

Nanostructured Materials as Anodes

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Project ID #
es_32_whittingham

Timeline

- Project start date: 06-01-2007
- Project end date: 05-31-2010
- Percent complete: Continuing

Budget

- Total project funding
 - DOE share: 100% \$
 - Contractor share: Personnel
- Funding received
 - FY08: 79k\$
 - FY09: 125k\$
- Funding requested
 - FY10: 130k\$

Barriers

- Barriers addressed
 - Cost
 - Safety, and
 - Volumetric capacity limitations of lithium-ion batteries

Partners

- SUNY Stony Brook, ANL,
- Primet, and other companies

- To replace the presently used carbon anodes
 - with safer materials that will be compatible with lower cost manganese oxide and phosphate cathodes and the associated electrolyte.
 - with materials having higher volumetric energy densities

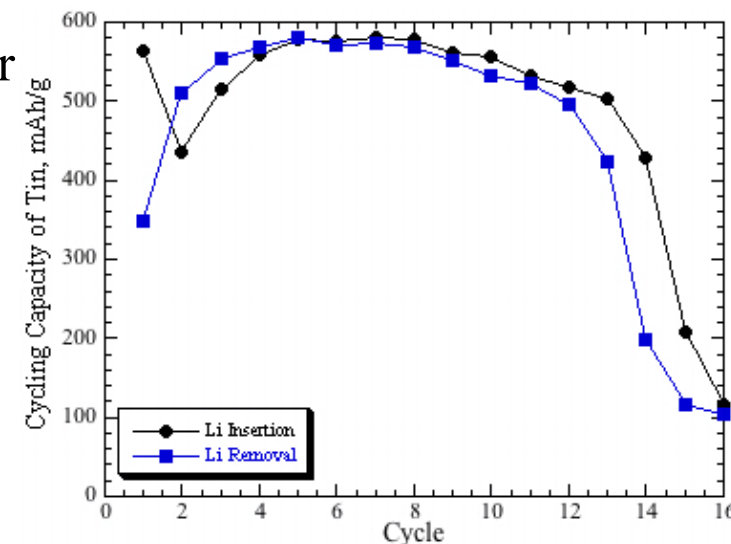


- a) Determine and understand impact of depth of cycling on capacity fade (HEV *vs.* EV) for both crystalline and amorphous Sn.
 - Feb. 2009 - **Nogo** on bulk crystalline tin even at low depths
 - Feb. 2009 – **Go** on nano amorphous tin
- b) Identify the structural and surface changes of Sn anodes during cycling.
 - Continuing with LBNL (R. Kostecki)
- c) Explore nano-size Sn/Si alloys and metal oxides to identify their cycling characteristics.
 - **Go** on all nano-sized materials, including conducting $\text{Li}_4\text{Ti}_5\text{O}_{12}$ – Feb. 2009
- d) Explore Co-free alloys.
 - Continuing

Approach to Replacing Carbon Anode

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- Explore, synthesize, characterize and develop inexpensive materials, that
 - Have a potential around 500 mV above pure Li
 - Have a higher volumetric capacity than carbon
- Compare both bulk and nanostructures
 - Emphasize tin, in foil form and as **nanostructures**
 - Look at nano-sized oxides
 - We reported on manganese oxide spinel last year
 - Cycle well
 - Extended to resistive titanium spinel



