Atomic Layer Deposition for Stabilization of Silicon Anodes

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DOE Vehicle Technologies Program

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Project I.D. # ES145

Overview

Timeline

- October 1, 2010
- September 30, 2014
- ~35%

Budget

- Total project funding
- Funding received:
- FY11 $ 440 K
- FY12 $ 470 K
- FY13 $ 495 K
- FY14 $ 495 K

P.I. Anne Dillon, NREL

Co-P.I.'s Se-Hee Lee and Steven George, University of Colorado, Boulder (sub contract)

Barriers

- Barriers addressed
  - Cost: Silicon is an inexpensive abundant element. Low cost processing and /or commercially available materials are employed.
  - High Gravimetric and Volumetric Capacity: Both have been achieved for thick electrodes that exhibit durable cycling.
  - Rate Capability: Stable cycling at C/5 has thus far been achieved.

Collaborators

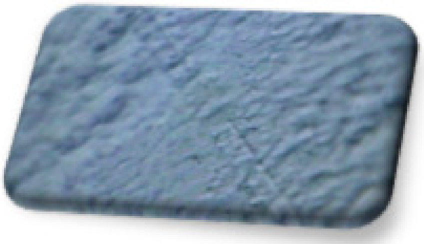
- M. Stanley Whittingham SUNY, Binghamton
- Stephen Harris, General Motors
- Gao Lui, LBNL
- Marca Deoff, LBNL
- Arumugam Manthiram, UT, Austin
- Michael Thackeray, ANL
- Vince Battaglia, LBNL
- Michal Toney, SSRL

Relevance / Main Objectives

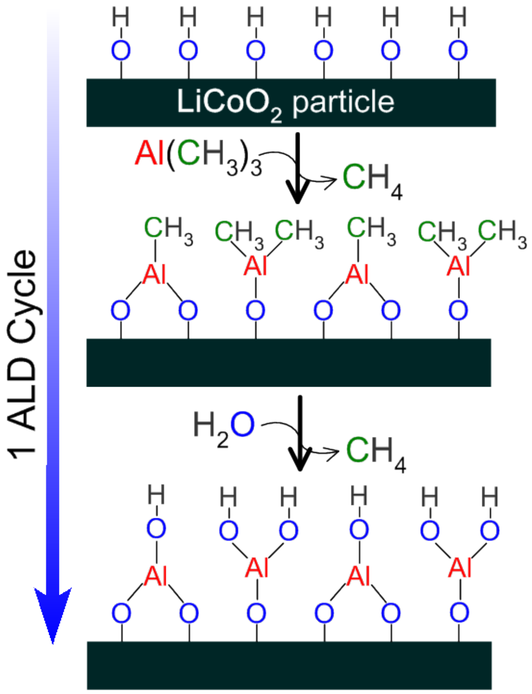
- Employ inexpensive techniques such as hot-wire chemical vapor deposition (HWCVD) or commercial particles to develop durable high capacity Si-based anodes for vehicles.

- Utilize atomic layer deposition ALD processes to further improve performance of Si-based anodes.

- Obtain better understanding of why Al_2O_3 ALD coatings work by both building full cells and obtaining *in situ* synchrotron X-ray diffraction techniques.



HWCVD a-Si



ALD of Al_2O_3

Milestones

FY11 Milestones

- **Demonstrate scale-up of HWCVD a-Si or nano-Si powder.**
  (January 2011) ***Complete***
- **Optimize HWCVD produced a-Si or nano-Si in conventional coin cell. (May 2011)** ***Complete***
- **Demonstrate an ALD coating for improved performance of Si anode. (July 2011)** ***Complete***
- **Optimize coated electrode and demonstrate durable cycling. (Sept. 2011)** ***Complete***

FY12 Milestones

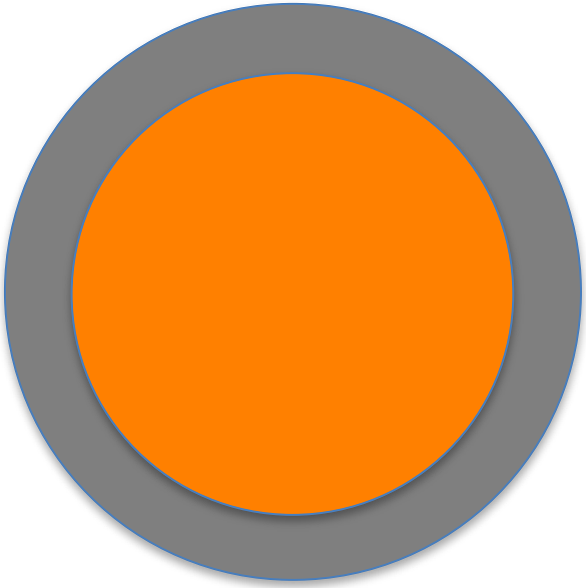
- **Demonstrate mechanistic information about ALD coatings via *in situ* techniques including Raman spectroscopy, X-ray diffraction, nuclear magnetic resonance and/or Time of Flight Secondary Ion Mass Spectrometry. (January 2012)** ***Complete***
- **Send an optimized thick electrode (≥ 15 μm) with a reversible capacity of at least 2000 mAh/g at C/20 to Dr. Vince Battaglia at LBNL for verification. (May 2012)** ***In Progress***
- **Demonstrate an ALD coating with rate performance of ≥ C/5 for a thick Si anode. (July 2012)** ***Complete (without ALD coating)***
- **Demonstrate at least 50 cycles at a minimum of C/3 rate. (Sept. 2012)**

Approach/Strategy

Major Issues with Si Anodes: 1. Large volume expansion → mechanical degradation with cycling. 2. Large initial irreversible capacity loss. 3. Poor Coulombic efficiency.

A Simple Solution

Nano-Si Core Shell Structure for Li-ion Battery Anode



Requirements for the outer layer

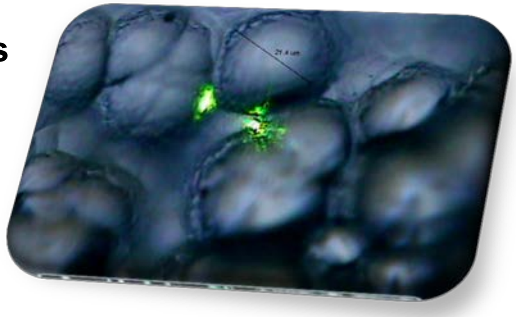
1. **Electronically conductive**
2. **Ionically conductive**
3. **Mechanically strong**
4. **Electrochemically stable**

Apply Facile Atomic Layer Deposition (ALD) Coatings for both improved mechanical integrity and reduced initial irreversible capacity loss.

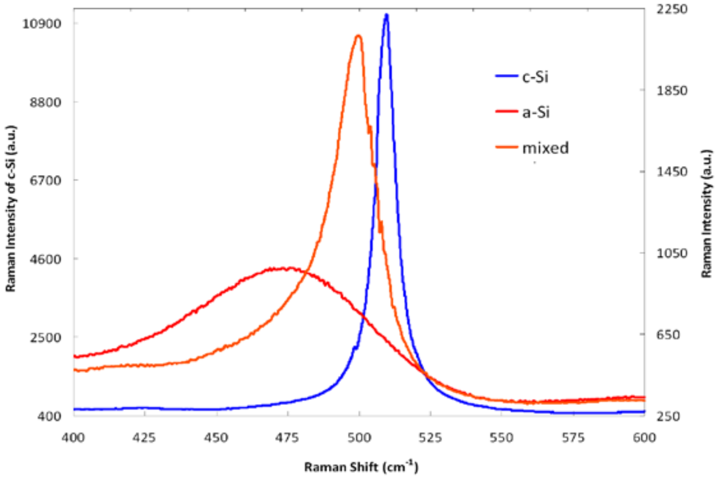
Note: That we are currently ahead of schedule in meeting our DOE Milestones.

Demonstration of Scale-up of HWCVD a-Si Powder

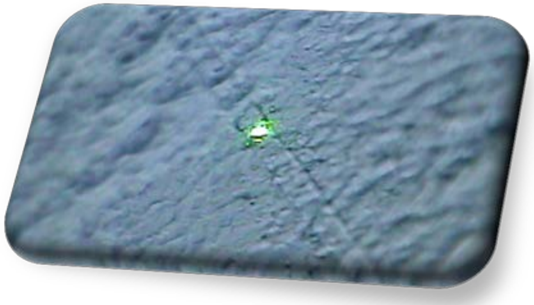
HIGH T_s



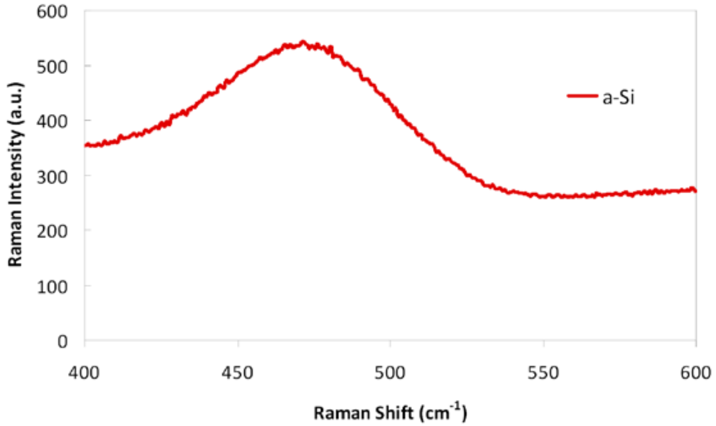
magnification of 100 x: crystals ~ 25 -35 μm



LOW T_s



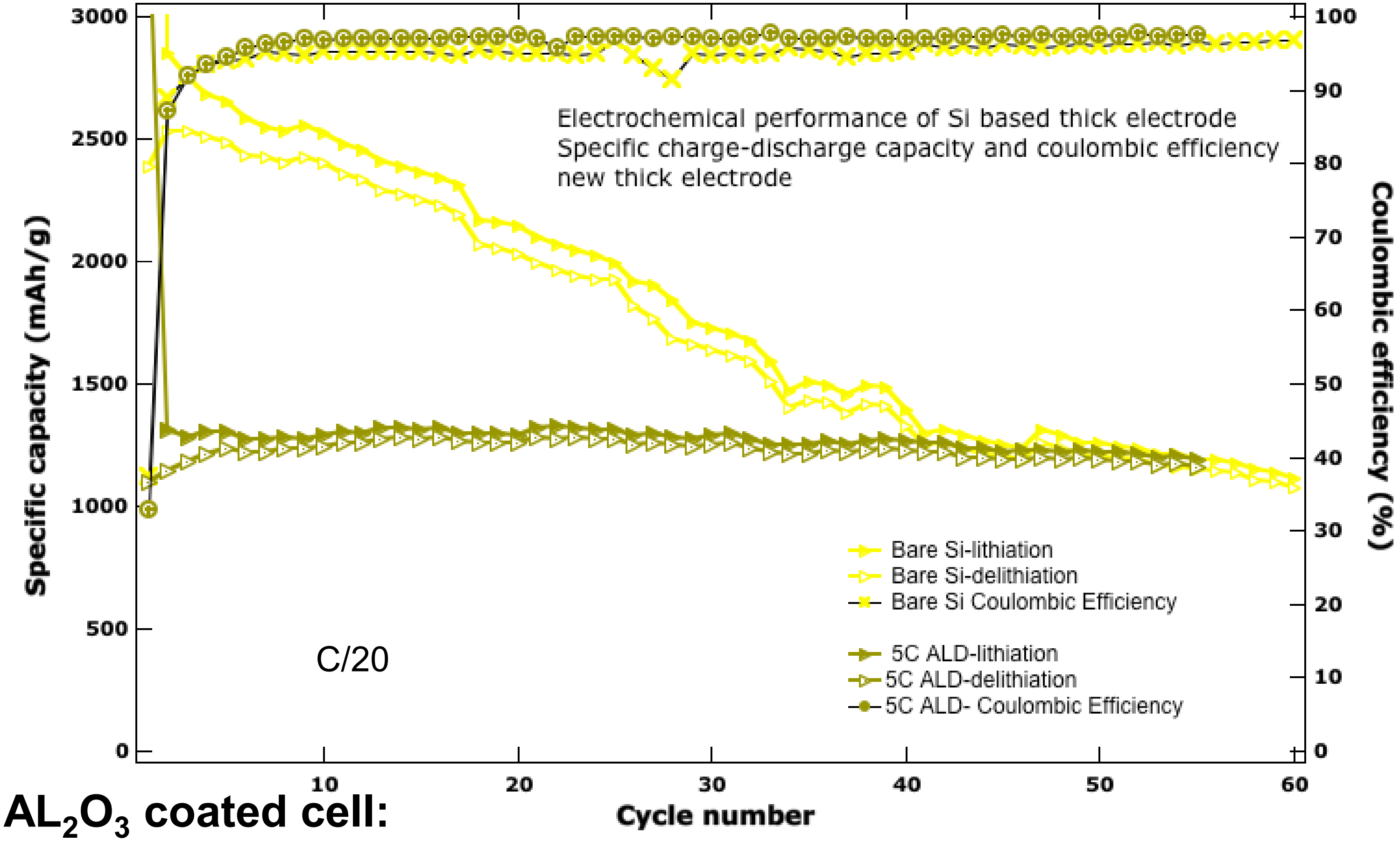
magnification of 100 x



- Initially HWCVD scale-up resulted in mixed crystalline phases.
- HWCVD synthesis conditions were optimized to produce all a-Si powder ~60 mg /h produced with a small-scale single filament system. Multi-filament HWCVD systems are available at NREL.
- Small spot Raman reveals substrate temperature (T_s) is critical to avoid crystalline silicon (c-Si) island formation.

This represented the completion of the January 2011 Milestone.

A Si/Cu Composite is formed by Simply Pressing “Organic” Copper with Si Followed by a Subsequent Anneal



ALD AL_2O_3 coated cell:

- ~98% Coulombic Efficiency

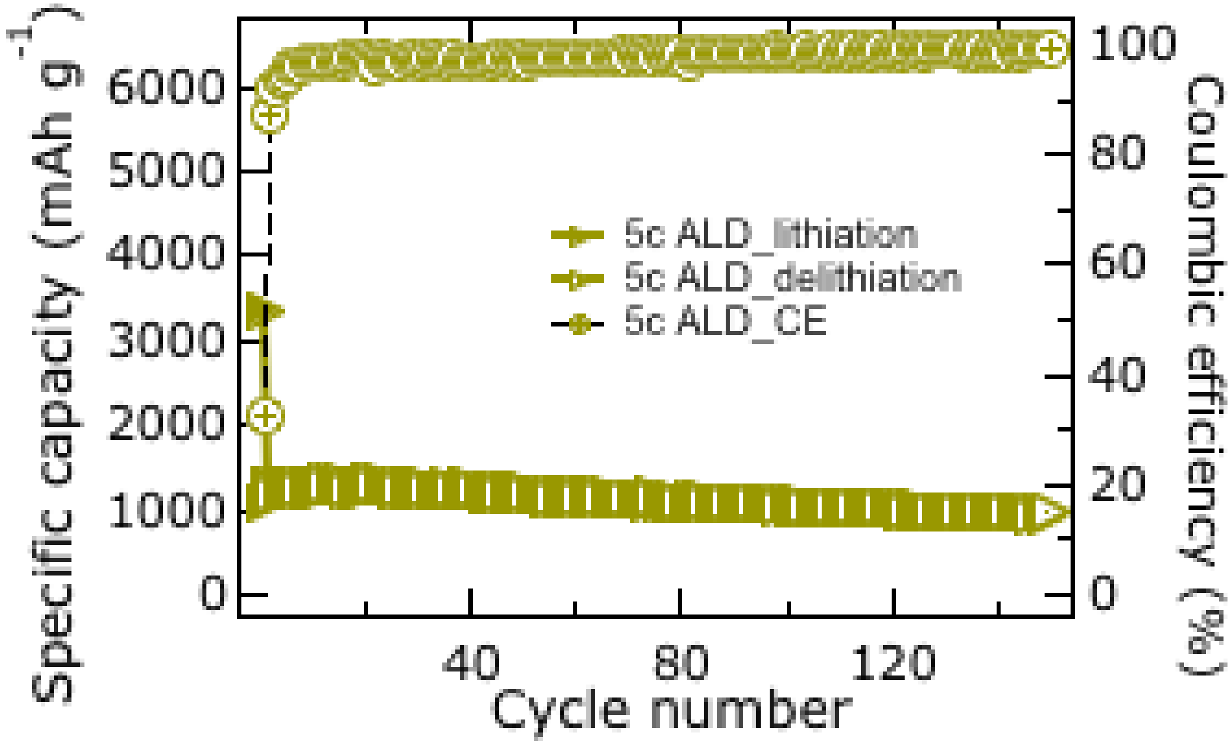
Bare cell:

- ~95% Coulombic Efficiency

Compressed to 8 metric tons

Annealing the organic copper creates void space and enables high capacity cycling. The ALD coating further stabilized the cell. This represented the completion of the January 2011 Milestone.

