Novel Anode Materials

Jack Vaughey

Aude Hubaud, Fulya Dogan, Lynn Trahey

Chemical Sciences and Engineering Division
Argonne National Laboratory
Argonne, IL 60439

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Project ID: ES143

Overview

Timeline

- Start: October, 2010
- End: September, 2014
- Percent complete: ~ 95%

Budget

- Total project funding
  - 100% DOE
  - FY11: $300K
  - FY12: $400K
  - FY13: $400K
  - FY14: $400K

Barriers

- Developing higher energy density electrodes
- Improving cycle life
- Increasing lithium battery safety

Partners

- Chris Johnson (ANL)
- Mike Thackeray, Zhenzhen Yang (CEES-EFRC)
- Dave Schroeder (NIU)

Collaborations

- Fikile Brushett (MIT)
- X. Xiao (APS microtomography)
- Gao Liu (LBNL)
- Russell Cook (Electron Microscopy Center)

Project Objectives - Relevance

To overcome problems associated with silicon-based electrodes for lithium-ion batteries – cycling stability, safety, and cycling efficiency - that slow its implementation into transportation energy storage technologies.

Project Areas:

- **Development of synthetic techniques to create stable three-dimensional silicon-based electrodes** where loadings, morphologies, and thicknesses can be varied.
- **Development of surface sensitive characterization tools** to better understand how the active materials interact with the electrolyte and binder.
- **Investigate how electrochemical cycling affects the stability** of the electrode surface and the composition of the SEI layer.
- **Investigate electrode deposition techniques** for developing silicon-based electrodes with controllable thickness, surfaces, and current collectors.

Milestones

1. Synthesize and evaluate a silicon-based electrode that utilizes a multilayer structure to stabilize the active silicon.
   (Dec. 2013) Completed

2. Synthesis and evaluation of at least three alternative electrode structures based on non-copper porous substrates.
   (Mar. 2014) Completed.

3. Utilize surface sensitive techniques to develop a model of the silicon - substrate interface on the alternative electrodes created.
   (Jun. 2014) On going.

4. Evaluate optimized electrode structure against BATT standard silicon electrode for rate capability and stability on cycling. Make recommendations to improve BATT standard electrode.
   (Sep. 2014) On going.

Approach/Strategy

APPROACH: Develop a detailed understanding of how *silicon-based electrodes* operate when constrained by other constituents, components, and active materials utilizing characterization tools that cross various length scales.

STRATEGY: Construct and characterize a series of silicon-based electrodes with a variety of structures in order to develop spectroscopic and electrochemical tools to look at the effect of cycling on the electrode.

- Electrode Formulation
  - Bulk Electrodes
    - 70% Si - 20% PVdF - 10% AB
  - Thin Film Electrodes
    - Si electrodeposition
    - Cu/Si PVD films
    - Cu/Si/Cu PVD heterostructures
  - Electrolytes
    - EC/EMC (3:7) 1.2M $LiPF_6$ (“Gen2”)
    - EC/DEC/FEC 1M $LiPF_6$ (“BATT-FEC”)

- Characterization
  - X-Ray tomography studies of Si-based electrodes
  - EQCM studies to evaluate electrolyte stability and SEI porosity
  - ^{29}Si NMR studies to identify surface functionality of deposited films
- Electrochemistry
  - Effect of electrode dimensionality
  - ^{29}Si NMR studies of silicon electrode /electrolyte interactions

Technical accomplishments: Protective Multilayers

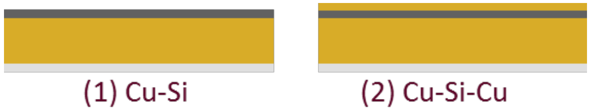
- Beneficial effects on the performance of electrodeposited Si electrodes were previously observed when SiO_2 or Si(OH) were identified as dominant surface species.

- We Investigated the use of thin layers of either porous or non-porous Cu in an effort to mediate the electrodes interactions with the electrolyte. Physical Vapor Deposition (PVD) techniques were used to give us more control over the Si electrode surface. Thickness of Si layer was approximately the same in both cases (0.1 mg/cm^2). Analysis of (2) indicated some active Si was lost to formation of Cu_3Si.