Technical Accomplishments: Barriers being Addressed

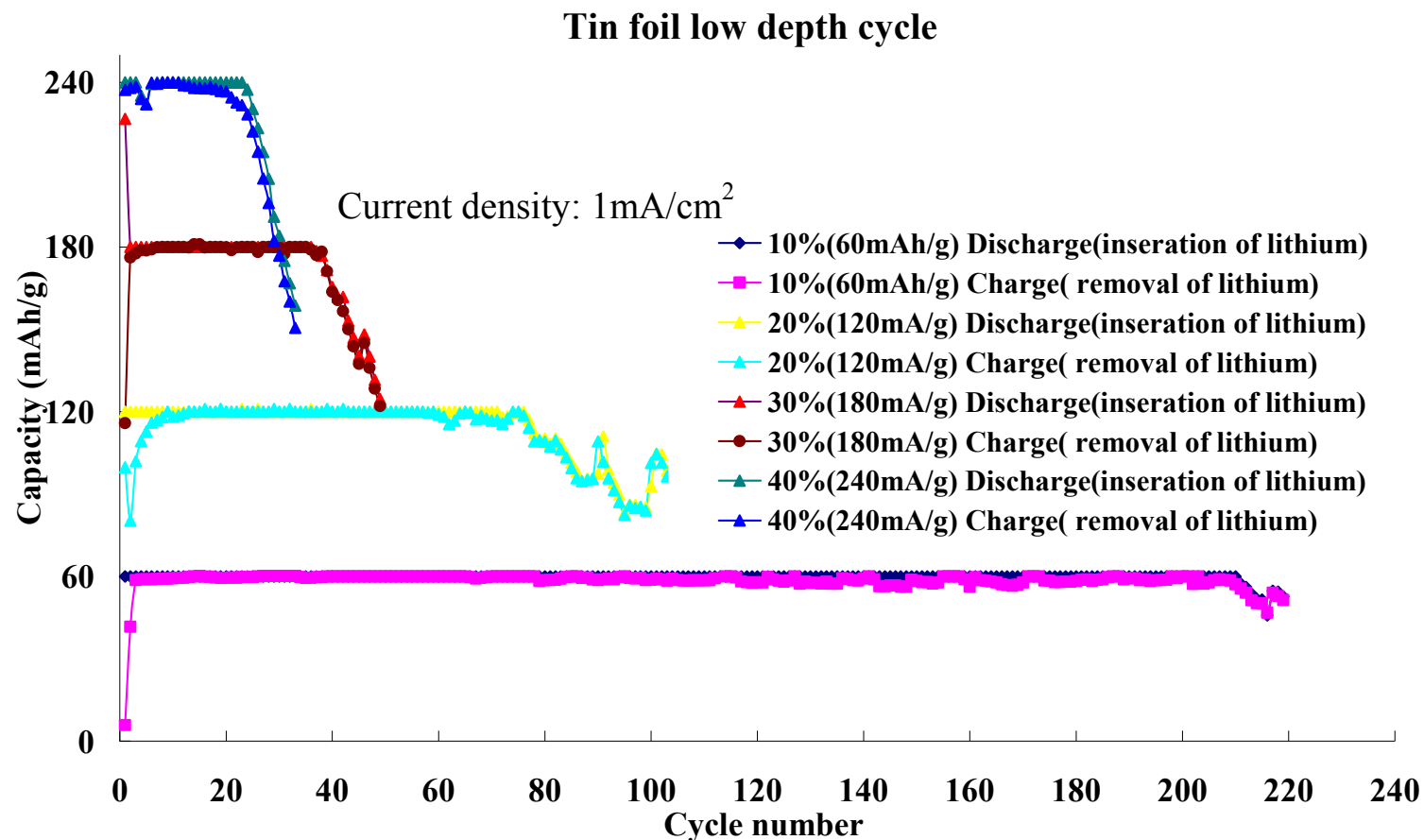
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- Replace the carbon anode presently used
 - Low **volumetric** energy density
 - Unsafe at high charge rates
 - Possibly plate out lithium metal, short out the cell
 - + **But, expands little and forms a coherent protective SEI layer**
 - + **Cycles well and accepted in market**
- Safer and lower cost materials
 - Higher **volumetric** energy density
 - Higher voltage vs lithium, giving safety margin
