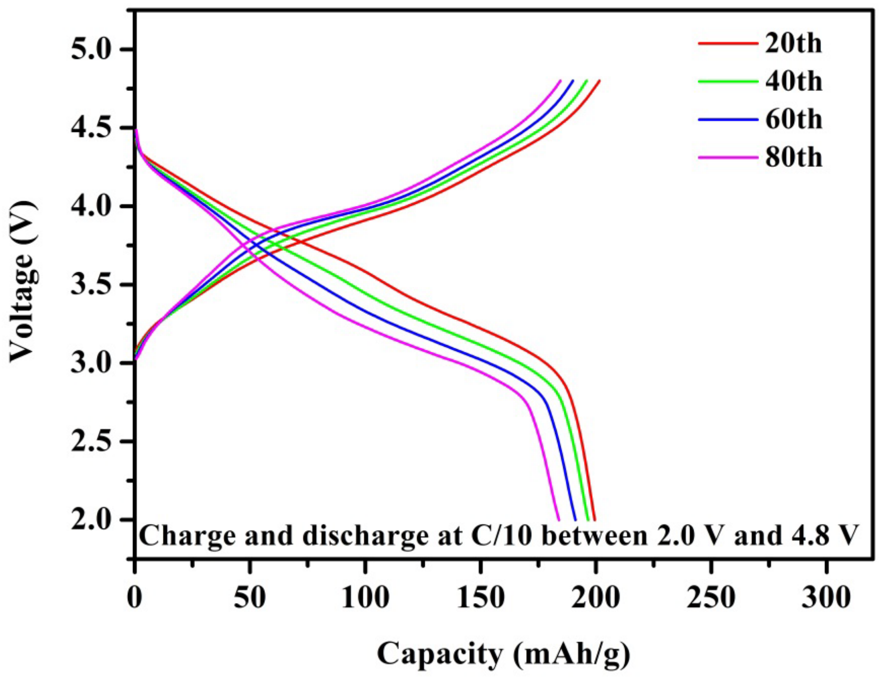
Non-morphology controlled sample: 3.26





Accomplishments to Date FY15
Impact of Morphology Control



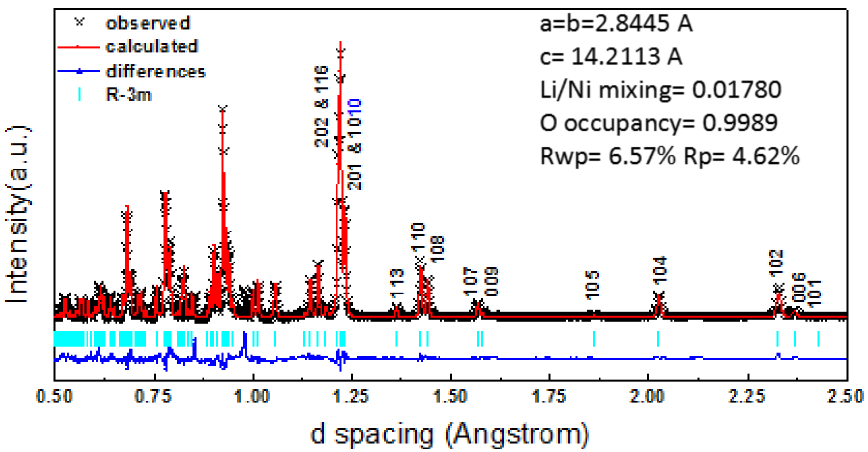


Much voltage stability

Optimizing more will achieve higher capacity

Accomplishments to Date FY15
Impact of Surface Modification

Pristine



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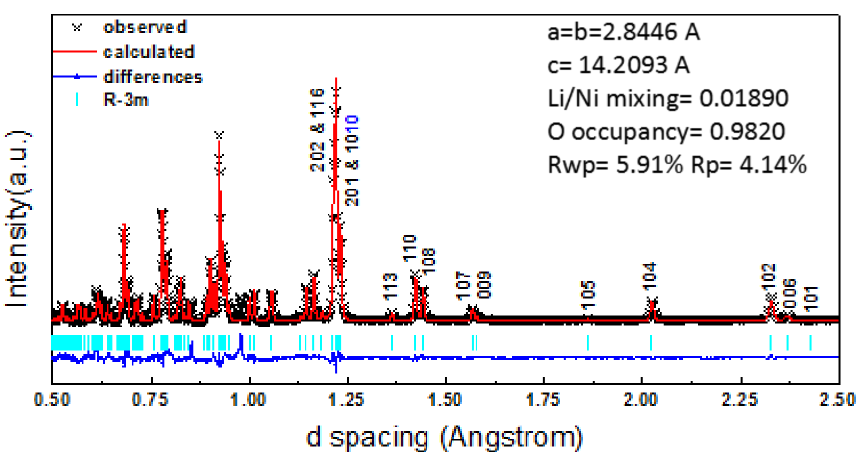
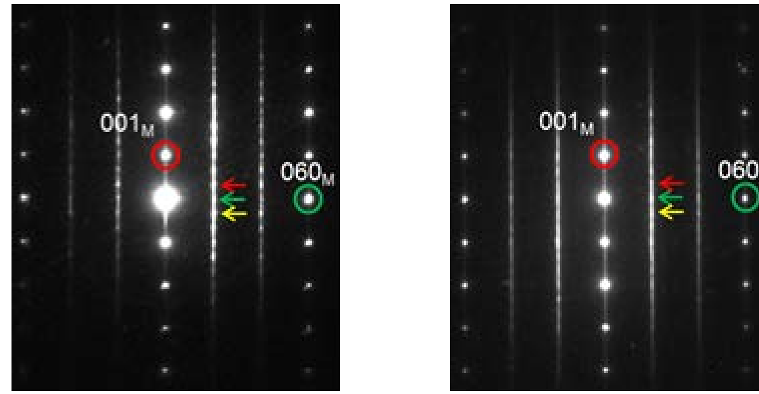


