

Atomic Layer Deposition for Stabilization of Silicon Anodes



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Project I.D. # ES145

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Overview

Timeline

- October 1, 2010
- September 30, 2014
- ~50%

Budget

- Total project funding
---100% by DOE
- Funding received:
FY12 \$ 440 K
FY13 \$ 440 K

Barriers: Strategy

Cost: Silicon is an inexpensive abundant element. Low cost processing and 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/3 has thus far been achieved.

Collaborators

- M. Stanley Whittingham, SUNY, Binghamton
- Michal Toney, SSRL
- Kang Xu, ARL
- Vince Battaglia, LBNL
- Anthony Burrell, ANL
- Nathan Neale, Qi Wang, NREL
- Nanosys Inc.

Main Objectives/Relevance

- Demonstrate durable high-rate cycling using our novel coating & electrode design;
- Utilize atomic layer deposition (ALD) processes to further improve performance of electrodes;
- Explore different hybrid ALD/MLD coatings to enhance battery performance for Si anodes;
- Investigate effects of nanoscale surface modification on irreversible capacity loss & structural evolution during cycling.

Addresses targets:

High Gravimetric and Volumetric Capacity: Both have been achieved for thick electrodes that exhibit durable cycling.

Rate Capability: Stable cycling at C/3 has thus far been achieved.

Milestones

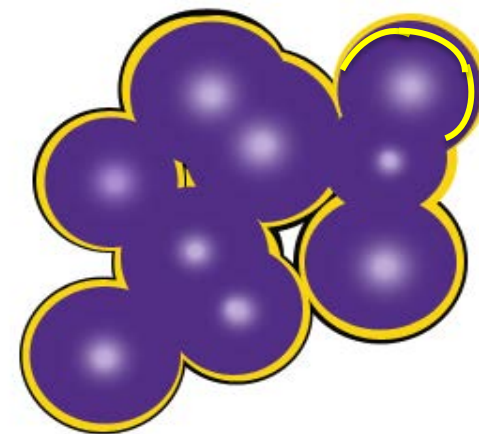
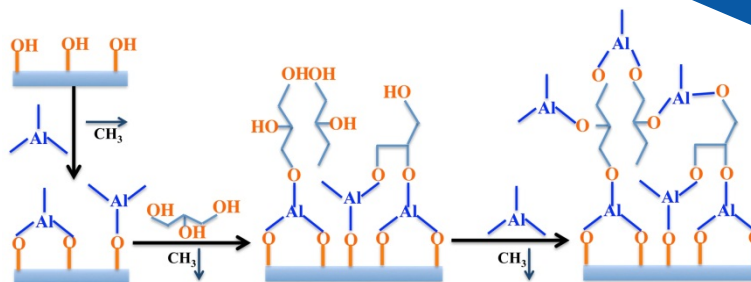
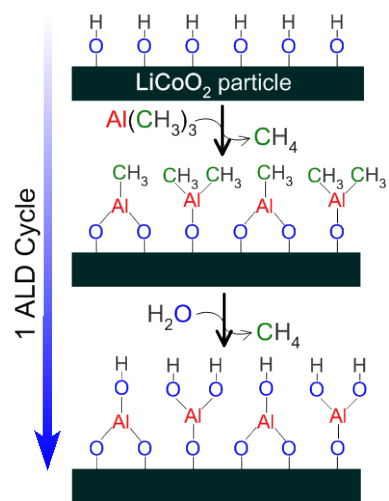
Milestone	Status	Date
Send an optimized thick electrode ($\geq 15 \mu\text{m}$) with a reversible capacity of at least 2000 mAh/g at C/20 to Dr. Vince Battaglia at LBNL for verification.	Complete	May 2012
Demonstrate an ALD coating with rate performance of $\geq \text{C}/5$ for a thick Si anode	Complete	Jul. 2012
Demonstrate at least 50 cycles at a minimum of C/3 rate	Complete	Sept 2012
Identify and characterize the MLD coatings on Si anode	Complete	Dec 2012
Demonstrate durable cycling (>100 cycles) of the surface-engineered thick Si anodes ($>15\mu\text{m}$) at C/3.	Complete	Mar 2013
Characterize the effect of MLD coatings on the Si anodes, and demonstrate MLD coated Si anode with reduced irreversible capacity loss at 1 st cycle	On track	Jul. 2013
Supply the optimized MLD-coated thick electrodes ($>20\mu\text{m}$) to LBNL for verification.	On track	Sept.2013

Approach/Strategy

Technical Approach:

Apply Atomic Layer Deposition (ALD) and Molecular Layer Deposition (MLD) coatings to high-capacity Si anode for both improved mechanical integrity and electrochemical performance

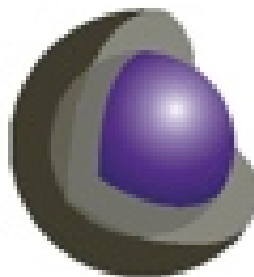
Robust Matrix by using ALD/MLD



Requirements for the shell/coating

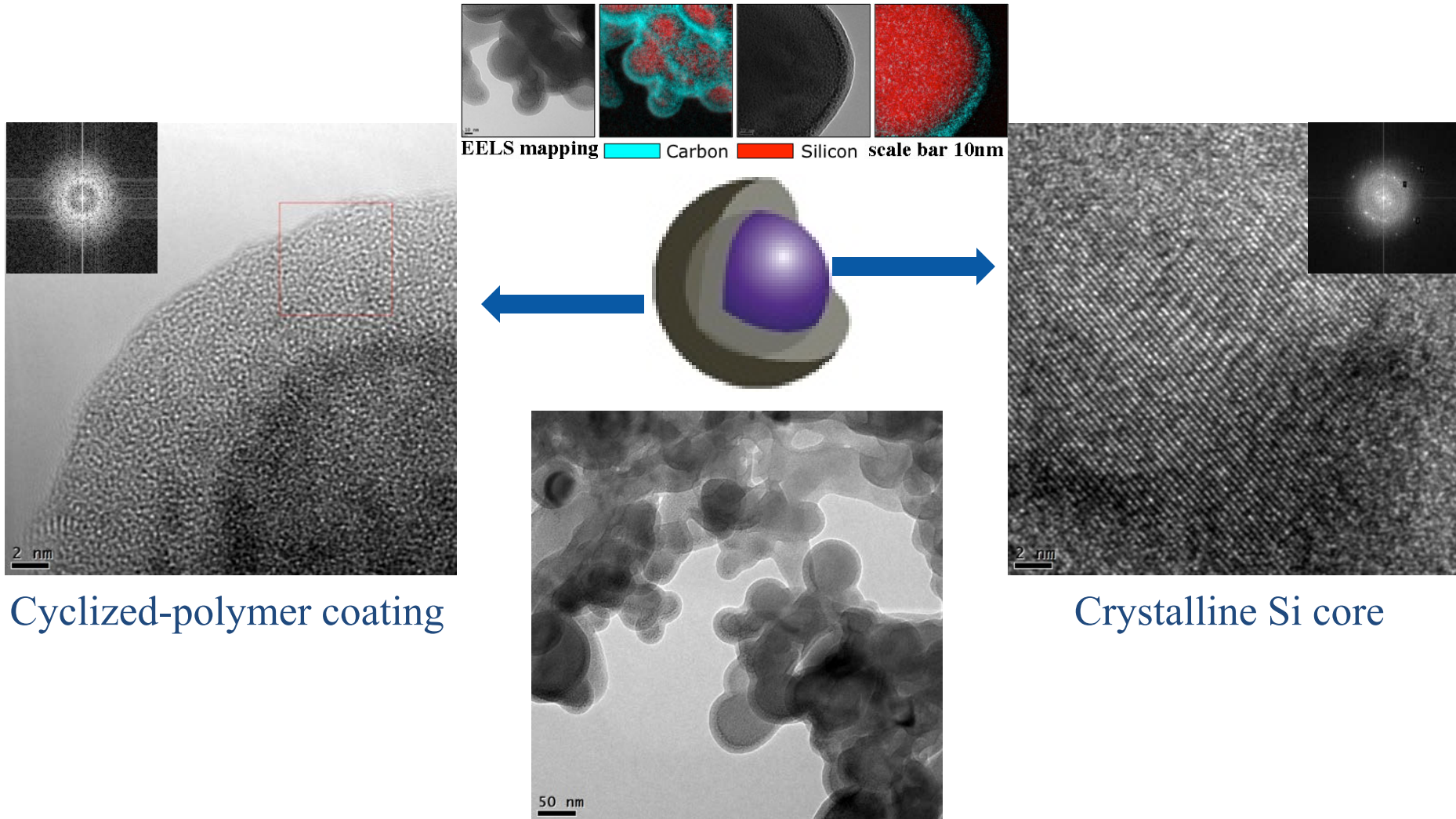
- ✓ **Electronically conductive**
- ✓ **Ionically conductive**
- ✓ **Mechanically strong**
- ✓ **Electrochemically stable**

