# Novel Anode Materials

**Jack Vaughey**

**Fulya Dogan, Lynn Trahey**

Chemical Sciences and Engineering Division

Argonne National Laboratory

Argonne, IL 60439

DOE Office of Vehicle Technologies Annual Merit Review

May 13 - 17, 2013

*Project Id: ES143*

# Overview

**Timeline**

- Start: October, 2010
- End: September, 2014
- Percent complete: 50%

**Budget**

- FY12: $400K
- FY13: $400K

**Barriers**

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

**Partners**

- Chris Johnson, Baris Key, Aude Hubaud (ANL)
- Mike Thackeray, CEES-EFRC
- Dave Schroeder (NIU)

**Collaborations**

- Fikile Brushett (MIT)
- X. Xiao (APS microtomography)
- Yi Cui (Stanford)
- Russell Cook (Electron Microscopy Center)
- Duminda Sanjeewa, Shiou-Jyh Hwu (Clemson)

# 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:

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

# Milestones

- Identify the thickness limits of electrodeposited silicon thin film electrode structures before spalling is observed (*completed*).
- Identify and demonstrate methodologies to incorporate higher levels (> 2 $mAh/cm^2$) of active Si into three-dimensional electrode structures (Sep 2013).
- Demonstrate an in-situ probe that can be used to correlate performance with sample preparation of an electrodeposited electrode. (Sept 2013).
- Synthesize, characterize, and evaluate the role of polymeric film coatings in increasing the cycle life of Si-based electrodes (Sept 2013).

# Approach/Strategy

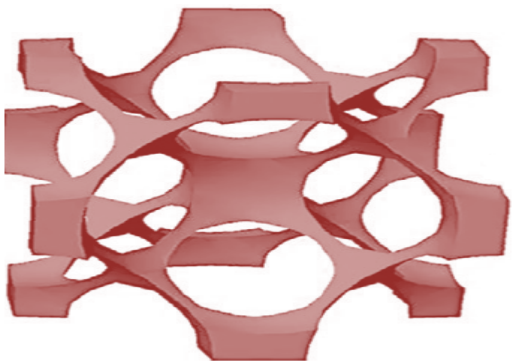
***APPROACH:*** Develop a detailed understanding of how *silicon-based electrodes* operate when constrained by other constituents, components, and active materials utilizing characterization tools that cross various length scales.

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

- Electrode Formulation
  - Bulk Electrodes
    - 70% Si - 20% PVdF binder - 10% AB
    - 70% Si - 30% Cu binder
  - Thin Film Electrodes
    - Si electrodeposition
    - Sn electrodeposition
    - Sn electroless deposition

- Characterization
  - X-Ray tomography studies of active electrodes
    - Complex Si-based electrodes as a function of cycling
    - Sn thin-film electrodes on cycling
  - Cycling Properties
    - Effect of binders on rate capability
    - $^{29}Si$ NMR studies of silicon/binder interactions
    - $^{29}Si$ NMR studies to identify surface functionality of electrodeposited films

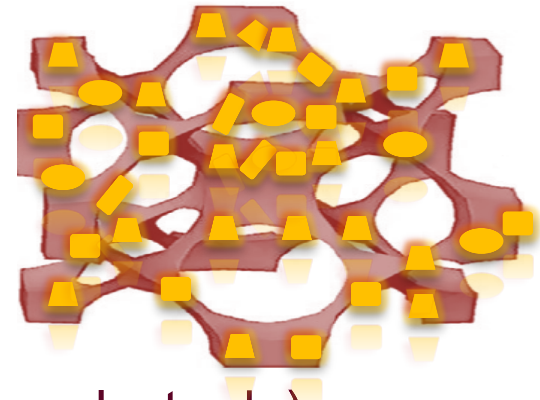
# Technical accomplishments: Silicon Electrodeposition in Confined Spaces



copper foam

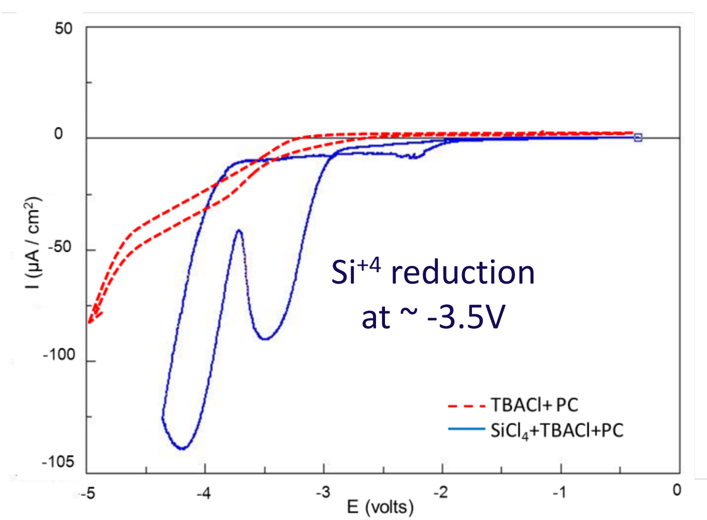
Silicon electrodeposition

1M $SiCl_4$, 0.5M TBACl, PC (0.5M TEACl)

