Three Dimensional Anodes and Architectures

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Project ID:
ES143

This presentation does not contain any proprietary or confidential information.

Overview

Timeline

- Start date: October, 2010
- End date: September, 2014
- Percent complete:
  - 33% complete

Budget

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

Barriers

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

Partners

- Fikile Brushett, Christopher Johnson, Baris Key (ANL), CEES-EFRC
- Yi Cui (Stanford, SLAC), Stan Whittingham (SUNY), Gao Liu (LBNL)
- Collaborations
  - R. Winarski, X. Xiao – APS tomography
  - Russell Cook (Electron Microscopy Center)

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:

- **Develop synchrotron tomography tools** to better understand how lithiated silicon interacts with its surroundings *within* a three-dimensional lithium-ion battery electrode on cycling.
- **Develop techniques to make three-dimensional silicon-based electrodes** with a variety of loadings, morphologies, and thicknesses.
- **Develop spectroscopic characterization tools** to investigate the interfacial regions within a silicon-based electrode.
- Investigate **electrodeposition as a synthetic technique** for copper, antimony, silicon, and tin-based three-dimensional electrodes.

Milestones

- Complete characterization of the interfacial region in Cu-Si metallic electrodes (completed Mar 2012)
- Characterize the phases formed and extent of electrode homogeneity for a series of electrodeposited Sn-based electrodes (completed Nov 2011)
- Assess the role of electrolytes and irreversible capacity and SEI formation in three-dimensional electrode structures (on going)
- Initiate nano- and micro-tomography synchrotron effort for three-dimensional electrodes including synthesis, cell design and cycling optimization (on going).

Approach/Strategy

APPROACH: Develop a detailed understanding of how *silicon-based electrodes* operate when constrained by other constituents, components, and active materials. How does volume expansion effect the local electrode environment and structure?

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

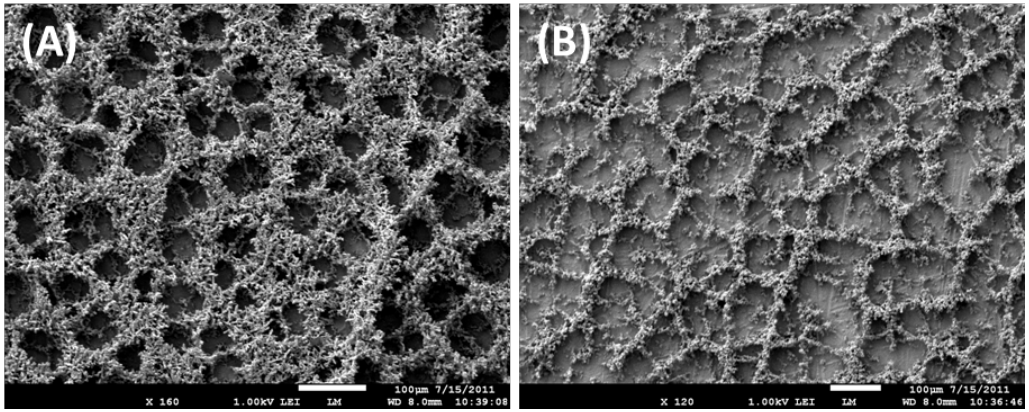
- Electrode Formulation
  - Bulk Electrodes
    - 25% nano-Si – 50% PvDF – 25% C
      (w/ G.Liu, LBNL) - BATT Anode Baseline
    - 70% Si (20-40 µm) - 20% PVdF binder - 10% AB
    - 70% Si (20-40 um) - 30% Cu binder
  - Thin Film Electrodes
    - Si electrodeposition
    - Sn electrodeposition

- Characterization
  - X-Ray tomography studies of active electrodes
    - Sn-based electrodes (improved XRD contrast)
    - Si-based electrodes
  - Cycling Properties

- Metallic binders
  - Effect of binders on rate capability
  - ^{29}Si NMR studies of active/binder interactions

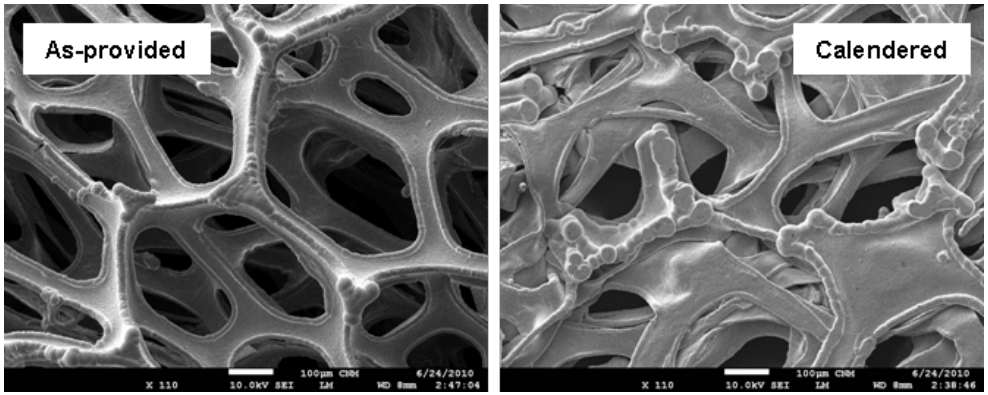
Technical accomplishments:

