NEXT GENERATION ANODES FOR LI-ION BATTERIES
FUNDAMENTAL STUDIES OF SI-C MODEL SYSTEMS

ROBERT KOSTECKI

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Next Generation Anodes for Li-ion Batteries
Fundamental Studies of Si-C Model Systems

• This presentation describes coordinated research task within the five National Laboratory consortium to develop practical Si-based Li-ion negative electrode. (Ref. ES261)

• The primary objective of this effort is to provide basic understanding and effective mitigation of key R&D barriers to implementation of silicon-based anodes.

• The technical approach involves fundamental diagnostic studies of basic properties of the Si anode active and passive components in model systems.

Timeline

- Start: October 1, 2015
  - Kickoff: January, 2016
- End: September 30, 2018

Budget

FY16 Total Funding: $4000K
The Silicon-Carbon Composite Electrode

- Si/C composite electrode is a complex multicomponent electrochemical systems that incorporate widely dissimilar phases in physical, electrical and ionic contact.
- Basic properties of constituent phases determine the behavior of the composite electrode and the entire Li-ion battery system.

Jones et al., Experimental Mechanics, 2014, 54, 971
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Diagnostic Evaluation of Si-C Anodes

Challenges

1. Inherent non-passivating behavior of Si in organic electrolytes
   - Large irreversible capacity loss
   - Gradual electrolyte consumption and lithium inventory shift in Si-based cells

2. Large volume changes of Si (320%) during cycling
   - Cracking and decrepitation of Si
   - Loss of electronic connectivity and mechanical integrity
Characterization Strategies for Si/C Anodes

- Design unique experimental methodologies for characterization of model Si, C and Si-C electrodes in a single particle, thin-film and monocrystal configurations.
- Apply ex situ and in situ optical and X-ray probes capable of sensing surface layers at a submonolayer sensitivity and resolution.
Function and Operation of Multipurpose Binders in Si/C Anodes

Electrochemical performance of Si/C electrodes varies strongly with different binders.

The rate and mechanism of the electrode degradation may depend on the binder properties.

Thorough understanding of the binder modes of operation cannot be gained solely through testing commercial-type devices.
Function and Operation of Binder(s) in Si/C Anodes

Model electrodes preparation and testing

1. Spin-coat PPALi, PVdF, PPy on Cu, p-Si wafer, glassy carbon substrates.

2. Carry out electrochemical measurements of model thin-film electrodes in baseline electrolyte(s).

3. Probe ex situ binder films after electrochemical tests (CVs, galvanostatic cycling etc)

4. Conduct ex situ and in situ studies of selected binder thin film electrodes to probe and monitor their phys-chem parameters.

5. Evaluate binders in tested composite Si-C electrodes.
Preliminary tests show that the model electrodes exhibit more side reactions than the baseline Si/C anodes.

Electrochemical response varies strongly with different Si-binder arrangements.

Origins of these interfacial phenomena will be the focus of future studies:

- Standard electrochemical measurements.
- Probing ionic and electronic conductivity of binders.
- Advanced spectroscopy and microscopy of C/binder and Si/binder interfaces and interphases.
Function and Operation of Binder(s) in Si/C Anodes

Testing mechanical properties of binders before and after electrochemical cycling

- Stress-strain curves for binder thin films.
- Indentation measurements
- Adhesion tests
- Morphology changes.

10 µL dispersion of polymer in NMP between two Si wafer pieces (1 x 1 cm). Adhesion measurements performed at 1 in/min rate.


<table>
<thead>
<tr>
<th>Binder</th>
<th>Dried at 120°C 15 h vacuum [lbf]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PPy</td>
<td>1.47 ± 0.4</td>
</tr>
<tr>
<td>PVdF</td>
<td>0.16 ± 0.05</td>
</tr>
</tbody>
</table>

How mechanical properties of the binder help withstand large volumetric changes in Si/C composites and assure composite electrode’s mechanical integrity?
Solid Electrolyte Interphase at Si/C Anodes

Solvent Reduction:

http://webb.cm.utexas.edu/research/research_SEI.html

“good” SEI formation
Li₂CO₃, Li₂O, RCO₂Li, alkoxides
-compact SEI, stable,
ionically conductive

“bad” SEI formation
(CH₂OCOLi)₂, insulating polymers
-unstable SEI, not ionically conductive

Typically 30-50 nm

SEI Interface:
Lithium Intercalation into Graphite

TEM Analysis of Discharged Si Particles after Formation

Si Anode in Gen2 +10% FEC Electrolyte

- SEI layer on Si is highly inhomogeneous and it displays poor passivating properties.
- The chemical composition, structure and function of the SEI are not well understood because of:
  - Fine structure and nonhomogeneous properties of electrode/electrolyte interphase.
  - Technical barriers associated with characterization methodologies.