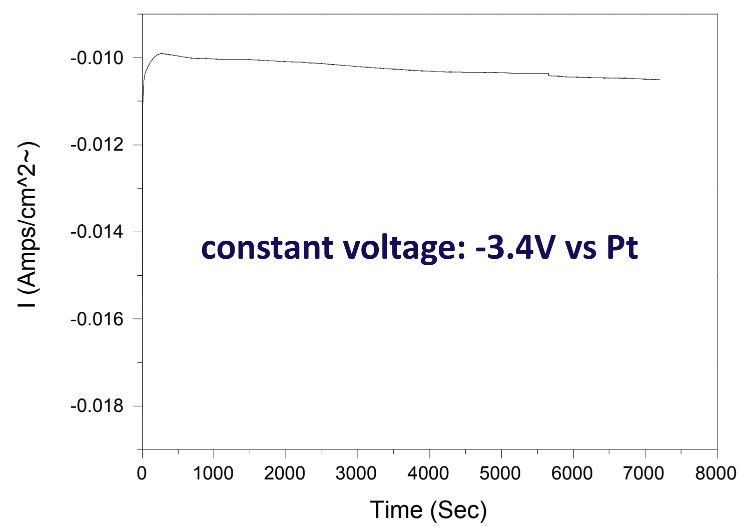


$$SiCl_4 + 4e^- \rightarrow \boxed{Si} + 4Cl^- \text{ (working electrode)}$$

$$4Cl^- \rightarrow 2\,Cl_2 + 4e^- \text{ (counter electrode)}$$

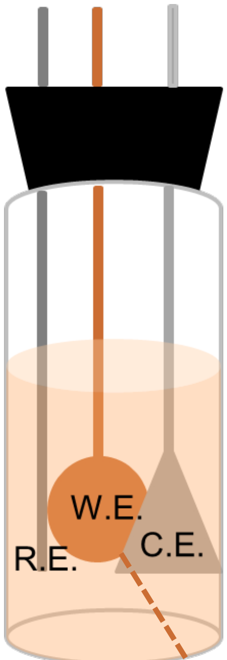



cyclic voltammograms for silicon electrodeposition solutions (with scan rate of 5 mV/s)




Chronoamperogram of electrodeposition of silicon on copper foam (1M $SiCl_4$, 0.5M TBACl solution)

# Technical accomplishments: Silicon Electrodeposition



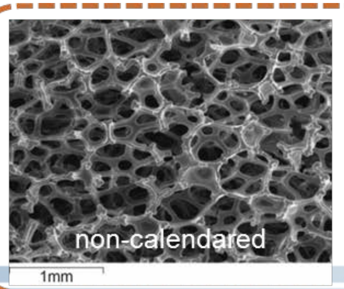

- Silicon was deposited on various thicknesses of copper foams via galvanostatic and potentiostatic electrodeposition.

- Effect of substrate thickness, deposition time, precursor concentration and cation size of supporting electrolyte on deposited silicon content, particle size/ thickness and structure has been studied.
- No oxide formation was observed under inert atmosphere (easily oxidized in contact with air/ oxygen)

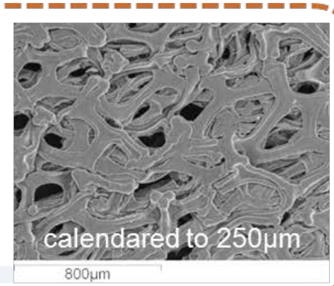
**The average efficiency of electrochemical silicon deposition in $SiCl_4$ solution is ≈ 35%**

side reaction - $SiCl_4 + 2H_2O \rightarrow SiOCl_3 + HCl \rightarrow\rightarrow SiO_2 + 4HCl$

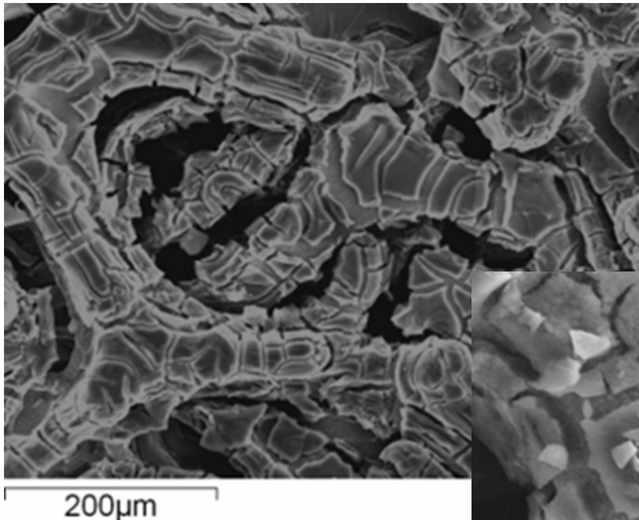
C.E.; Pt mesh,
R.E.; Pt wire,
W.E.; Cu foam