Substrates: Copper foam synthesis



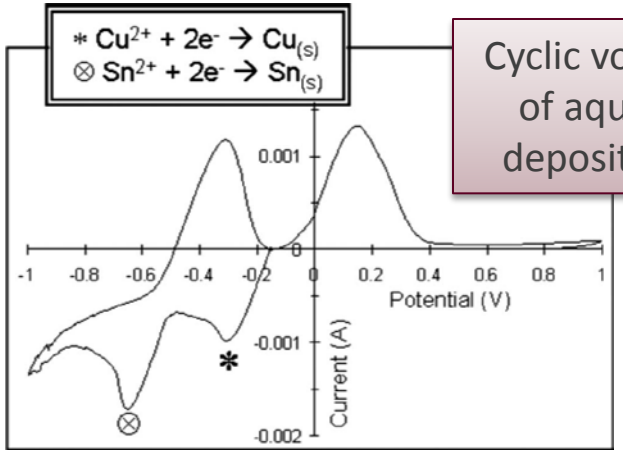
(left) Electrodeposited Cu foams with same Sn deposition performed on each. (A) 1mM chloride concentration in Cu bath, (B) 4 mM chloride concentration in Cu bath

(right) Calendered commercial foams (CircuitFoil) before and after calendaring to 100 µm.

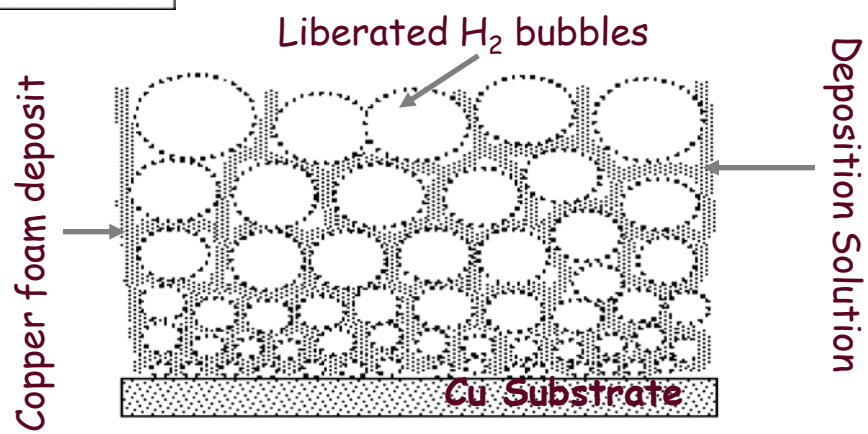


The porosity, thickness, and surface roughness of homemade foams is highly tunable. Commercial foams, however, offer the ease of reproducibility. More commercial vendors will be sought in order to have varying porosities.

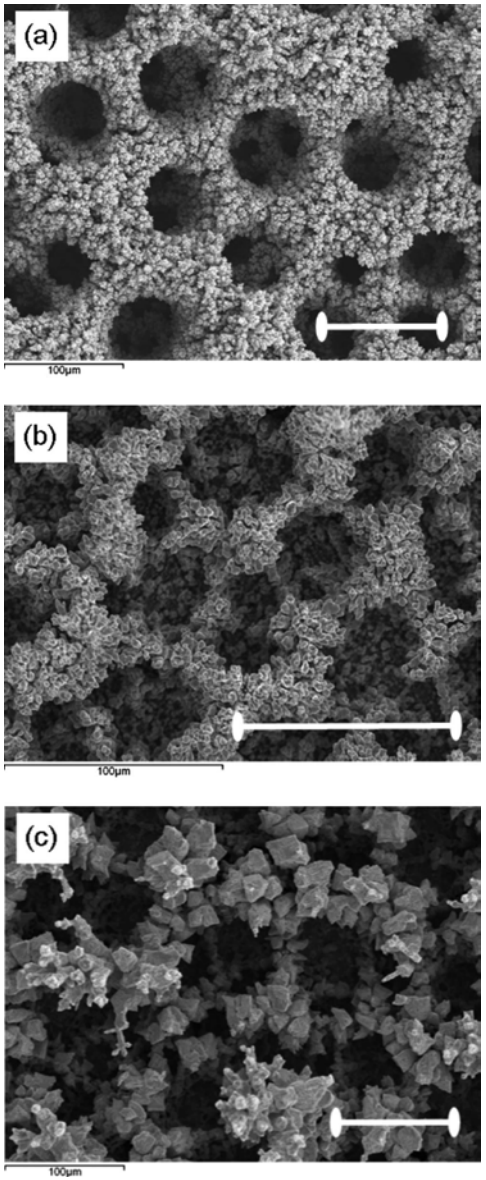
Technical accomplishments:
Tin Electrodeposition in Confined Spaces