Si core shell nanostructure



Technical Accomplishments

Formation of Si-Polyacrylonitrile (PAN) Composite Materials



Composite Si-PAN anode without other additives

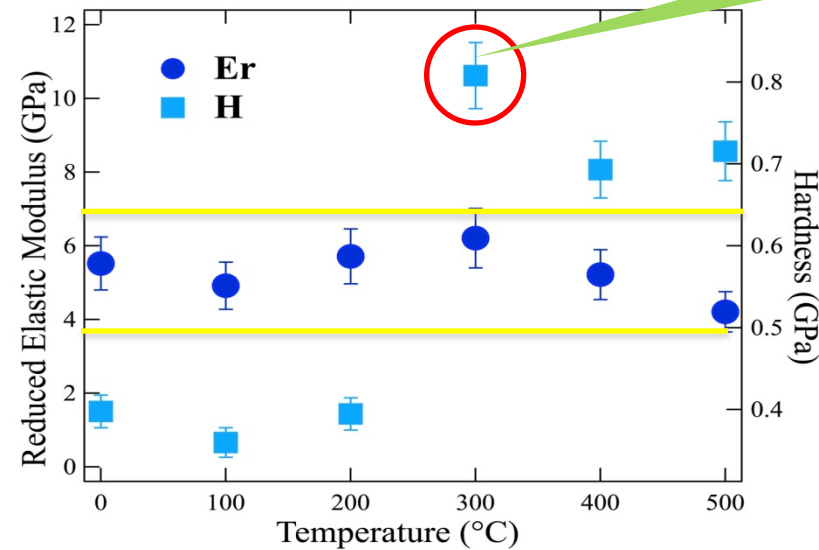
Technical Accomplishments

Improved Performance of Si-PAN Thick Anodes

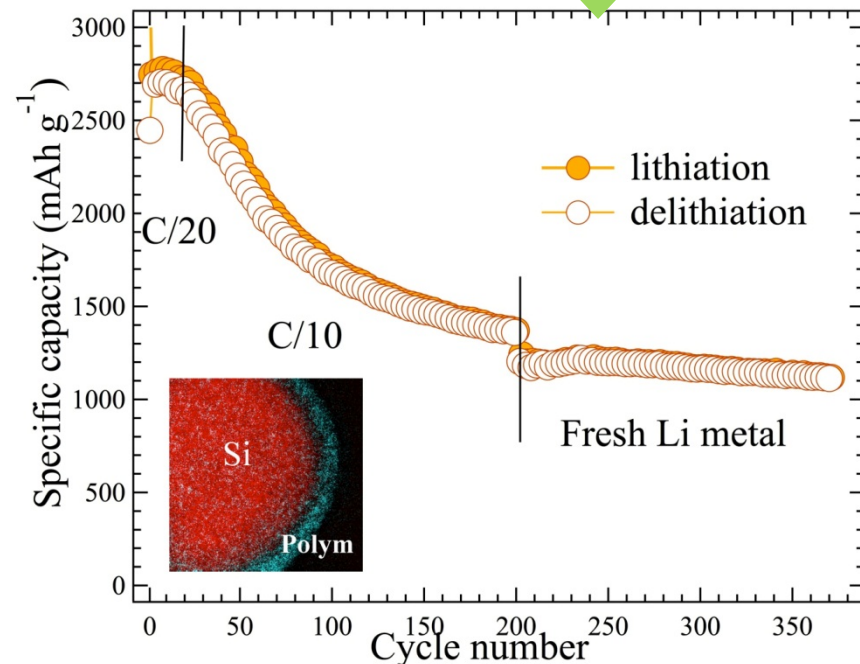
Optimization of mechanical properties of PAN polymer shell during the annealing process

Increased hardness in *polymer-like coating*

Accommodates volumetric Change



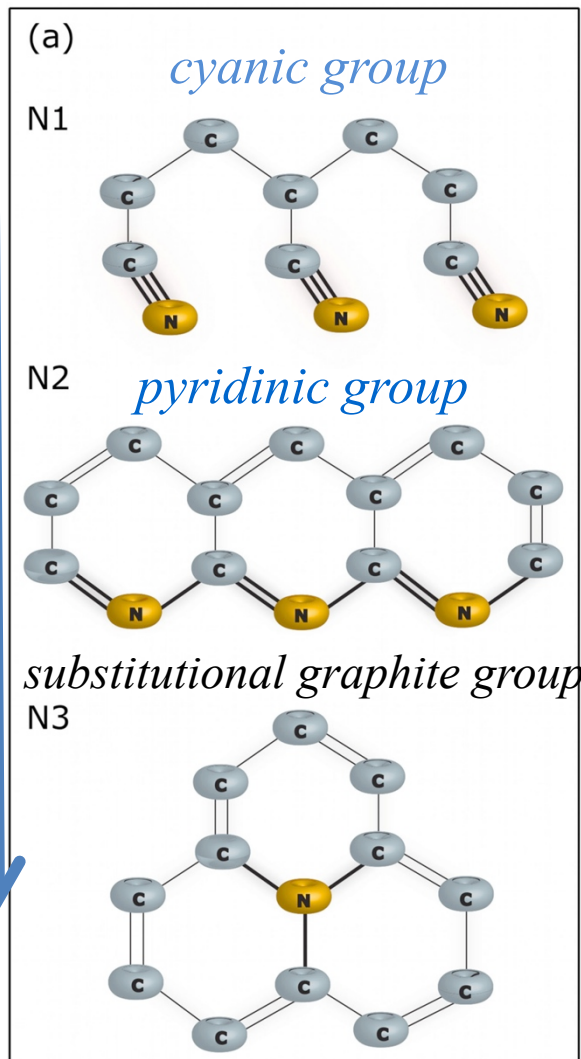
The hybrid core-shell nano-structure has demonstrated stable cycling performance over hundreds of cycles.