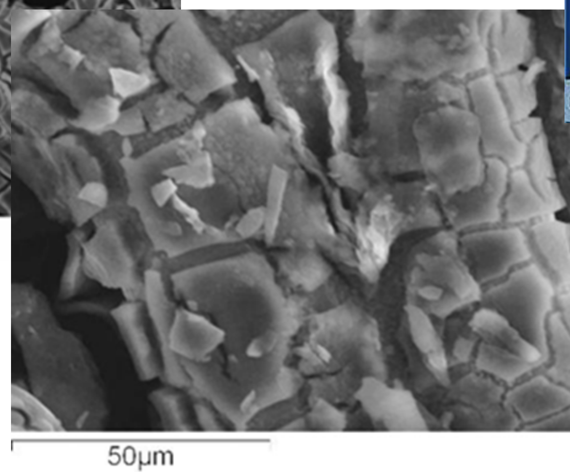

- commercial foams are initially studied
- calendared to various thicknesses

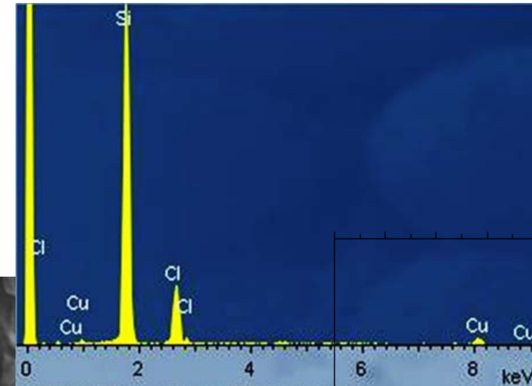


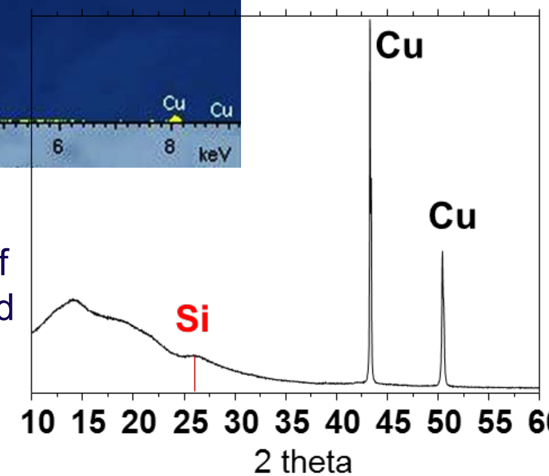
# Technical accomplishments: Silicon Electrodeposition in Confined Spaces