 - **Volume expansion of most materials on reaction with lithium causes fast electrochemical cycle fade**
 - Tin and other materials lose capacity after 10-12 cycles
 - Find materials that cycle without losing capacity
 - Needs an effective SEI layer

Milestone: Crystalline vs Amorphous Tin

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- Crystalline tin foil
 - Capacity fades even for low-depth cycling
 - About 10 - 20 deep cycle equivalents

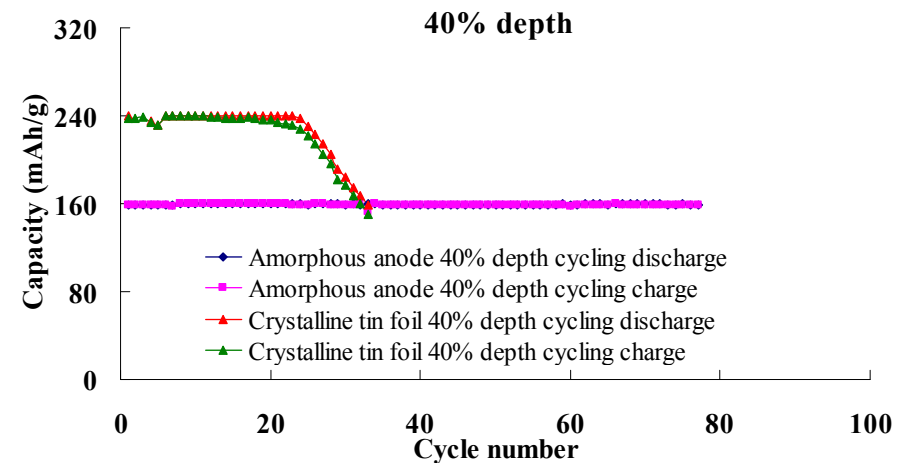
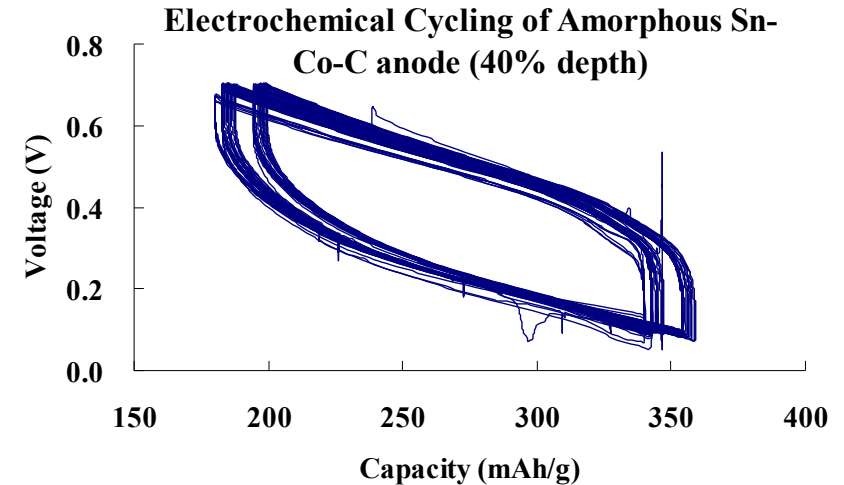