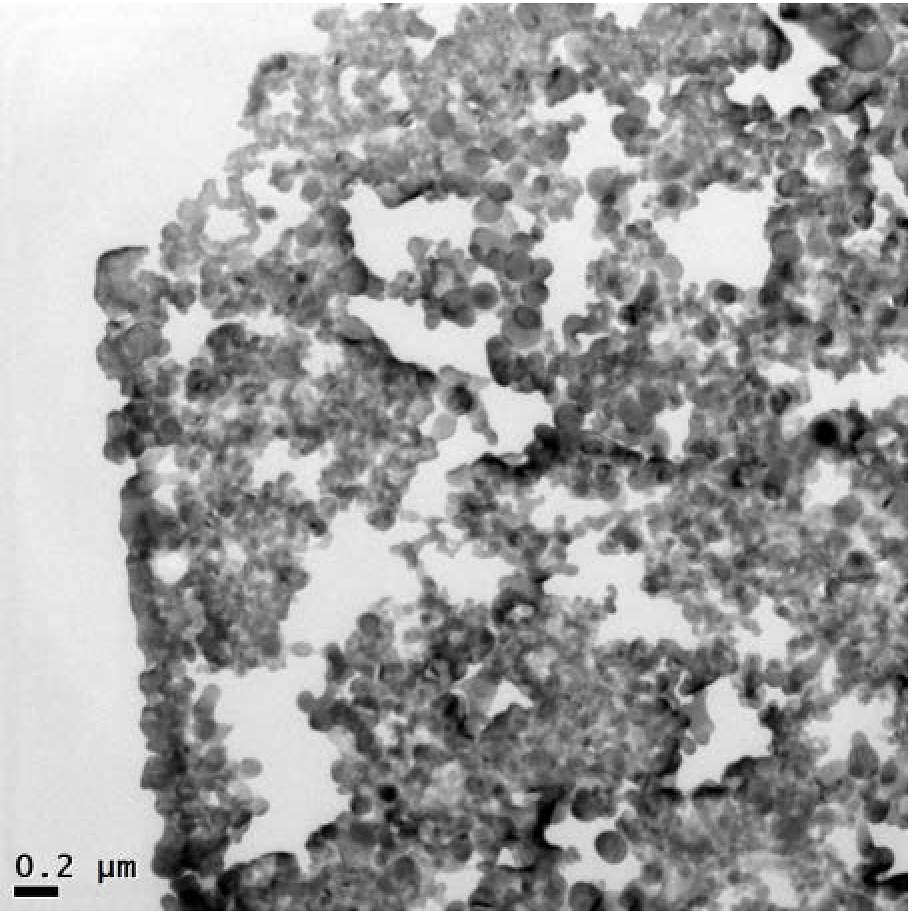
ALD Al_2O_3 was Demonstrated to Stabilize Si/Cu Electrodes



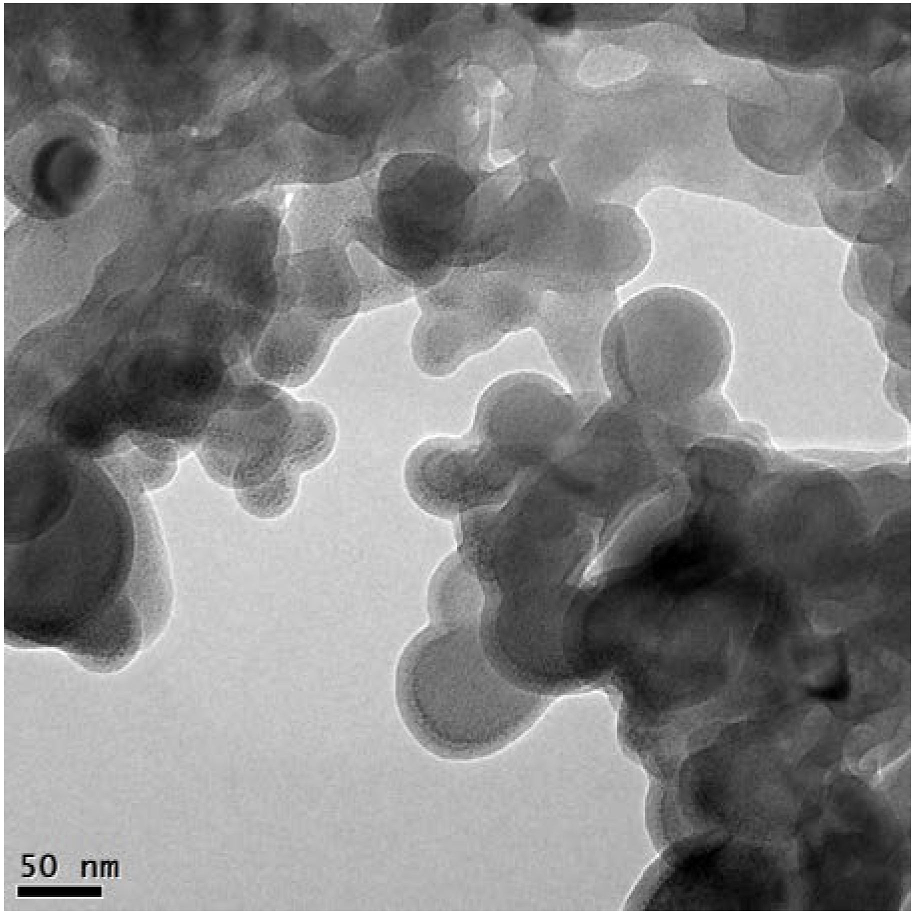
5 cycles of ALD Al_2O_3 (~1 nm) was found to be the optimal coating thickness. Capacity of Si is *constrained* to ~1000 mAh/g but Coulombic efficiency is improved to > 99%.

Various thicknesses of coatings were tested and 1 nm (5 cycles) was found to be optimal. This represented the completion of the January 2011 Milestone

TEM Images of C/Si Core Shell Structures



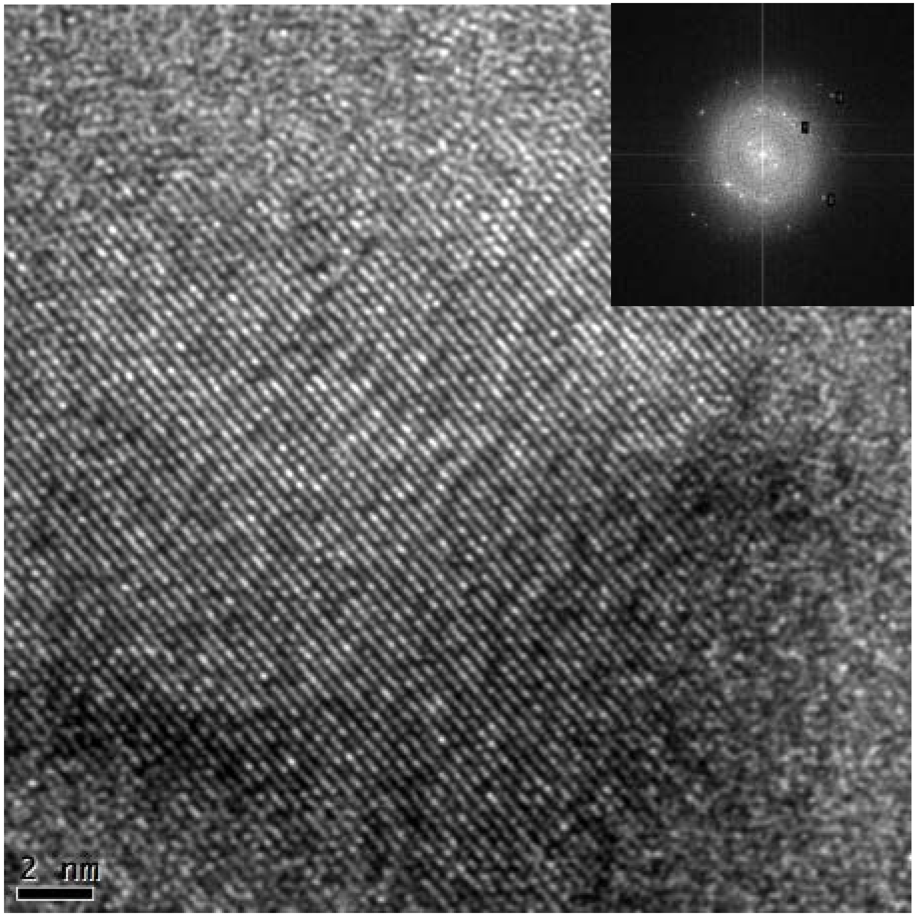
x4.5K

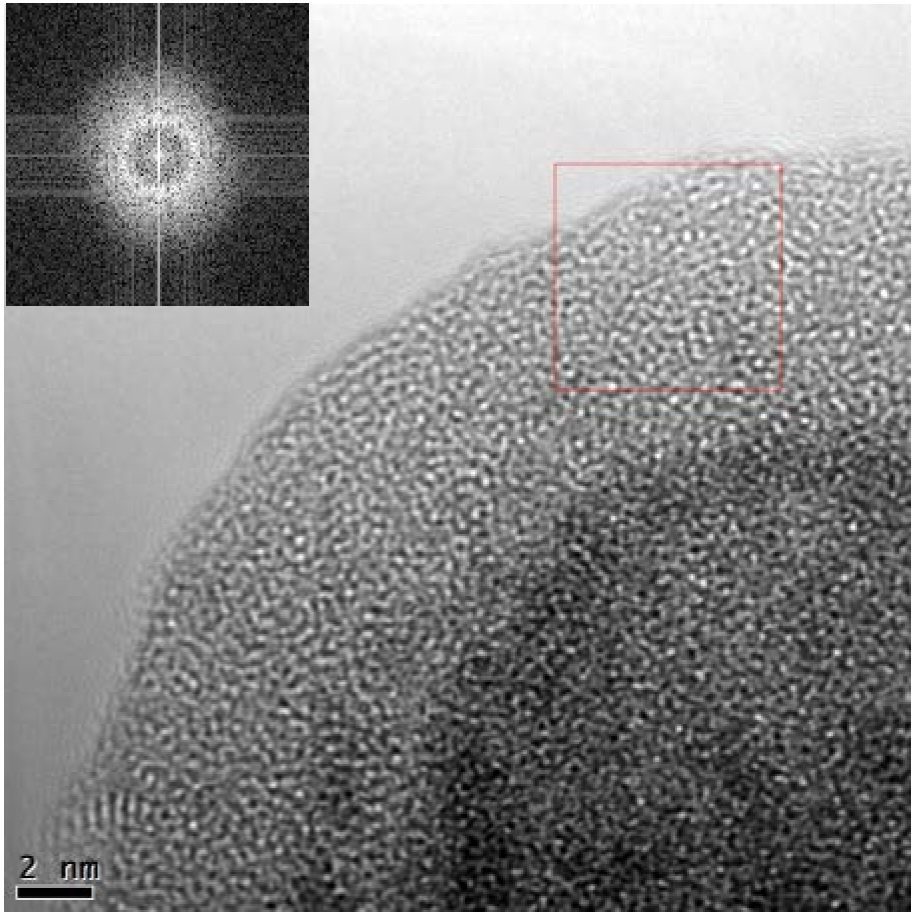


x13.5K

Carbon / Silicon core shell structures were created with a simple annealing process. The composition is 70% Aldrich Nano-Si and ~ 30% carbon with no other binder or conductive additive.

HRTEM Images of Core Shell Structures



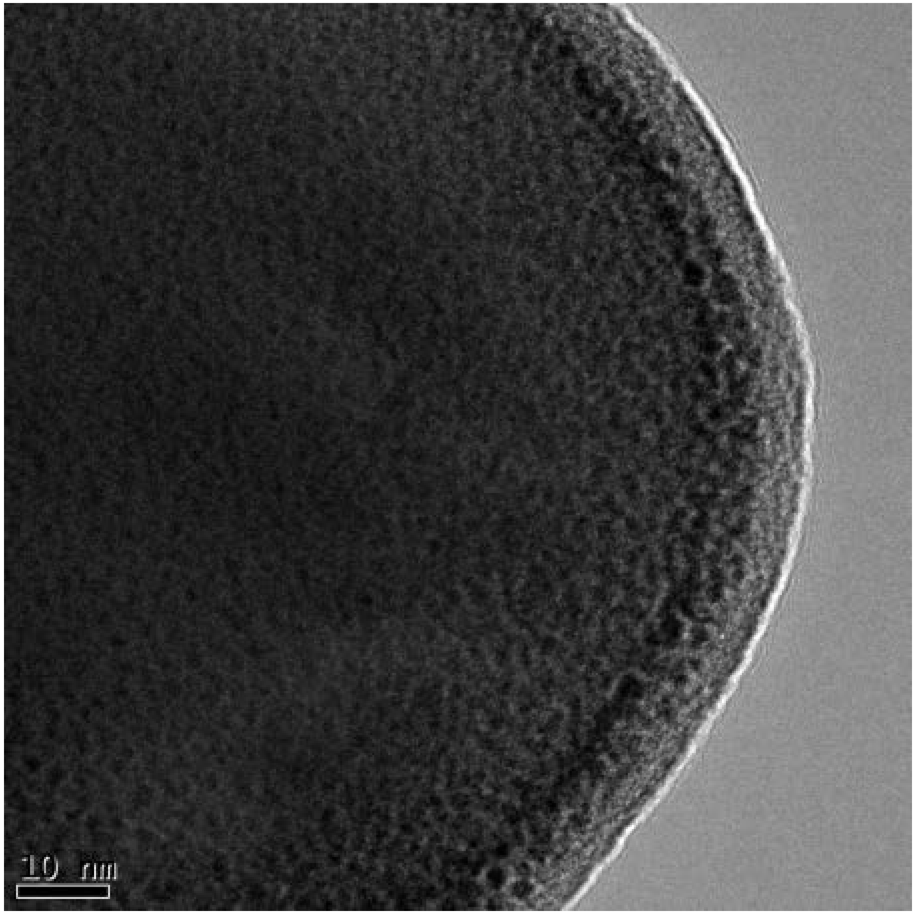


HRTEM of Aldrich crystalline Si core particle with electron diffraction.

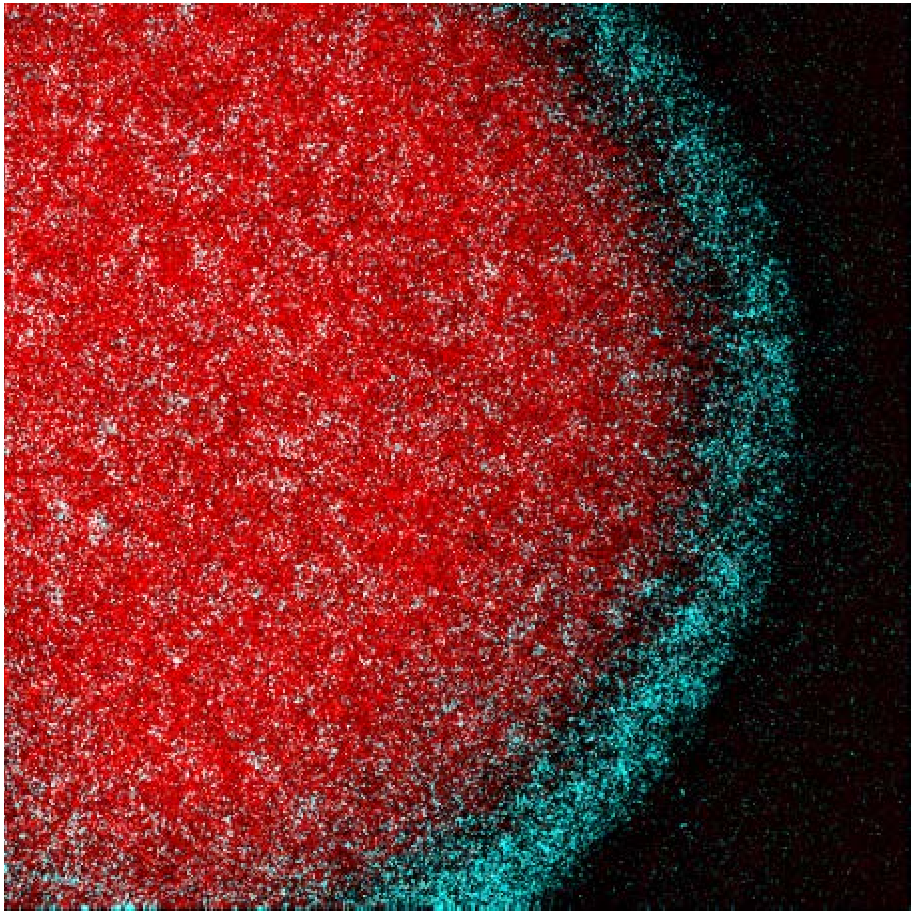
HRTEM of carbon shell where small spot electron diffraction (red box) shows the shell is amorphous.