Technical Accomplishments

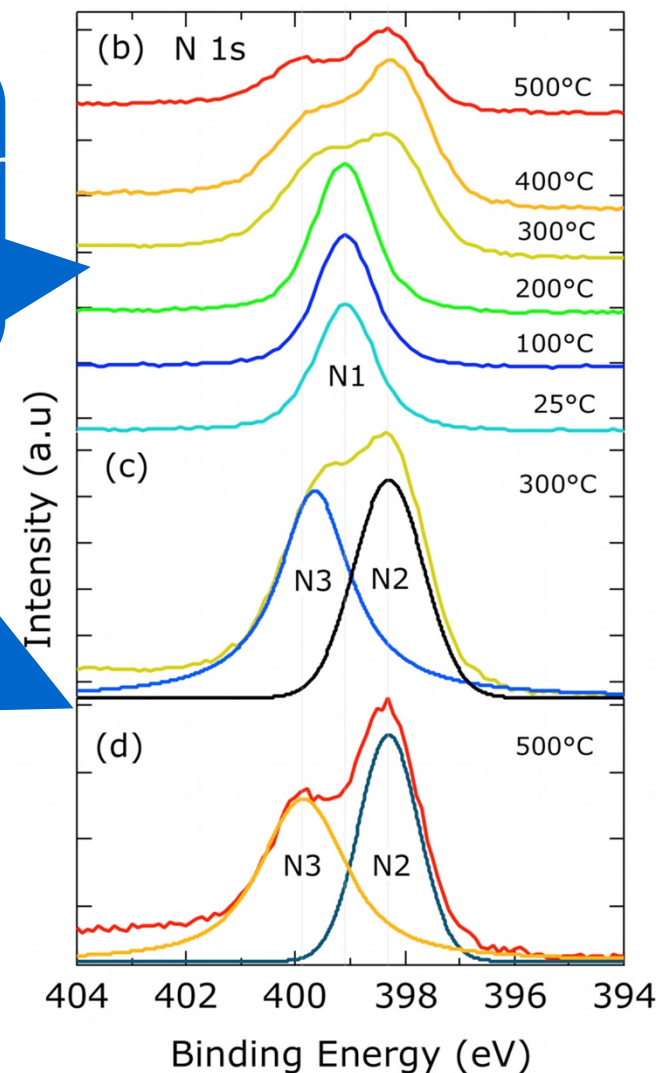
Enhanced Properties of Si-Cyclized PAN Nanostructure

Cyclization



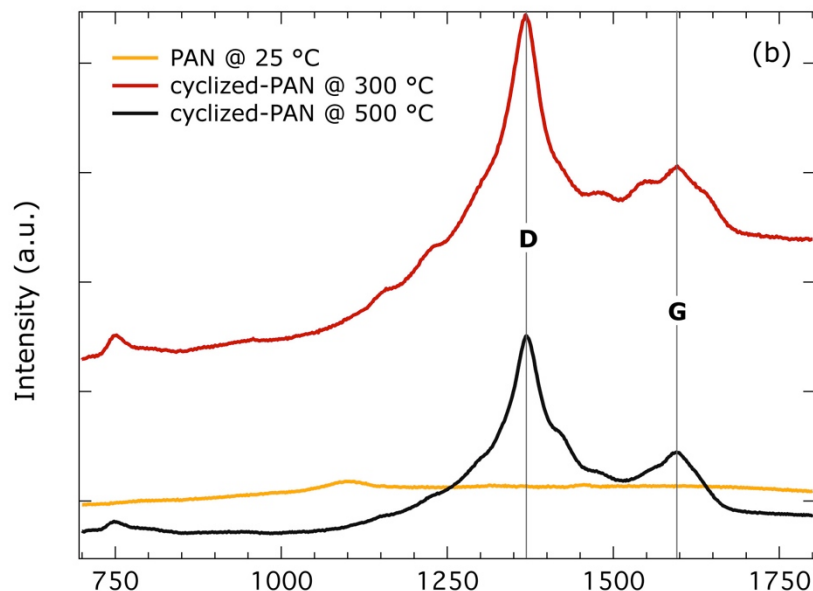
N 1s XPS spectra of PAN shell material with increasing treatment temperature.

(c)&(d) show the Gaussian-Lorentzian fits to contributions from N2 and N3 groups.

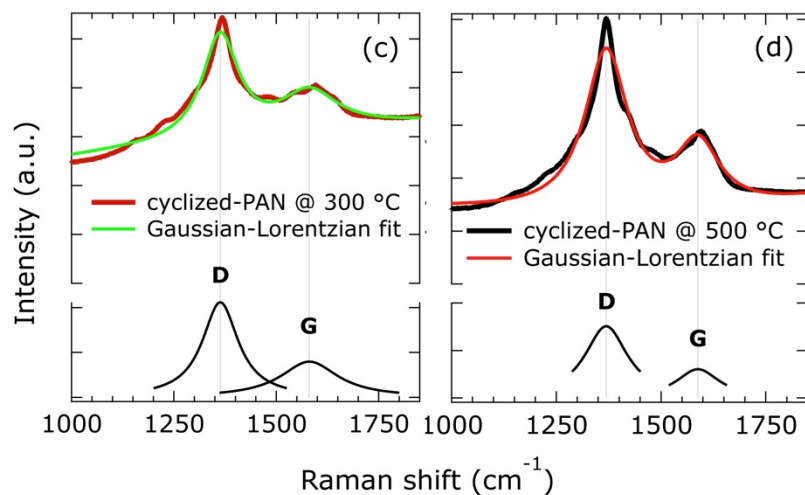


Technical Accomplishments

Evolution of Graphitic-Type Structure in PAN Outlayer



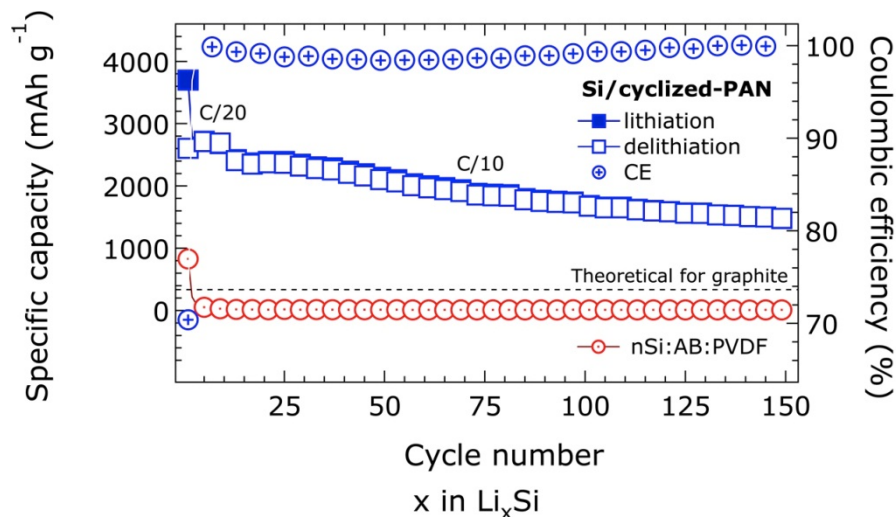
Raman spectra of untreated PAN films (orange), PAN films treated at 300°C (red) and PAN films treated at 500°C (black). The observation of graphite D and G bands confirms sp² bonding and a cyclic structure for heat-treated samples.



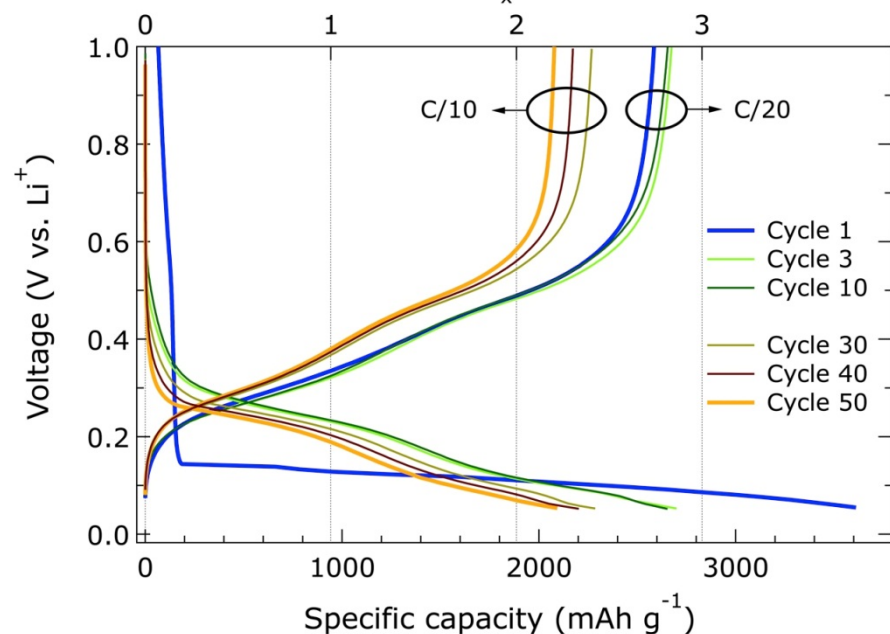
Fitted D and G bands used to calculate the I_D/I_G ratio. A smaller ratio at 500°C (2.50) than at 300°C (2.66) indicates that a more graphite-like crystalline structure is achieved at higher heat treatment temperatures.