Amorphous Tin cycles well at 40% DoD

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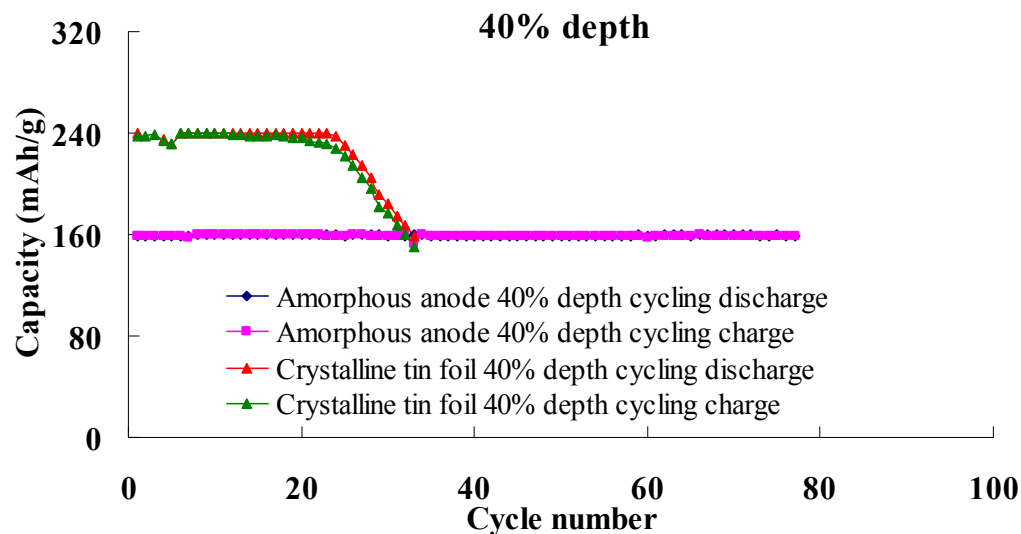
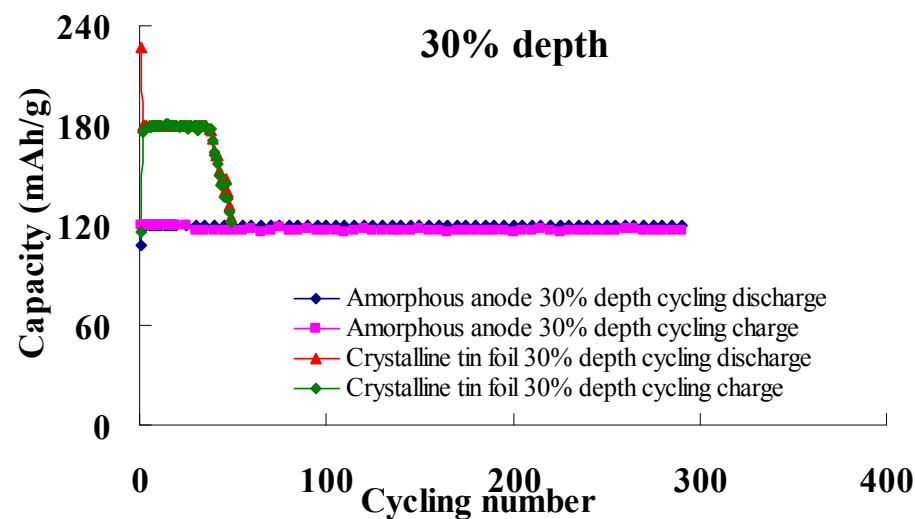
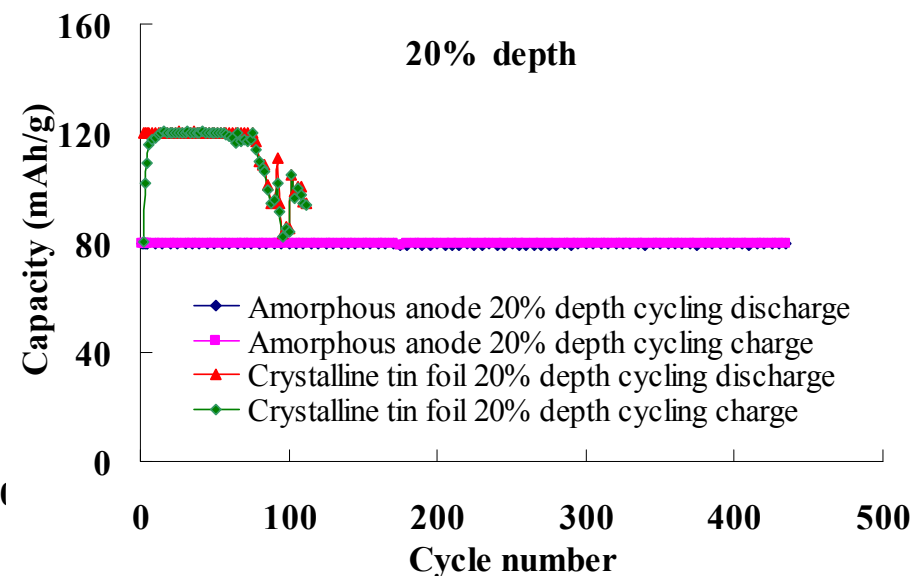
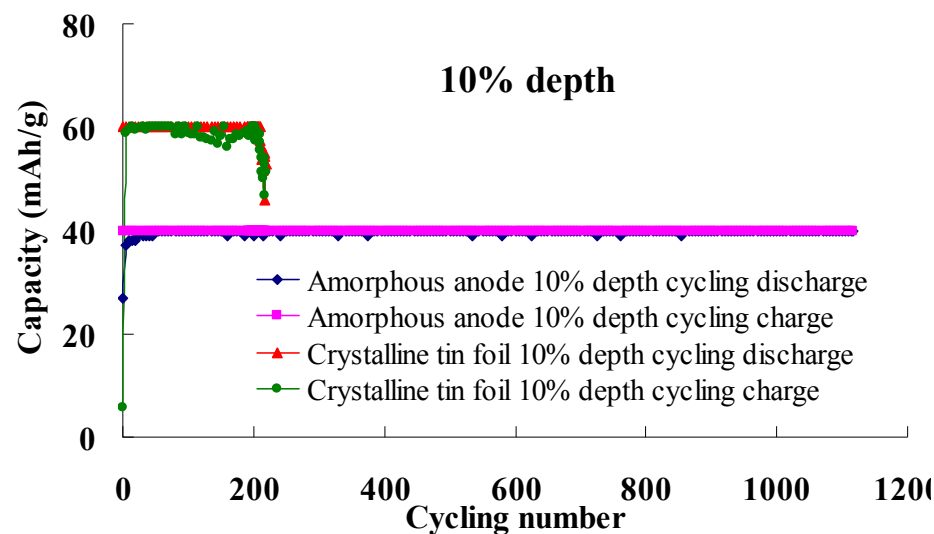
Nano-amorphous tin shows:

- Smooth cycling curve
 - No two-phase regions
- No loss of capacity on cycling



Nano-Amorphous Tin cycles well at all DoD

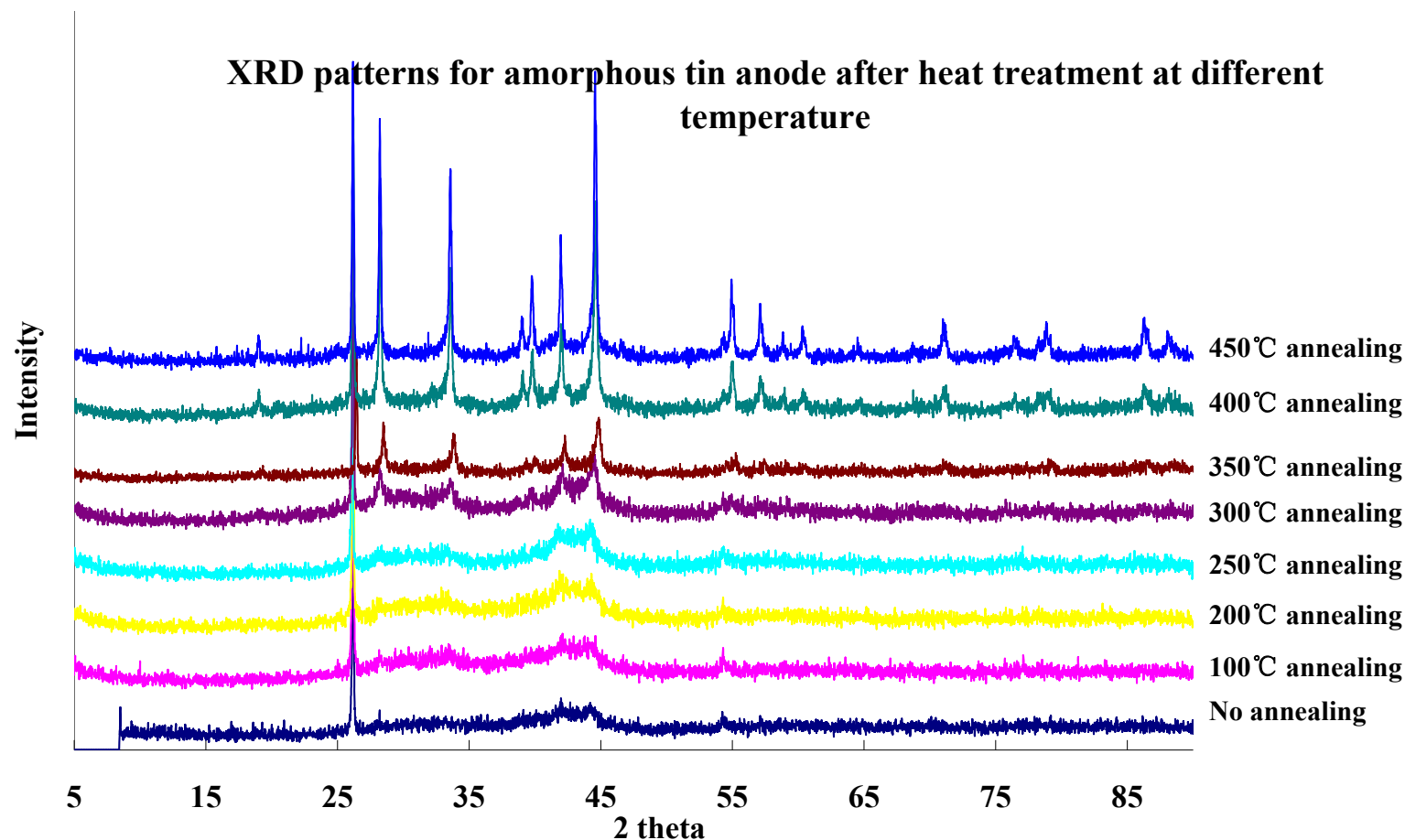
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Why is the Nexelion Anode not Viable?

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- Amorphous nano-tin probably meets technical needs of PHEV
 - However, fails to meet cost and materials availability targets
 - Essentially SnCo alloy
 - Also questions about cost of large-scale manufacturing
- Need to understand what makes the Sn-Co amorphous alloy special?
 - Crystalline Sn-Co does not cycle well
 - Annealing amorphous Sn-Co causes particle growth, and capacity loss.