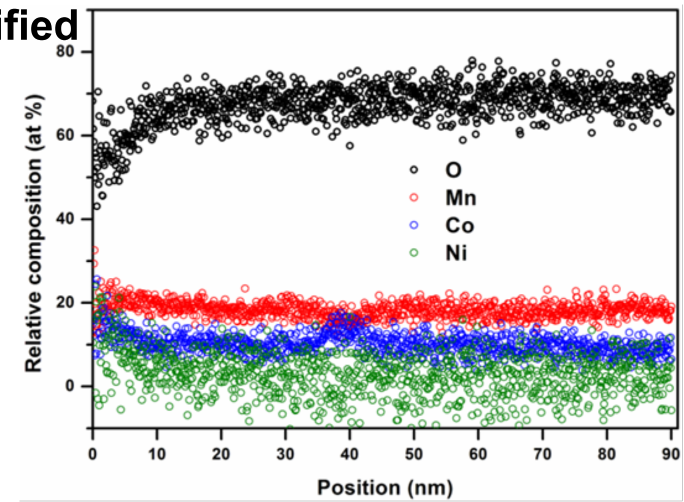
Partnered with NIMTE

B. Qiu and M. Zhang et. al submitted, 2015

Pristine **Modified**



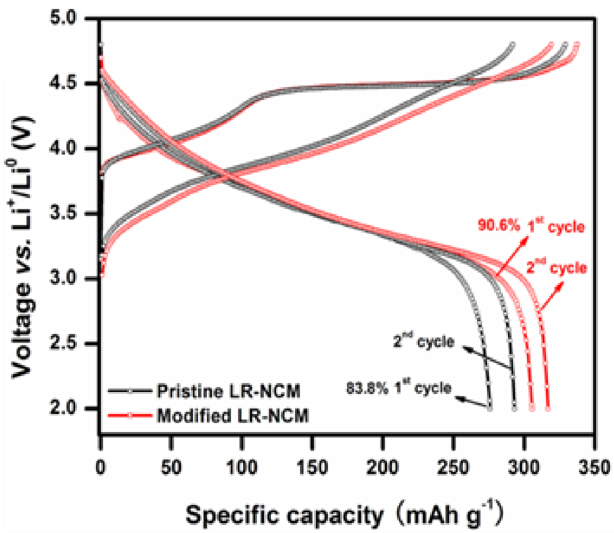
Modified

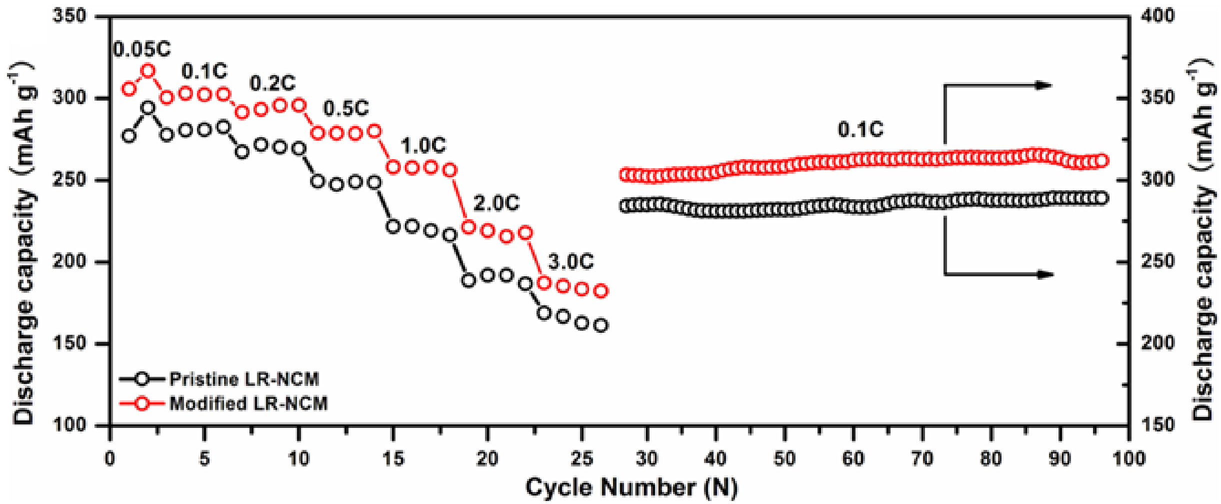


Both ND and STEM/EELS results show oxygen vacancies formed on the surface without noticeable bulk-structure interruption through a novel interface reactivation

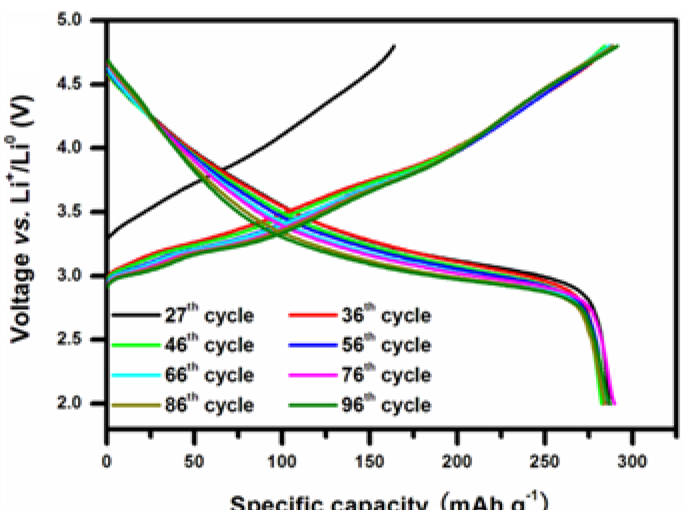
Accomplishments to Date FY15
Impact of Surface Modification