Technical Accomplishments

Stable Electrochemical Performance of Si-PAN Anode



Si/cyclized-PAN composite electrode has a specific charge capacity of $\sim 1500 \text{ mAh g}^{-1}$ and a CE approaching 100% after 100 cycles.



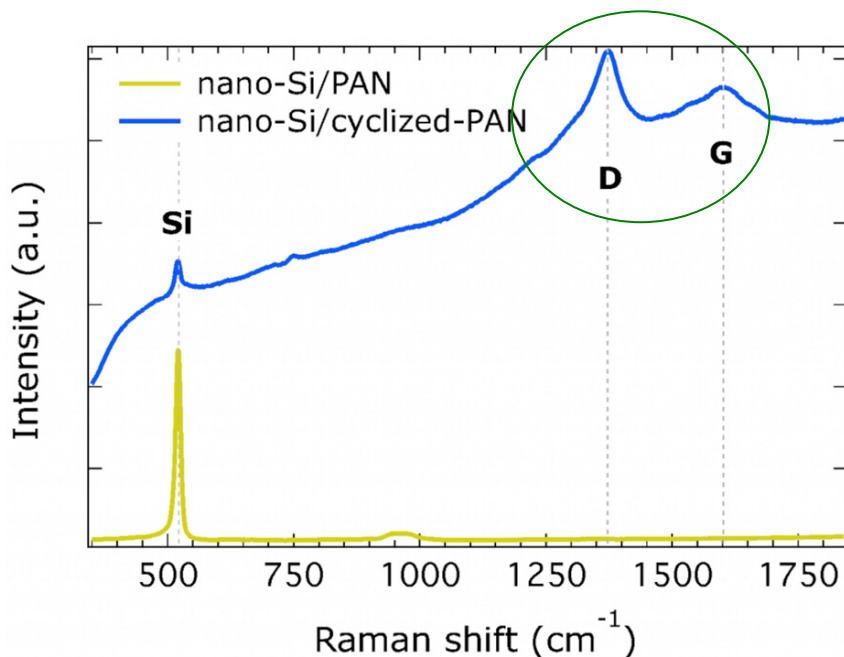
The Si/cyclized-PAN electrode shows a minimal overpotential at C/10

The composition is 70% Aldrich Si and $\sim 30\%$ commercially available polymer without other additives.

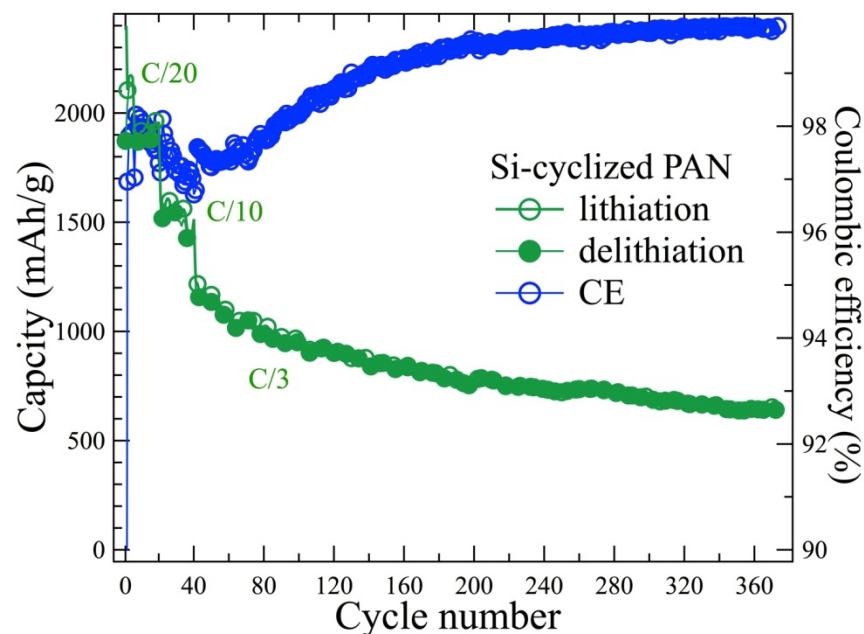
Technical Accomplishments

Durable Cycling Performance of Si-PAN Anode at C/3

The hybrid material with good mechanical resiliency and graphite-like properties accommodate volumetric expansion during cycling.



Only Si-cyclized PAN core-shell composite shows the D and G delocalized sp^2 π bands.

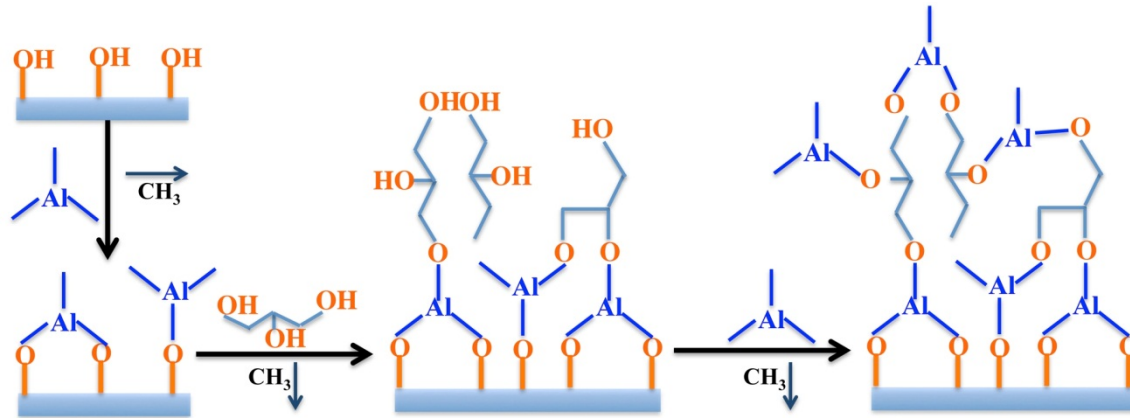


Durable high-rate cycling performance observed for the thick Si/C anode ($>15\mu\text{m}$).

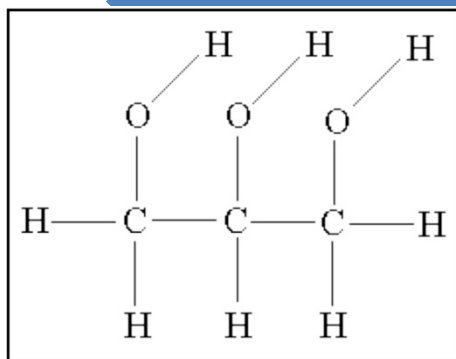
Technical Accomplishments

Developed Hybrid Coatings by ALD/MLD

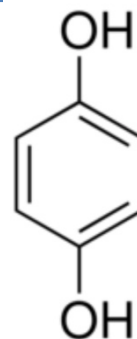
Developed stable, conductive, and elastic framework by using ALD/MLD to enhance mechanical integrity with improved electrochemical performance.