Small spot electron diffraction shows that the Aldrich Si core is crystalline and that the carbon coating is amorphous.

Small Spot EELS : Si and Carbon Map



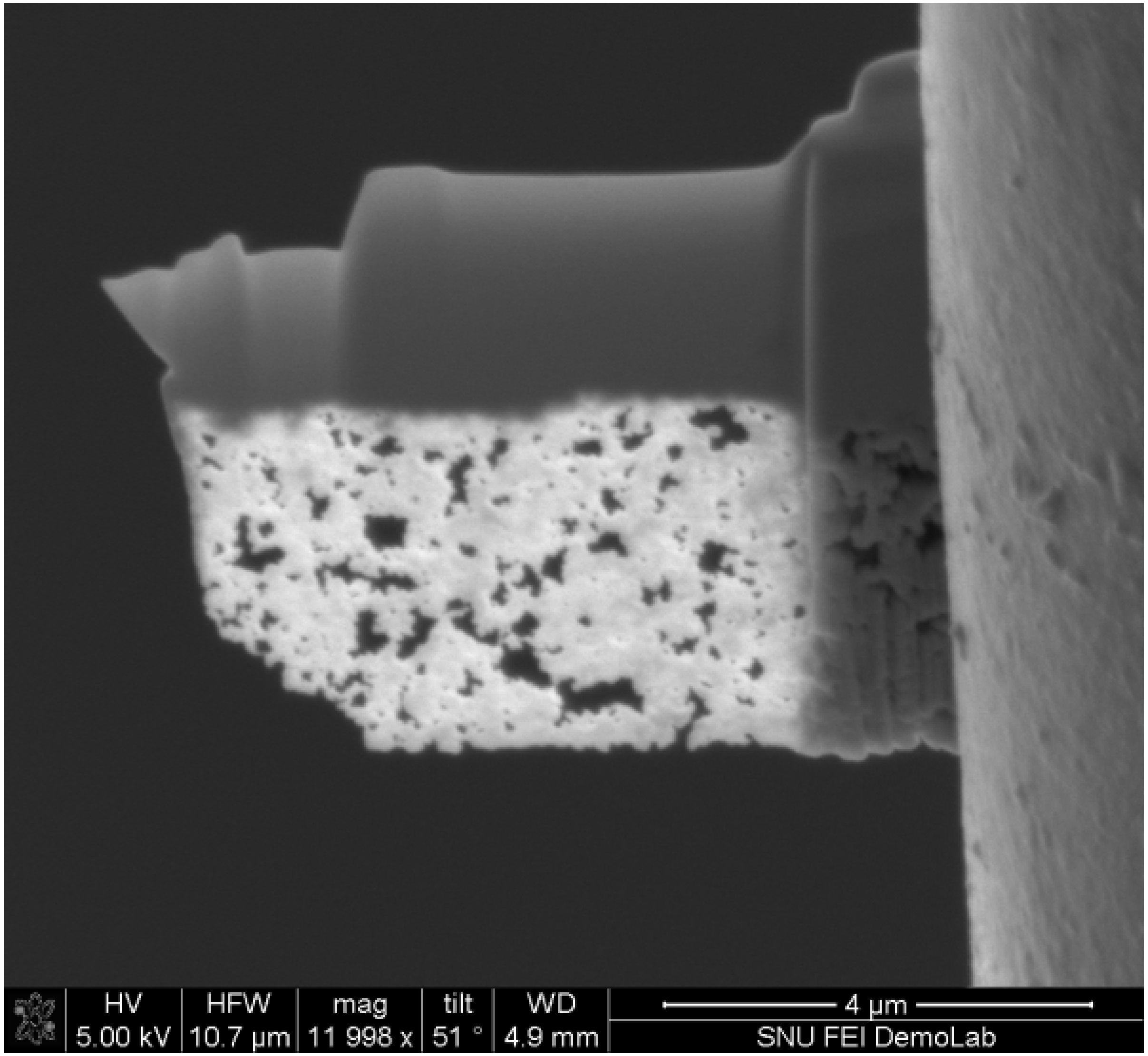
x440K



Red : Si
Blue : C

Carbon core shell importantly surrounds the commercial crystalline silicon, maintaining excellent electronic conductivity and enabling fabrication of a thick electrode.

Cross Sectional Image of Thick Electrode Fabricated From Core Shell Particles



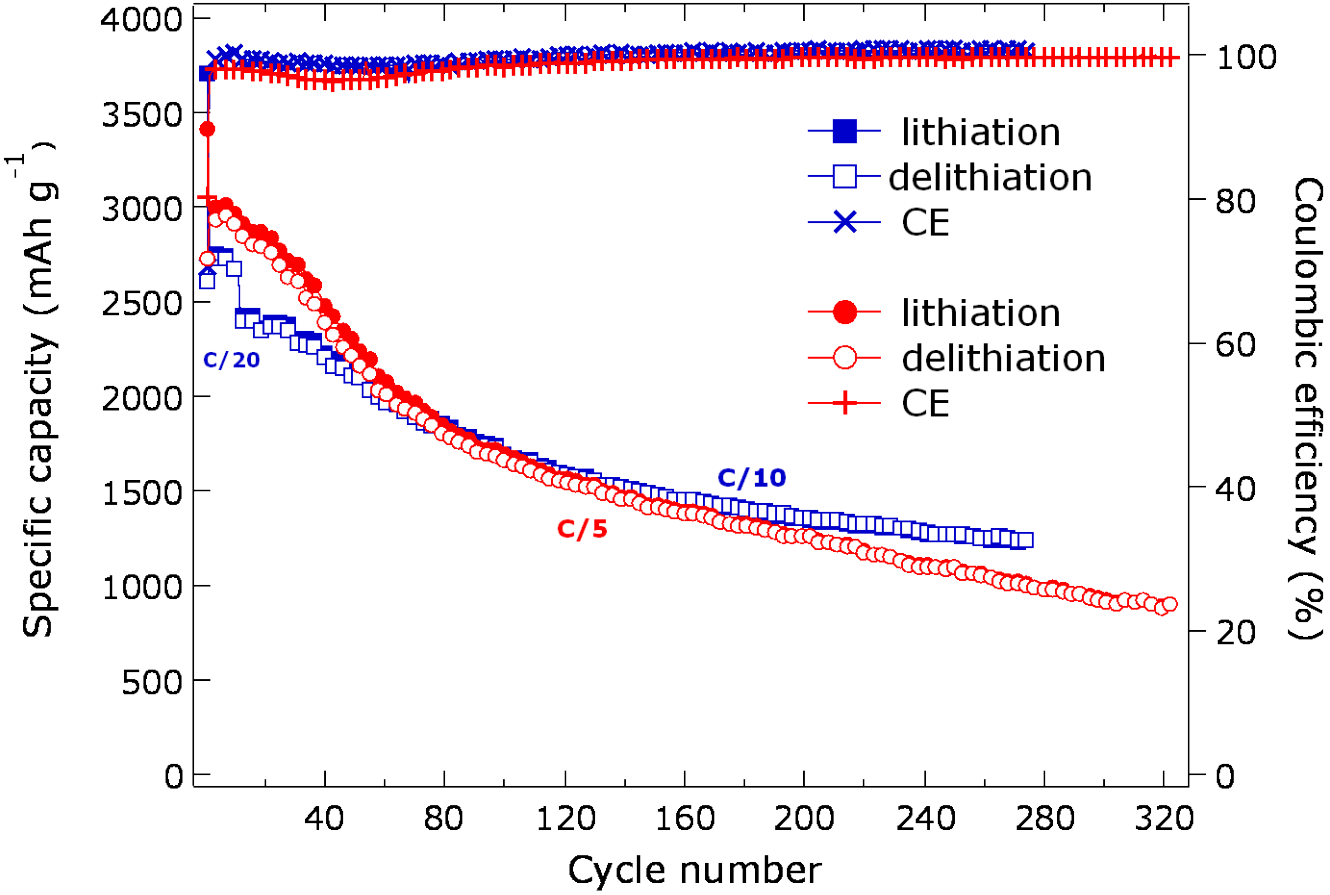
- Mass loading of particles is 70% Si and 30% carbon with no binder required.

- Mass loading in coin cells that have been tested to date is 1-2 mg / cm^2

- From the voltage profiles the Si appears to become amorphous in the first cycle.

Fabrication of a thick Si/C electrode 70:30 with high Si mass loading is achieved.

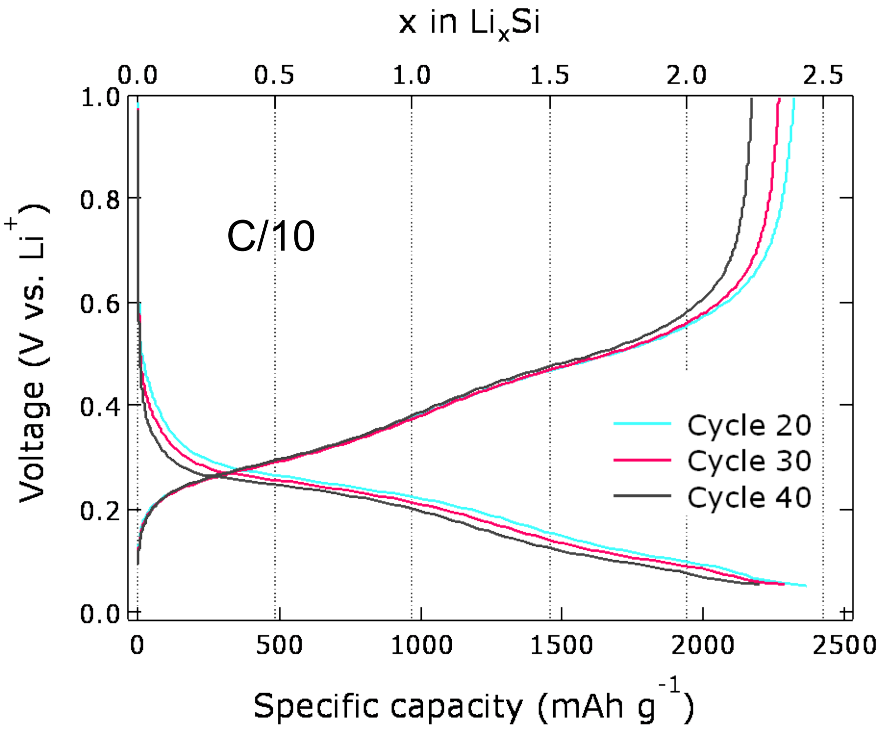
Cycling Data of Thick Core-Shell Electrodes

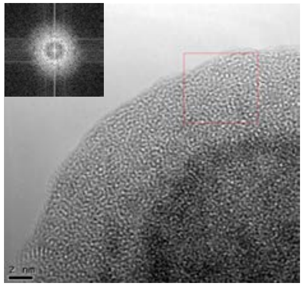


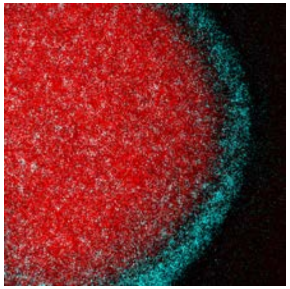
- **Coulombic Efficiency is > 99.99%.**
- **Capacity fade is likely due to particles falling off the electrode due to mechanical strain.**
- **An atomic layer deposition coating will likely alleviate this problem.**

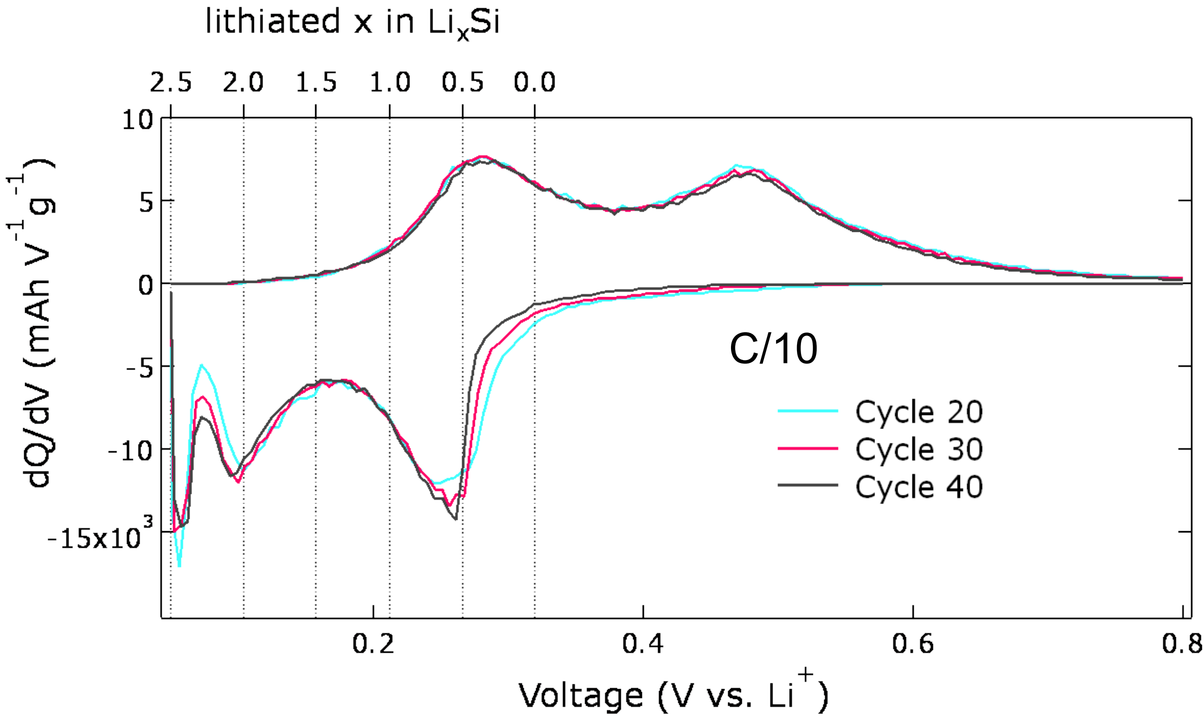
The cycling Data at C/5 represents early completion of the July 2012 Milestone (without an ALD coating).

