Atomic Layer Deposition for Stabilization of Silicon Anodes

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

<table>
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<tr>
<th>Milestone</th>
<th>Status</th>
<th>Date</th>
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<tr>
<td>Send an optimized thick electrode ($\geq 15 \mu m$) with a reversible capacity of at least 2000 mAh/g at C/20 to Dr. Vince Battaglia at LBNL for verification.</td>
<td>Complete</td>
<td>May 2012</td>
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<tr>
<td>Demonstrate an ALD coating with rate performance of $\geq C/5$ for a thick Si anode</td>
<td>Complete</td>
<td>Jul. 2012</td>
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<td>Demonstrate at least 50 cycles at a minimum of C/3 rate</td>
<td>Complete</td>
<td>Sept 2012</td>
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<td>Identify and characterize the MLD coatings on Si anode</td>
<td>Complete</td>
<td>Dec 2012</td>
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<tr>
<td>Demonstrate durable cycling ($&gt;100$ cycles) of the surface-engineered thick Si anodes ($&gt;15\mu m$) at C/3.</td>
<td>Complete</td>
<td>Mar 2013</td>
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<tr>
<td>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</td>
<td>On track</td>
<td>Jul. 2013</td>
</tr>
<tr>
<td>Supply the optimized MLD-coated thick electrodes ($&gt;20\mu m$) to LBNL for verification.</td>
<td>On track</td>
<td>Sept.2013</td>
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**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**

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

**Requirements for the shell/coating**

**Si core shell nanostructure**
Technical Accomplishments
Formation of Si-Polyacrylonitrile (PAN) Composite Materials

Cyclized-polymer coating

Composite Si-PAN anode without other additives

Crystalline Si core
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.
Technological Accomplishments
Enhanced Properties of Si-Cyclized PAN Nanostructure

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

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

The composition is 70% Aldrich Si and ~ 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 of the thick Si/C anode (>15um).
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

Tetraflorohydroquinone
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.

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

1. Bare electrode showing the presence of Si.
2. Sample with a peak at 2 keV indicating the presence of Si.
3. Sample with a peak at 0 keV indicating the presence of C.
4. Sample with peaks at 0 and 2 keV indicating the presence of C and Si.
Technical Accomplishments
Uniform MLD Alucone Coating on Si Electrode

Al detected on coated electrodes

MLD coated Si anode

1. Graph showing elements C, Fe, O, and Al detected.
2. Graph showing elements C, F, O, and Si detected.
3. Graph showing elements C, F, O, and Al detected.
4. Graph showing elements C, F, O, and Si detected.

NATIONAL RENEWABLE ENERGY LABORATORY
**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 ~1500mAh/g over a hundred cycles.

  Demonstrated the durable high-rate cycling performance of the thick Si/C anode (>15um). The Si-C anode with mass loading of ~ 1 mg/cm2 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 ~99% in the MLD coated Si electrode.
Technical Back-Up Slides
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)
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

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
The thin Al$_2$O$_3$ ALD coating on polymer separators results in **significantly suppressed thermal shrinkage**, which lead to improved safety of Li-ion batteries. Demonstrated **wettability** of Al$_2$O$_3$ ALD-coated separators in an extremely polar electrolyte (propylene carbonate PC solvent).

Comparison of bare and Al$_2$O$_3$ ALD coated separators in PC and LiPF$_6$-PC electrolytes.