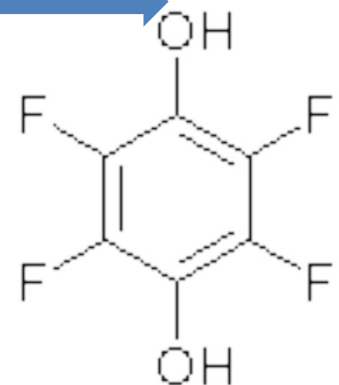
Tune the mechanical properties by using different precursors



Glycerol



Hydroquinone

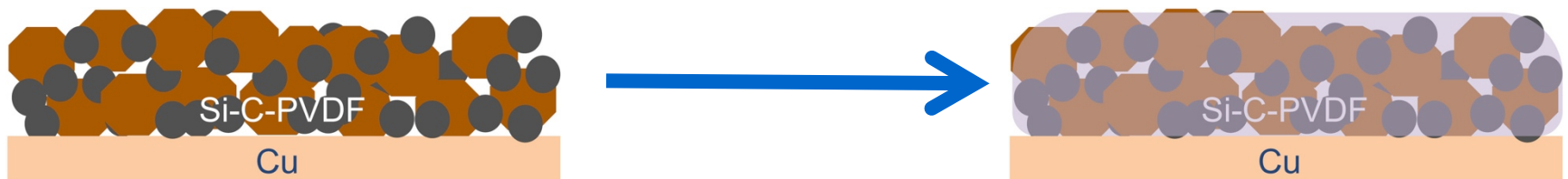


Tetrafluorohydroquinone

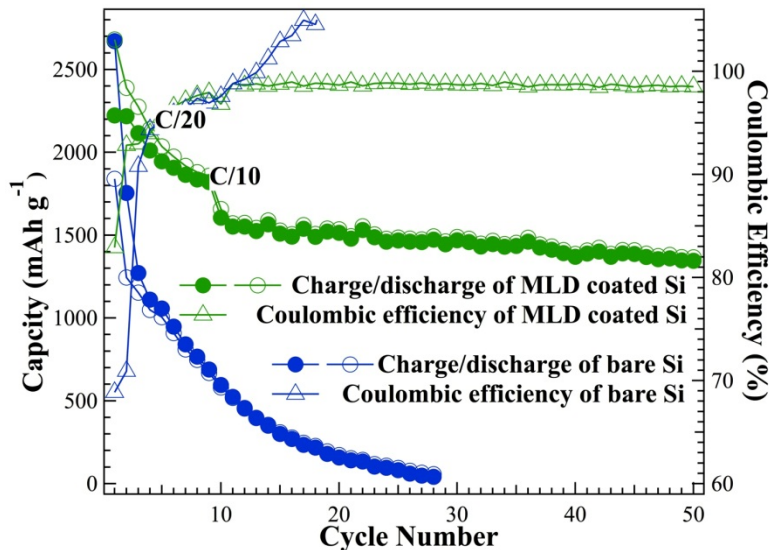
Technical Accomplishments

Stabilization Si Anode by Alucone Coating

- An aluminum alkoxide polymer (Alucone) coating can be grown by sequential exposures of trimethylaluminum (TMA) and glycerol;
- Alucone MLD-coated Si electrodes show significantly improved cycling stability.



Nanoscale surface modification



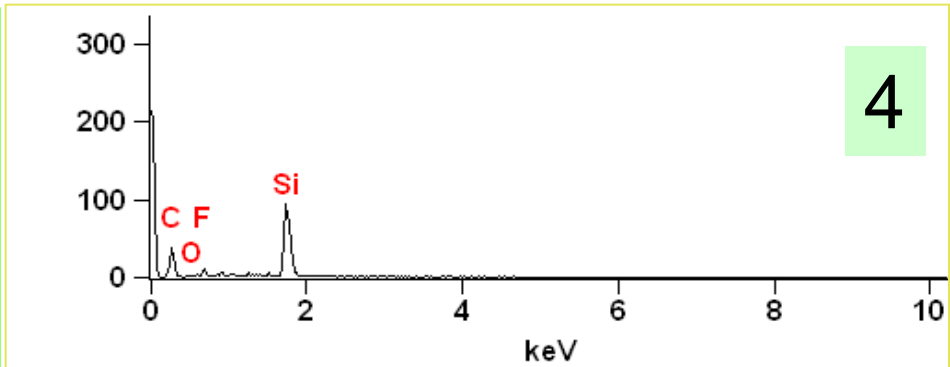
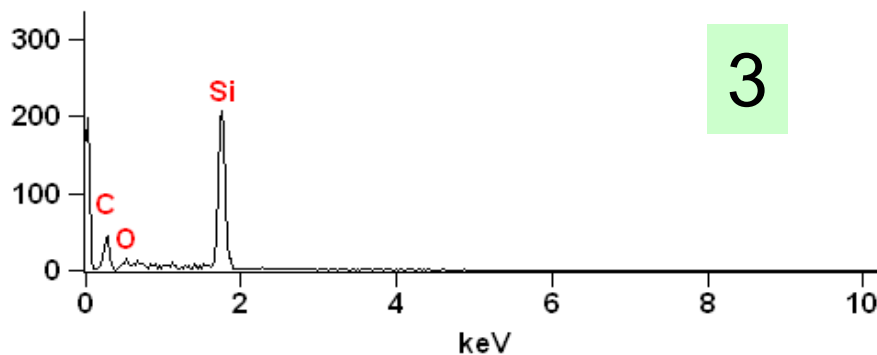
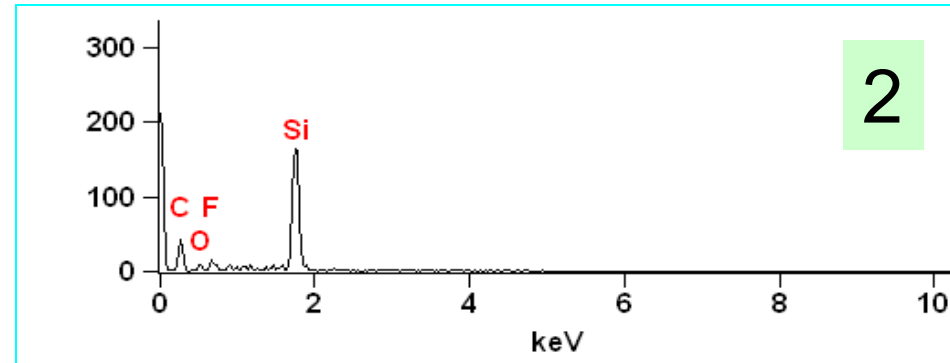
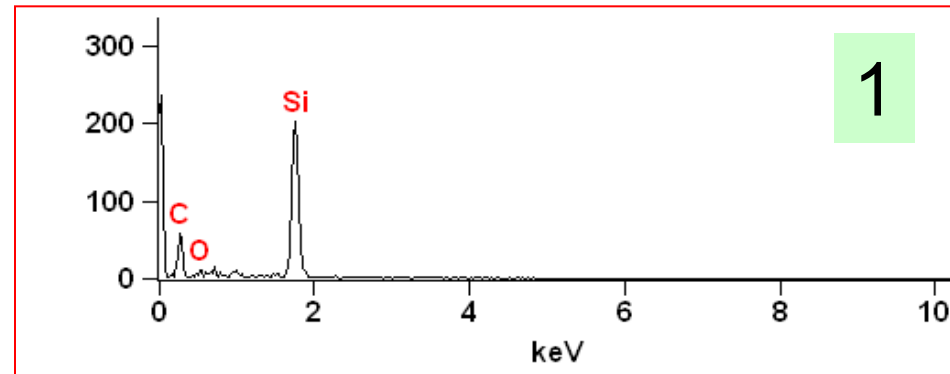
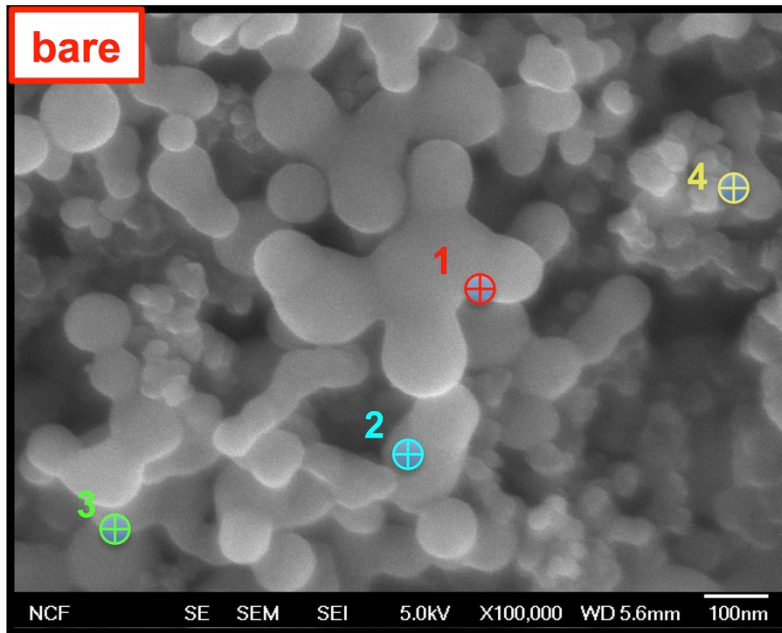
Coating 20cycle MLD Alucone
on Si-C-PVDF electrode; **cycling**
conditions: 175 mA/g (C/20)
350 mA/g (C/10), 0.05-1V.