Nano-C/Si Composite Anode



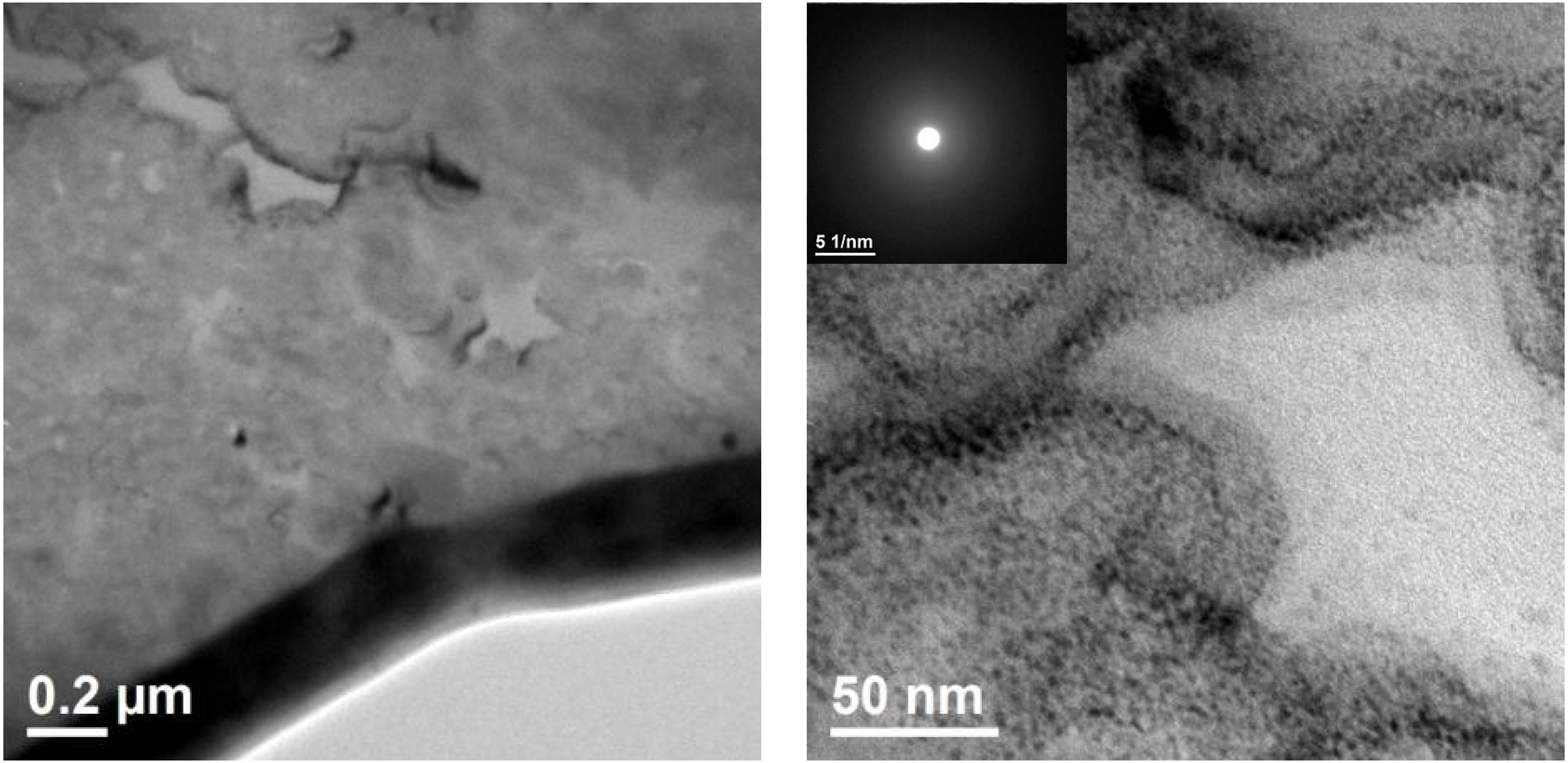






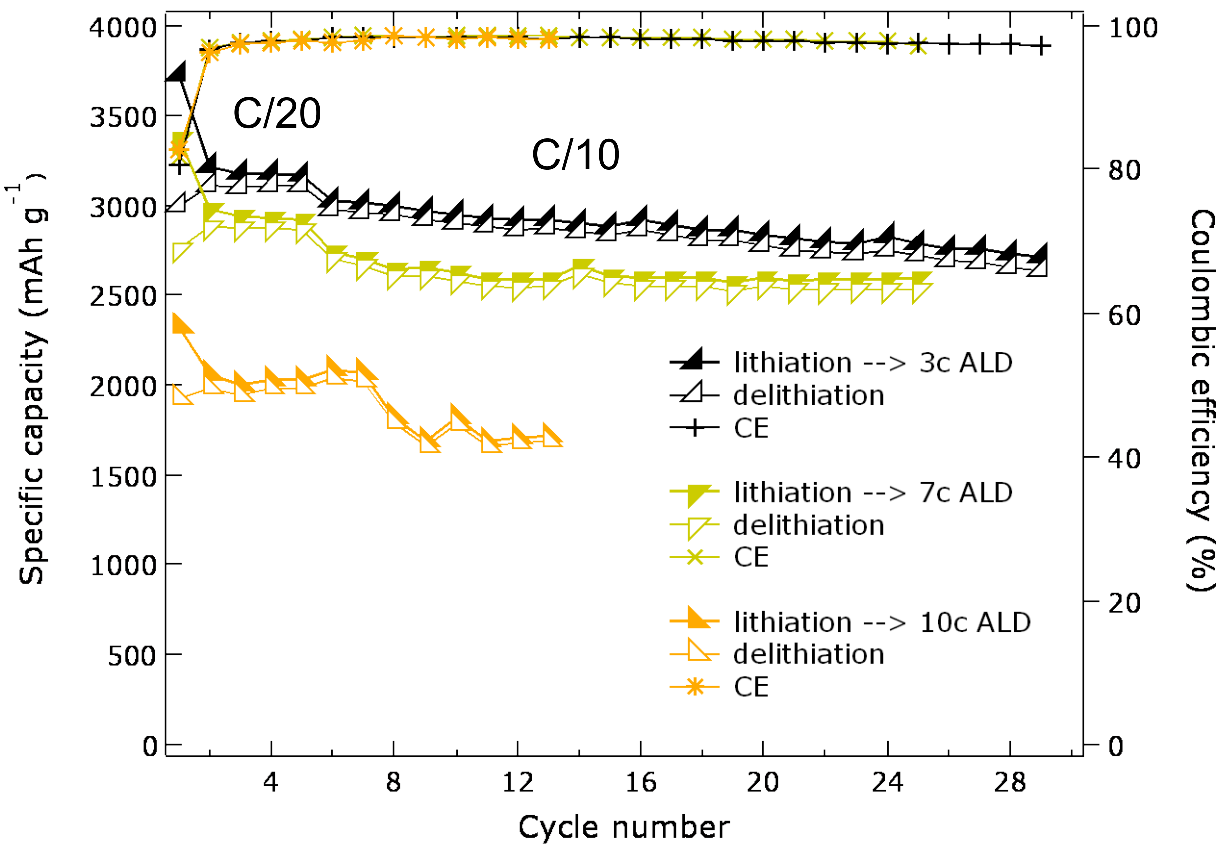
Electrochemical data suggests that the particles become amorphous after the first cycle, but that little structural degradation occurs in subsequent cycles.

TEM Images of C/Si Core Shell Anodes After 20 Cycles in a Coin Cell at C/5



The cycled TEM data shows that the electrode is largely intact, but that the Si does indeed become amorphous upon cycling.

Cycling Data of ALD Coated Core-Shell Electrodes



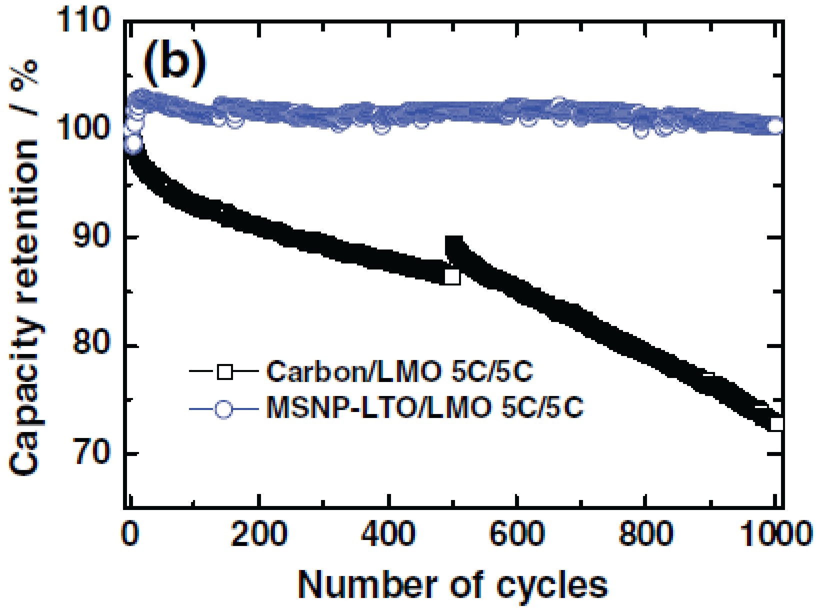
- ALD Al_2O_3 Coatings of different thicknesses were applied to the core shell anodes.
- Three cycles of ALD corresponding to a coating of ~ 0.6 nm was found to be optimal.
- The mechanical integrity appears to be dramatically improved, and the first cycle irreversible capacity may be also slightly better.

An ~0.6 nm thick Al_2O_3 coating improves the mechanical integrity of of thick C/Si core shell anodes with a mass loading of ~1 mg/ cm^2.

Full Cells vs. Half Cells Provide Interesting Insight into ALD Coating

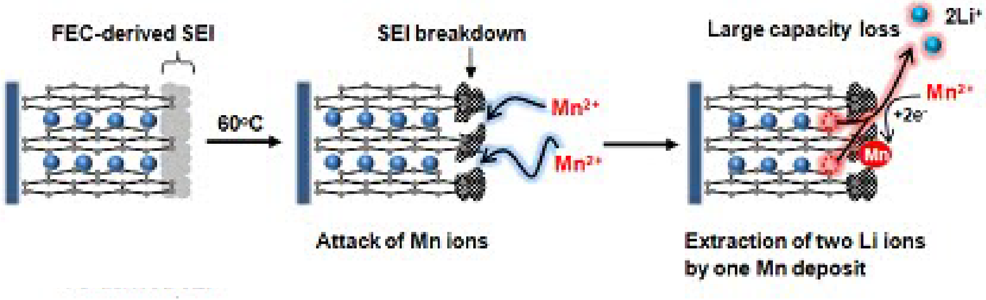
	Half cell	Full cell
Capacity Fading	Working electrode (assume degradation from Li metal, counter electrode negligible)	Both electrodes
Degradation mode	Electrode degradation	Electrode degradation Loss of Li from cathode
Interpretation	Less complex	**More complex**

Example) $LiMn_2O_4$/carbon *vs.* $LiMn_2O_4/Li_4Ti_5O_{12}$



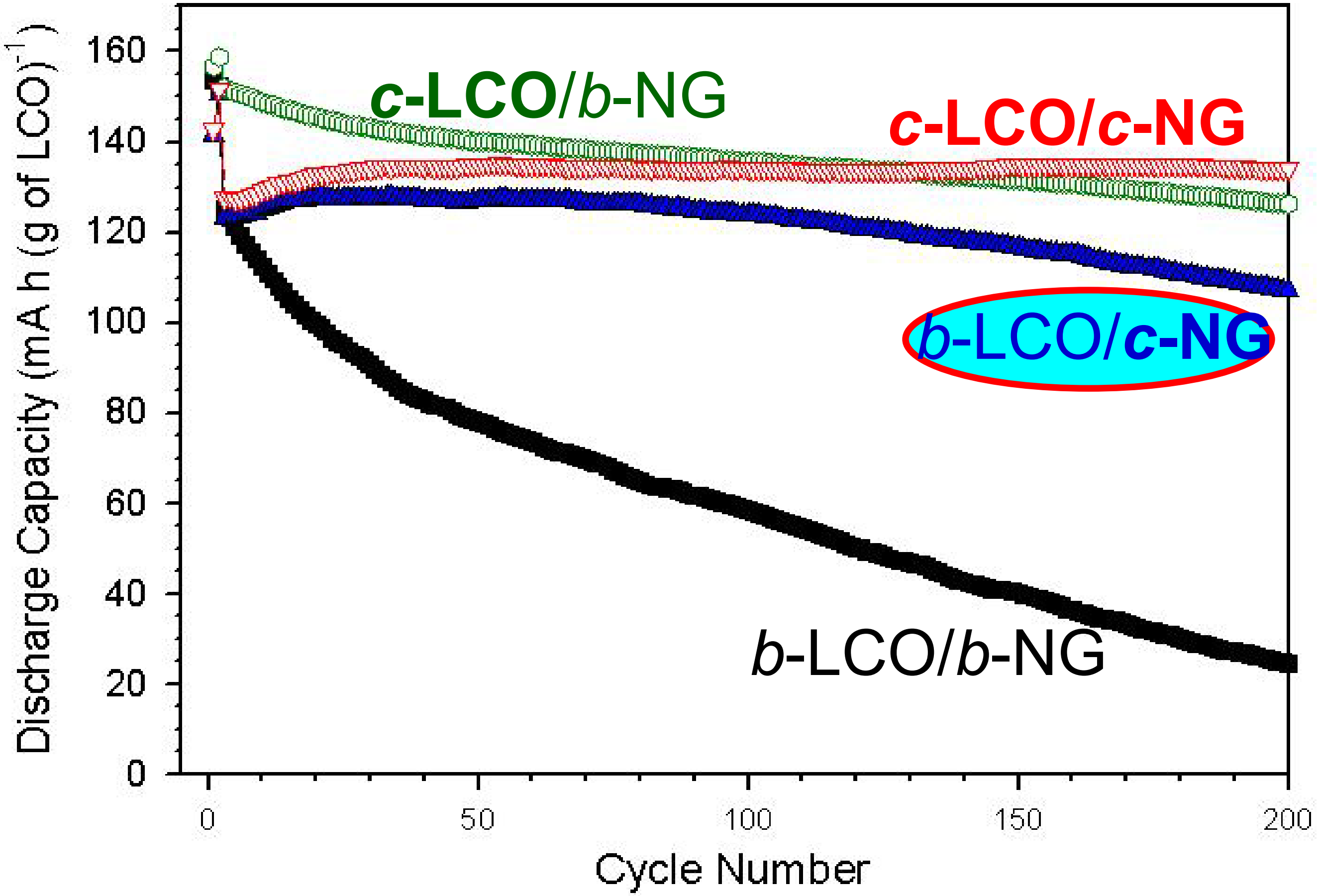
K. Amine, et. al., *Adv. Mater.* **2010**, *22*, 3052.

Deposition of dissolved Mn^{2+} from LMO on carbon surface at <1 V (*vs.* Li/Li^+) deteriorates the SEI film.



I. H. Cho, et. al., *Electrochem. Solid-State Lett.* **2010**, *13*, A168.

Cycling Performance of LCO/NG Full Cells



c-LCO: 2 Al_2O_3 ALD
c-NG: 5 Al_2O_3 ALD

Severe condition for LCO!

3.25-**4.45** V

0.2C – 1.0C
(1C = 140 mA (g of LCO)$^{-1}$)
Charge/discharge in 1hour

***c*-LCO**/*b*- or ***c*-NG** - >> *b*-LCO/*b*-NG

- *c*-LCO/*c*-NG ehhibits **no capacity fading**!
- Most fade is likely due to LCO
- Why doe b-LCO/c-NG improve so much?