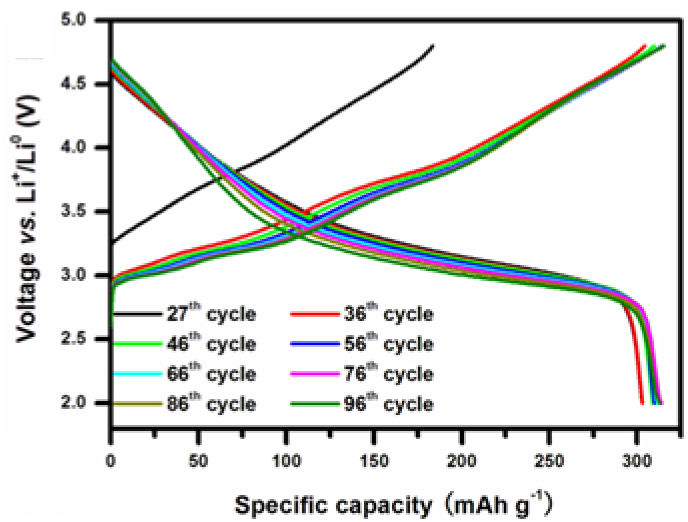
Room Temperature





300 mAh/g capacity maintained after 100 cycles, minimized voltage decay





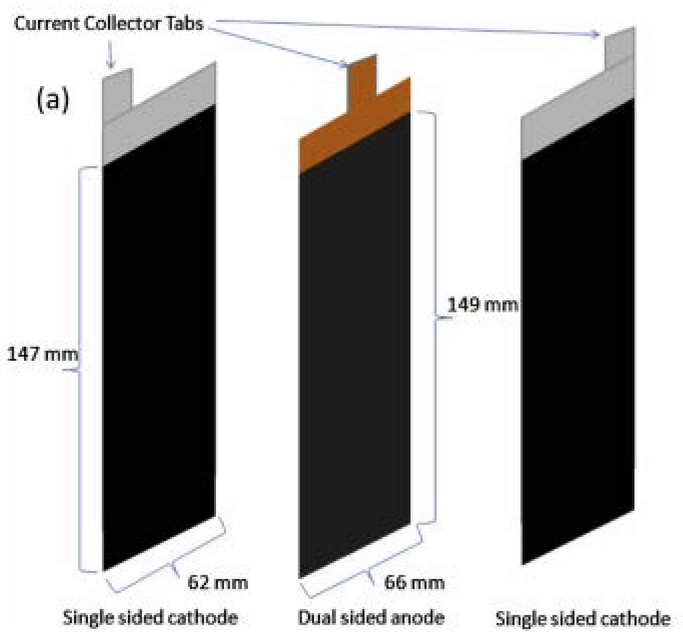
Partnered with NIMTE

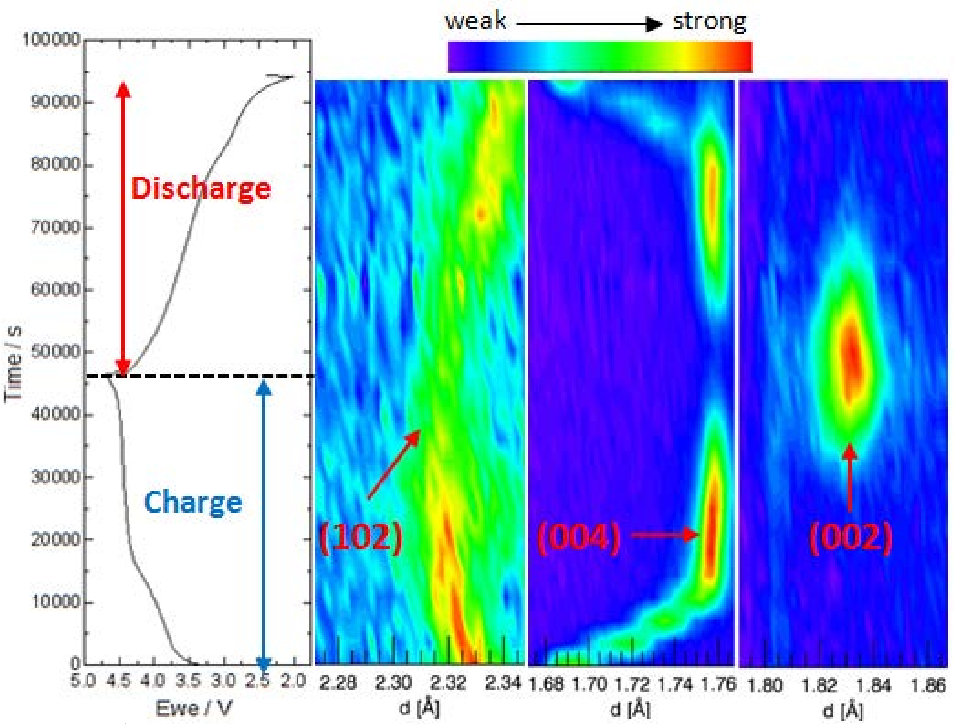
B. Qiu and M. Zhang et. al submitted, 2015

Technical Achievements
First Gen Operando Neutron

Single layer pouch cell

Only (102) peak from cathode





(a): 1st cycle charge/discharge curve of Lithium-rich / C cell and surface contour plots of (b): Lithium-rich (102); (c): Li_xC_6 (004); (d): LiC_6 (002) Neutron Diffractions.