No major capacity fade observed
for MLD coated Si anode

Technical Accomplishments

Uniform MLD Alucone Coating on Si Electrode

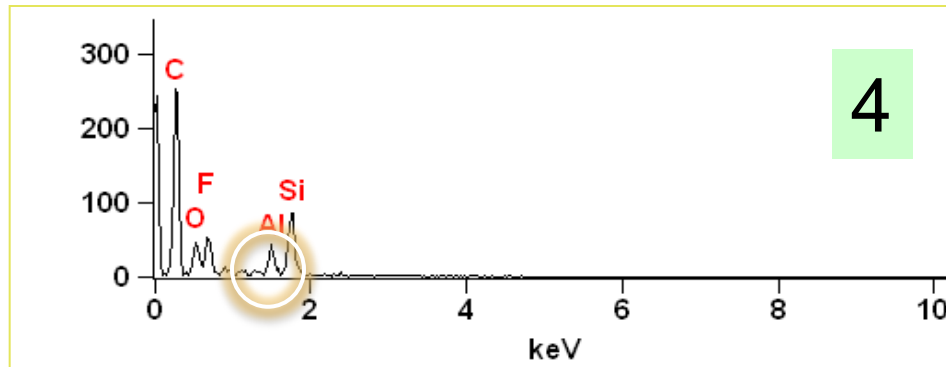
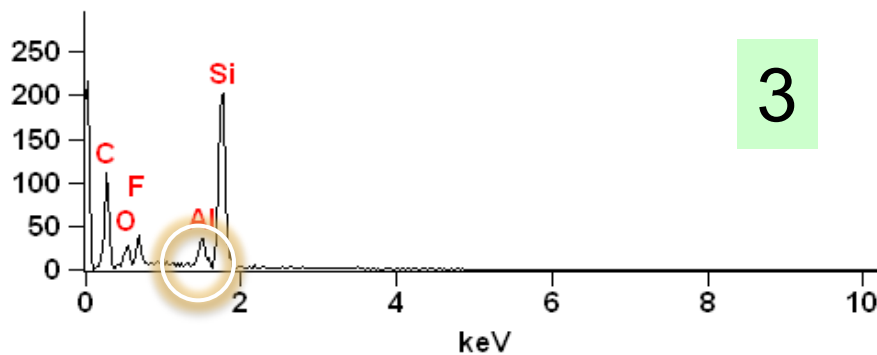
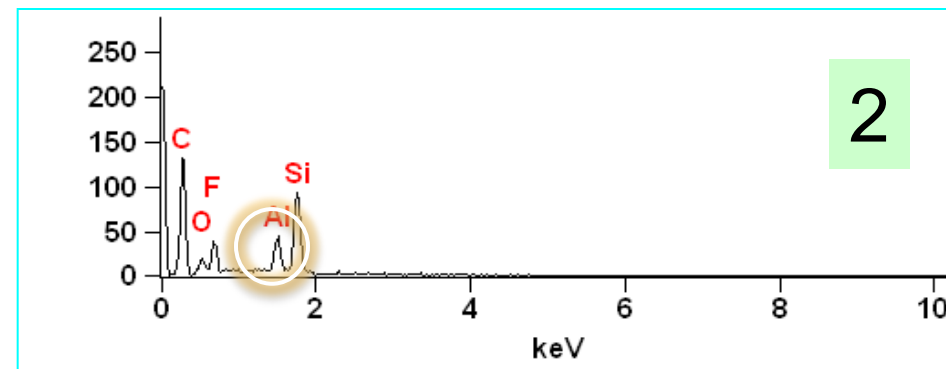
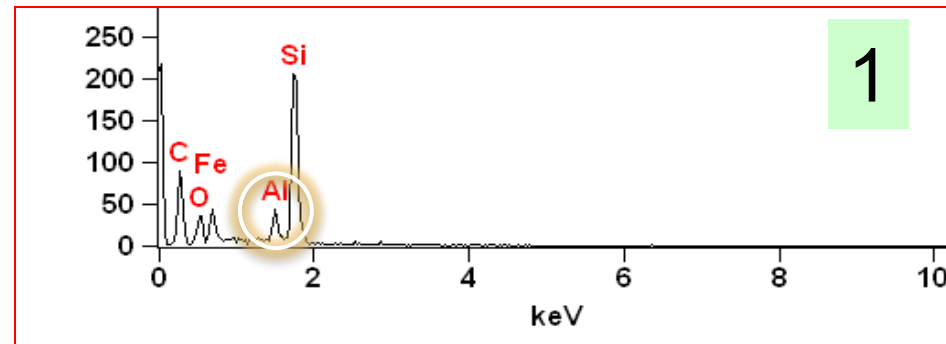
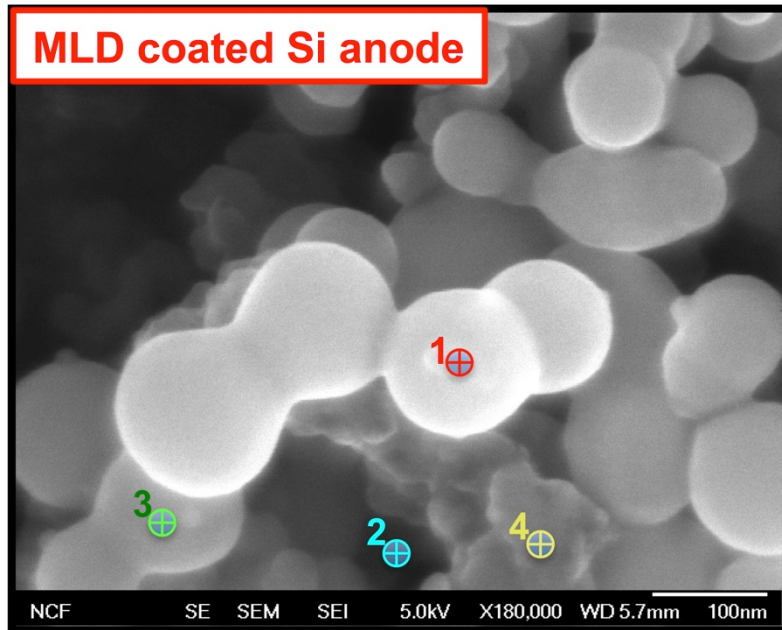
EDS analysis on bare electrode



Technical Accomplishments

Uniform MLD Alucone Coating on Si Electrode

Al detected on coated electrodes



Collaborations

SUNY, Binghamton: Prof. M. Stanley Whittingham provided us layer-cathode material. We demonstrated the improved rate performance and also investigated the effect of ALD coating on high-voltage cycling performance. Enhanced performance on cathodes finally help the full-cell chemistry by using our high-energy Si anodes.

Stanford Synchrotron Radiation Light Source (SSRL): We collaborated with Dr. Michal Toney at SSRL to get *in-situ* synchrotron x-ray diffraction, in-situ XANES of ALD coated electrodes in order to study the ALD coating on the structural evolution during cycling.

Army Research Laboratory (ARL): Working with Dr. Kang Xu on the electrolytes, we are able to further improve the cycling performance for the Si anodes and high-voltage cathodes.

Argonne National Lab (ANL): We are working with Dr. Anthony Burrell on high-voltage Li-excess cathode materials to identify the coating effect on the voltage fading.