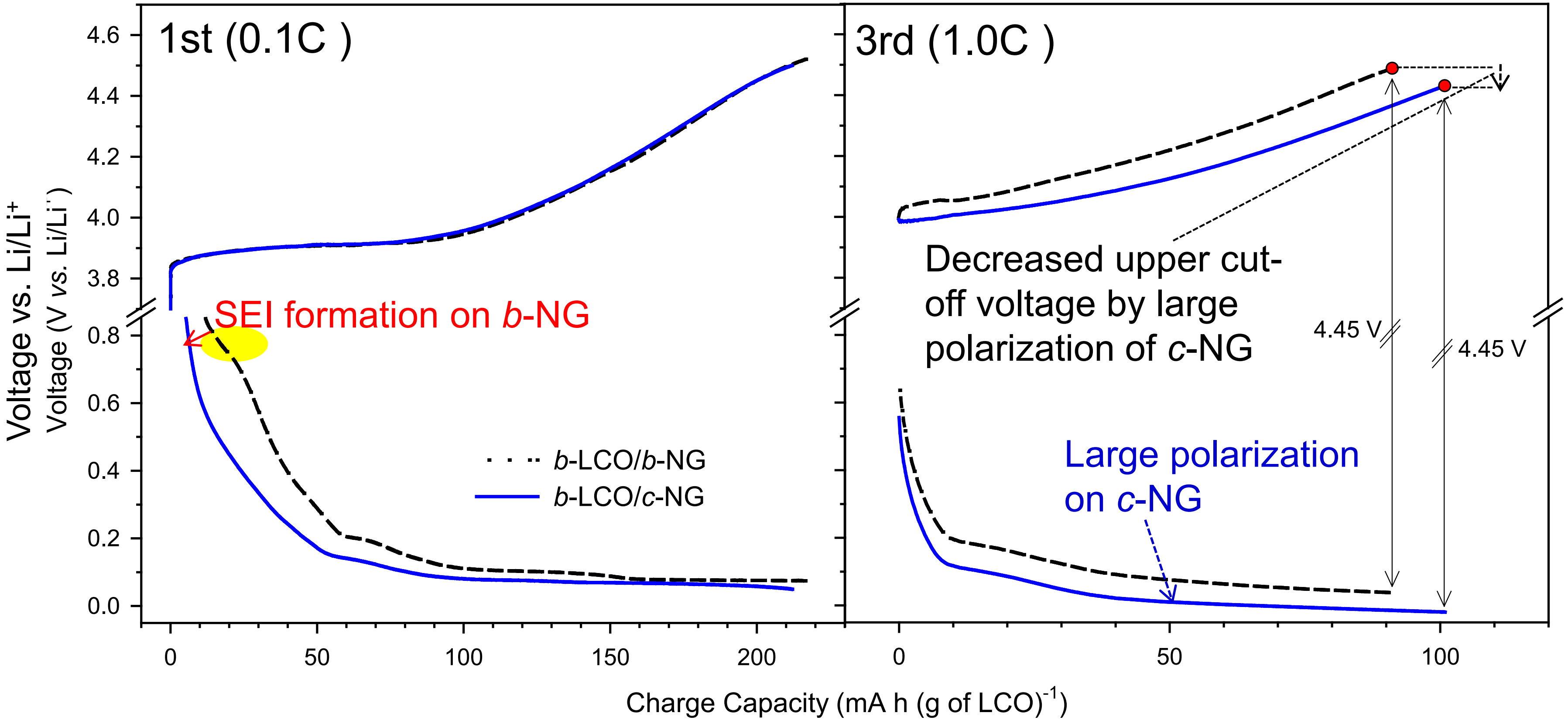
b-LCO/***c*-NG** >> *b*-LCO/*b*-NG

#1. Different cutoff voltage of b-LCO *vs.* Li/Li⁺

#2. Degradation occurs at *b*-NG significantly

#3. Unexpected role of *c*-NG

Possibility #1: LCO/Li/NG 3-Electrode Cell

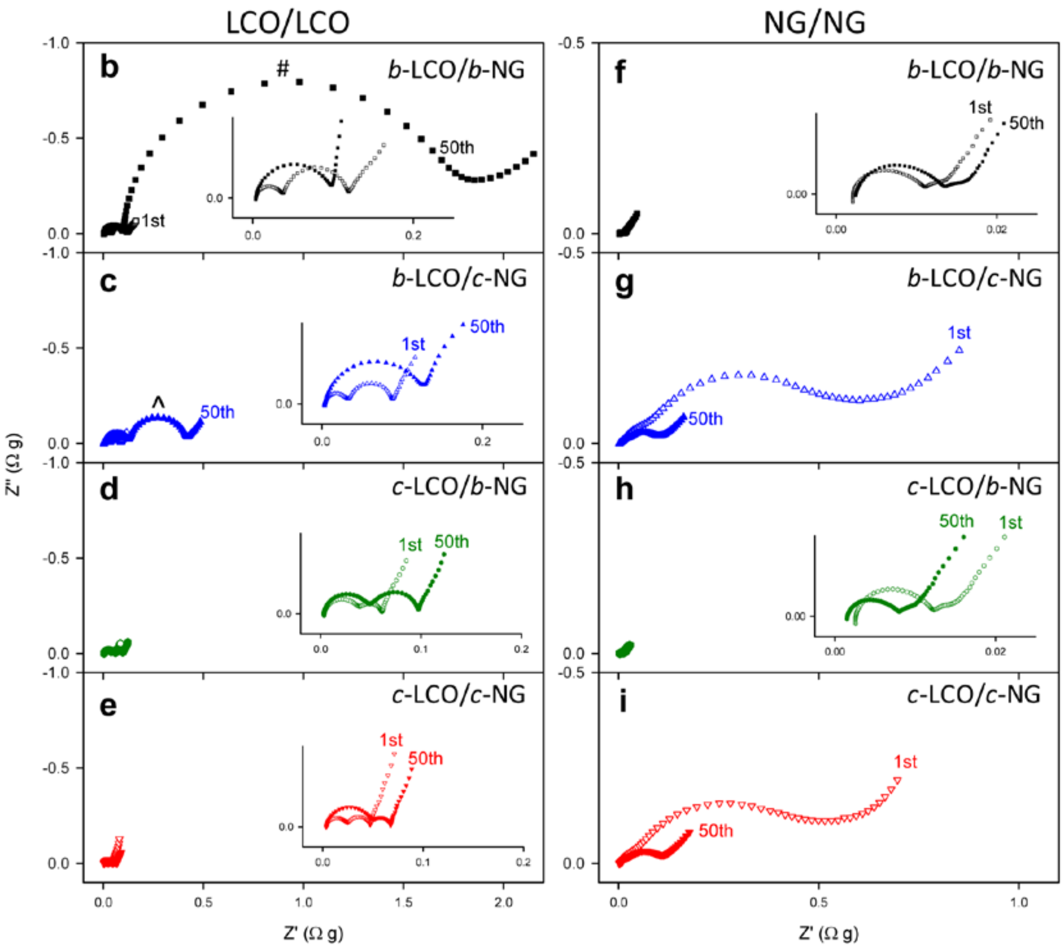


	Upper cut-off voltage of LCO [V *vs.* Li/Li$^+$]		
	1st (0.1 C)	2nd (0.1 C)	3rd (1.0 C)
b-LCO/*b*-NG	4.52	4.53	4.49
b-LCO/***c*-NG**	**4.50**	**4.52**	**4.43**

Voltage Polarization *vs.* Li/Li$^+$ difference is only ~60 mV

Possibility #2: EIS Using Symmetric Cells

Disassembled LCO/NG full cell after 50 cycles and reassembled symmetric cells: to separate degradation mechanisms.

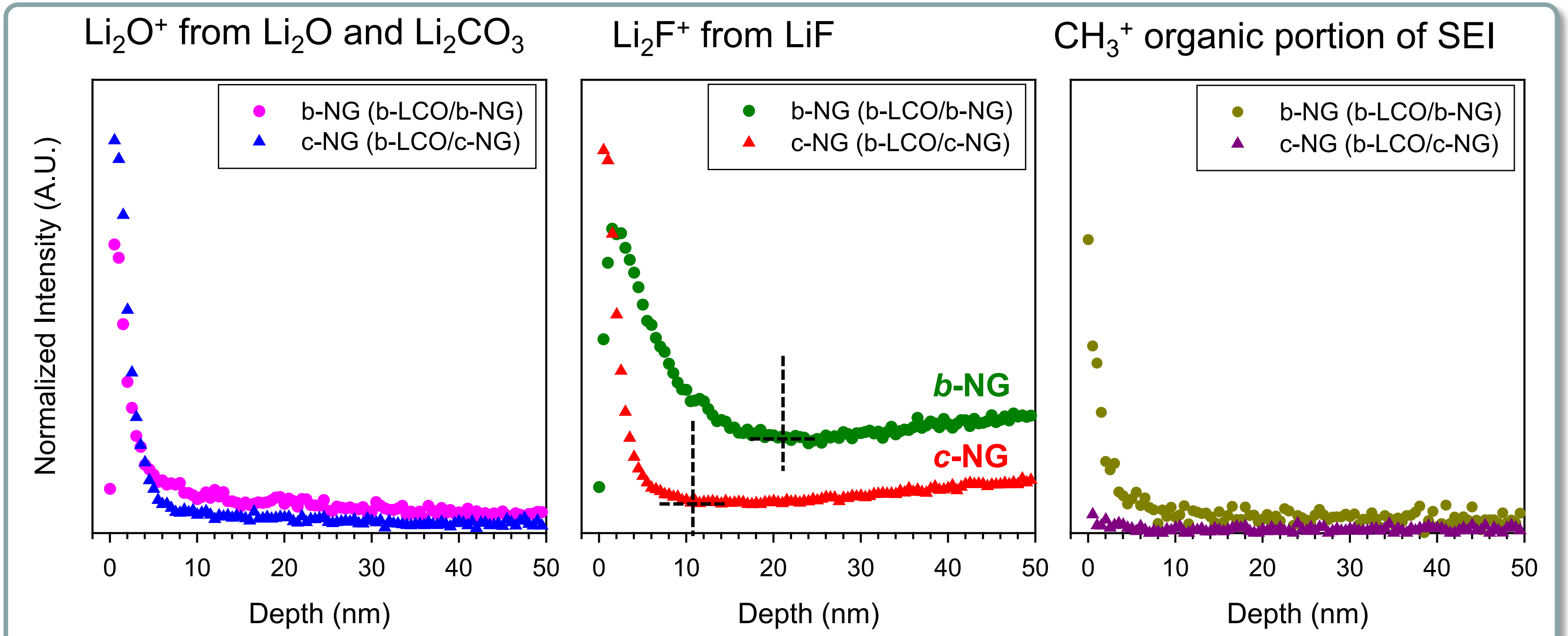


- ✓ Increase of charge transfer resistance is noticeable for LCO, not NG → Degradation occurs at LCO, not NG
- ✓ LCO electrodes: *b*/*c*-NG shows negligible increase in resistance after cycling
- ✓ Bare LCO with coated NG has much lower resistance compared to b-LCO and *b*-NG after cycling

Coating even on NG can mitigate the increase of resistance in LCO!

Possibility #3: TOF-SIMS for NG

After 15 cycles between 3.25-4.45 V at 0.1C.



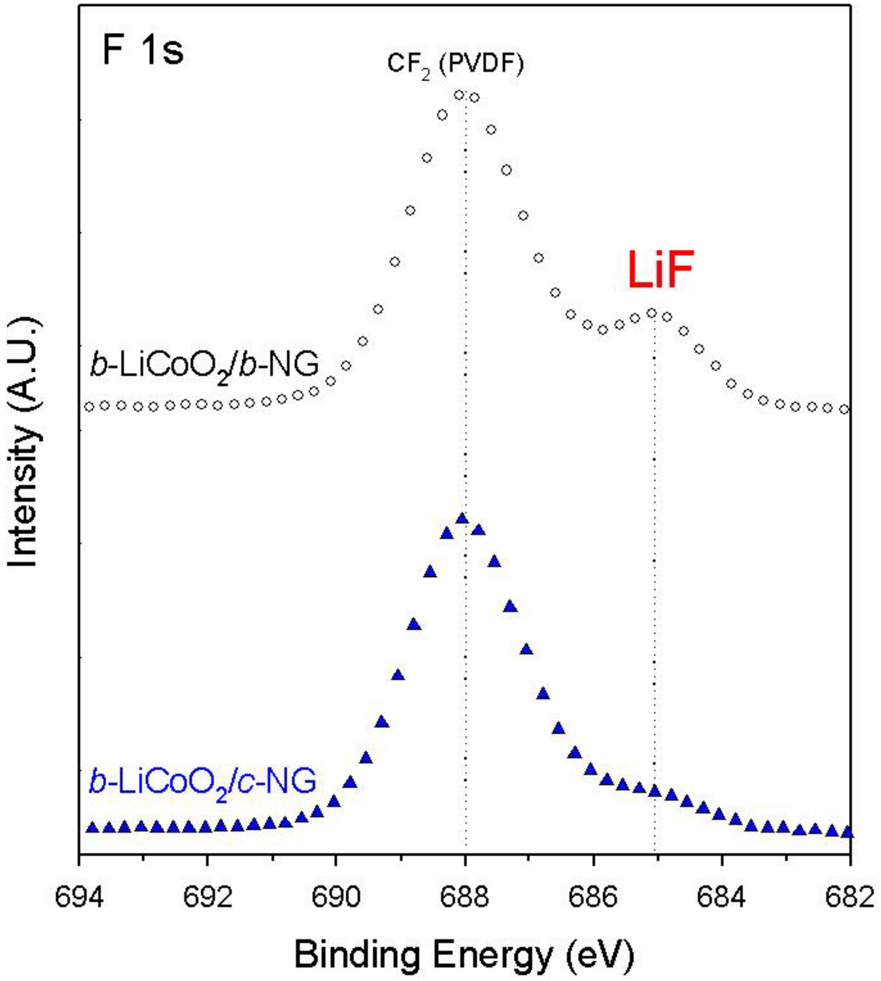
Courtesy of P. Lu and S. J. Harris

Side reaction is much more severe on *b*-NG than on *c*-NG

- Much thicker LiF layer on *b*-NG (~20 nm) than on *c*-NG (<10 nm).
- Much higher signals from organic components of SEI (CH_3^+) on *b*-NG than on *c*-NG

Possibility #3: *Ex-situ* X-ray Photoelectron Spectroscopy (XPS) for LCO

SIMS data showed that the SEI layer on Coated NG is changed



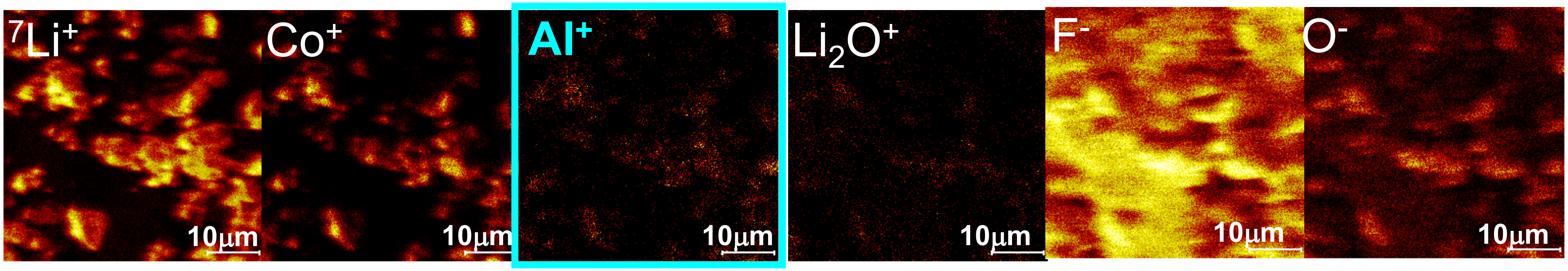
After 15 cycles between 3.25-4.45 V at 0.1C

- **Signals of C 1s, Co 2p, F 1s, Li 1s, O 1s for cycled LCO were comparable.**
- **The F 1s signal is the major striking difference.**
- **Coating the NG alters the surface species on the LCO.**

Formation of LiF on LCO may be main cause of degradation for LCO.