- Cycling efficiencies:
  - Cu-Si film ~86%
  - Cu-Si-Cu multilayer (> Cyc 5) ~96%
  - Si(OH) terminated electrodeposited Si films >99.7%

Inhibiting material losses and electronic isolation by decreasing parasitic surface reactions increases cycling efficiency, although a better model system is required.

Electrodes fabricated by PVD on stainless steel substrates:



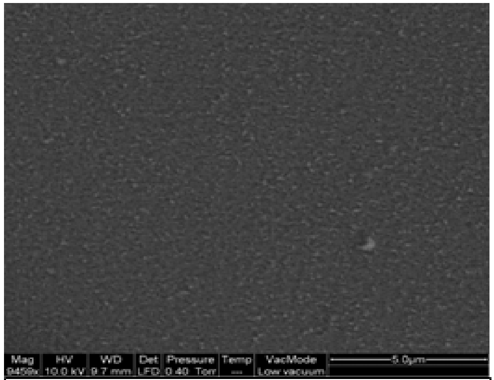


Figure 1. Top down view of the Cu surface of the Cu-Si-Cu multilayer

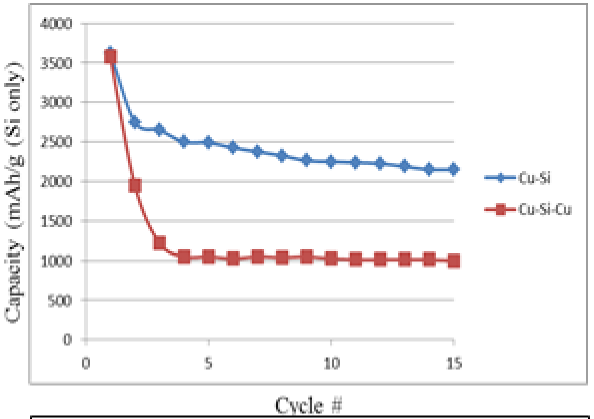
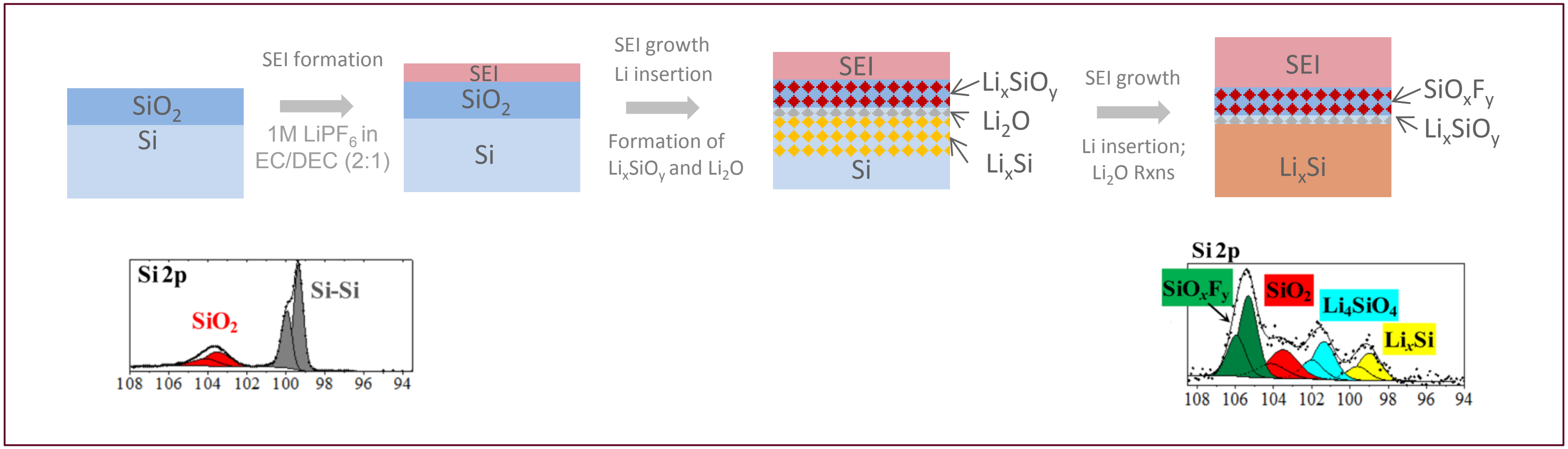


Figure 2. Cycling comparison of the two different Cu/Si electrode multilayers.