Cyclic voltammogram of aqueous Cu:Sn deposition solution



Shin, H.C., Dong J., Liu, M; *Advanced Materials*, 2003, 15, 1610-1614



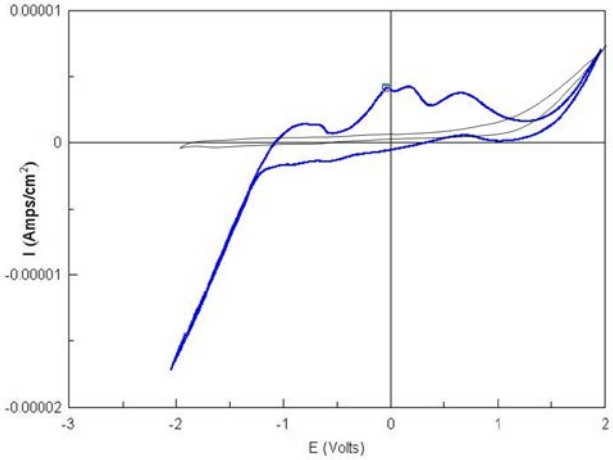
Techniques to make the copper foams and Cu_6Sn_5 porous electrodes foams were developed at Argonne as part of a previous BATT-Anode program and the CEES-EFRC

(a) SEM micrographs of a copper foam, as-grown, (b) sintered copper foam 500°C, and (c) electrodeposited Cu_6Sn_5–Sn film on sintered copper foam. Scale bar = 100 um.

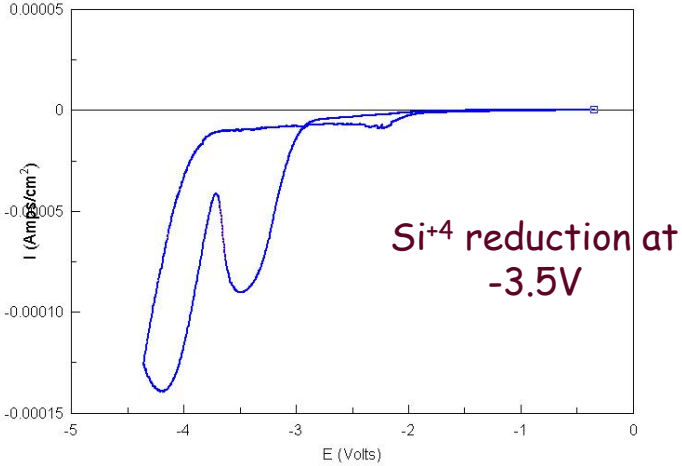
Technical accomplishments:

Silicon Electrodeposition in Confined Spaces

$Na_4[Si_4] \longrightarrow 4Si + 4\,Na^+ + 4\,e^-$



$SiCl_4 + 4e^- \longrightarrow Si + 4Cl^-$



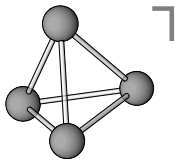
deposition: Si anion vs Si cation

<u>Synthesis</u>: 4 Na + 4 Si → $Na_4[Si_4]$

Sealed Ta tube, 500 C / 12 hrs.

Solvent: glyme

Notes: Very low solubility



<u>Synthesis</u>: $SiCl_4$

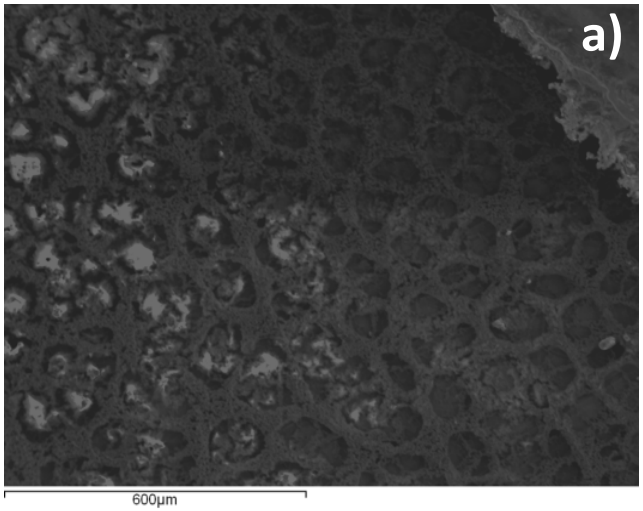
(Sigma-Aldrich, 99.99%)

Solvent: PC

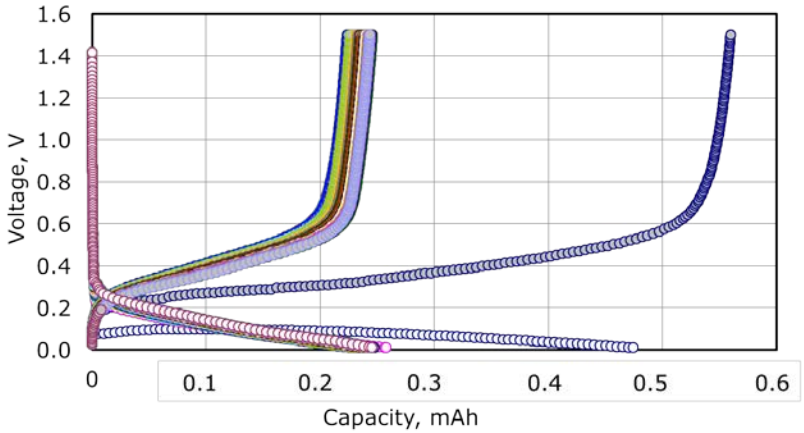
Solubility: Moderate

Technical accomplishments:

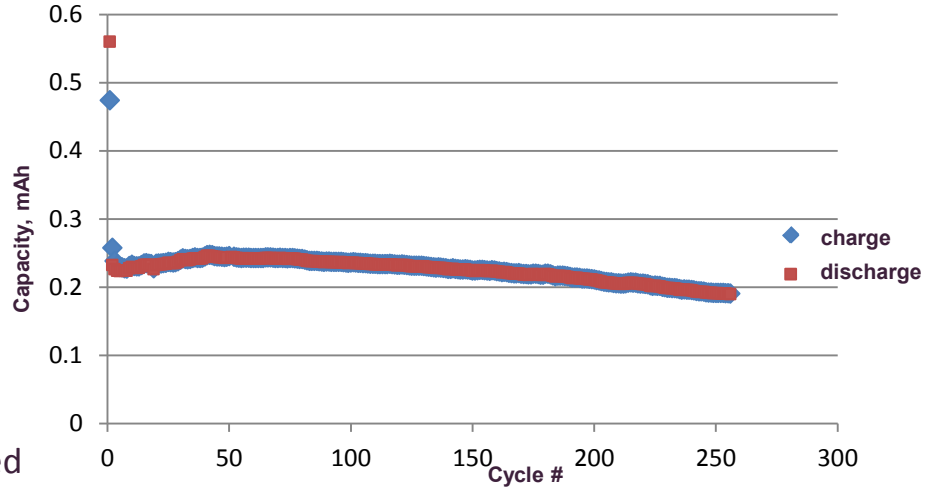
Silicon Electrodeposition in Confined Spaces



SEM micrographs of electrodeposited silicon a) on synthesized copper foam, pore sizes ~ 50µm b) on commercial foam (calendared) , pore sizes ~ 300µm



Voltage profile for electrodeposited silicon electrodes (commercial foam) at a constant current of 50µA. First cycle activity indicates~ 0.17mg

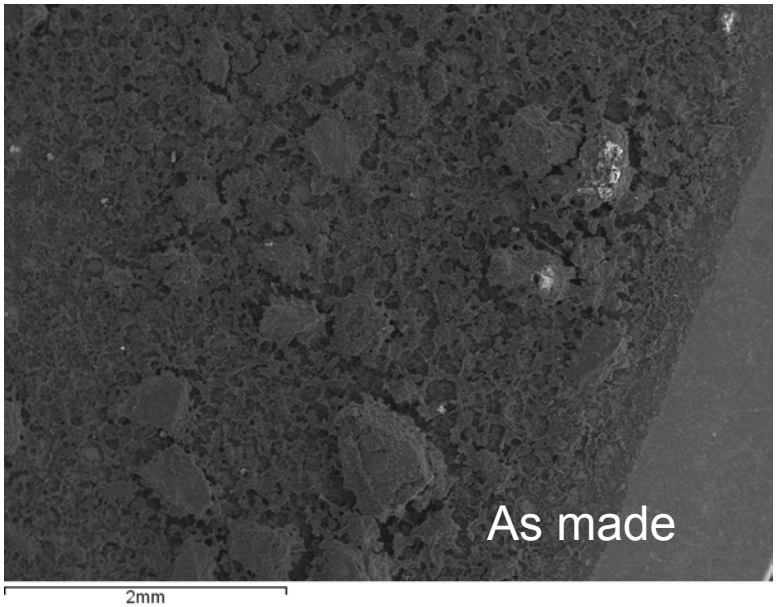


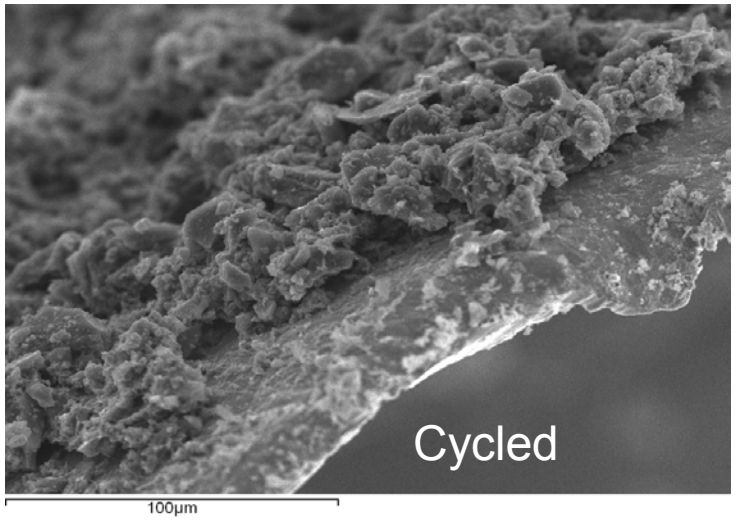
Cycle performance of electrodeposited silicon (1.5V-10mV vs Li) on commercial copper foam

Technical accomplishments:

Metallic Copper Binders – Simpler Electrodes

Deduce the effect of the polymeric binder on the electrical resistance of the electrode while cycling