H. Liu , C.R. Fell, K. An, L. Cai, and Y.S. Meng, Journal of Power Sources **2013**, 240, 772-778.

Technical Achievements
Second Gen Operando Neutron

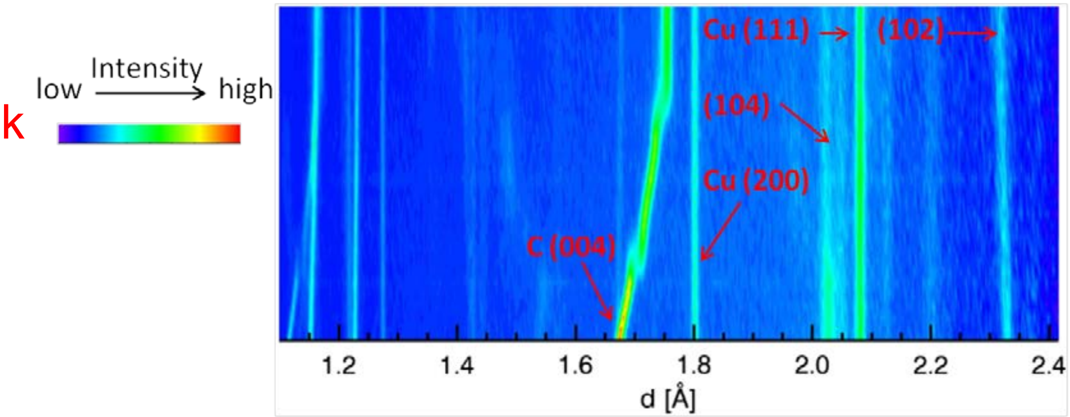
Single layer pouch cell

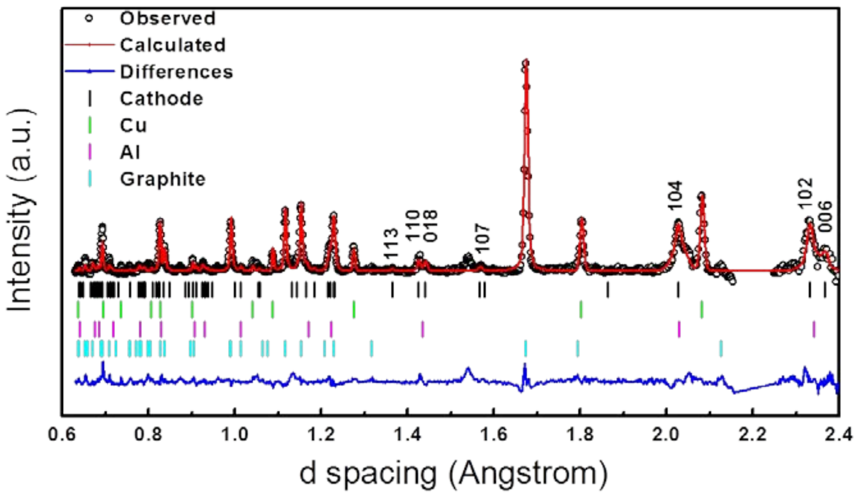
Only (102) peak from cathode

⇩

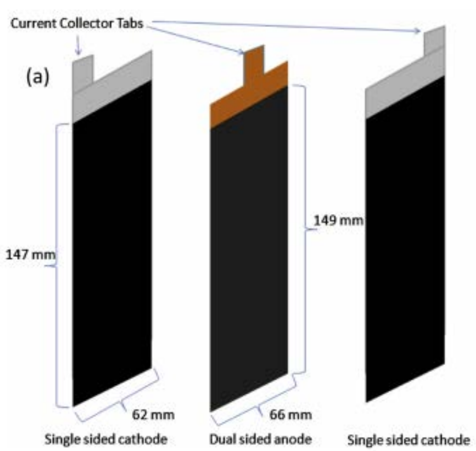
Multi layer pouch cell (C)

Data can be refined, graphite introduce complex phases





12*



R_{F2} = 11.81% R_{wp} = 1.2% Chi^2 = 1.702

H.D. Liu, … Y. S. Meng, "Probing the activities of Li and O in advanced Li-ion batteries via operando neutron diffraction", to be submitted, 2015

Technical Achievements
Third Gen Operando Neutron

Single layer pouch cell

Only (102) peak from cathode

⇩

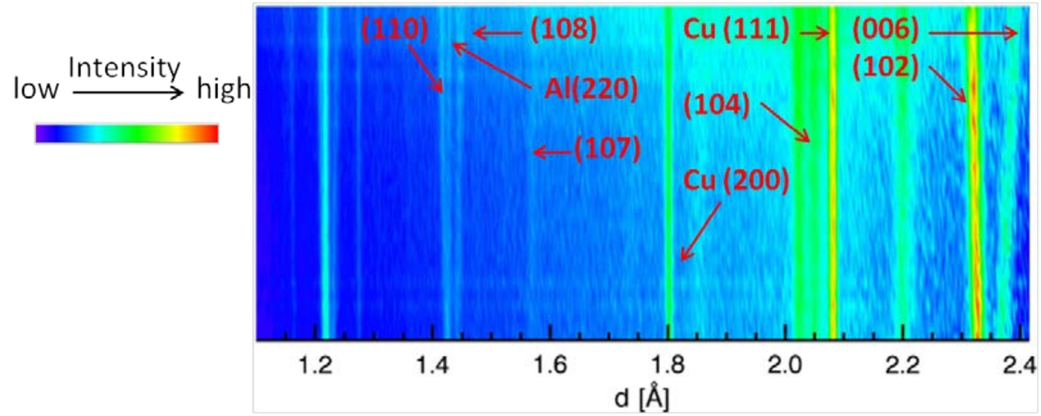
Multi layer pouch cell (C)

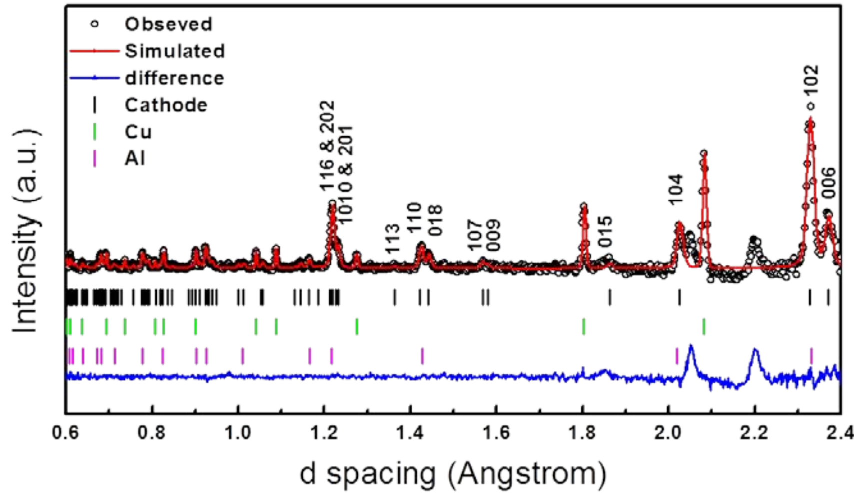
Data can be refined, graphite introduce complex phases

⇩

Multi layer pouch cell (a-Si)