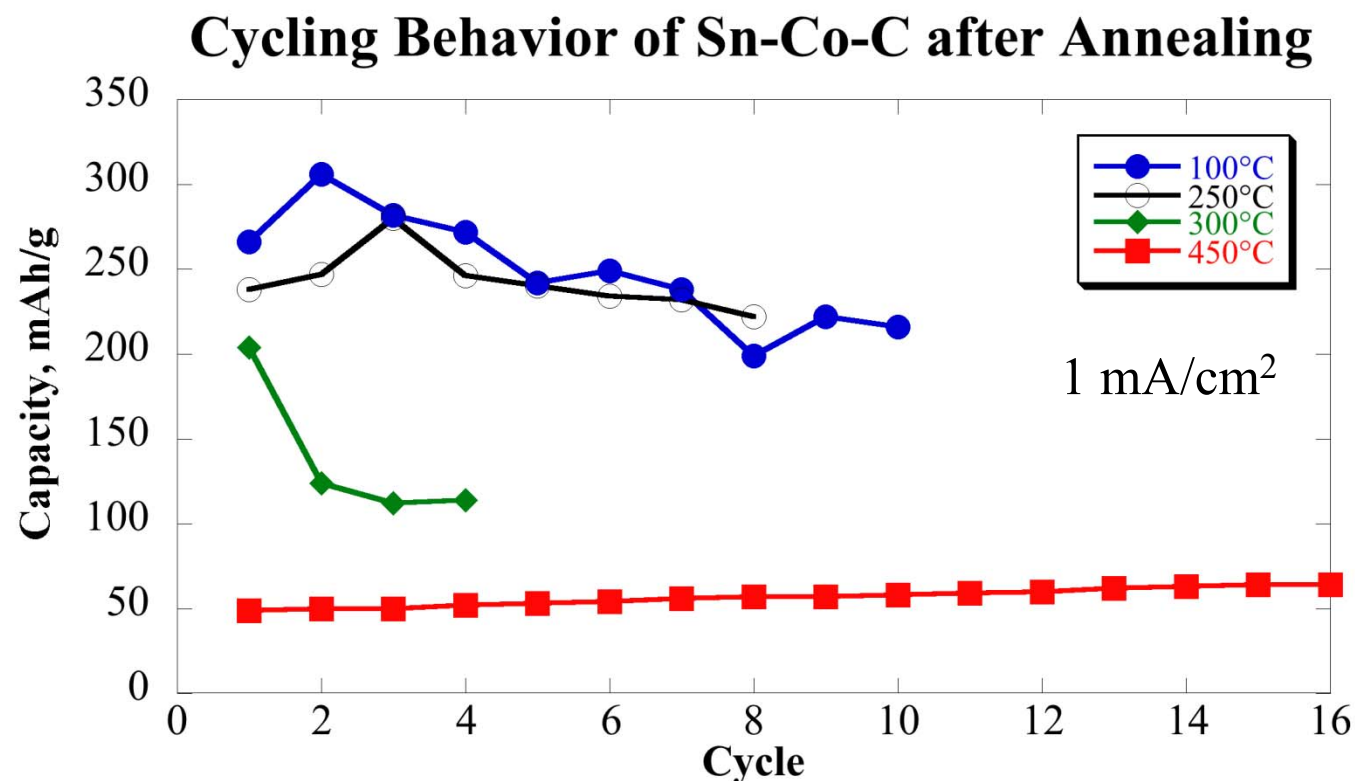
- Grains become crystalline and larger

Annealing temperature (°C)	No Annealing	100	200	250	300	350	400	450
Crystalline size (nm)	5	—	—	—	21	33	38	44

Annealing causes capacity loss

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- Amorphous tin loses capacity on crystallization and grain growth
 - Which is it – crystallization or grain growth?
 - Capacity falls as soon as diffraction lines appear