Proposed Mechanism II – Al-species Found on *b*-LCO

Ions maps of *b*-LCO electrode from *b*-LCO/*c*-NG via TOF-SIMS



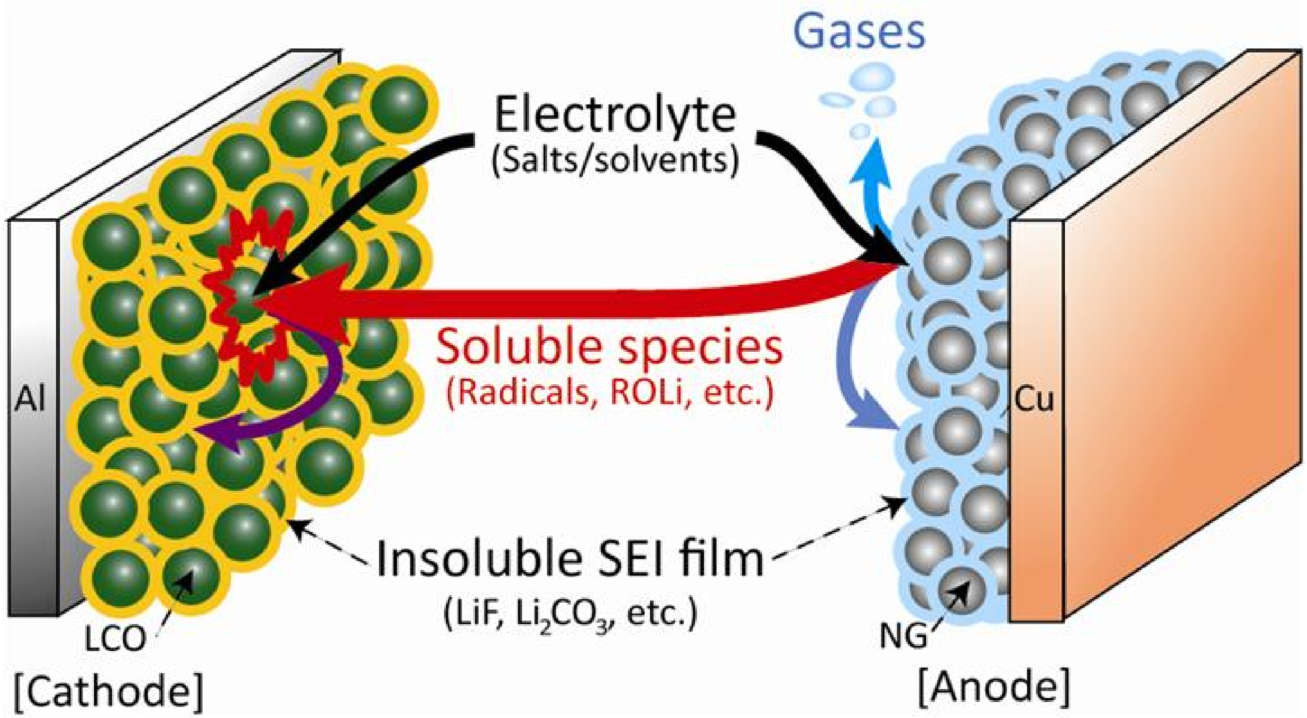
Courtesy of P. Lu and S. J. Harris

Presence of Al on even b-LCO surface

- Direct evidence on anode-cathode interaction
- The ALD Al_2O_3 layer on NG may be reduced, dissolved by HF, migrate, and oxidized/deposited on LCO.
- The deposited of Al-species may contribute to mitigating undesirable side reactions. This shows that coating only the anode in a full cell is still very beneficial.

Surface reactions on anode and cathode likely interact!

Proposed Mechanism – Coupled Side Reactions

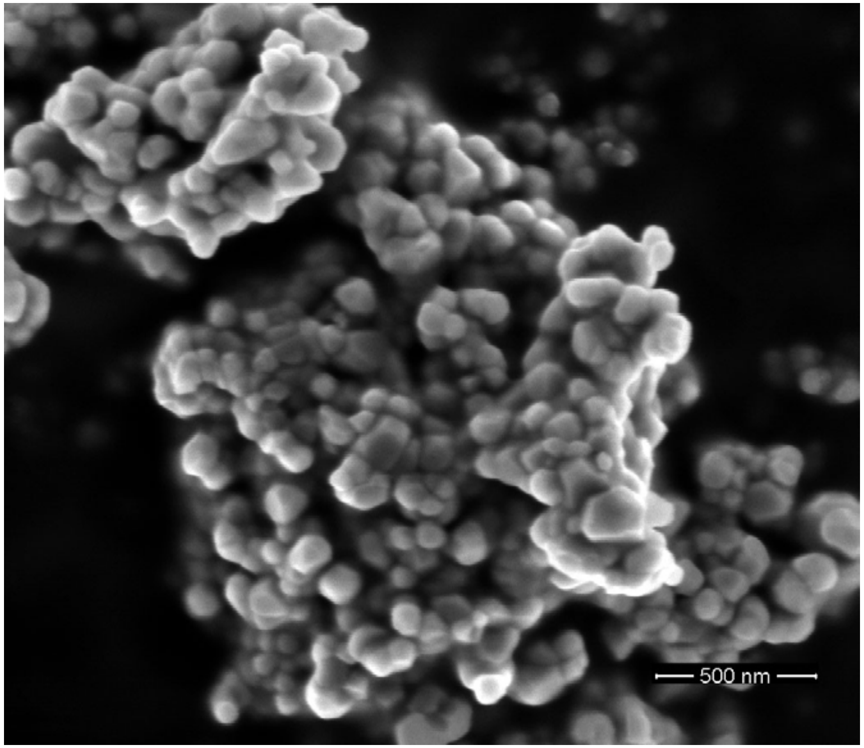


Undesirable side reactions on LCO may be coupled with side NG reactions

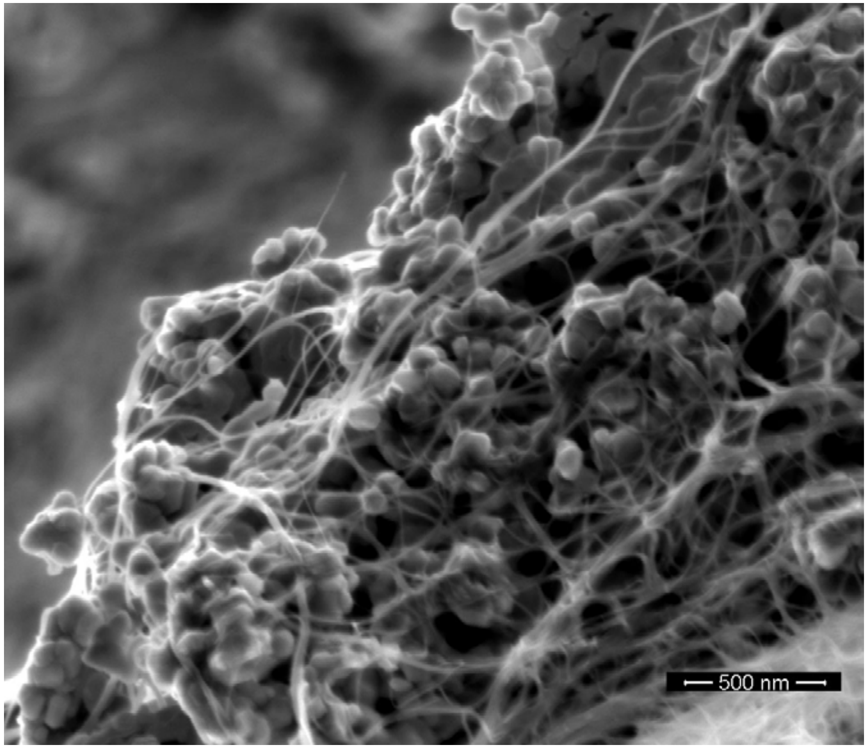
→ Soluble byproducts from side reaction on NG may reach LCO, and actually help prevent undesirable oxidative decomposition reaction on LCO.

Y.S.Jung et. al. *Advanced Energy Materials* (Submitted).

$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ with 5 wt.% SWNTs



SEM images of $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ particles. Nanoparticles agglomerate into µ-sized clusters



$LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ dispersed with 5 wt.% Carbon single-wall nanotubes (SWNTs). Note that SWNTs are highly interlaced

Through a collaborative effort a "binder-free" electrode containing 95 wt.% active material and 5 wt.% SWNTs was demonstrated.

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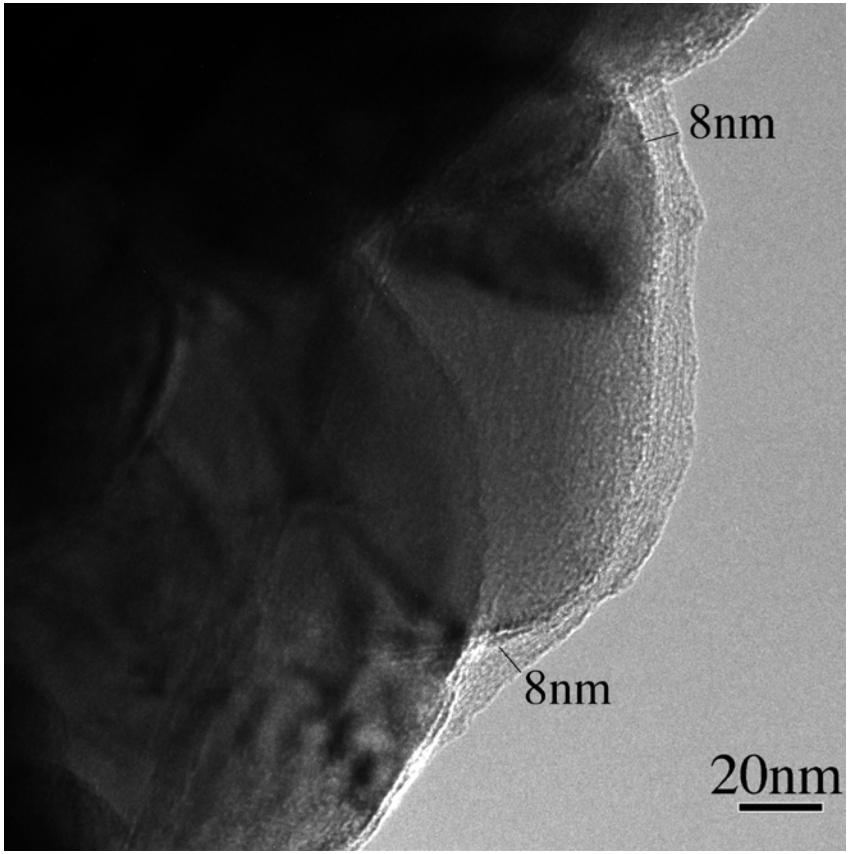
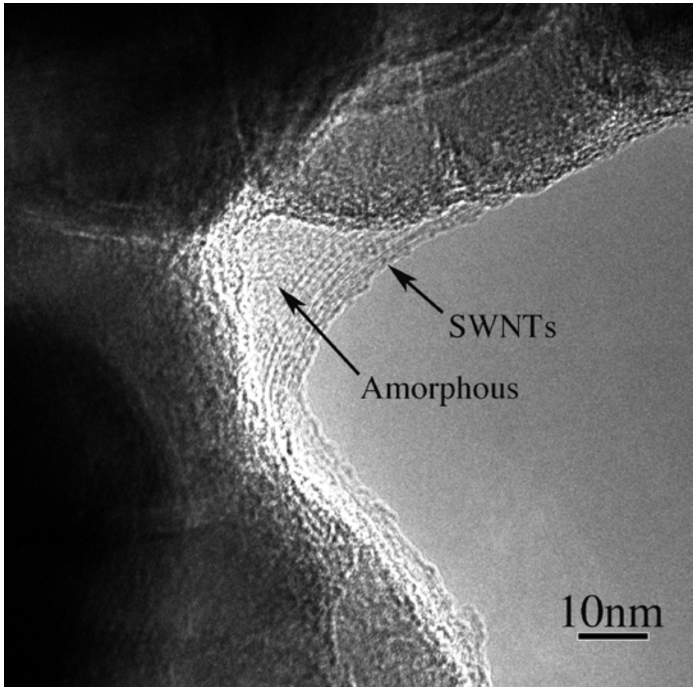
LiNi $_{0.4}$Mn$_{0.4}$Co$_{0.2}$O$_2$ with 5 wt.% SWNTs



HRTEM image showing that the SWNTs seamlessly adhere to particle surfaces. A bundle containing ~ 8 SWNTs is observed.



HRTEM showing that the SWNTs also encapsulate an amorphous pocket of Li_2CO_3 that is formed during electrode fabrication.

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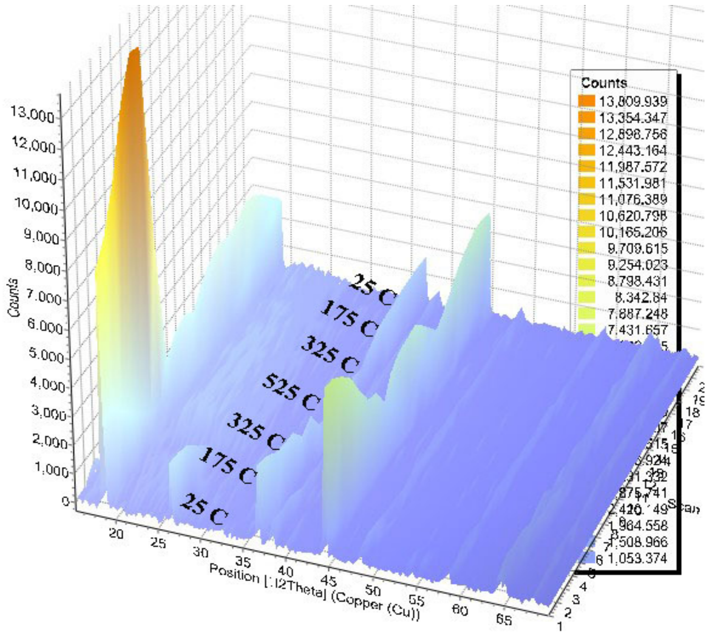
SWNTs trace the particles and improve electronic conductivity.

In-situ High-temperature XRD Indicates SWNTs also Stabilize Surface



Preparation cond.	*a* (Å)	*c* (Å)	*c/a* (Å)
As-prepared	2.8693(1)	14.259(2)	4.969
Annealed in air	2.8696(1)	14.259(1)	4.969
As-prepared	2.8702(2)	14.254(2)	4.966
Annealed in air	2.8715(2)	14.271(3)	4.970

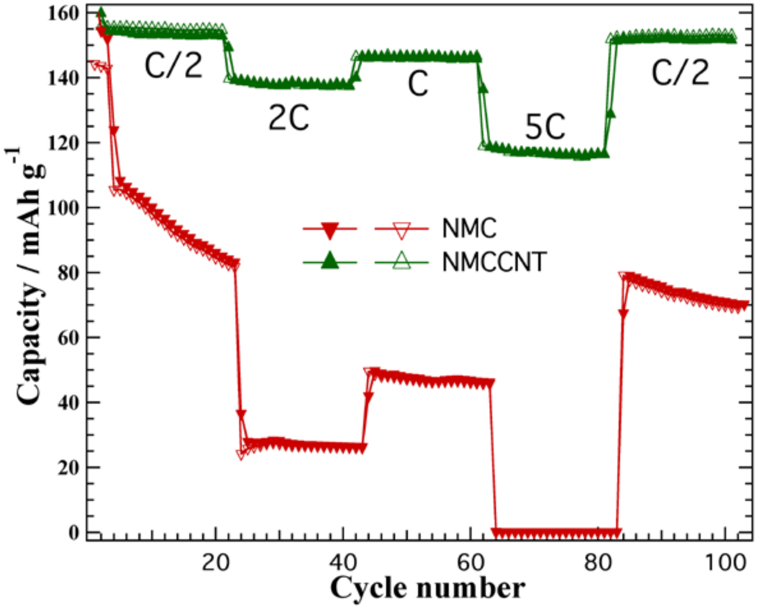
There is a change in lattice parameters following heating and cooling between 25-525˚C suggesting an elongation in the M-O bonds.

html
HIGH TEMPERATURE MATERIALS LABORATORY

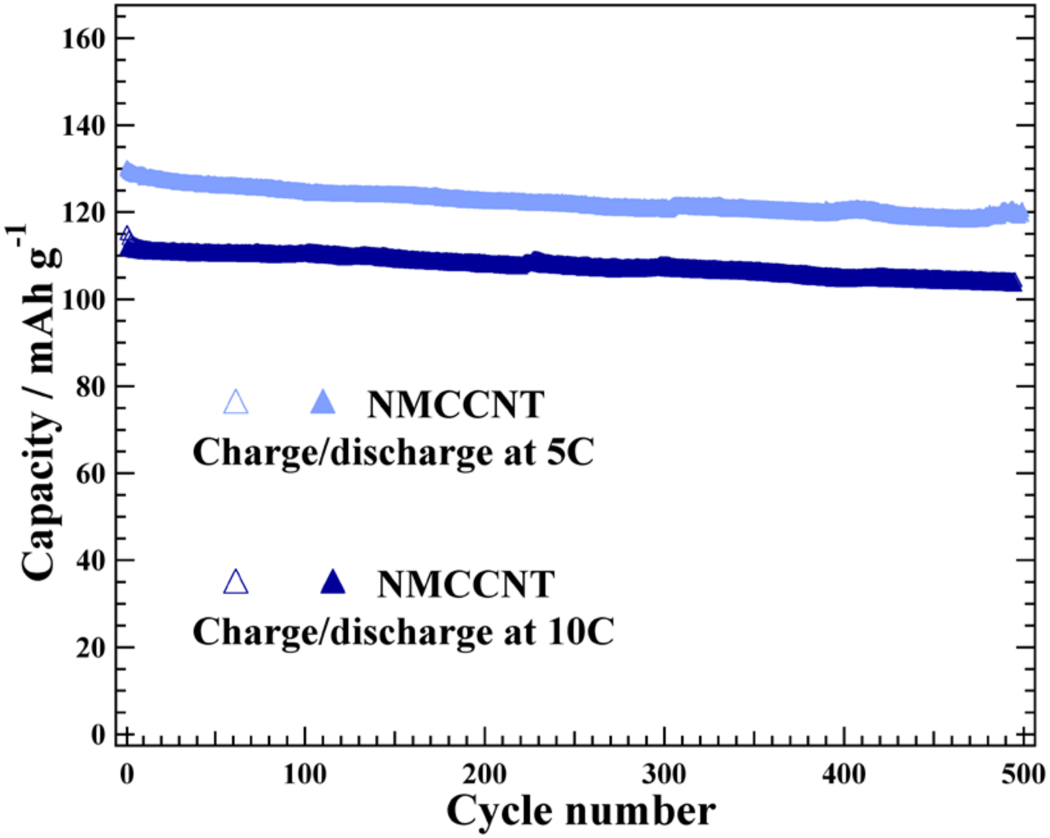
The elongated M-O bonds, is likely due to interaction with SWNT carbon atoms and assists in surface stabilization.