Data can be refined, Improved reliable factor focus on cathode

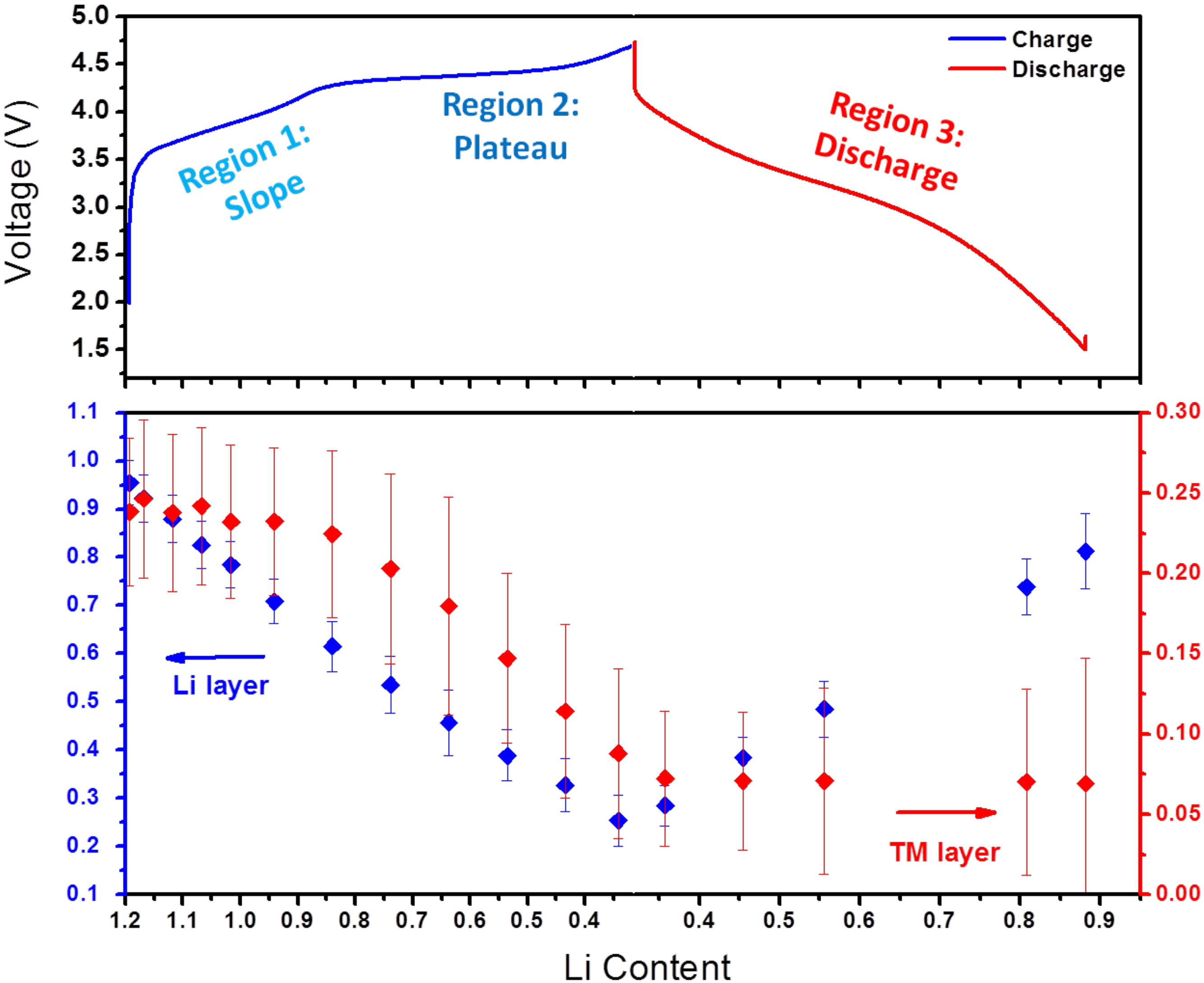




R_{F2} = 9.27% R_{wp} = 1.16% Chi^2 = 1.358

H.D. Liu, … Y. S. Meng, "Probing the activities of Li and O in advanced Li-ion batteries via operando neutron diffraction", to be submitted, 2015

Accomplishments to Date FY15
Directly Probing Li and O

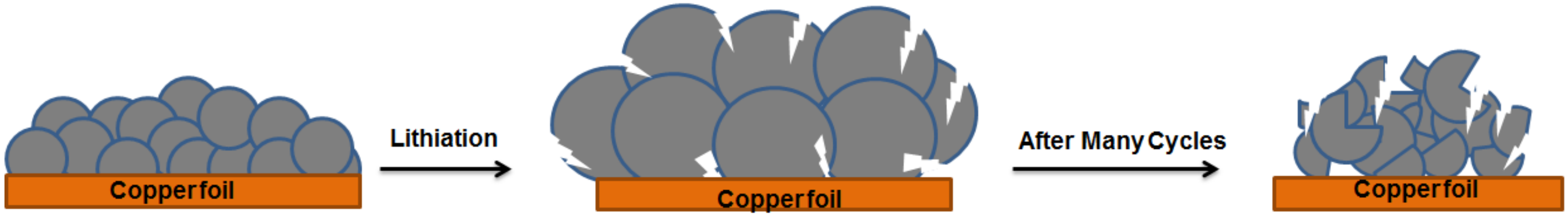


1. Li in Li layer extracted out first
2. Most of Li in TM layer extracted out during plateau region
3. Li inserted back to Li layer during discharge

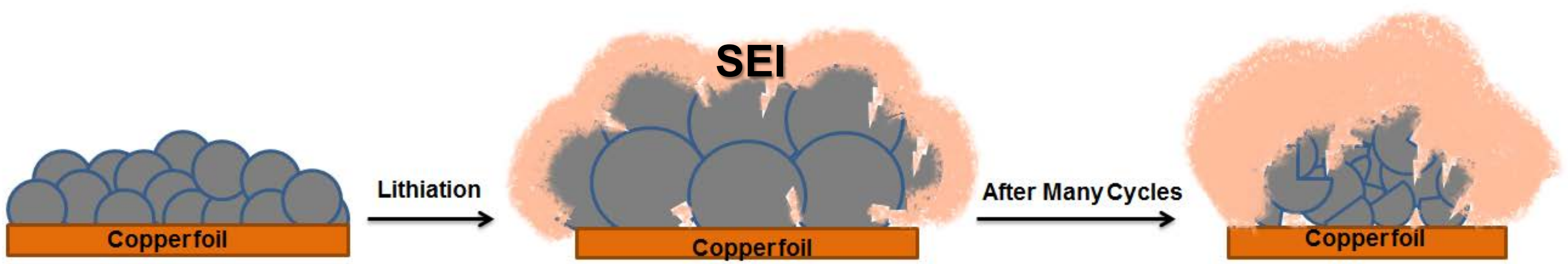
H.D. Liu, … Y. S. Meng, "Probing the activities of Li and O in advanced Li-ion batteries via operando neutron diffraction", to be submitted, 2015