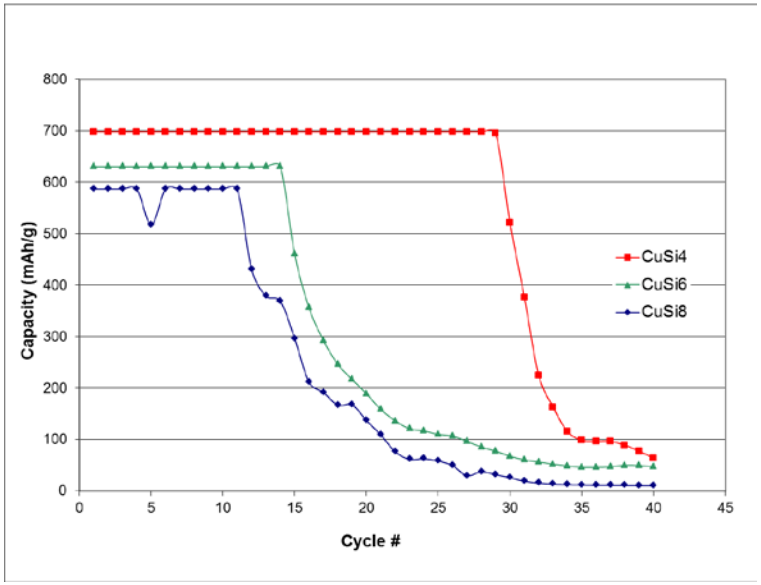


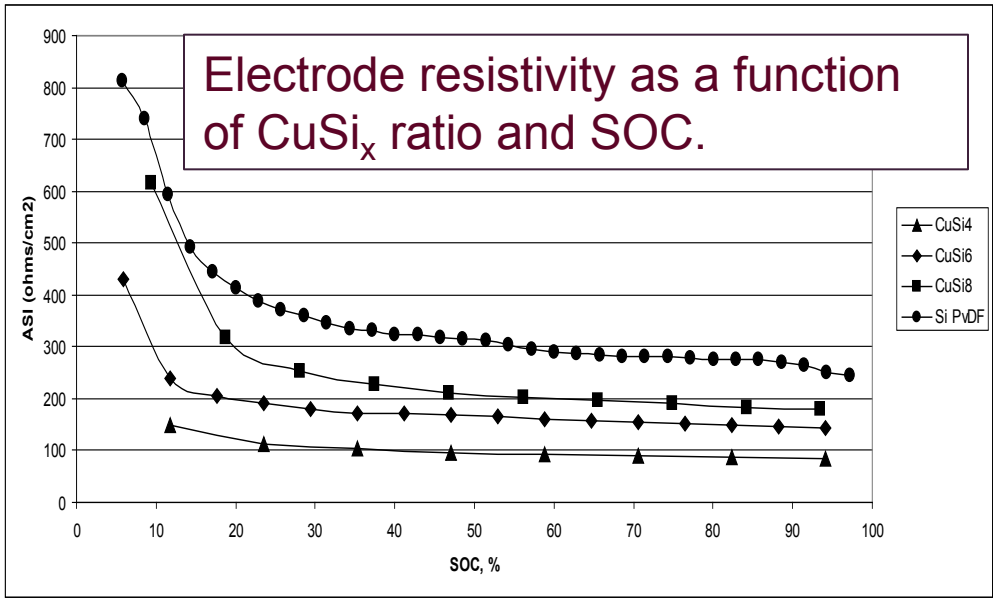
$$Si + Cu(NO_3)_2 \xrightarrow[\text{water}]{H_2C=O} CuSi_x \ (x = 4,6,8)$$

- Cast a mixture of $CuSi_x$ in an 24% PVA/NMP solution onto Cu foil
- Heat laminate > 400 C to burn out PVA
- Heat laminate 500 ≤ x ≤ 700C to anneal to Cu foil backing

Technical accomplishments:

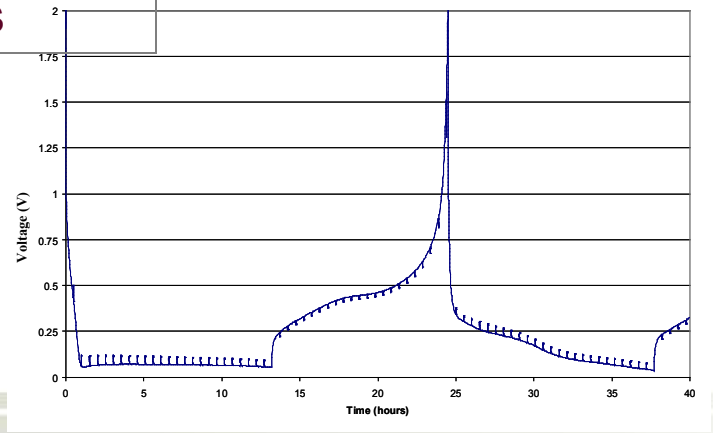
Metallic Copper Binders – Simpler Electrodes





Electrode resistivity as a function of $CuSi_x$ ratio and SOC.