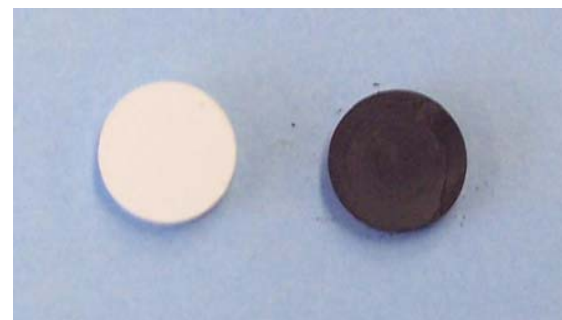


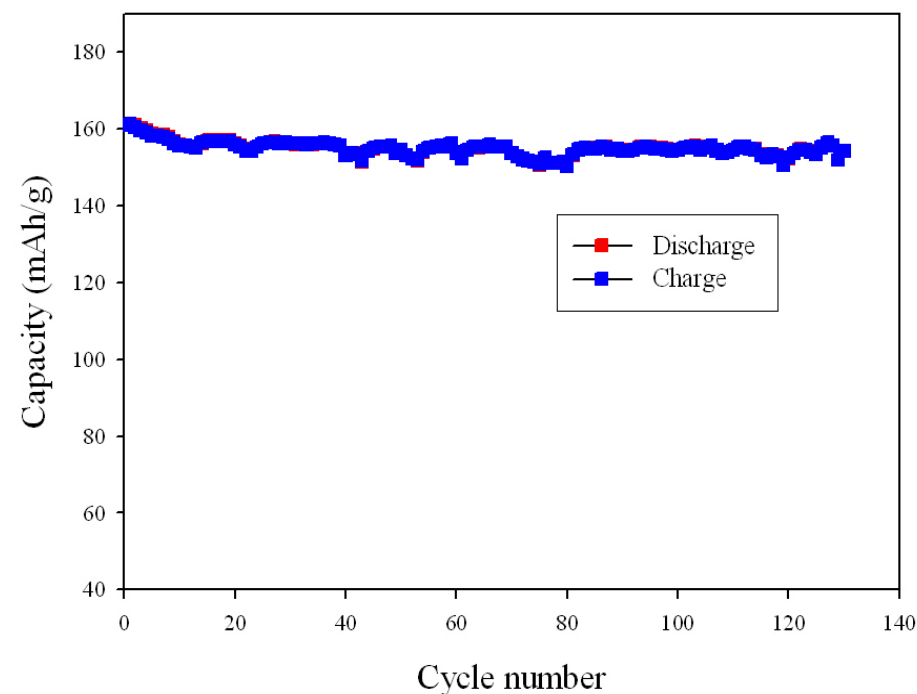
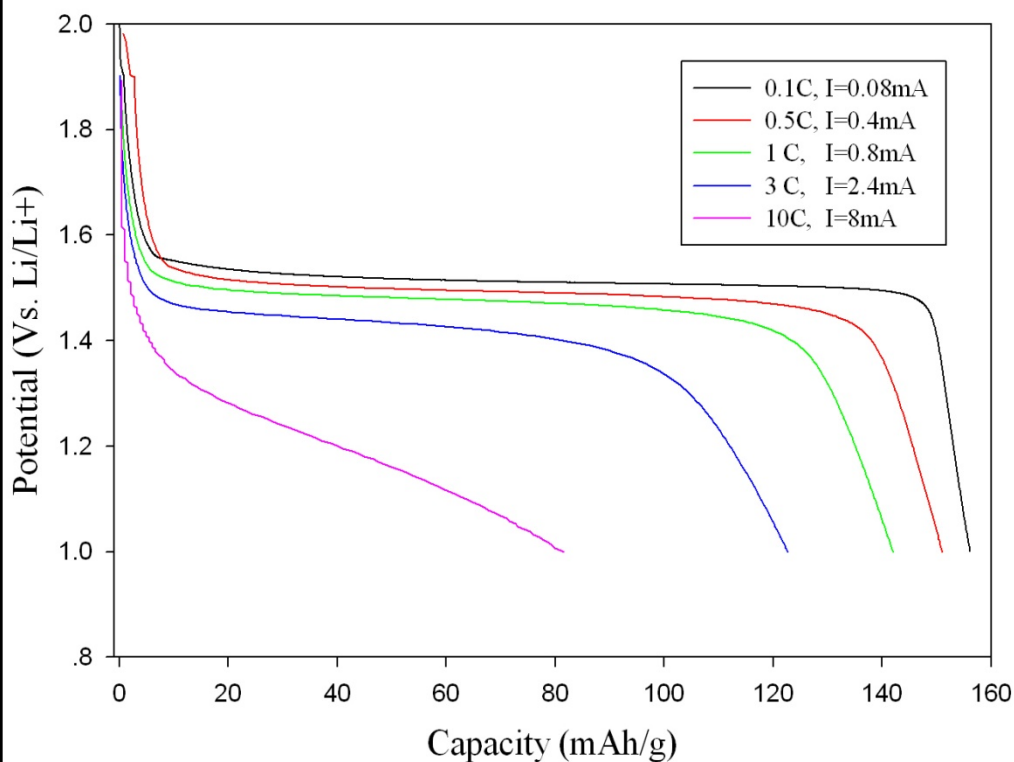
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Crystalline size (nm)	5	—	—	—	21	33	38	44

Milestone: Go on Nano-Amorphous

- Results show that nano-amorphous the direction to go for tin
 - Not clear yet whether amorphous is more important than nano
- Future effort will be focused on tin compounds
- Last year reported on nano MnO_x
 - Excellent capacity retention
 - Partially crystalline
- This year report on nano $\text{Li}_4\text{Ti}_5\text{O}_{12}$
 - Structure retention electrode
 - Intercalation electrode

- Nanosize titanium oxide
 - Safe high-rate anode
 - But, exhibits insulating behavior, when fully charged
- Goal
 - Make $\text{Li}_4\text{Ti}_5\text{O}_{12}$ more conducting
- Approach
 - Use a reducing atmosphere
 - Resistance reduced to 10^6 ohm-cm