Technical accomplishments: Interfacial phases

Harris, et al., recently assessed the solubility of Li-containing SEI products generated on a graphitic carbon anode as a route towards understanding gradual lithium loss[1,2]. Silicon based anodes have similar SEI components and gradual losses (CE ~ 98-99%) are also observed. Recent XPS work by Edström et al, identified $Li_4[SiO_4]$ as a component of the Si interfacial layer from cells [3,4]. The formation of $Li_4[SiO_4]$ results from the reaction of the native SiO_2 passivation coating with "Li_2O" on charge.



Reactivity of this interfacial phase with electrolyte or SEI components could be a source of the gradual loss of active silicon on cycling seen as non-ideal cycling efficiency.

1) K. Tasaki, et al., *J. Electrochem Soc.* **156**, A1019 (2009); *2) J. Phys Chem C* **114** 8076 (2010)
3) B. Philippe, et al., *J. Am. Chem. Soc.*, **135**, 9829 (2013); 4) *Chem . Mater*. **25**, 394 (2013).

Technical accomplishments: Synthesis & Characterization

Synthesis of identified Si(IV) surface species: Li_4SiO_4, $Li_6Si_2O_7$, Li_2SiO_3

- Solid-state synthesis: LiOH / SiO_2, 800 °C, air atmosphere
- Solution/freeze drying synthesis: LiOH / SiO_2, 400 °C, air atmosphere
- Thin film Sputtering (PVD): Si + Li + O_2 (reactive gas) → Si, SiO_2, or Li_xSiO_y films

Reactivity with Electrolyte Solvents

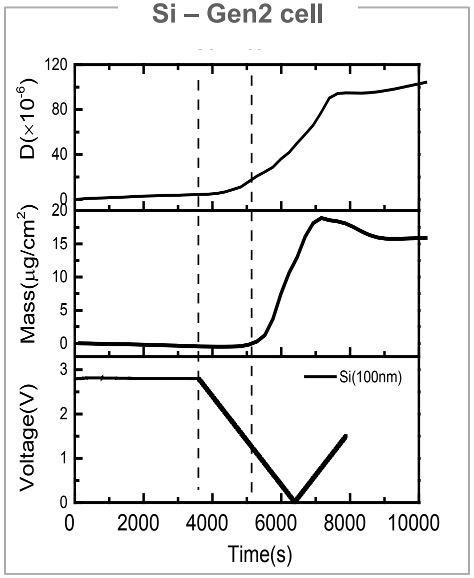
- Li_4SiO_4
- $Li_6Si_2O_7$
- Li_2SiO_3

Samples were exposed to PC,DME, 'Gen2', EMC, EC/EMC, and pentane for 1d & 7d periods, RT & 60°C, and stirred and unstirred conditions.

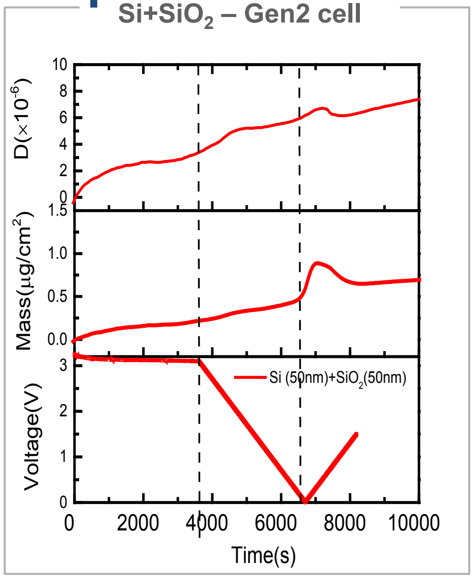
^{29}Si NMR Studies (solution, solid)

Compound	Silicate Anion Form	^{29}Si Chemical Shift
SiO_2	$[SiO_{4/2}]$	-108 ± 2
Li_2SiO_3	$[SiO_{2/2}O_{2/1}]_\infty$	-75 ± 2
$Li_6Si_2O_7$	$[SiO_{3/1}O_{1/2}]$	-70 ± 2
Li_4SiO_4	$[SiO_{4/1}]$	-65 ± 2