Silicon electrodeposited on copper foams



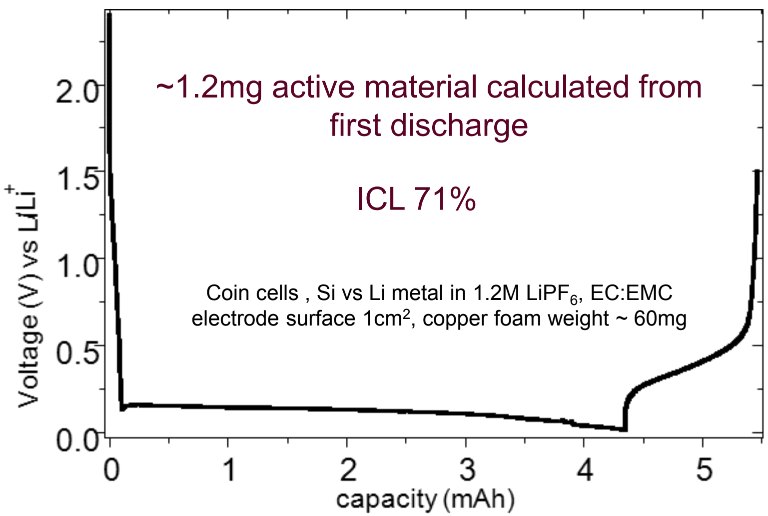



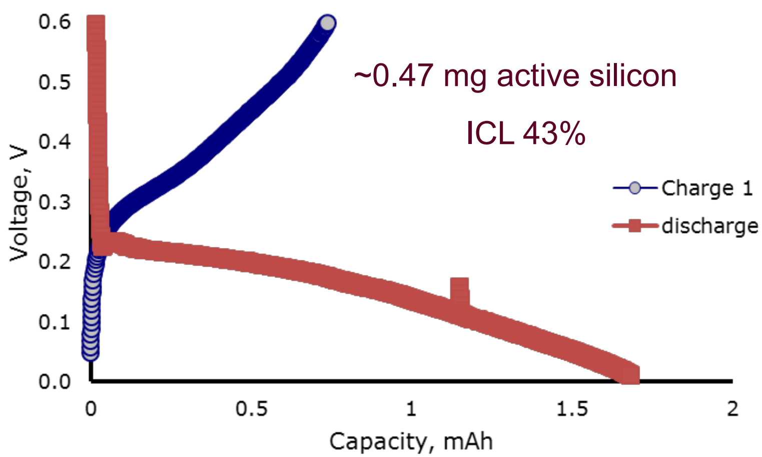

EDX and XRD spectroscopy of electrodeposited silicon

- Up to 2.5 mg active silicon (calculated by first full discharge) was obtained per $cm^2$
- SEM images show non-uniform silicon deposits with plate-like structures with silicon thicknesses of 1.5 – 4 µm
- **The electrodeposited silicon shows semi-crystalline / amorphous structure and the cation size of supporting electrolyte affects long range order**

# Technical accomplishments: Effect of Supporting Salts



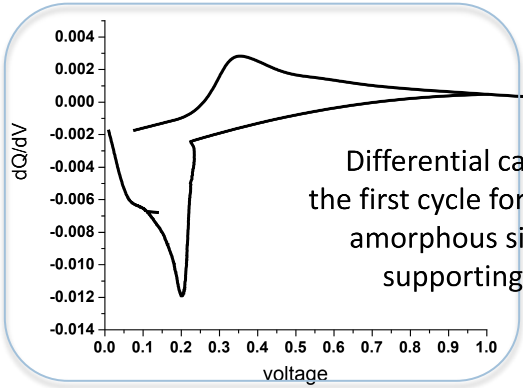

1[st] cycle voltage profile for electrodeposited silicon **TBACl** as supporting electrolyte




1[st] cycle voltage profile for electrodeposited silicon **TEACl** as supporting electrolyte

## TBACl as supporting electrolyte

- Electrochemical characterization shows crystalline silicon character with first discharge (lithiation)
- Irreversible Capacity Loss (ICL) for the first cycle varies between 65- 80% and can be correlated with the silicon loading level

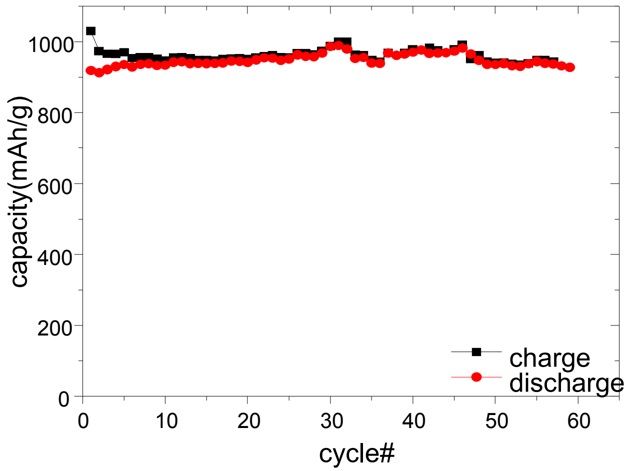


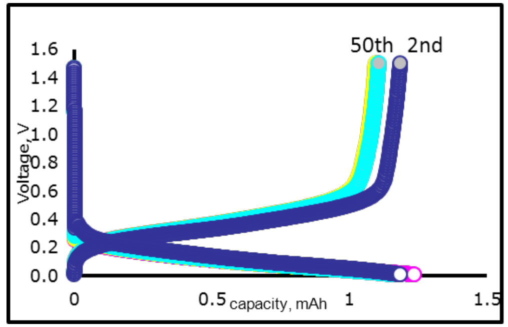

Differential capacity curve of the first cycle for electrodeposited amorphous silicon (TEACl as supporting electrolyte)

## TEACl as supporting electrolyte

- Electrochemical characterization shows amorphous silicon character with first discharge
- Irreversible Capacity Loss (ICL) for the first cycle varies between 40-55% and can be correlated with the silicon loading level
- Higher retention for the first cycle with amorphous electrodeposited silicon