Cycling of selected capacity limited $CuSi_x$ electrodes

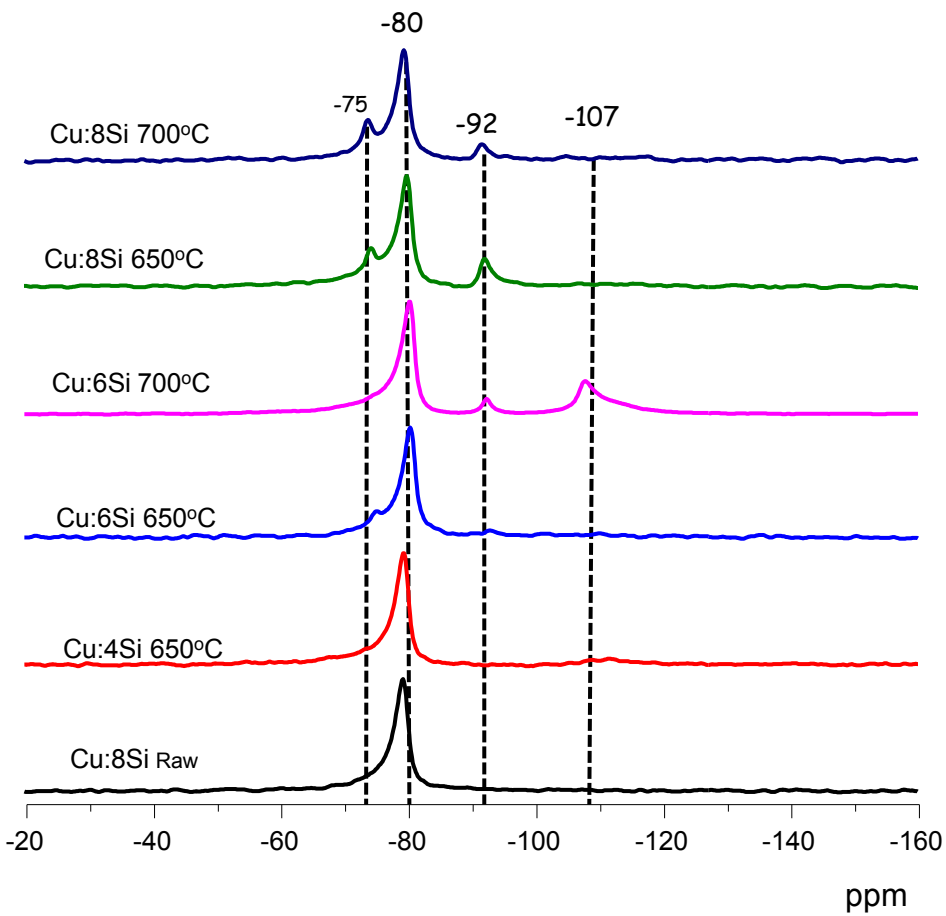


Cycling profile of a $CuSi_4$ electrode

Technical accomplishments:

Metallic Copper Binders – Simpler Electrodes

^{29}Si MAS NMR



^{29}Si MAS NMR of $CuSi_x$ samples annealed at varying temperatures

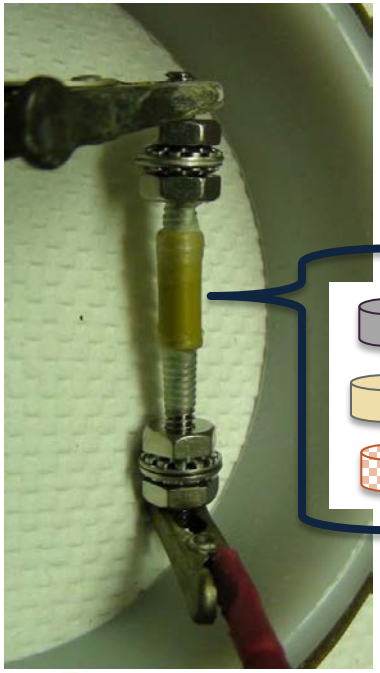
^{29}Si NMR is much more sensitive to interfacial phase formation than bulk techniques such as powder XRD.

The best electrodes (cycling stability) appear to have none or a minimal amount of Cu_3Si intermetallic formation and variation of silicon local environment.

This is consistent with VLS-derived Si nanotubes where the intermetallic glue formed is localized at the base of the electrode.

Technical accomplishments:
Tomography – Looking inside the Electrode

- Unlike SEM and TEM, tomography sheds light on material behavior in sub-surface positions of porous electrodes, while cycling in realistic battery environments. [1]
- Severe volume changes in silicon and tin can be observed.
- Changes in porosity can be determined.
- Thicker electrodes are currently being investigated as a means to lower battery costs. [2] Tomography will be useful in evaluating depth-dependent material utilization and failure modes.



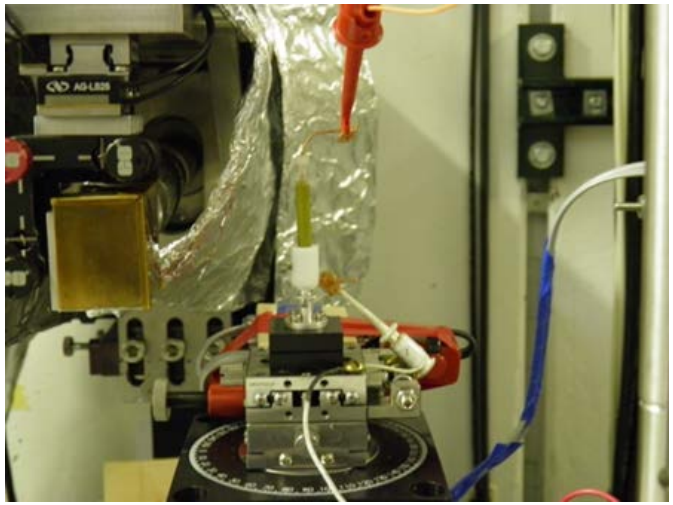
Cells are constructed in miniaturized form within a Torlon® tube (X-ray transparent) and with flattened stainless steel screw leads.