Lawrence Berkeley National Laboratory (LBNL): Dr. Vince Battaglia help testing some of our Si/C core shell electrodes for verification.

Internal collaborations: Dr. C. Ban and Dr. S. M. George are working with Dr. R.C. Tenent to develop an inexpensive atmospheric pressure technique that will be easy to incorporate into a battery line; Dr. Nathan Neale and Dr. Qi Wang at NREL provided the Si nanocrystalline and Si thin-film samples.

Nanosys Inc. Provided Si/C materials.

Planned Future Work

- Characterization and analyses will be performed to understand the ionic diffusion and mechanical properties of the ALD/MLD coatings.
- Investigate the effect of coating on the formation of Solid Electrolyte Interphase (SEI) to reduce the irreversible capacity loss due to the inferior SEI reactions.
- The optimal composition and structure of the ALD/MLD surface coatings will be established to improve the surface stability of Si particles as well as increase the integrity of Si electrodes.
- A thick Si anode with the appropriate ALD/MLD coatings will be demonstrated to have a high durable capacity as well as high rate capability.
- In-situ structural characterization will be further performed to better understand the structural evolution of the coated electrodes during cycling.

Summary

- ✓ Utilized cyclized PAN for Si-PAN composite anode to address Si large expansion and enable greatly improved cycling performance.

Achieved sustainable cycling of the Si-PAN composite anode with a reversible capacity of $\sim 1500 \text{ mAh/g}$ over a hundred cycles.

Demonstrated the durable high-rate cycling performance of the thick Si/C anode ($> 15 \mu\text{m}$). The Si-C anode with mass loading of $\sim 1 \text{ mg/cm}^2$ delivers a stable cycling at C/3 for over 300 cycles, and the Coulombic efficiency reaches 99.9%.

- ✓ Developed uniform MLD Alucone coating on porous electrode by using trimethylaluminium and glycerol precursors.

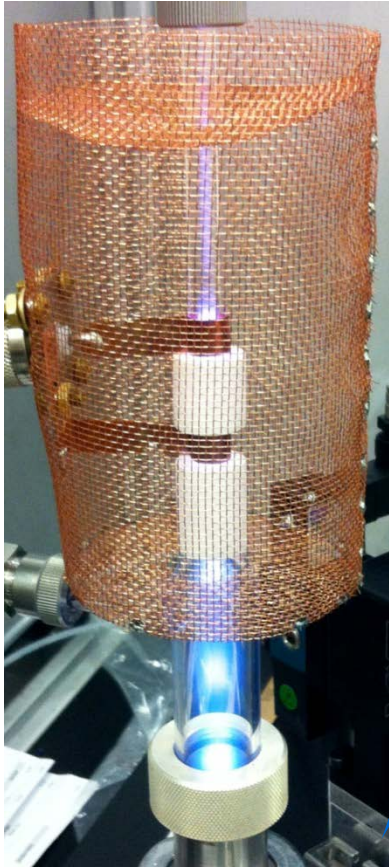
Significantly improved the cycling performance of conventional Si-C-PVDF electrodes. The capacity obtained at a cycling rate of 0.1C has been stabilized in the MLD-coated Si electrode.

No major capacity fade observed after 50 charge-discharge cycles. And the Coulombic efficiency reaches $\sim 99\%$ in the MLD coated Si electrode.

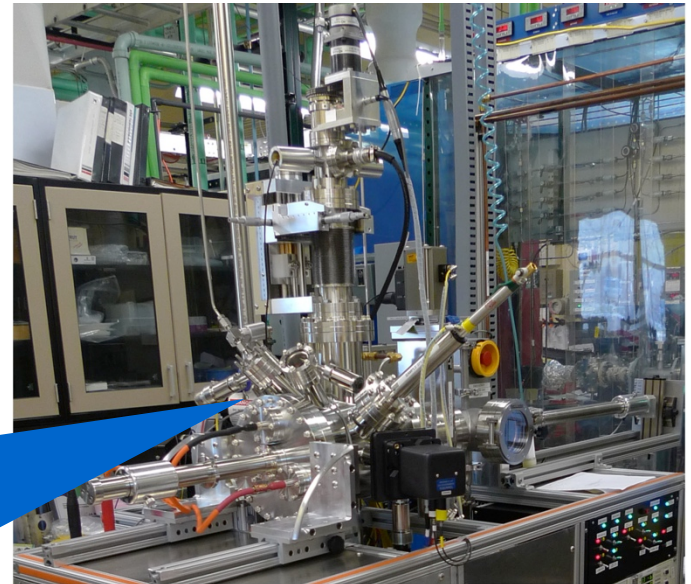
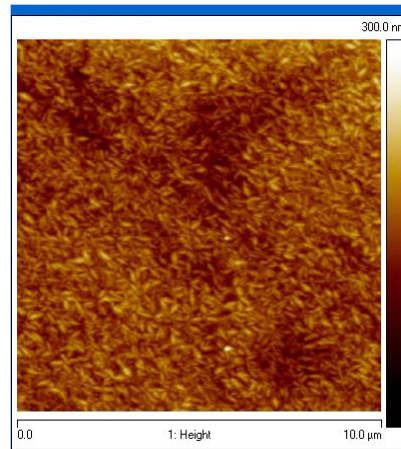
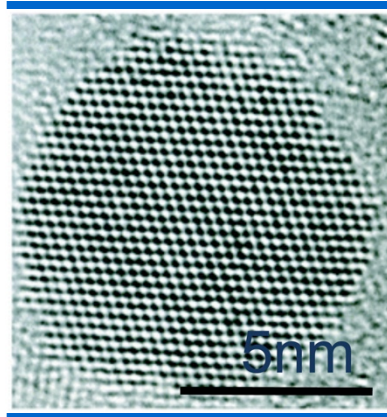
Technical Back-Up Slides

Synthesis of Si Nanoparticles, Si Thin Film

High-quality Si nanoparticles have been successfully synthesized by:
RF-enhanced plasma reactor and Si nanocrystalline thin-film prepared by using Hot Wire Chemical Vapor Deposition (CVD)



RF reactor
Courtesy of Nathan Neale

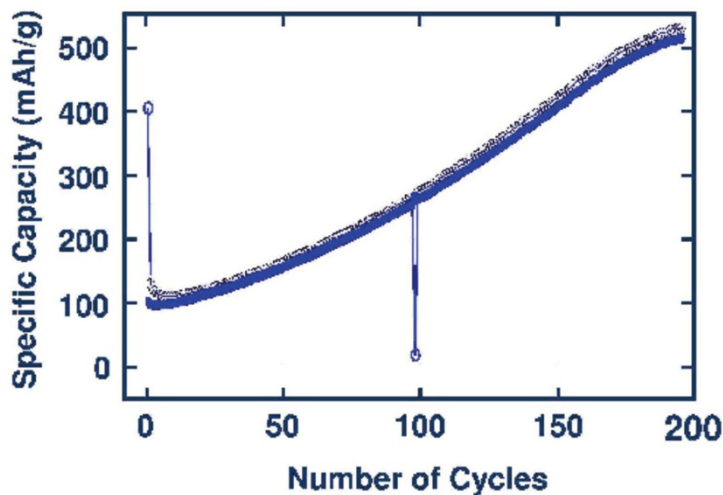


HWCVD

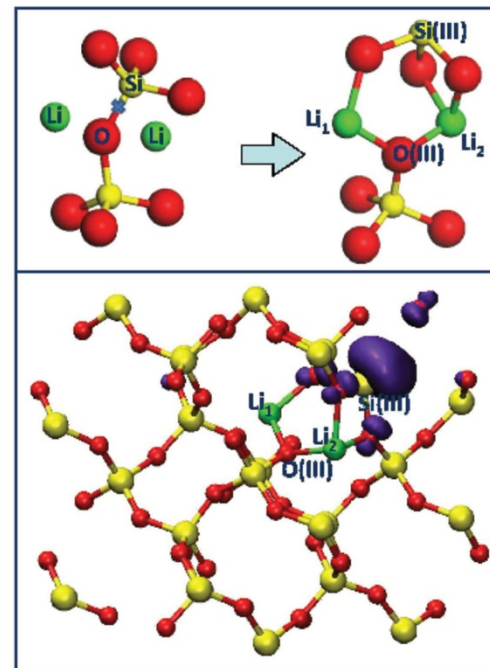
Density functional theory (DFT) simulations of lithiation in silica

- Observed the continuous capacity rise of SiO₂ anode;
- Proposed a new mechanism for SiO₂ lithiation, based on molecular dynamics and density functional theory simulations

Li effectively break a Si-O bond and become stabilized by oxygen, thus partially reducing the SiO₂ anode: leading to increased anode capacity.