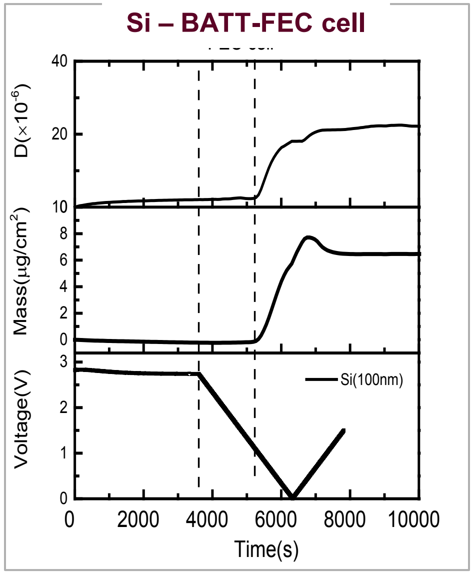
Technical accomplishments: EQCM Studies


Si – Gen2 cell

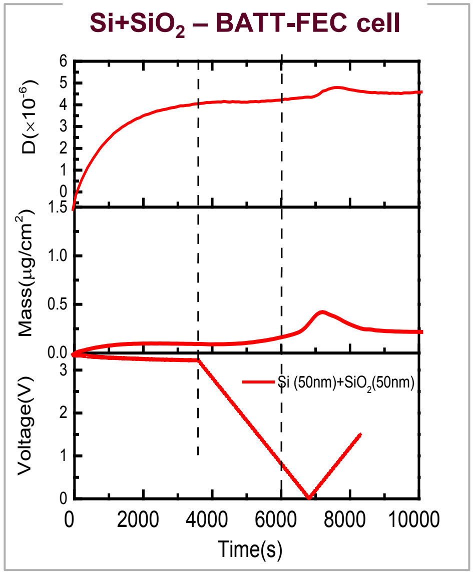
m_{Li}=4.12μg/cm2


Si+SiO_2 – Gen2 cell

m_{Li}=1.43μg/cm2

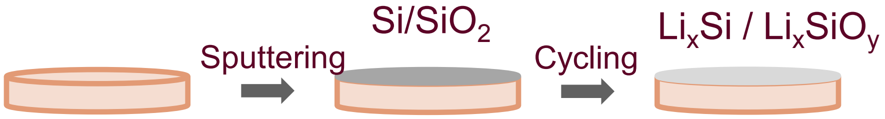

Si – BATT-FEC cell

m_{Li}=3.36ug/cm^2


Si+SiO_2 – BATT-FEC cell

m_{Li}=1.39ug/cm^2

The reactivity of $Si/SiO_2/Li_xSiO_y$ anodes with common electrolytes was evaluated using a combined thin film / EQCM-D study. Various Si or Si/SiO_2 thin films were sputtered (100 nm total film thickness) on Cu-coated quartz crystals by Physical Vapor Deposition (PVD) and cycled as the weight and porosity of the electrodes were monitored as a function of SOC.