Si Anode Challenges

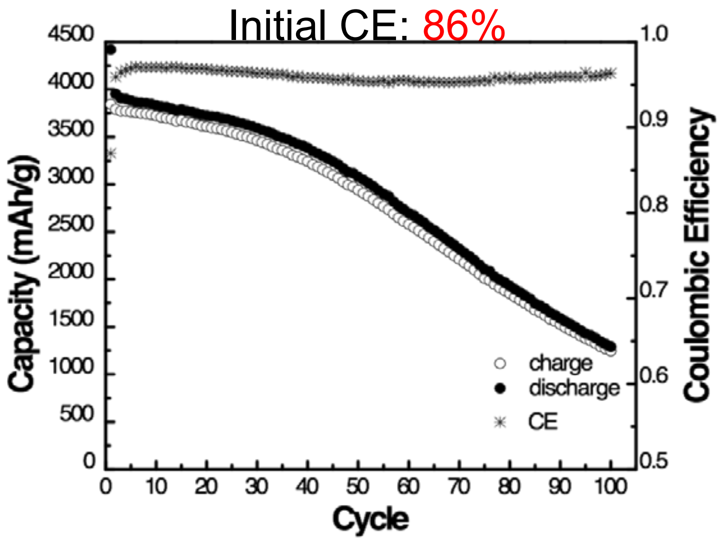
Mechanical

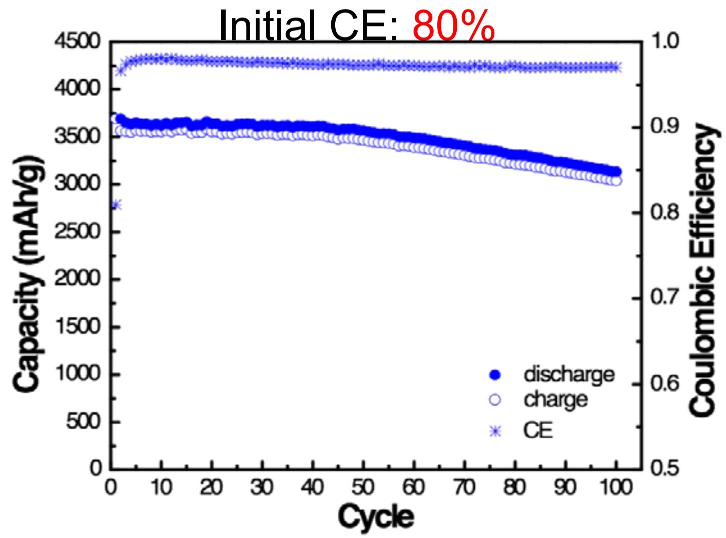


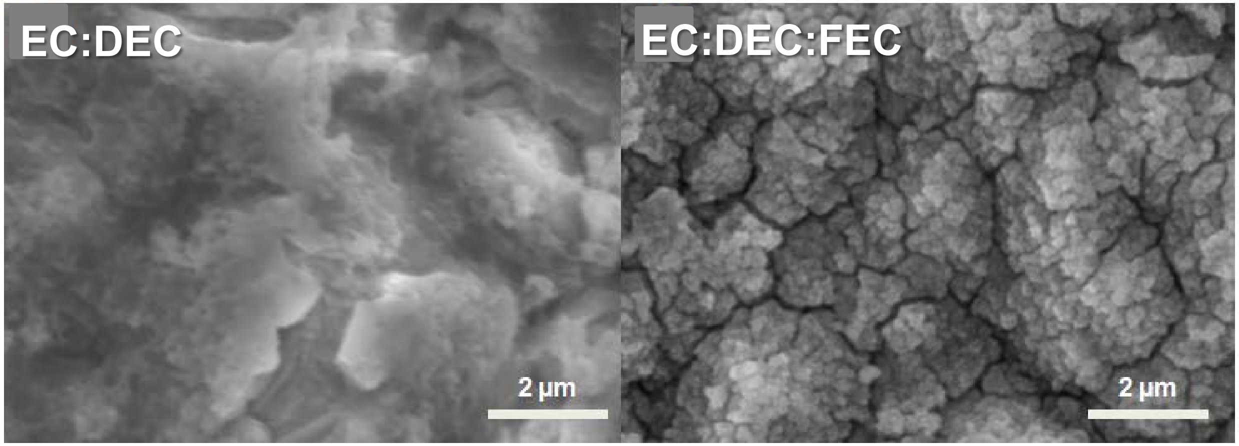
Chemical



Accomplishments to Date FY15
Impact of FEC on a-Si Thin Film

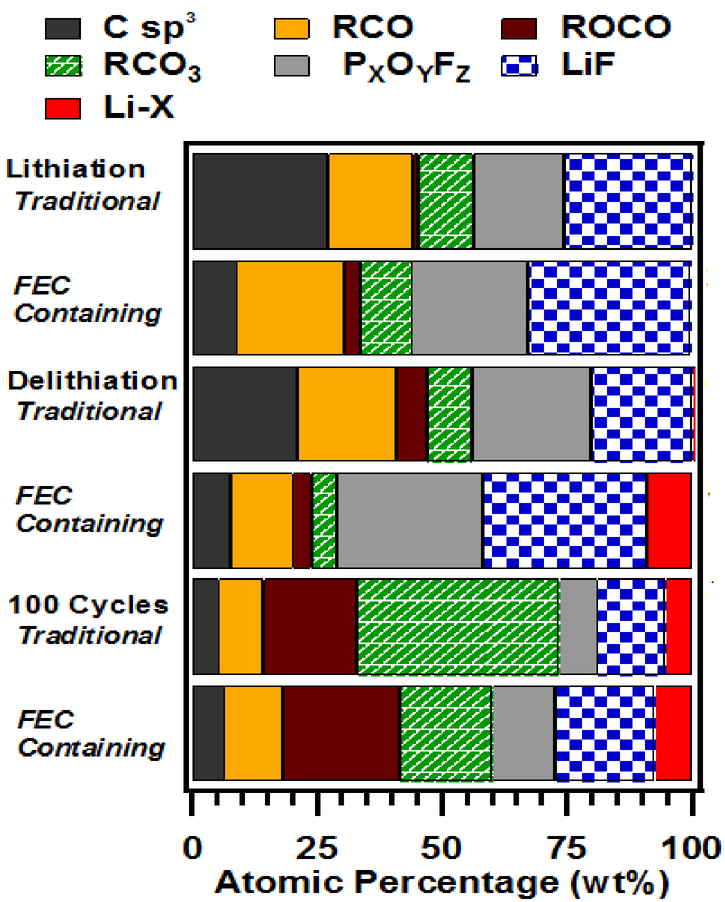




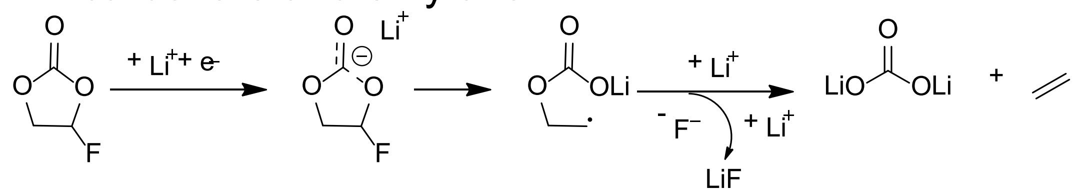


- **Lower initial CE is attributed the consumption of Li-ions as a result of FEC decomposition**
- Mechanically stable a-Si thin films avoid delamination during electrochemical cycling
- After 100 cycles FEC containing electrolyte forms more inorganic species resulting in a brittle dense SEI