Continuously capacity rise over 200 cycles

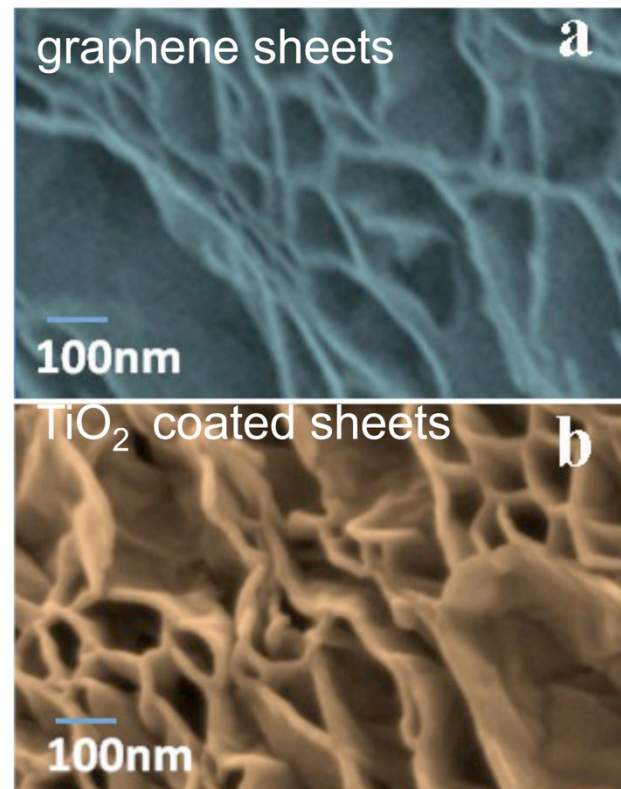
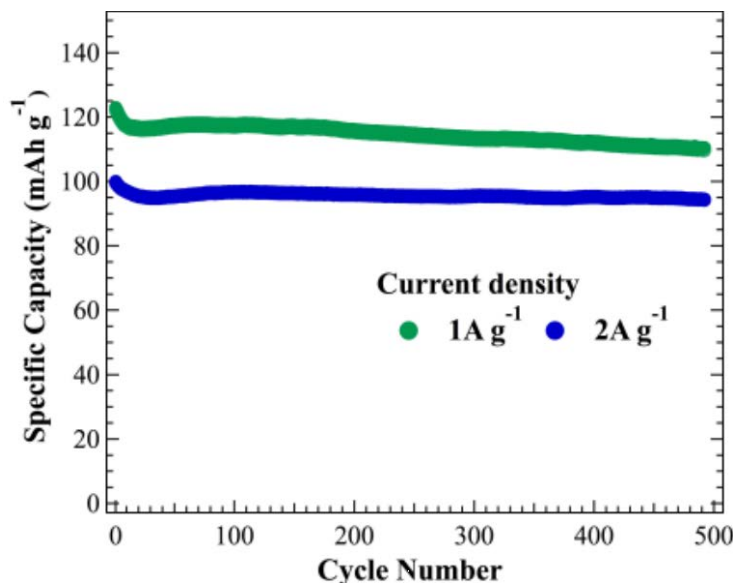


Intercalation of Li in SiO₂ through partial reduction

➤ C. Ban, *Appl. Phys. Lett.* (2012) 100, 243905

ALD of Amorphous TiO_2 on Graphene as a Li-ion Anode

Greatly improved rate performance by using ALD nano TiO_2 –Graphene anode.



New approach for synthesis electrode materials:

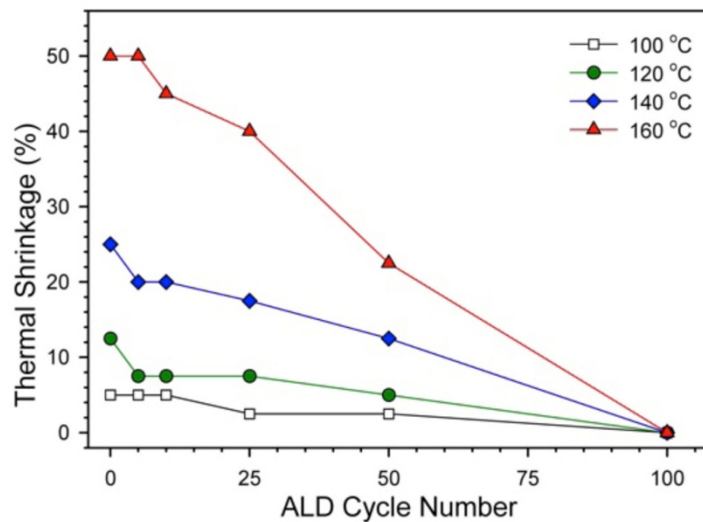
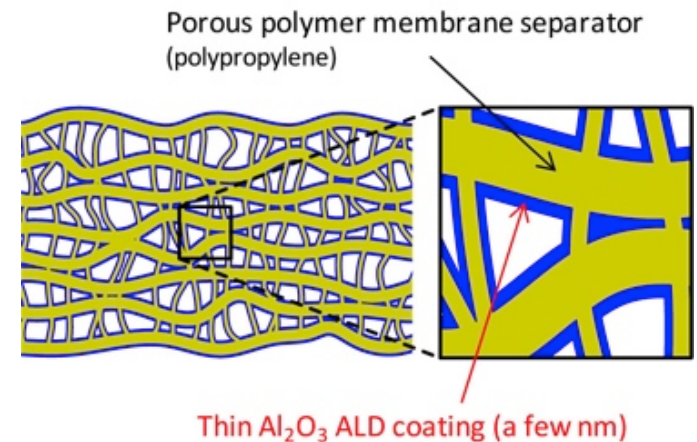
Using ALD depositing Li-ion electrode materials on high surface area substrates to enable high-rate cycling performance.

C. Ban et al. Nanotechnology, accepted

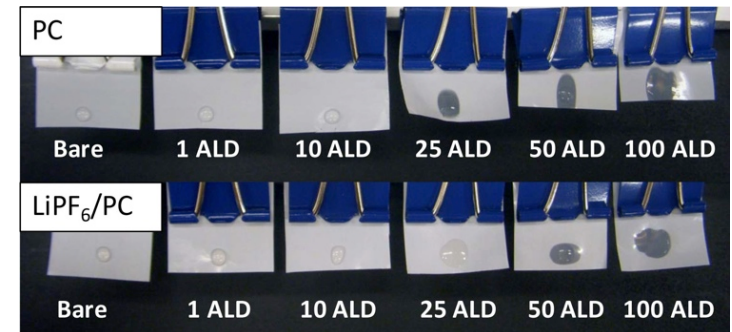
ALD Coated Li-Ion Separators

The thin Al_2O_3 ALD coating on polymer separators results in *significantly suppressed thermal shrinkage*, which lead to improved safety of Li-ion batteries.

Demonstrated *wettability* of Al_2O_3 ALD-coated separators in an extremely polar electrolyte (propylene carbonate PC solvent).



Thermal shrinkage as a function of ALD cycle number and temperature



Comparison of bare and Al_2O_3 ALD coated separators in PC and LiPF₆-PC electrolytes.

Y.S. Jung, et al. *Adv. Energy Mater.*, 2: 1022–1027. 2012