C. Ban, Z. Li, Z. Wu, M. J. Kirkham, L. Chen, Y. S. Jung, E. A. Payzant, Y. Yan, M. S. Whittingham, A. C. Dillon Advanced Materials 1 (2011) 58.

Durable High-Rate Capability



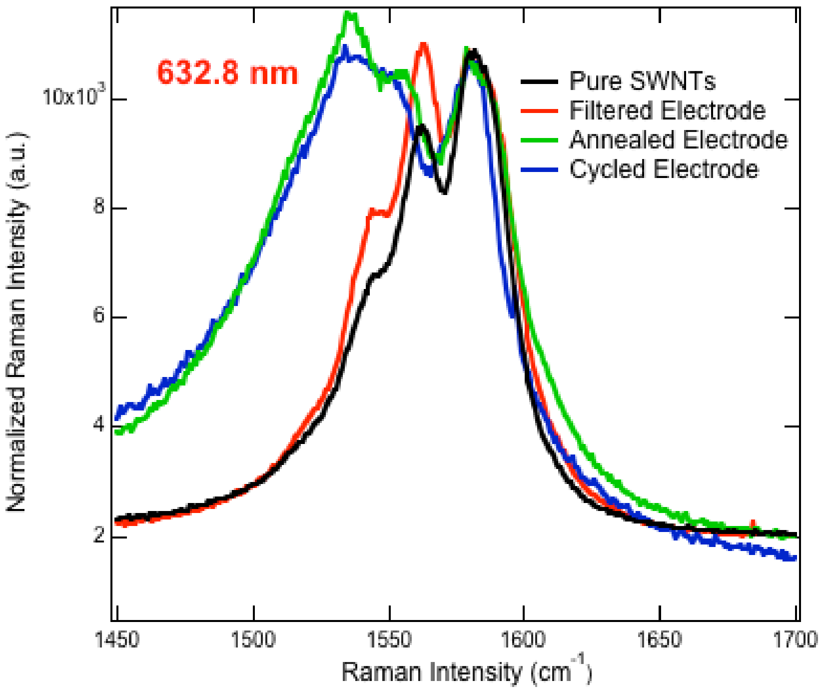
The cathode composed of layered $LiNi_{0.4}Mn_{0.4}Co_{0.2}O_2$ and SWNTs (LMOSWNT) is shown to have markedly improved rate capability than a conventional electrode (LMO)

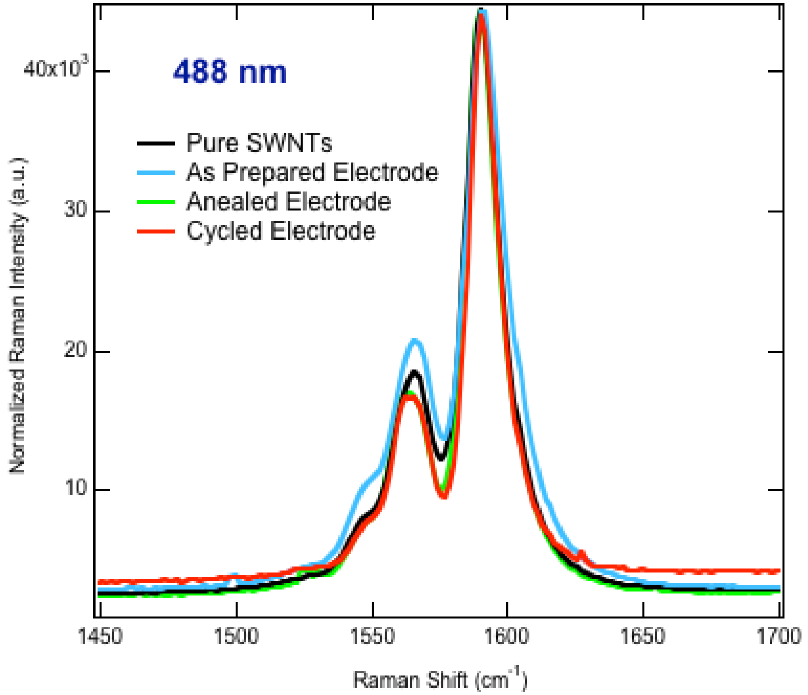


120 mAh/g at 10C (charge / discharge in 6 minutes) and 130 mAh/g for 500 cycles at 5C (charge/discharge in 12 minutes)

C. Ban, et al. *Advanced Energy Materials* 1 (2011) 58.

Raman Spectroscopy Suggests at Least Some of the SWNTs may be Bound to the Surface

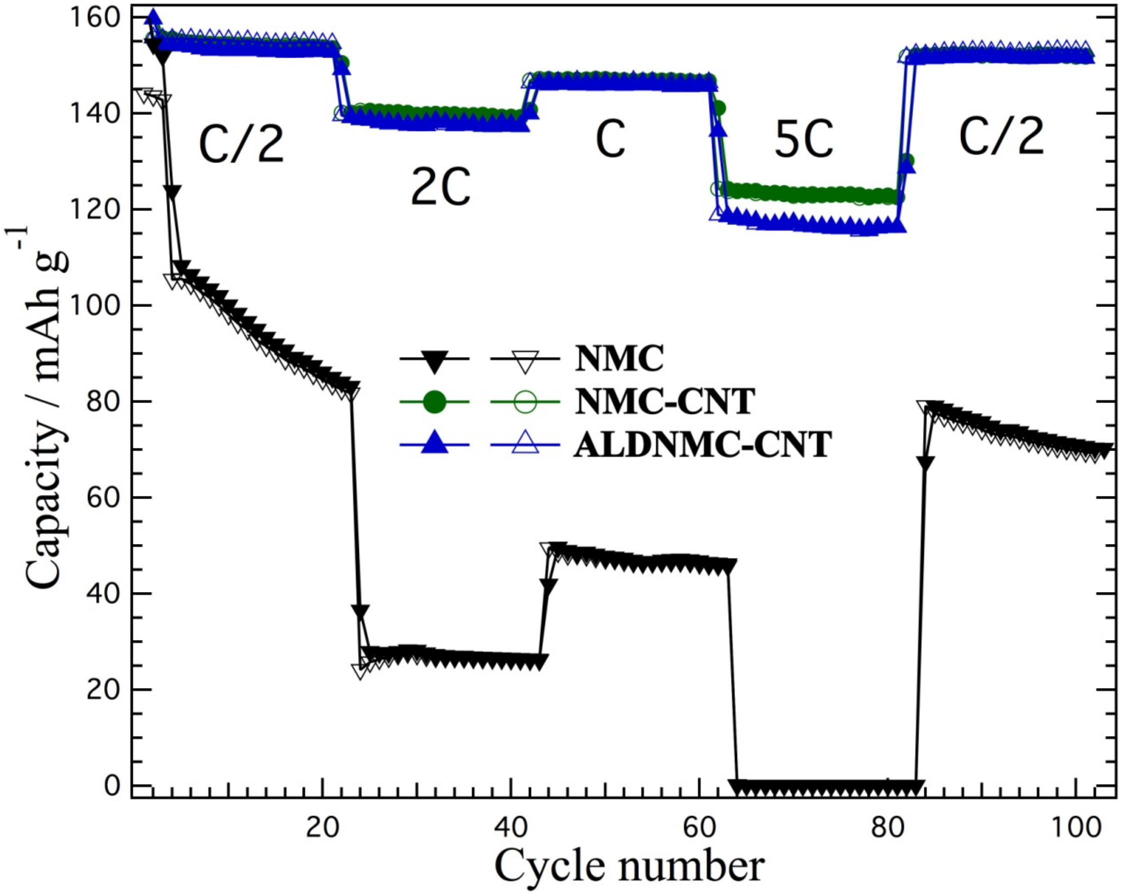




- No quenching is expected as reversible Li$^+$ insertion does not occur at higher voltage.
- Note also the SWNTs appear undamaged after cycling.

Large shift in the SWNT Raman lines is only observed after annealing at 632 nm, indicating that significant charge transfer / chemical bond only forms with certain nanotubes.

Rate Capability for both NMC-CNT and ALDNMC-CNT Cathodes



ALD Al_2O_3 Coating ~ 0.5 nm

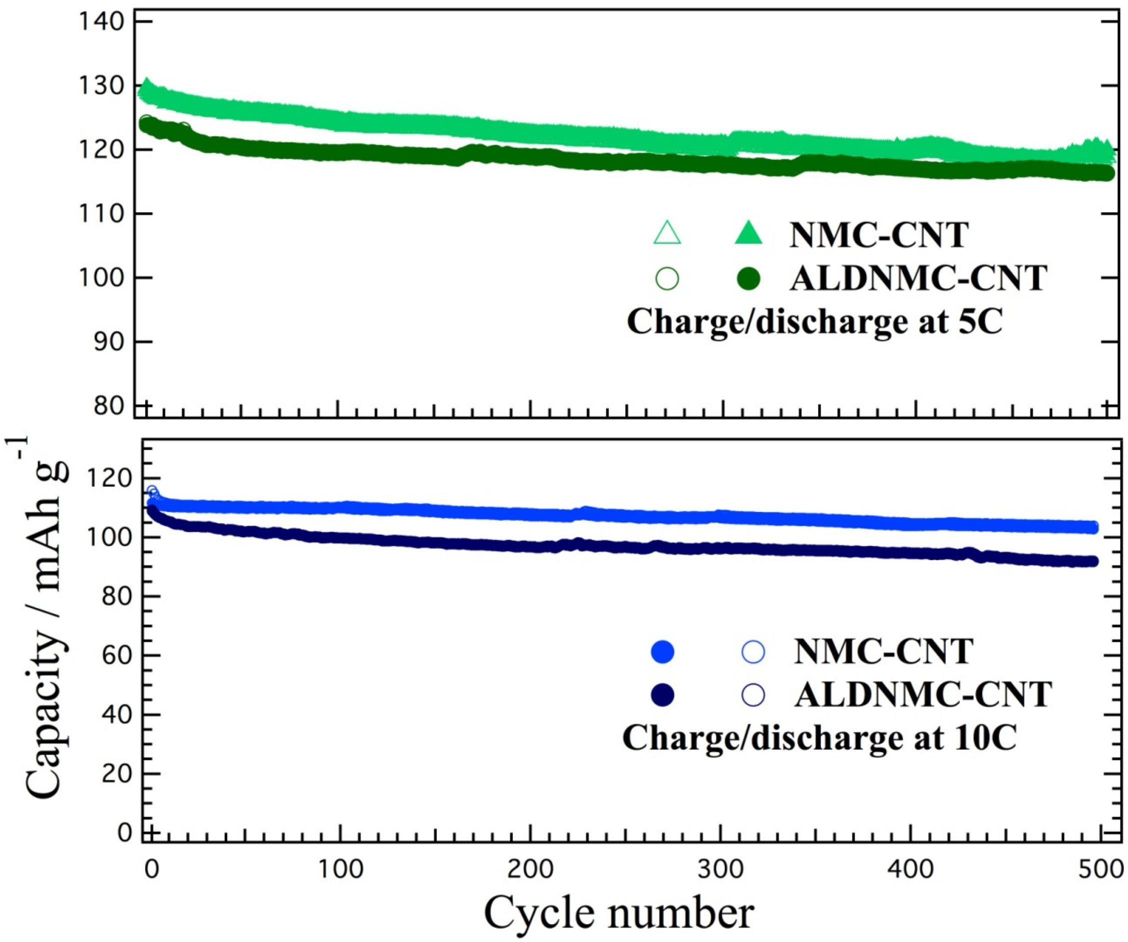
High conductivity is enabled by using SWCNT as 5 wt.% additive.

Higher Coulombic efficiency indicates the stable surface of the NMCSWNT cathode.

Al_2O_3 thin coatings do not effect mid-rate performance.

All cells were cycled between 3 and 4.2V

Durable High-Rate Capability



Cycled between 3 and 4.2V

High performance achieved for both cathodes:

- ✓ Stable high-rate cycling attributed to fast charge transfer with SWNTs
- ✓ The ALD-NMCSWNT cathodes have a capacity of ~ 130 mAh/g at 5C and nearly 120 mAh/g at 10C, both for over 500 cycles. (2mg-3mg/cm^2)

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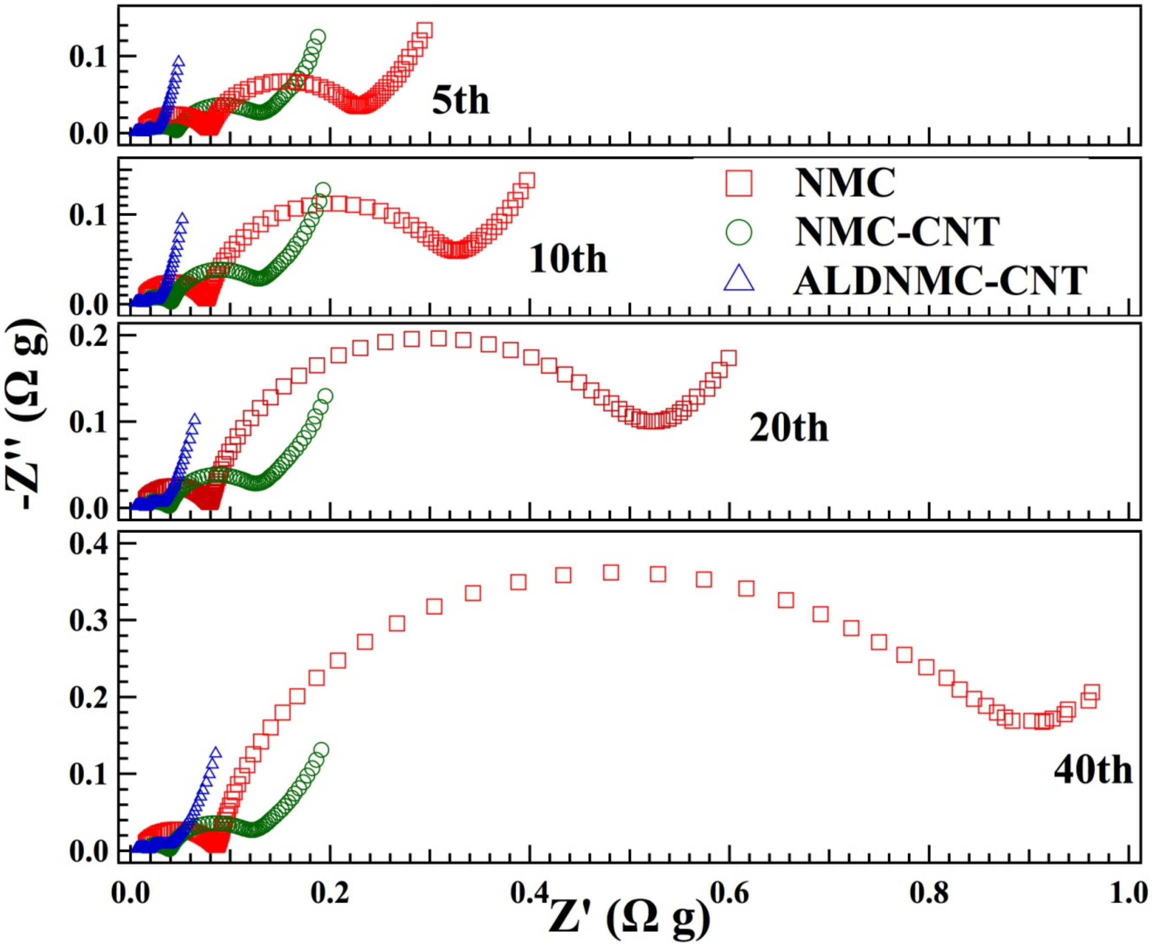
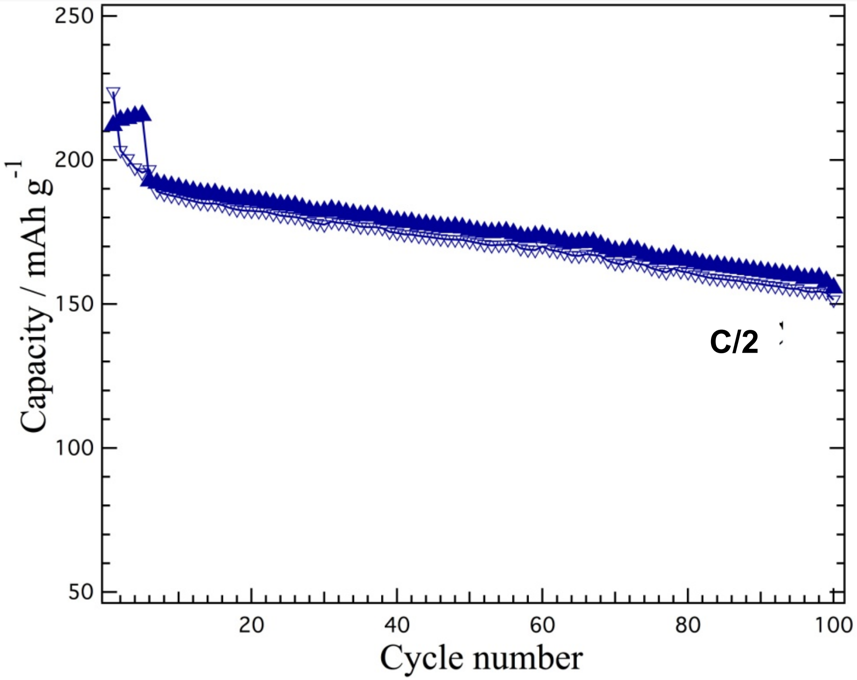
Comparison of EIS for Different Electrodes