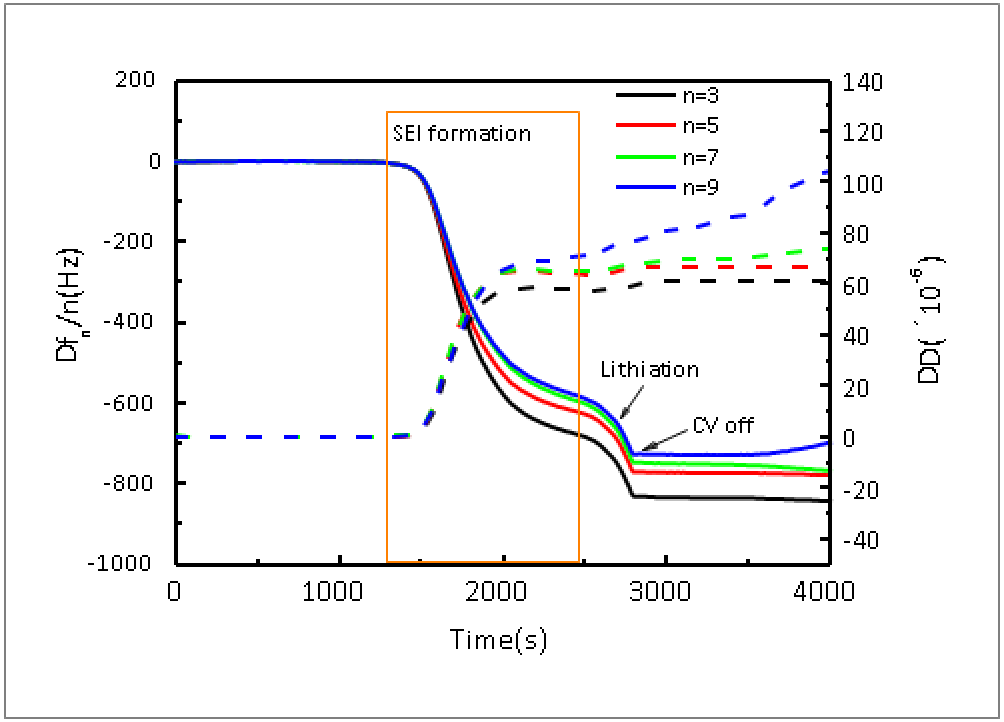


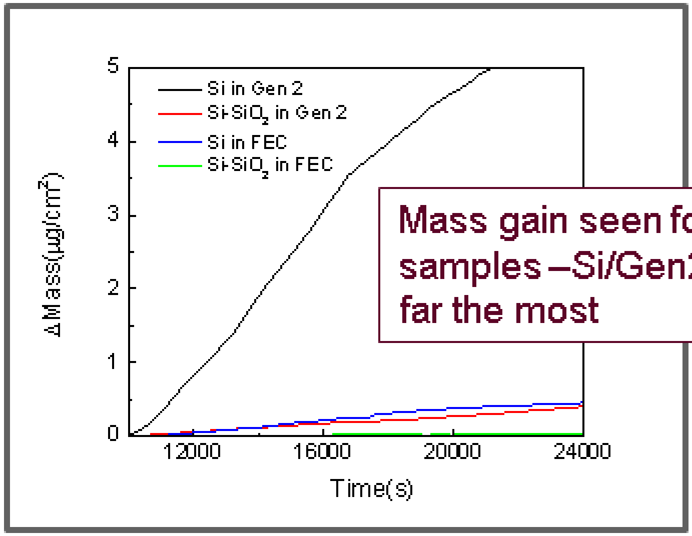
Cu-coated quartz crystals

Time dependence of the (1) mass change and (2) energy dissipation shifts (change in hardness), ΔD, during the initial OCP measurement and the first CV cycle. Utilizing third (n=3) overtones.

- Electrodes: Si and Si/SiO_2 (via PVD)
- Electrolytes: Gen 2 and BATT-FEC.
- Scan rate: 1mV/s.

Technical accomplishments: EQCM Studies





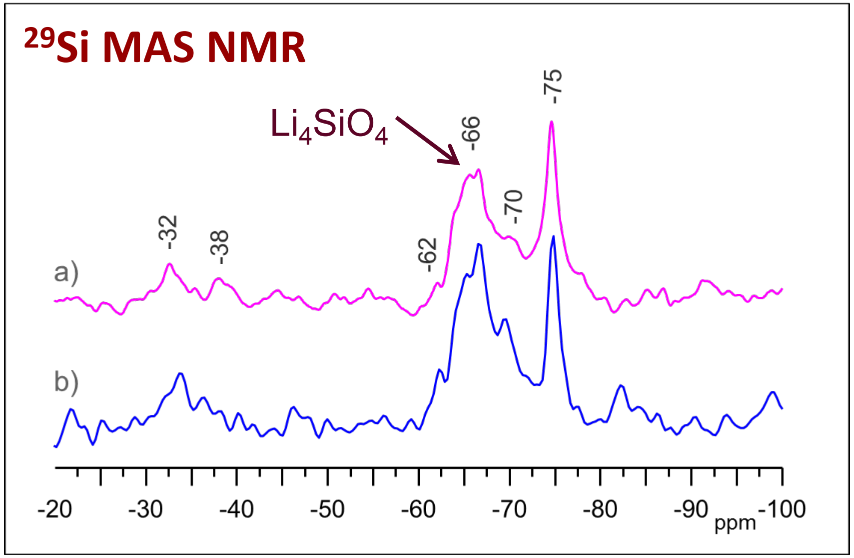
Mass gain seen for all samples – Si/Gen2 by far the most

(Left) EQCM-D response for Si electrode in Gen 2
(Top) Mass change after CV cycling by holding the cell in the electrolyte. Data is offset by the value at 10000s to show the relative change.