# Technical accomplishments: Electrochemical Performance



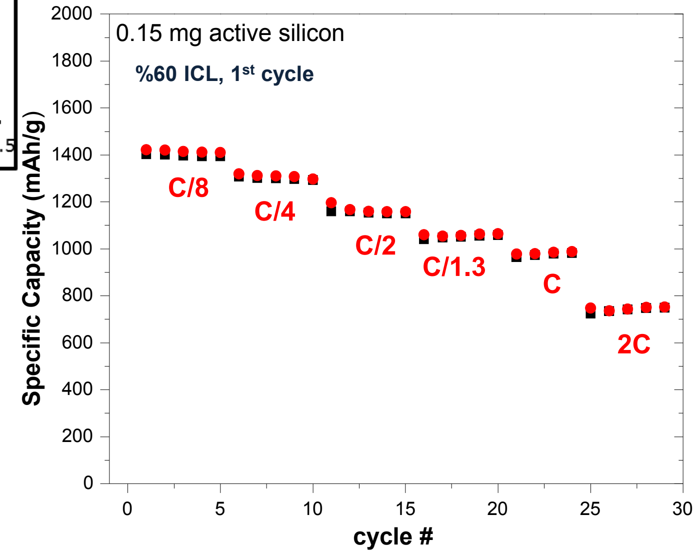



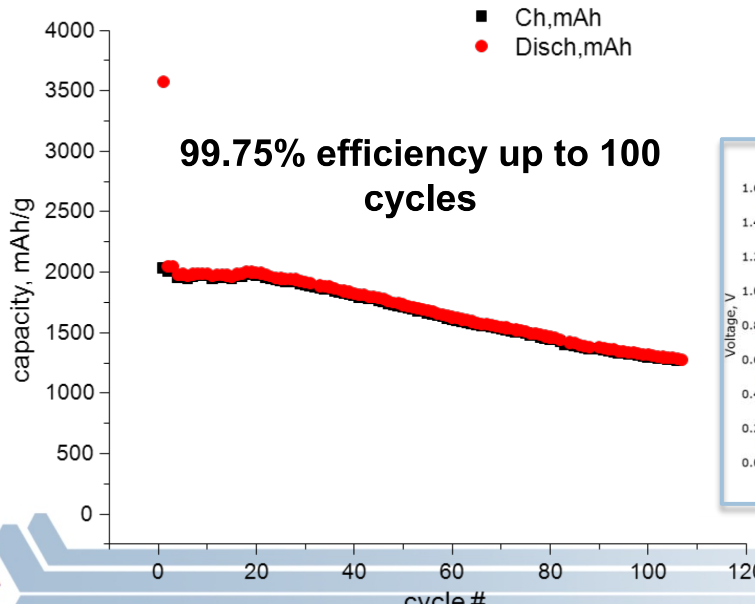

Voltage profile for electrodeposited silicon electrode

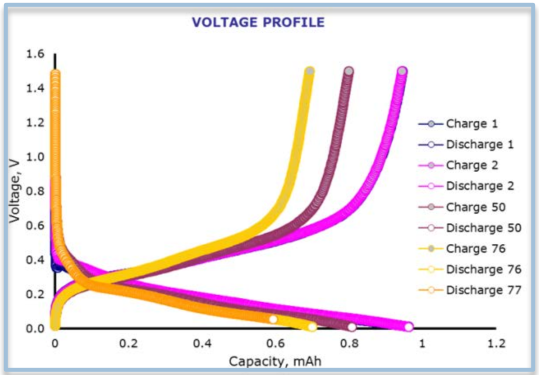
Cycle performance of electrodeposited silicon

prepared with TBACl (↑) TEACl (↓)