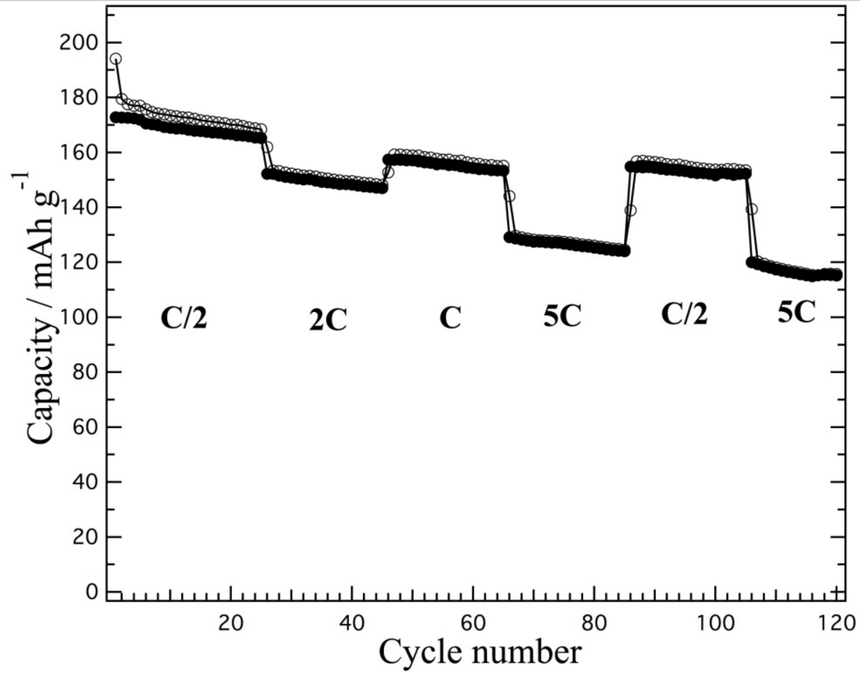


EIS taken after charging to 4.2 V

- ✓ Continuous growth of SEI contributes to increasing medium-frequency semicircle detected on NMC electrode.
- ✓ Small medium-frequency semicircles in NMC-CNT and ALDNMC-CNT electrodes indicates reduced charge-transfer resistance.
- ✓ Surface reactions or structural changes during lithiation are limited by Al_2O_3 conformal coating.

Electrochemical Behavior of *High-voltage* Cycling between 2.5 V and 4.5 V





NMC-CNT electrode:

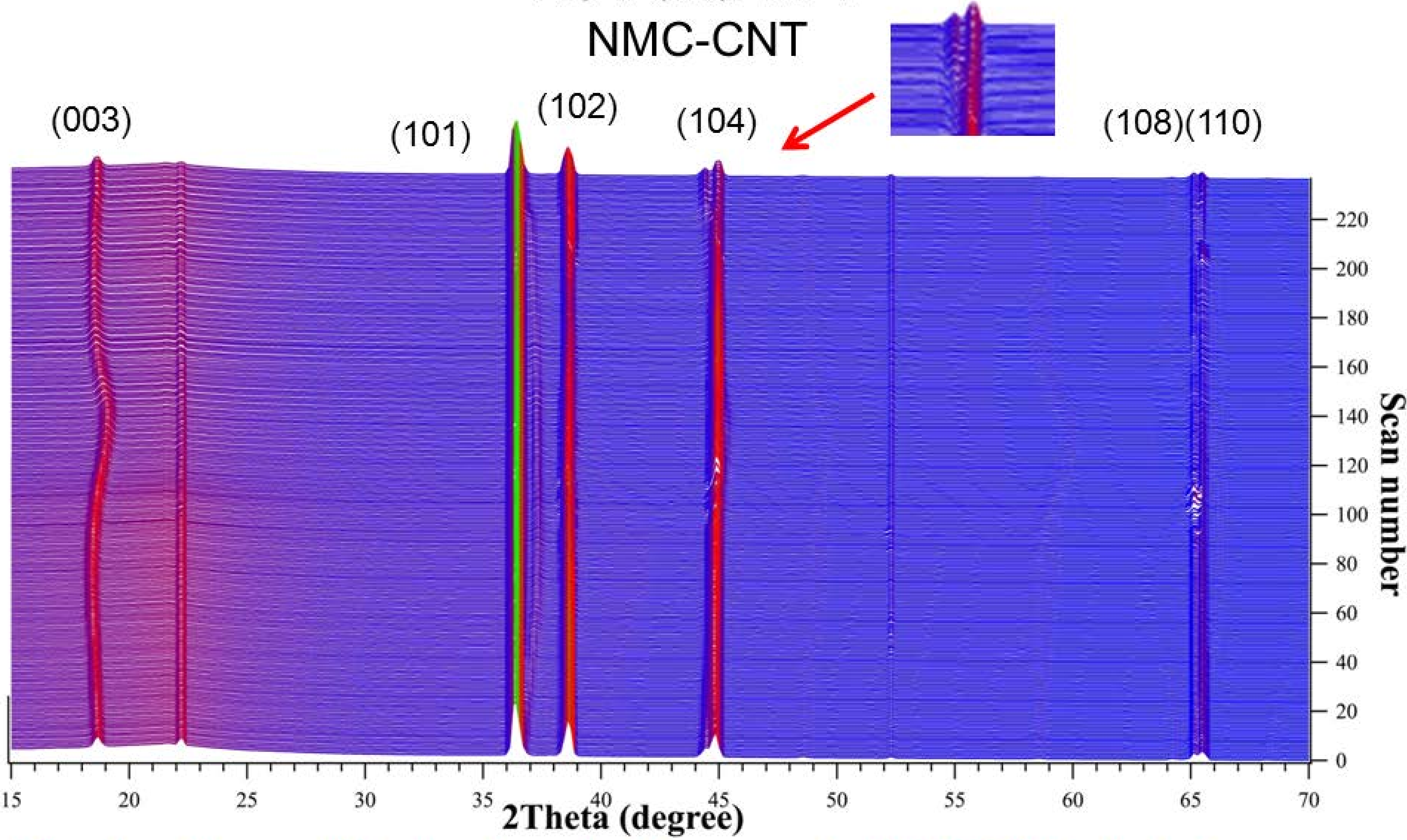
- higher capacity in the first cycle.
- Fast degradation.
- Lower Coulombic efficiency.
- No stable cycling at med./high rates.

ALD-NMC-CNT electrode:

- Lower capacity in the first cycle
- Slowly degrading at medium rates.
- Capacities of 180 mAh/g, 130 mAh/g obtained at C/2 and 5C, respectively when cycled to 4.5 V.

In-situ **Synchrotron X-ray Diffraction** During cycling between **2.5 V and 4.7 V**

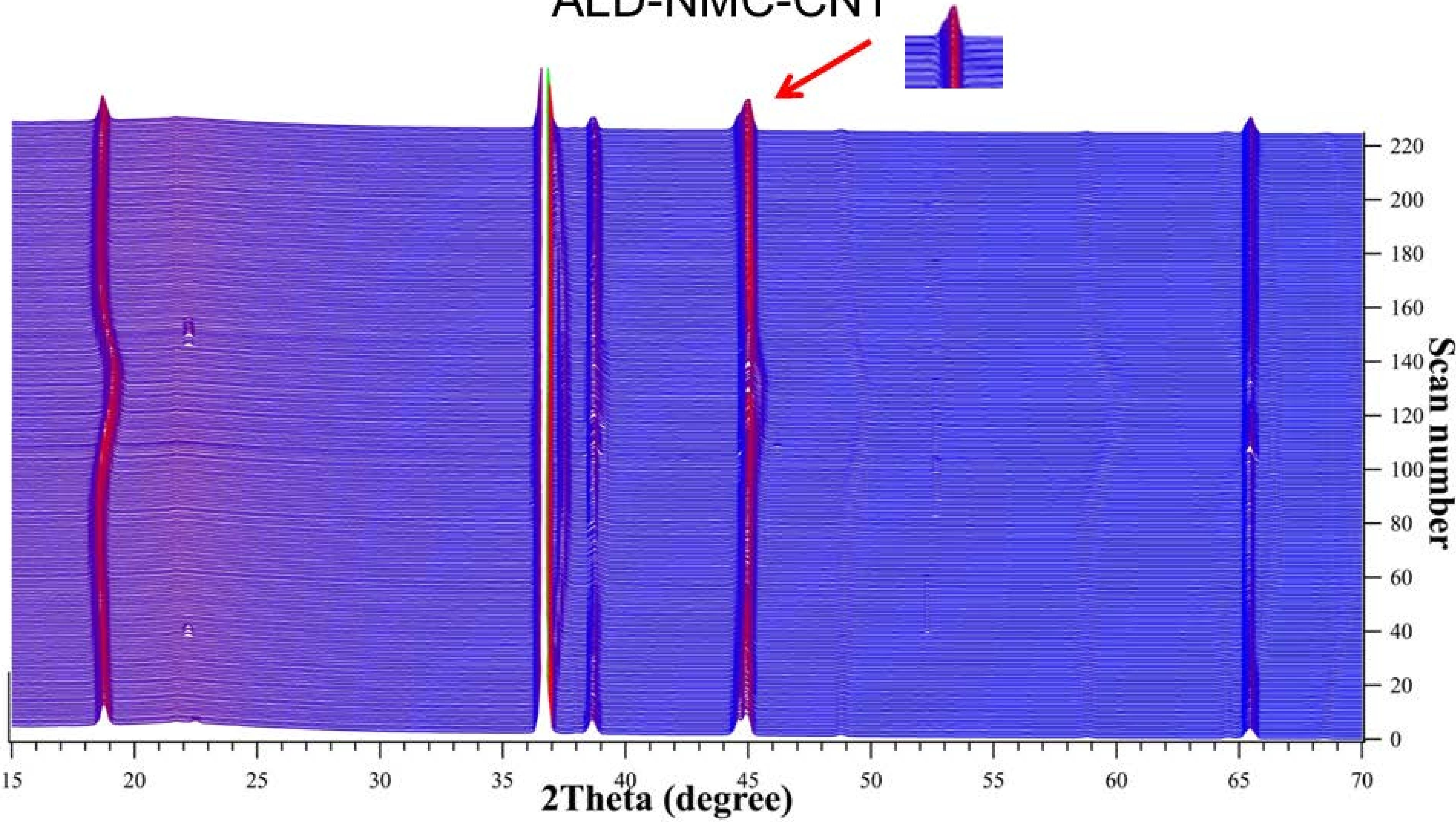
NMC-CNT



Structural degradation is shown for the uncoated NMC-CNT electrode after only one discharge and charge at 1C.

In-situ Synchrotron X-ray Diffraction During cycling between 2.5 V and 4.7 V

ALD-NMC-CNT



The ALD coating preserves the variation in lattice parameters after one cycle. This represents completion of January 2012 milestone.

Collaborations

SUNY, Binghamton: M. Stanley Whittingham provided us with an NMC cathode material. We demonstrated improved rate performance with this material by using our binder-free electrode fabrication process. He provided us with more material and we coated it with ALD, and extended the voltage window.

General Motors (GM): Stephen J. Harris and Peng Lu performed TOF-SIMS measurements on our ALD coated full cells and helped us establish that it may only be necessary to coat one electrode. GM is patenting this with NREL co-authors.

LBNL: We coated several Si electrodes for Gao Lui and the preliminary data suggests that the thick electrodes wer stabilized some (more work is needed). Lui and Dillon are also co-organizing a batter symposium for the Sprin 2013 Materilas Research Society Meeting.

LBNL: We have performed several low-temperature spray depositions in support of Marc Deoff's spray pyrolisis project to make inexpensive high voltage cathodes.

University of Texas, Austin: We coated several cathode materials for Arumugam Manthiram.

ANL: We are preparing to coat some of Michael M. Thackeray's Li-excess cathode materials.

LBNL: We sent Vince Battaglia some of our Si/C core shell electrodes for vefication and completion of the 2012 May milestone

Stanford Synchrotron Radiation Light Source (SSRL): We collaborated with Michal Toney at SSRL to get *in situ* synchrotron x-ray diffraction of ALD coated electrodes in order to satisfy our January 2012 milestone.

Proposed Future Work

- It is becoming apparent that the volume expansion issues for Si that lead to mechanical degradation are going to be more easily addressed than the first cycle irreversible capacity loss. We would therefore like to work with DOE and redirect some of our coatings and materials efforts in FY13 towards reducing the first cycle irreversible capacity loss.
- We are continuing to work with General Motors, and are patenting our core Si/C shell process, that GM will likely license.
- We have already met our July 2012 milestone and have made substantial progress towards making our year-end milestone. "Demonstrate at least 50 cycles at a minimum of C/3 rate."
- We realize ALD could be expensive to integrate into a battery line. A.C. Dillon is working with R.C. Tenent to develop an inexpensive atmospheric pressure technique that will be easy to incorporate into a battery line via a new NREL ABR award. (See oral presentation ES162, Tenent)

Summary

- Demonstration of thick electrodes (~10 μm) that contain Si/C core shell structures with a ratio of 70:30 Si:C and a mass loading of ~ 1 mg/cm^2 cycle stably at C/5 for over 300 cycles. Coulombic efficiency is >99.99.
- Capacity degradation is still observed in above likely due to mechanical degradation and particles falling off the electrode. However, an Al_2O_3 coating ~0.6 nm thick reduces mechanical degradation, and a stable capacity of ~ 3000 mAh/g is observed for 30 cycles, thus far, at C/5 (testing still underway).
- Mechanistic understanding of the Al_2O_3 coating has been obtained via TOF-SIMS analysis of ALD coated full cells as well as *in situ* synchrotron x-ray diffraction.

	Gravimetric Capacity (mAh/g)	Volumetric Capacity (mAh/cm^3)
Si /C Core shell	3000 (C/5)	~ 1660
Commercial	370 (graphite)	770 (graphite)