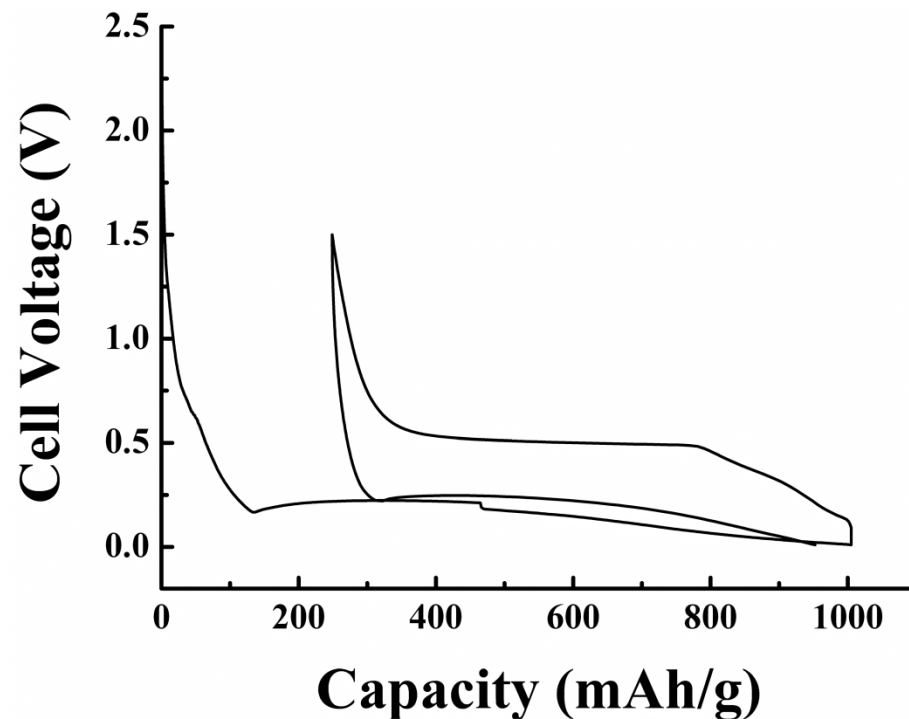
Results

- Capacity stable for many cycles
- However, less than 1% conductive titanium

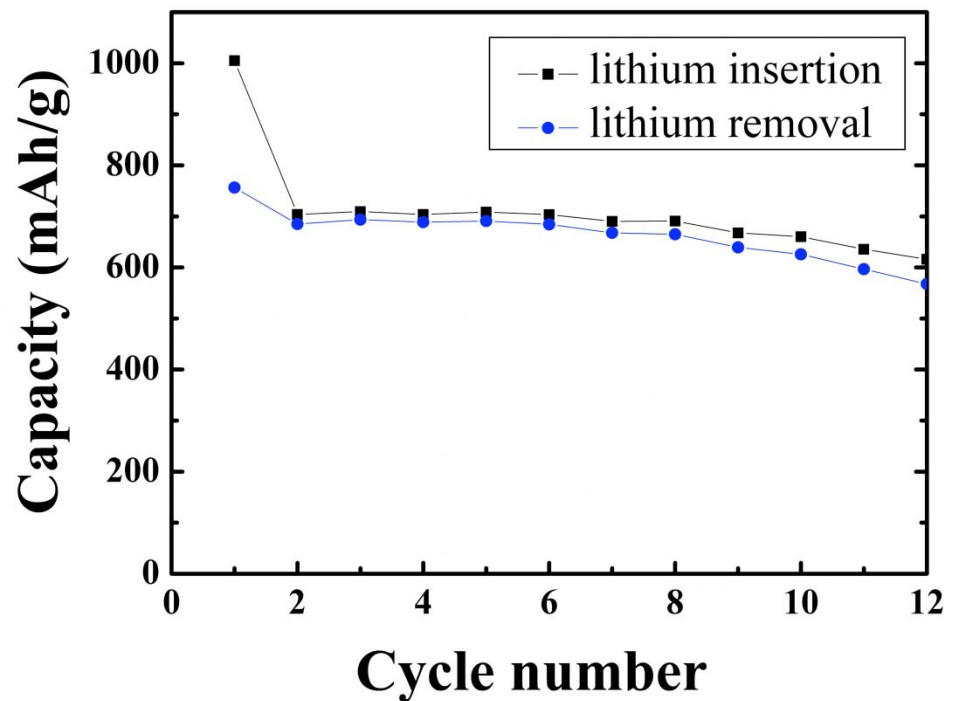
Challenge

- Improve conductivity further
 - Increase number of isolated conductive Ti^{3+} ions
 - Reduce the Ti^{3+} - Ti^{3+} ion pairs that do not contribute to the conductivity □

- Work continuing on silicon-based anodes
- Successfully formed an aluminum based anode
 - Cycles much better than pure aluminum in carbonates
 - A clue that aluminum may yet work



First cycle of Al-M-C material



Cycling capacity of Al-M-C material.

- Determine whether nano and/or amorphous is key to the charge retention of anode materials.
 - Design the ideal experiment to differentiate
- Determine the rate capability of amorphous tin materials.
 - Both on lithium insertion and removal
- Explore nano-size tin and determine if cobalt-free materials are viable. (ANL and BNL)
- Ascertain the optimum reduction level in $\text{Li}_4\text{Ti}_5\text{O}_{12}$.
 - Can we control?
- Identify the structural and surface changes of tin anodes during cycling working collaboratively with LBNL.
- Continue to explore new anode host materials.

- Some clues have been obtained that may allow the eventual replacement of the carbon anode in batteries
 - Nano materials approach seems to be effective,
 - Better cycling than micron-size materials, at full or partial cycling depth
 - Physical and electrochemical properties can be modified
 - All have **higher volumetric energy** densities than carbon
 - Gravimetric energy density equal to or better than carbon
- Technology transfer being accomplished
 - Ex-student in battery company working on anodes
 - Collaboration underway with Primet on anodes
 - Publications to transfer knowledge
- Collaborations with National Labs
 - LBNL – Robert Kostecki on changes of tin surfaces on cycling
 - ANL – Pete Chupas on structure of amorphous materials
 - BNL – Xiao-Qing Yang on plans to study silicon systems