Cycling performance of electrodeposited silicon at various rates after 15 cycles

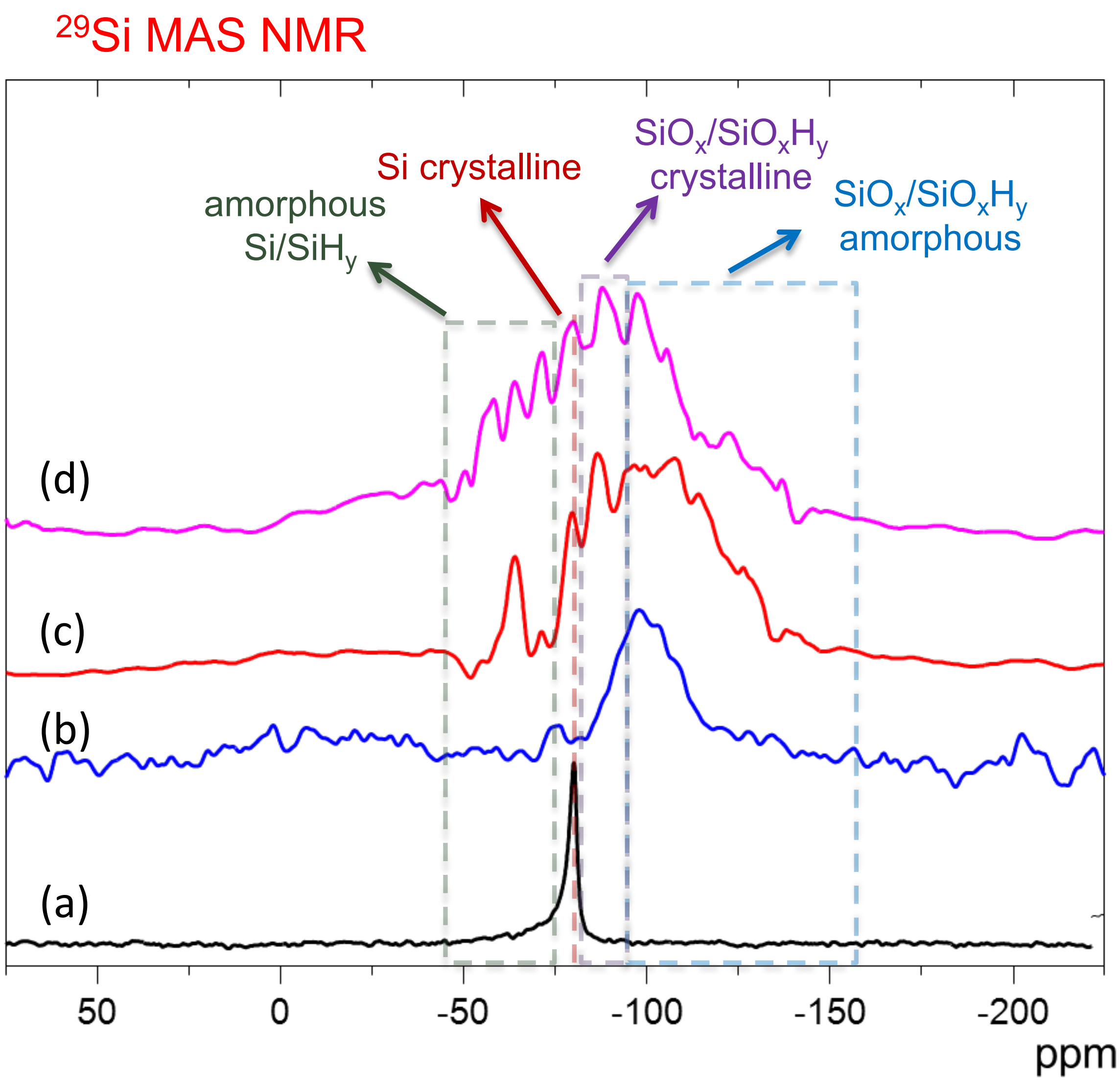



Capacities up to 2100 mAh/g with amorphous electrodeposited silicon

# Technical accomplishments: $^{29}$Si NMR Studies

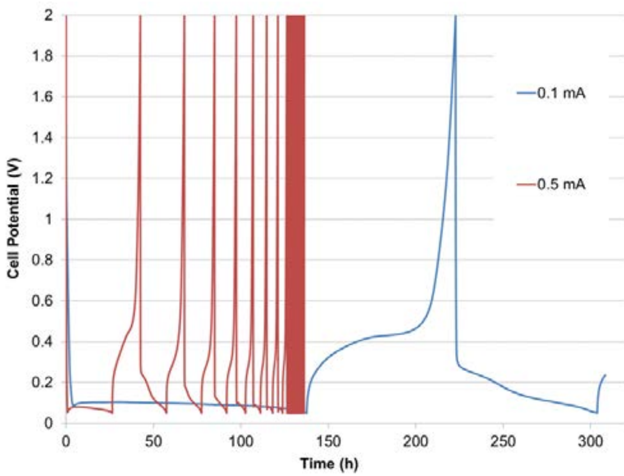


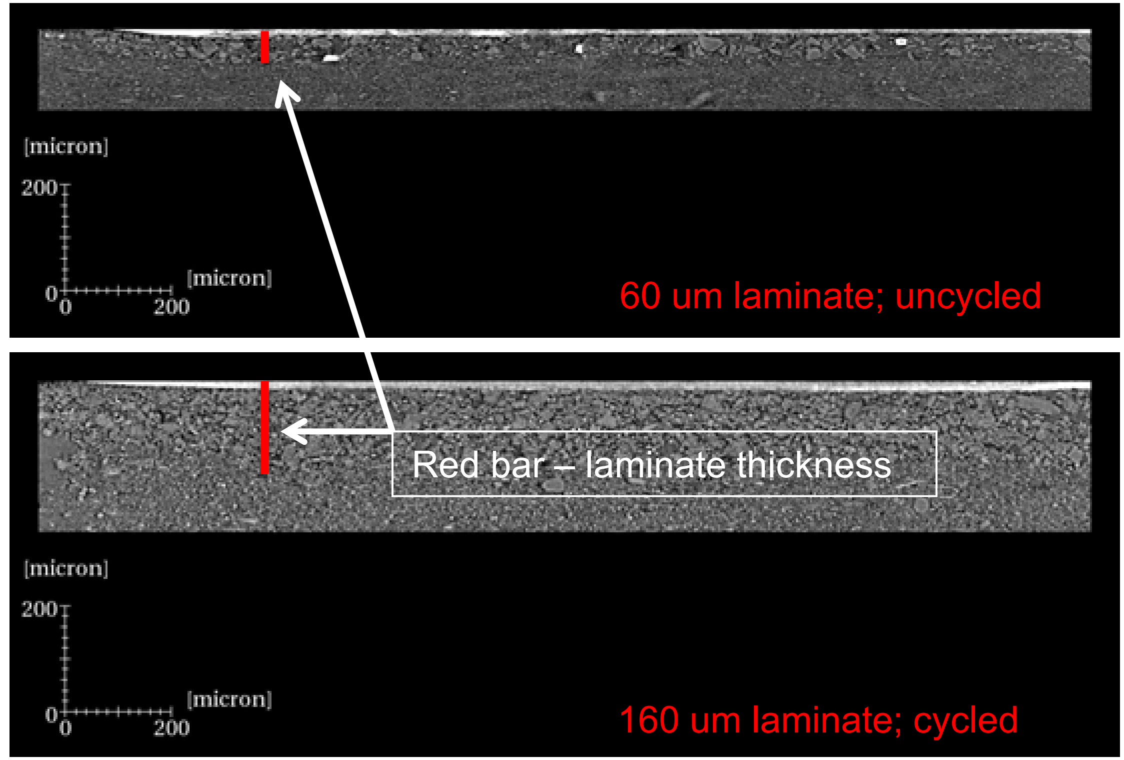

**$^{29}$Si MAS NMR** a) silicon powder b) electrodeposited silicon (oxidized) c) electrodeposited silicon (with TBACl) d) electrodeposited silicon (with TEACl)

## Characterization

- A $^{29}$Si MAS NMR local characterization study has been initiated on electrodeposited silicon on copper foams
- Combination of various MAS NMR techniques will be used for the assignment of silicon environment observed.