Lithium (2 mm diameter)

Glass fiber separator (3 mm)

Sn / Si electrode (2 mm)

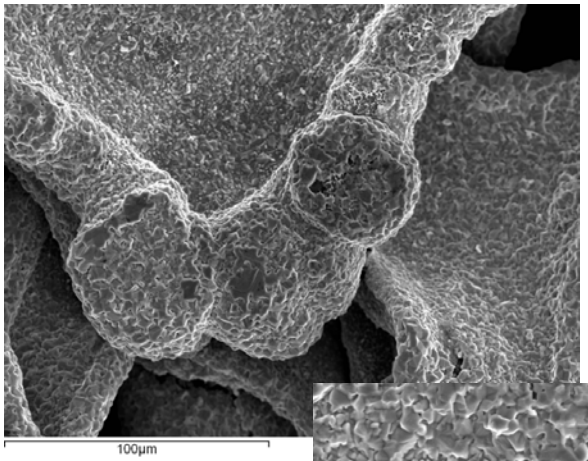
Cell ready for testing at Sector 2-BM at the APS

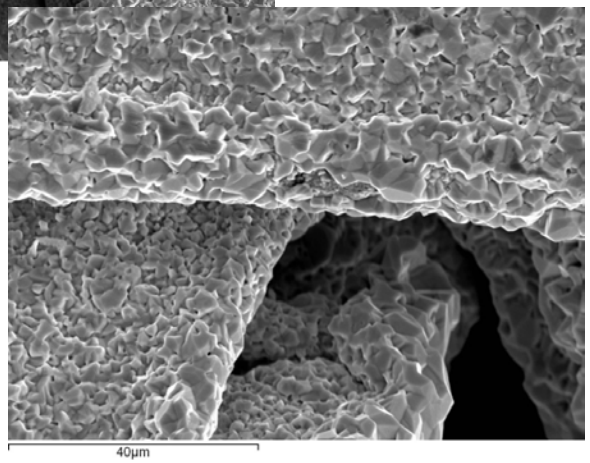


[1] P. Shearing, Y. Wu, S.J. Harris, N. Brandon, *The Electrochemical Society- Interface* (Fall 2011) 43-47.
[2] J.S. Wang, P. Liu, E. Sherman, M. Verbrugge, H. Tataria, *J. Power Sources*, 196 (2011) 8714-8718.

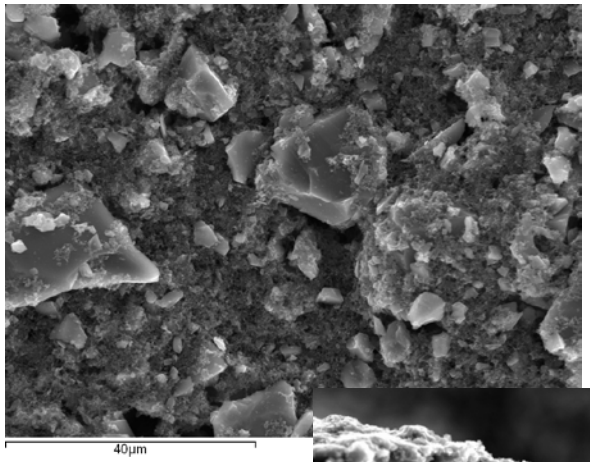
Technical accomplishments:

Tomography – Looking inside the Electrode





Binder-free Sn on Cu foil

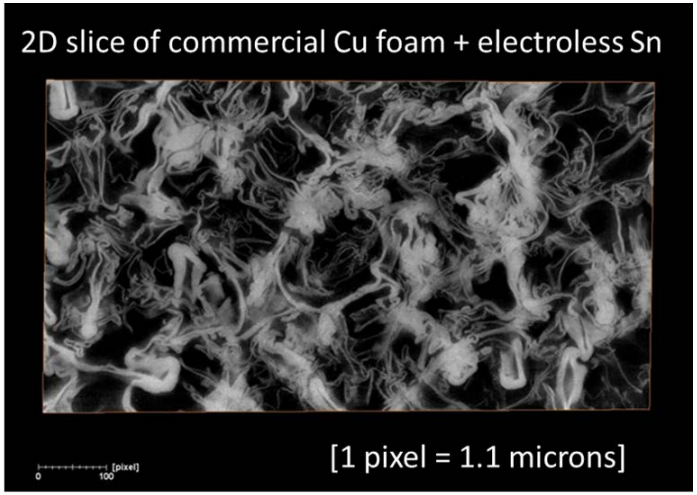


Silicon particles (Aldrich) laminated on Cu foil

- Electrodes being evaluated have included electrolessly deposited tin on commercial copper foams and silicon particles laminated with 70% active material on copper foil.
- 2 mm punches of both electrodes can be cycled at 10- 20 µA and exhibit typical electrochemical behavior of Sn and Si.

