Nanostructured Materials as Anodes

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Project ID #
ES063

Overview

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Timeline

- Project start date: 06-01-2007
- Project end date: 12-31-2010
- Percent complete: Continuing

Budget

- Total project funding
  - DOE share: 100% $
  - Contractor share: Personnel
- Funding received
  - FY09: 125k$
  - FY10: 141k$
- Funding requested
  - FY11: 172k$

Barriers

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

Partners

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

Objectives of Work

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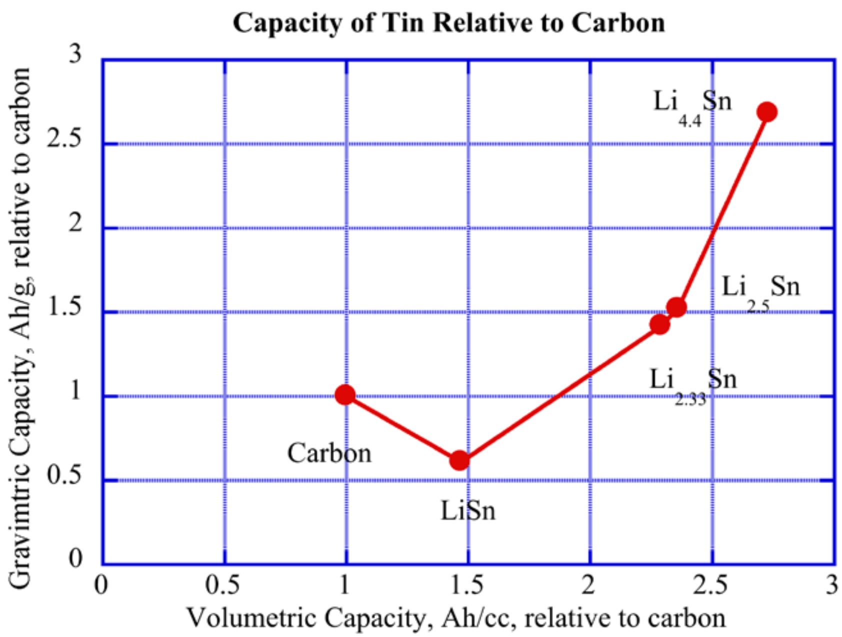
- To replace the presently used carbon anodes
  - with safer materials that will be compatible with lower cost manganese oxide and phosphate cathodes and the associated electrolyte.
  - with materials having higher **volumetric** energy densities, twice carbon
    - 1.6 Ah/cc
    - Gravimetric ≥ 0.5 Ah/g



Milestones

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a) Determine the limitations, besides cost, of the Sn-Co-C nanostructured anode. Complete
- **March 2010 - Nogo for high rate charging and cost**
- **March 2010 – Go on maintenance of capacity on cycling**

b) Explore nano-size tin/silicon alloys and metal oxides to identify their cycling characteristics.
- **Continuing**

c) Explore cobalt-free alloys to identify lithium active stable phases.
- **Continuing**

d) Identify the structural and surface changes of tin containing anodes during cycling working collaboratively with LBNL – R. Kostecki.

Approach to Replacing Carbon Anode

- Explore, synthesize, characterize and develop inexpensive materials, that
  - Have a potential around 500 mV above pure Li
  - Have at least double the volumetric capacity of carbon
  - Have a higher gravimetric capacity than carbon
- Build on know-how generated from Co-Sn anode
  - Emphasize nanostructures
    - Tin **nanostructures**
      - Devise novel synthetic approaches
    - Compare with silicon based nanostructures
    - Keep aware of oxide-based anodes
      - We showed that Mn_3O_4 cycles well

Technical Accomplishments: Barriers being Addressed

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- Replace the **low capacity** carbon anode presently used
  - Increase volumetric capacity to 1.5 Ah/cc
    - Double the low volumetric capacity of carbon
    - Significantly increases energy density of battery
- Reduce the **cost** of the anode
  - Use low cost materials, and low cost synthetic approaches
- Increase the **safety** relative to carbon
  - Higher voltage vs lithium, giving safety margin
  - Tin releases less energy than silicon on combustion
    - ΔG for SnO_2 formation half that of SiO_2
    - Sn and Si both release much less energy on combustion than carbon per mole of lithium stored

Milestone: Determine the Limitations of the Sn Nanostructured Anode

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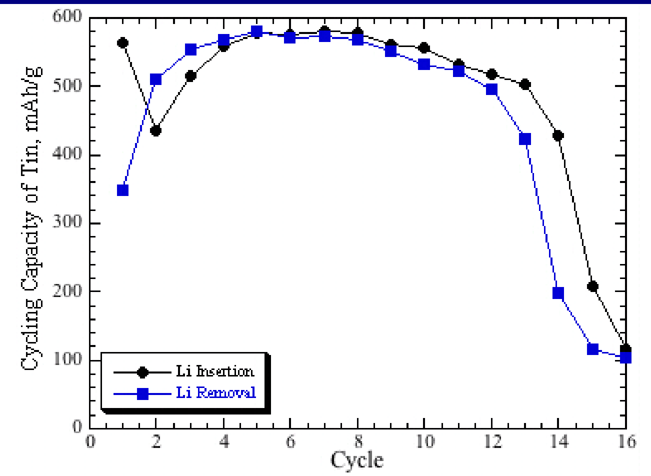
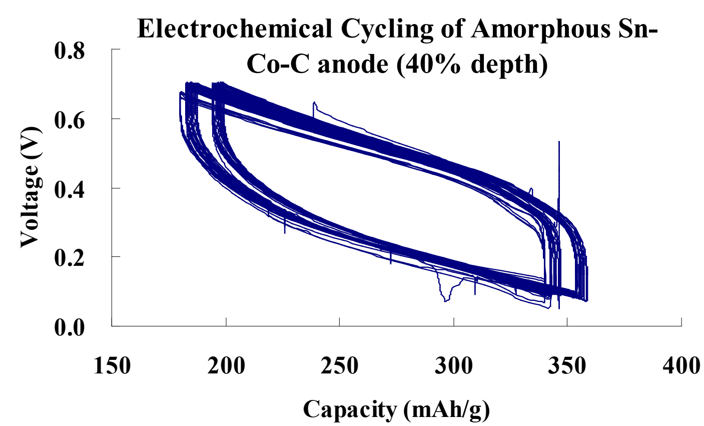