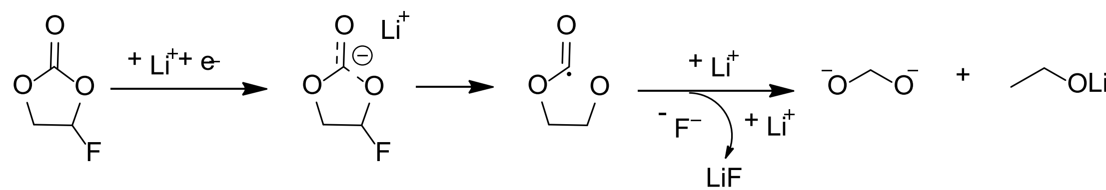
Accomplishments to Date FY15
Tracking SEI Composition by XPS



Reaction 1. Electro-reduction of fluoroethylene carbonate to form lithium fluoride, lithium carbonate and ethylene



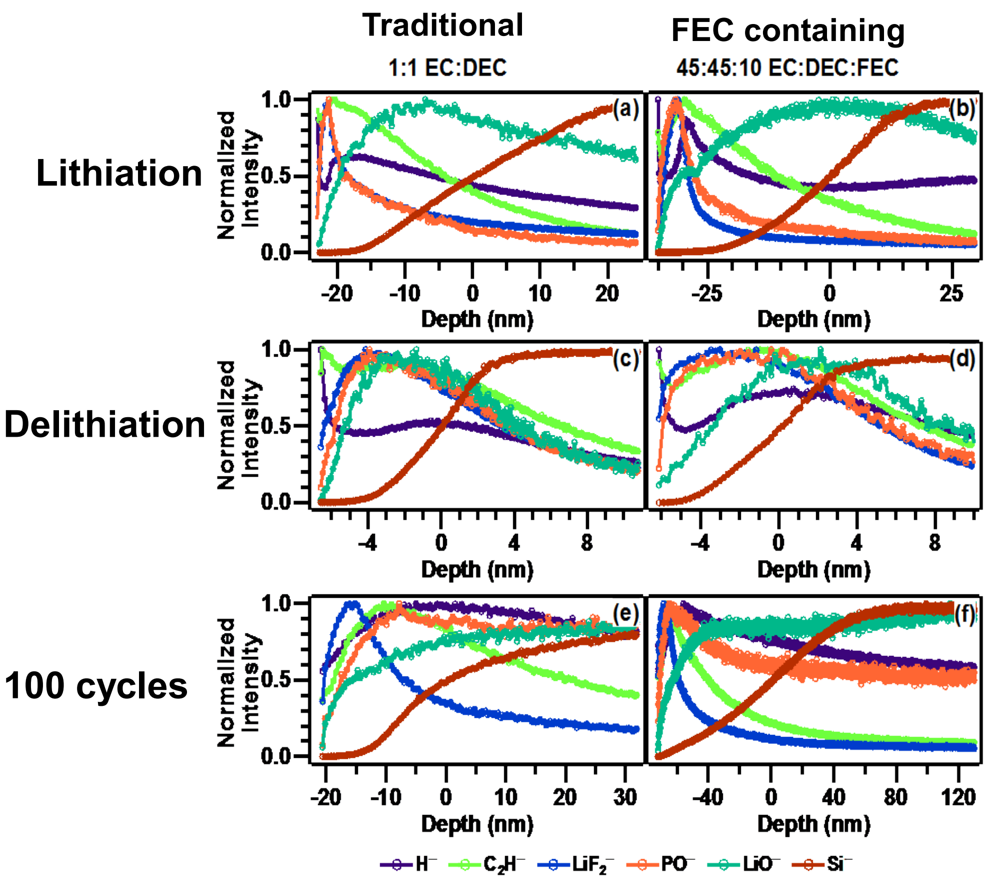
Reaction 2. Electro-reduction of fluoroethylene carbonate to form lithium fluoride, methylenedioxyl ion (or alternately carbon dioxide) and lithium ethoxide

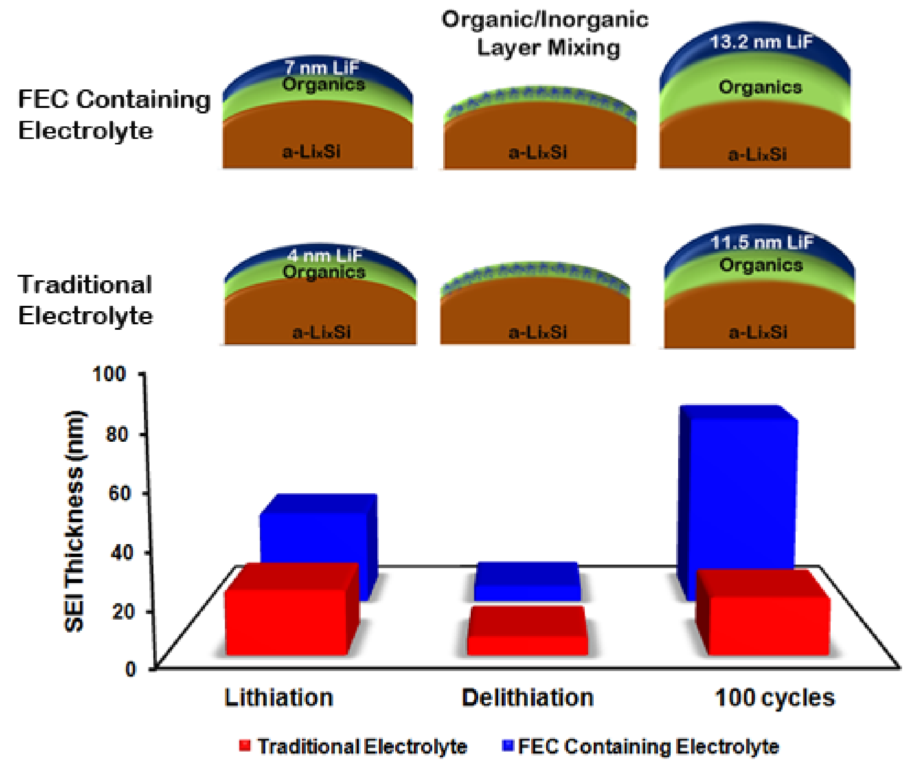


These results are consistent with calculations conducted by Balbuena and co-workers which suggests a kinetically fast formation of neutral radical carbonate and fluoride via a ring opening mechanism leading to the rapid formation of LiF

Schroder, K; Alvarado, J et al. "**The Effect of Fluoroethylene Carbonate as an Additive on the Solid Electrolyte Interphase on Silicon Lithium-ion Electrodes" to be submitted**