- For both Si and Si/SiO_2 samples, less mass is produced with the BATT-FEC electrolyte
- For both Si and Si/SiO_2 samples, the SEI is *harder* (⇔ smaller dissipation change) in the BATT-FEC electrolyte than in Gen2
- Mass change on Si/SiO_2 samples *at early stages of lithiation* is *less* than the expected based on the amount of lithium added.

Technical accomplishments: ^{29}Si NMR Studies

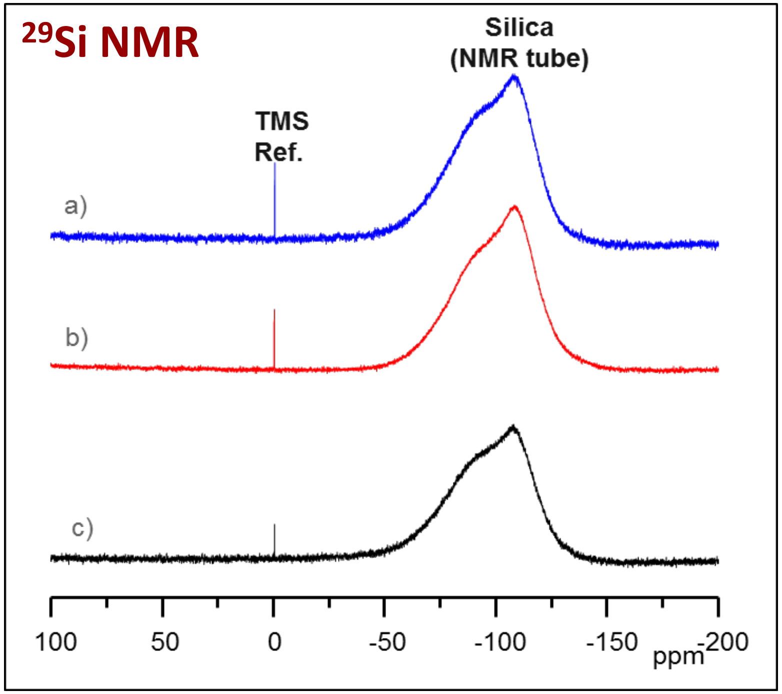
Does $Li_4[SiO_4]$ react on contact with electrolyte solvents?



^{29}Si MAS NMR of a) synthesized Li_4SiO_4 stirred in DME, filtered, washed and dried b) as synthesized Li_4SiO_4

^{29}Si MAS NMR studies of sample s of a mixed phase Li_4SiO_4 / Li_2SiO_3 before and after 7d exposure to DME at RT. After exposure the ratio of species changed **generating Li_2SiO_3 at the expense of Li_4SiO_4**.

^{29}Si solution NMR of Li_4SiO_4 mixed with different solvents did not show any significant soluble silicon species



^{29}Si solution NMR of synthesized Li_4SiO_4 mixed in a) DME b) PC and c) in Gen 2

Technical accomplishments: Analysis

Synthesis:

- Inert dry atmosphere synthesis of $Li_4[SiO_4]$, $Li_6[Si_2O_7]$, $Li_2[SiO_3]$
  - white hygroscopic crystalline solids.
- Exposure to electrolyte solvents was done using closed Al containers
- After exposure and isolation – polar solvents appeared yellow.
- After exposure - silicate samples were difficult to dry and lost crystallinity.

EQCM:

- SiO_2 capping layer samples have denser SEI layers than uncoated samples.
- BATT - FEC electrolytes create a denser SEI layer than Gen2 electrolytes.
- Mass balance of Si/SiO_2 samples indicates *less* mass than expected based on the amount of lithium added.

^{29}Si NMR:

- Solvents isolated after exposure do not contain a soluble silicon species
- Solid isolated after exposure has changed – week long exposure to polar solvents results in an increase in the amount of $Li_2[SiO_3]$ at the expense of $Li_6[Si_2O_7]$ and $Li_4[SiO_4]$.