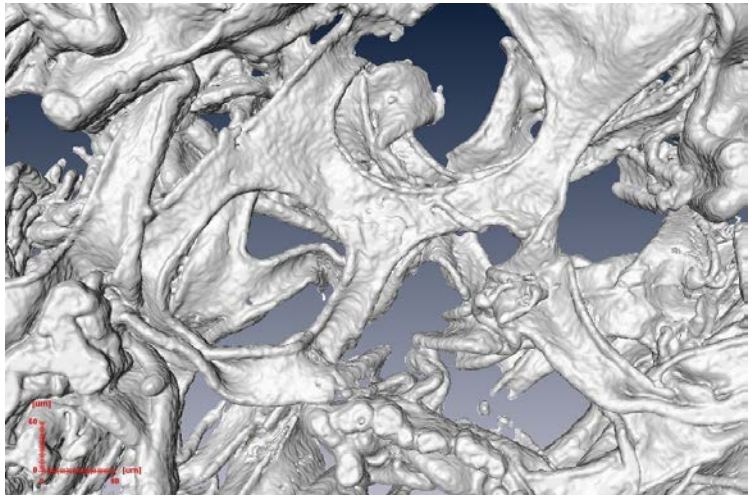
Technical accomplishments:

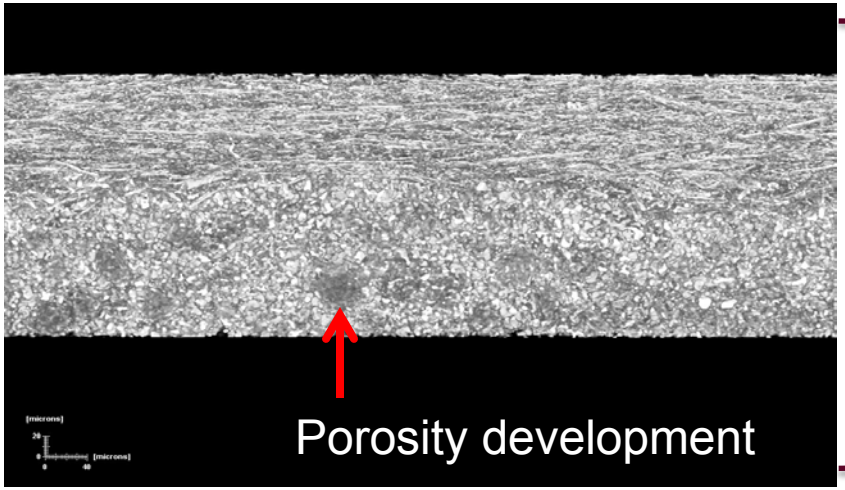
Tomography – Looking inside the Electrode



3D reconstruction →

Surface area : Volume changes as a function of electrode depth (distance from counter electrode) are being analyzed to determine the effects of unequal Li^+ diffusion to electrode regions.





- Silicon laminates have been imaged before and after cycling.
- Particle pulverization and evolution in porosity has been observed.
- Electrolyte degradation tests show no major changes in electrolyte due to beam, thus *in situ* experiments are underway.

Collaboration and Coordination with Other Institutions

- **Partners**
  - BATT Anode Diagnostics
    - Yi Cui (Stanford, SLAC)
    - Gao Liu (LBNL)
  - BATT Anode Tin Electrodes
    - Stan Whittingham (U Binghamton, New York)
    - Mike Thackeray (ANL)
  - User Facilities:
    - John Muntean (CSE-NMR Center)
    - R. Winarski, X. Xiao – APS, Tomography
    - Russell Cook (Electron Microscopy Center)

Future Work

- Methodology development:
  - Utilize new NMR capabilities to improve understanding of the microstructure of Si-based electrodes.
  - Collaborate with Advanced Photon Source staff to improve the data resolution.
  - Optimize synthetic techniques to improve sample quality and investigate morphological variables on the system

- Silicon-based electrodes
  - Continue efforts to use X-Ray tomography to study the internal properties of electrodes. Extend work to the all-inorganic electrodes developed.
  - Work with BATT-Anode group partners to better understand capacity fade in a variety of electrode environments.

Summary

We have initiated a combined synthesis – characterization approach to better understand the effect of cycling on a silicon-based lithium-ion battery electrode.

- Synthesis
  - Conventional bulk microcrystalline silicon lithium-ion battery electrodes have been compared using X-Ray tomography to ones based on silicon nanoparticles.
  - We have developed a new all-inorganic Si lithium-ion battery electrode that uses metallic Cu as the binder.
    - This new electrode type has 75% lower resistivity than a conventional electrode
    - Has similar cycle life to PVdF electrodes at 120% volume expansion.
- Characterization
  - We have initiated collaboration with microtomography development beamline scientists at the Advanced photon Source at Argonne.
    - Developed a cell fixture, sample preparation, and electrochemical characterization techniques.
    - Initiated methods to selectively deposit Si on a tungsten sample tip.
  - Utilized ^{29}Si NMR techniques combined with powder X-Ray diffraction to better understand the Cu-Si phase diagram and the phases formed at the interface of Cu-Si lithium-ion battery electrodes.