![Image of TEM analysis of discharged Si particles]

![Graph showing X-ray energy vs. counts]

Si Particle Edge 2 (mostly SEI)
**In situ EQCM-D Studies of SEI on Model Si Electrodes**

Goals:
1. Evaluate the effect of electrolyte composition, surface composition and morphology on the formation and properties of the SEI.
2. Assess physico-chemical properties of binders.

Preliminary measurements during initial cycles indicate gradual changes of the mass and mechanical properties of the surface film.

*PVD Si thin-film (100 nm) electrode, Gen-2 electrolyte, v=1mVs⁻¹*
**In Situ Neutron Scattering (SANS) Studies of the SEI**

- SEI in presence of FEC electrolyte is ~4x thinner than in base electrolyte. It consists mostly of LiF.
- SEI thickness in base electrolyte varies greatly with cycling.
Si Nanowires Model Electrode for Interfacial Studies

Diameter: 30-60 nm; Length ~ 10 µm

XPS show SiO\textsubscript{x} surface layer of thickness < 10 nm that can be removed by a simple etching process.

- **In operando** Electrochemical Acoustic Time of Flight (EAToF) on Si-NMC cells (collaboration with Dan Steingart, Princeton University).
- Soft X-ray microscopy and nanotomography of cycled/degraded silicon and silicon-carbon composite electrodes.
Spectral Individuation of the LiBOB-Induced Passivation Film on Si-111 by Near-Field IR Spectroscopy

Si(111) wafer at 1.5 V in 1M LiPF$_6$ + 2 % LiBOB, EC:DMC [1:1]

- High lateral and axial resolution of the near-field optical probe enable spectral and chemical selectivity to select out peaks associated with a single compound.
- Matching early-stage near- and far-field IR spectra allows isolation of the passivating oligomer LiB$_2$C$_{10}$O$_{20}$, confirms its presence in the “inner SEI”, establishes structure-function relationship.
Studies of Solid Electrolyte Interphase at Si/C Anodes

Model Si/C electrodes preparation and testing

1. Use photo-lithography to produce micro-patterned Si/C electrode.

2. Carry out electrochemical tests of model Si/C electrodes in baseline electrolyte(s).

3. Apply ex situ and in situ optical and X-ray probes capable of sensing surface layers at submicron resolution.

4. Monitor and analyze local SEI formation on silicon, carbon and Si-C boundaries.

Probes interfacial properties and evaluate (in)compatibility of Si and C surface chemistry on the electrochemical performance of Si/C composite electrodes.
Summary

Initiating Extensive Diagnostic Studies of Model Silicon System

1. Formed collaborative multi-National Lab team to study fundamental phenomena that control the performance of Silicon composite electrodes.

2. Established new and unique experimental capabilities to produce Si, Si/binder, Si/C model electrodes. Initiated integrated electrochemical and analytical diagnostic studies on model systems.

3. Preliminary tests of model Si/PPy electrodes show that the PPy binder is electrochemically stable during initial cycles.

4. More fundamental studies is needed to probe, characterize and evaluate interfacial behavior of model Si/C systems vs. electrochemical performance of the composite silicon anode.
Future Work

- Explore and study range of silicon and silicon-carbon model systems materials to establish correlations between properties of active and passive components and electrochemical performance of Si composite anode.
- Assess failure modes in Si and Si-based materials and electrodes.
- Establish general rules of the surface-structure-composition-property relationships for Si-based materials and electrodes.
- Develop new and expand existing in situ and ex situ diagnostic approaches:
  - Far- and near-field optical micro-spectrometry of electrode/electrolyte interfaces at molecular resolution.
  - Advanced EELS to study lithium transport phenomena in bulk particles, across interfaces, and through grain boundaries.
  - Surface sensitive techniques such as synchrotron XPS, soft XAS, atom probe tomography (APT) and neutron reflectometry to study the composition of interfacial layers as a function of state-of-charge, electrolyte composition, etc.
  - $^1\text{H}$, $^2\text{D}$, $^6\text{Li}$, $^7\text{Li}$, $^{13}\text{C}$, $^{19}\text{F}$, $^{31}\text{P}$ Multinuclear Correlation NMR spectroscopy and new in situ MAS NMR techniques
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Contributors
- Daniel Abraham
- Eric Allcorn
- Chunmei Ban
- Javier Bareno
- Ira Bloom
- Anthony Burrell
- James Ciszewski
- Claus Daniel
- Dennis Dees
- Fulya Dogan Key
- Zhijia Du
- Alison Dunlop
- Trevor Dzwiniel
- Kyle Fenton
- Kevin Gallagher
- James Gilbert
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- Jianlin Li
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