Translating Data and Observation to a Model

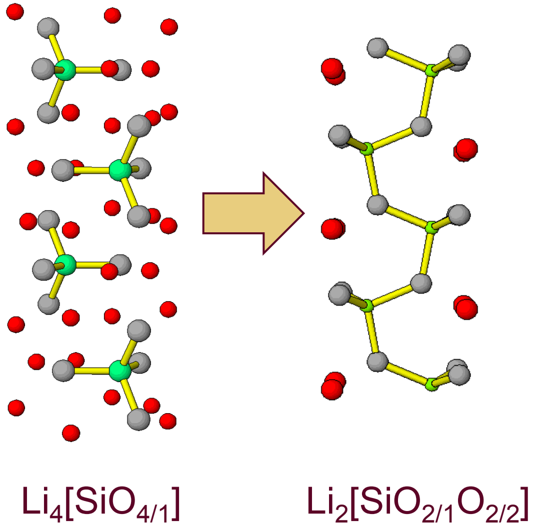
XPS data indicates that $Li_4[SiO_4]$ forms at the interface from the reaction of the silica passivation layer on silicon with 2 Li_2O equivalents on first discharge

$Li_4[SiO_4]$ solvates on contact with polar solvents.

- The solvation probably destabilizes the highly charged silicate tetrahedra
- Available protons may protonate terminal oxides on the $[SiO_4]^{4-}$ to lower the formal charge, e.g. $[SiO_3(OH)]^{3-}$, which is susceptible to condensation forming Si-O-Si bonds.

EQCM data indicates gradual mass loss of lithium silicates samples after electrochemical cycling

- The $Li_x[SiO_y]$ coating may be effective at shielding bulk Li_xSi from the electrolyte. The ionic conductivity of Li_4SiO_4 is several orders of magnitude higher than the more condensed Li_2SiO_3.[5]



^{29}Si NMR data shows that after exposure to polar solvents no silicon-containing species are in solution however the bulk lithium silicate has started formally losing oxide by a simple condensation reaction that maybe release water back in to the system.

Alkali metal hydroxides catalyze the decomposition of organic carbonates.[6]

5) I. Raistrick, C. Ho, R.A. Huggins *JES* **123** 1469 (1976) 6) A. A. G. Shaikh, S. Sivaram, *Chem. Rev.* **96** 961 (1996).

Summary

- We have investigated how compounds that form at the interface between Si and the SEI layer can influence the performance of Si-based LIB electrodes.
  - Thin intermetallic Cu_xSi coatings showed good electronic conductivity and stability to electrolyte but their brittleness limited their durability.
  - Metallic Cu binders enhanced conductivity and power but had no effect on the surface degradation that contributes to capacity fade. Adding capping Cu layers (Cu-Si-Cu) showed improvements in cycling efficiency but lower capacity due to interfacial Cu_3Si formation.
  - The natural SiO_2 passivation layer on silicon is transformed to a good lithium ion conductor, Li_4SiO_4, on first charge. This phase is stable does not transform back to SiO_2 on discharge.
  - The lithium silicate initially formed (Li_4SiO_4)gradually reacts with the electrolyte through a gradual process of solvation and condensation to form a denser phase (Li_2SiO_3). The reported ionic conductivity differences between these starting and ending interfacial phases is > 10^4 S/cm.

Collaborations and Coordination with Other Institutions

Tomography Studies:

- Xianghui Xiao (ANL/APS Microtomography @ 2BM)
- Fikile Brushett (MIT)

EQCM Studies:

- Zhenzhen Yang (ANL - CEES EFRC)

Silicon Electrode Formulation:

- Joseph Kubal, Bryant Polzin (ANL - CAMP)
- Dave Schroeder (NIU)
- Russell Cook (ANL / NST - Electron Microscopy Center)

Future Work

- Continue to investigate how interphase layers on silicon influence the performance of Si-based LIB electrodes. Initial work on Cu and Cu_xSi coatings led to examination of the lithium-ion conducting lithium silicates and how they interact and gradually degrade within the electrochemical cell environment.

- Identify conditions to limit degradation caused by lithium silicates reactivity in the electrochemical cell.

- Identify more stable materials that may influence the degradation pathways and lead to a better performing Si-based electrode.

- Wrap up Studies: Evaluate and report on the role of surface, surface coatings, and interfacial species on the performance of a silicon electrode and report on methods to improve the BATT baseline electrode.