# Tomography of silicon laminate electrodes

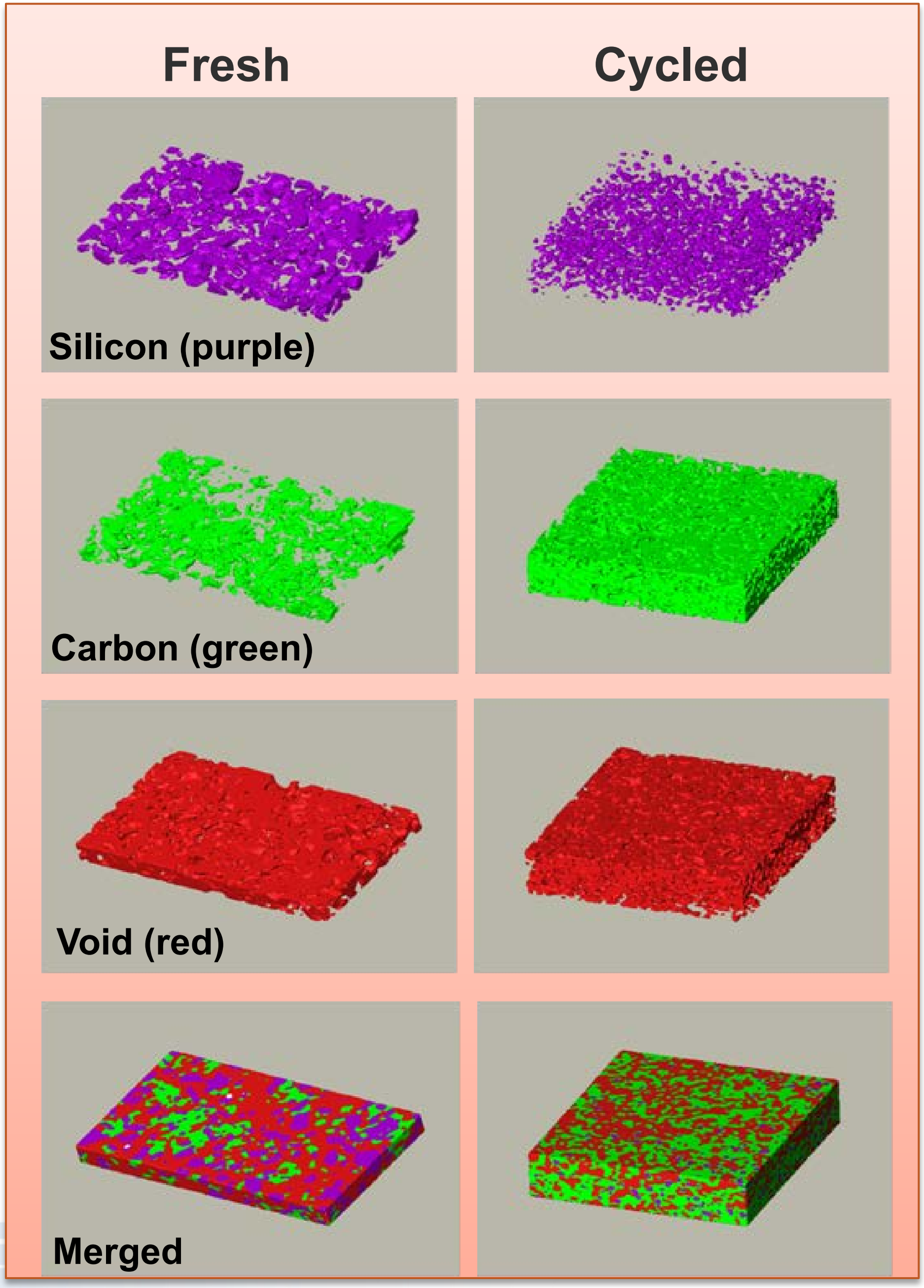



- Silicon laminates (Aldrich, 325 mesh), with its wide array of particle sizes, were used to establish the ability to distinguish silicon from carbon, binder, and electrolyte using X-Ray tomography.
- The laminates were cycled in coin cells offline at different rates. Fresh vs. cycled laminates were compared using 50 keV monochromatic X-rays in *ex situ* tomography (2-BM at APS).
- Qualitative comparison of the silicon laminate thickness is straightforward. Uncycled laminates were ~60 µm thick and cycled laminates ~160 µm (see red bars above). Laminate cycled to cell death.

# Seeing Inside a Silicon Laminate using Tomography

- To enhance the contrast of Si particles against carbon we take advantage of partial coherence from synchrotron radiation source.
- Propagation phase contrast is therefore rendering Si particles from the surrounding materials.
- Using Paganin phase retrieval algorithm, semi-quantitative phase maps can be obtained in which Si particles can be easily distinguished from the binder material matrix.
- Porosity and tortuosity calculations on silicon laminates are currently underway.
- The ongoing APS upgrade will increase the resolution (currently 1 µm) and decrease the time per data collection, reducing beam damage to electrolyte during *in situ* experiments.




*Right:* Silicon (purple), Carbon (green), Void (red), and merged components of fresh and cycled laminates.

# Collaborations and Coordination with Other Institutions

**Tomography Studies**:

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

**Silicon Electrode Formulation:**

- Duminda Sanjeewa, Shiou-Jyh Hwu (Clemson)
- Joseph Kubal (ANL - CFF)
- Dave Schroeder (NIU)
- Russell Cook (ANL / NST - Electron Microscopy Center)

# Future Work

- Examine the effect of different supporting electrolyte/solvent combinations on the formation of local silicon environments - TEM evaluation with ANL / NST–EMC staff.
- Develop 2D $^{29}Si(H)$ NMR techniques to help correlate silicon local environments and surface functionality with electrochemical performance. Assess role of electrolytes and additives, e.g. FEC.
- Apply tomography techniques developed using in-house electrodes to BATT-Anode silicon standard – with Gao Liu (LBNL).
- Examine effect of substrate surface treatment on deposition film quality and performance – with Dave Schroeder (NIU)

# Summary

- SEM images show non-uniform silicon deposits with plate-like morphology with silicon thicknesses of 1.5 – 4 µm; up to 2.5 mg / $cm^2$ active silicon (by first cycle capacity).

- The cation size of **supporting electrolyte** strongly affects the long range order of the electrodeposited silicon – from semi-crystalline to amorphous – and this has significant implications for the first cycle irreversible capacity losses.

    - TBACl → crystalline silicon character on first discharge w/ a first cycle irreversible capacity loss (ICL) between % 65- 80 and can be correlated with the silicon loading level

    - TEACl → amorphous silicon character with first discharge w/ a first cycle irreversible capacity loss (ICL) between between %40-%55 and can be correlated with the silicon loading level. 99.8 % capacity retention after first cycle.

    - $^{29}Si$ MAS NMR has shown that the countercation in the supporting electrolyte salt has a tremendous effect on the electrodeposited silicon surface functionality. Preliminary assignments: TBACl – more oxygen rich surface, TEACl - more proton-rich surface.

- X-Ray tomography studies show the extent silicon particle pulverization happens at the electrode surface and 'moves' through the laminate with continued cycling.