Accomplishments to Date FY15
Tracking SEI Composition by TOF-SIMS



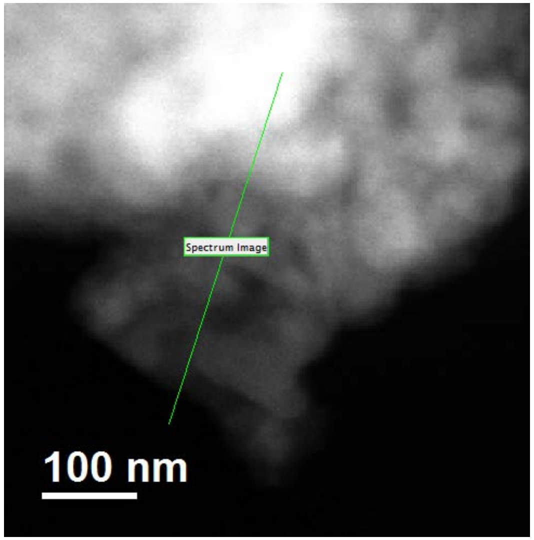


- There are two tentative structural differences: **(1) the traditional electrolyte SEI appears to have a thicker organic stratum on top of the inorganic species compared to the FEC containing electrolyte SEI and (2) there is a thicker stratum of LiO^- species in the traditional electrolyte SEI than the FEC containing electrolyte SEI**
- Depth profiles suggests that the FEC containing electrolyte formed more irreversible and more stable inorganic species

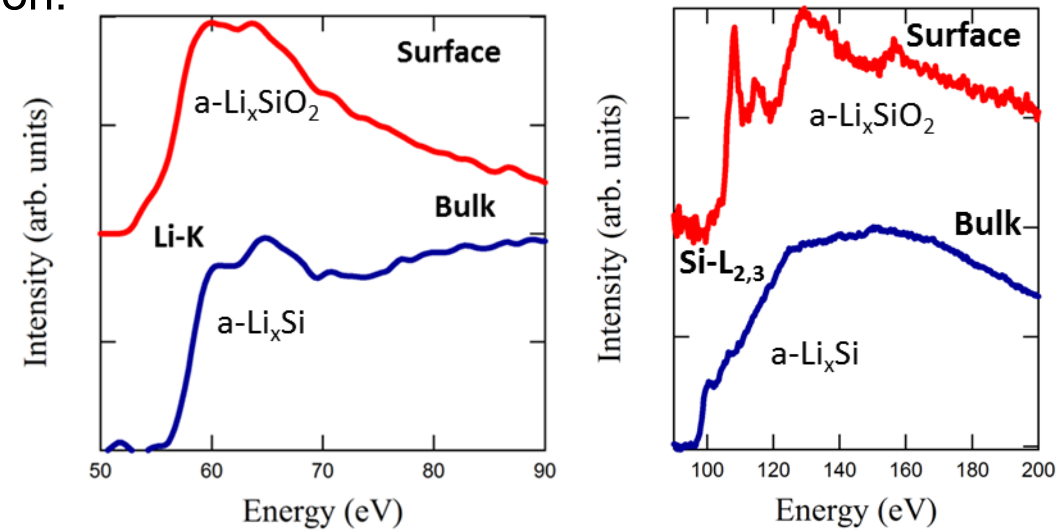
Schroder, K; Alvarado, J et al. "**The Effect of Fluoroethylene Carbonate as an Additive on the Solid Electrolyte Interphase on Silicon Lithium-ion Electrodes" to be submitted**

STEM-EELS analysis from cycled Si

STEM-EELS: is a powerful technique for characterizing Si anode in Li-ion batteries.
Challenge: Li_xSi alloys and SEI are extremely beam sensitive, therefore STEM/EELS conditions were optimized to minimize beam damage and achieve high spatial resolution.



ADF-STEM from the lithiated Si after 5 cycles.



Two different fine structures have been observed for Si-L and Li-K edges

1- Li_xSiO_2 formation at the surface of particle.
2- Presence of Li_xSi alloy in the bulk.

Responses to Previous Year Reviewers' Comments

Comment: The reviewer stated that the combination of scanning transmission electron microscopy/electron energy loss spectroscopy (STEM/EELS), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS) and first principle computations is a powerful approach to understanding the structure of important materials as well as understanding the effect of structure on properties such as voltage fade and material instability.
Response: We hope to continue demonstrating the reviewer's point.

Comment: The reviewer commented that unlike the title, no ion transport data was present although the project had been going on more than a year. The reviewer then wanted to know when the data/calculations concerning ion transport in the materials are gathered.
Response: We presented the ion transport data in terms of the excellent rate performance data in optimized Li rich layered oxides. We also reported the ion transport barriers in FP computation. The detailed data is shown in publication #7.

Comment: This reviewer was not sure how the PI had the resources to conduct these studies in sufficient depth.
Response: We listed each partner institutional roles. UCSD designed the experiments and we performed all these experiments and analyzed data together with our partners/collaborators.

Collaborations

Dr. An Ke (SNS – Operando ND)

Dr. Nancy Dudney and Dr. J.C Li (a-Si thin film)

Dr.Subramanian Venkatachalam (Multilayer Operando Neutron Cell)

Dr. Keith Stevenson and Dr. Kjell Schroder (XPS, TOF-SIMS access)

Dr. Chunmei Ban (MLD coatings)

Dr. Zhaoping Liu (Surface Modification)

OAK RIDGE NATIONAL LABORATORY
Managed by UT-Battelle for the Department of Energy

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TMI TEXAS MATERIALS INSTITUTE
Materials Science & Engineering

NREL

CNITECH
Ningbo Institute of Industrial Technology, CAS

Remaining Challenges and Barriers

- TEM/STEM Beam Sensitivity of Lithiated Si Anode
- Beam time access limit on transmission X-ray microscopy
- Sample variety (thin film vs. powder)

Future Work

- Investigate the secondary particle size effects on electrochemical performance via TXM. TXM provide larger field of view and is complementary to TEM

- Identify the mechanisms of MLD coated silicon anode for their improved chemical stability upon cycling. Rationalize the improvement of columbic efficiency

- Utilizing STEM/EELS to further understand the effects of FEC containing electrolyte on SEI layer composition.

Summary

- Developed a novel and facile synthesis method for Li-rich cathodes to improve voltage stability upon cycling

- Probed Li^+ de/intercalation activities of Li-excess via operando Neutron scattering

- Our diagnostic tool suite consisting STEM/EELS, XPS, and TOF-SIMS are effective at identifying the SEI compositions in Si-based anode materials

- By using amorphous silicon thin film model system, we have investigated the effect of FEC co-solvent and other additives in promoting a stable SEI formation