- Crystalline tin foil
  – Capacity fades even for low-depth cycling
- Nanotin shows some excellent behavior
  - Reported May 2009
    - Capacity maintained at all depths of discharge
    - Crystallizes on heating to around 300°C
      - Capacity lost



- Questions raised last year
  - Safety relative to carbon anode
  - Low temperature operation
    - Not studied, as Army Research Laboratory determined to be safe, operates well at low temp. and suitable for military use
  - What is rate capability?

Amorphous Tin shows Excellent Lithium Release Rate

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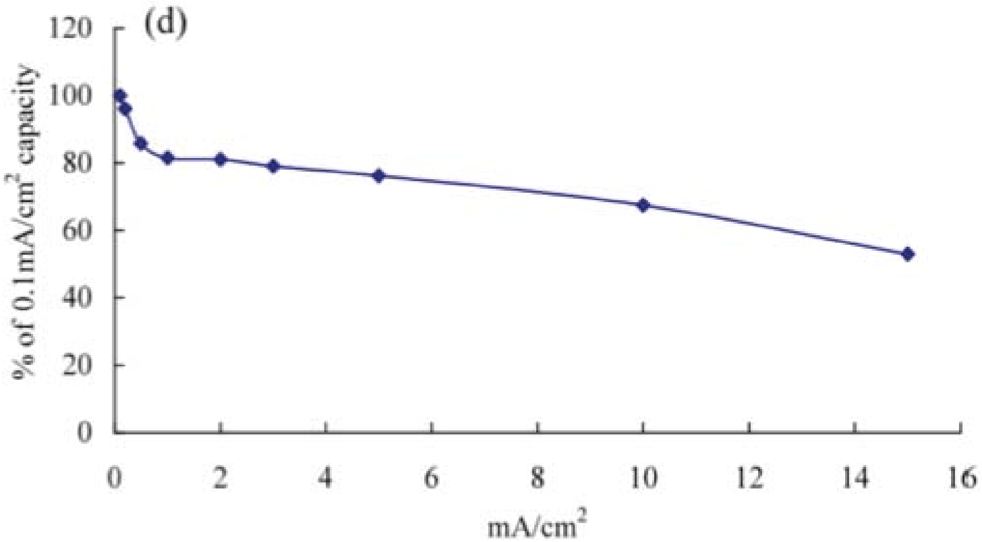
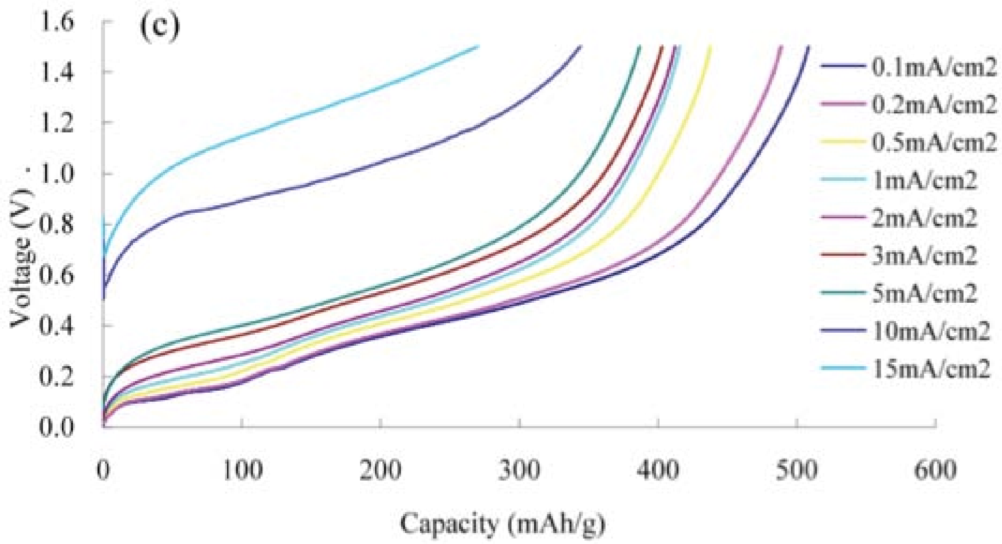
Nano-amorphous tin shows:

- Very high lithium release rate
  - Still 60% of capacity at 15 mA/cm^2
- Allows high discharge rates when used as anode





Amorphous Tin shows Limited Lithium Insertion Rate

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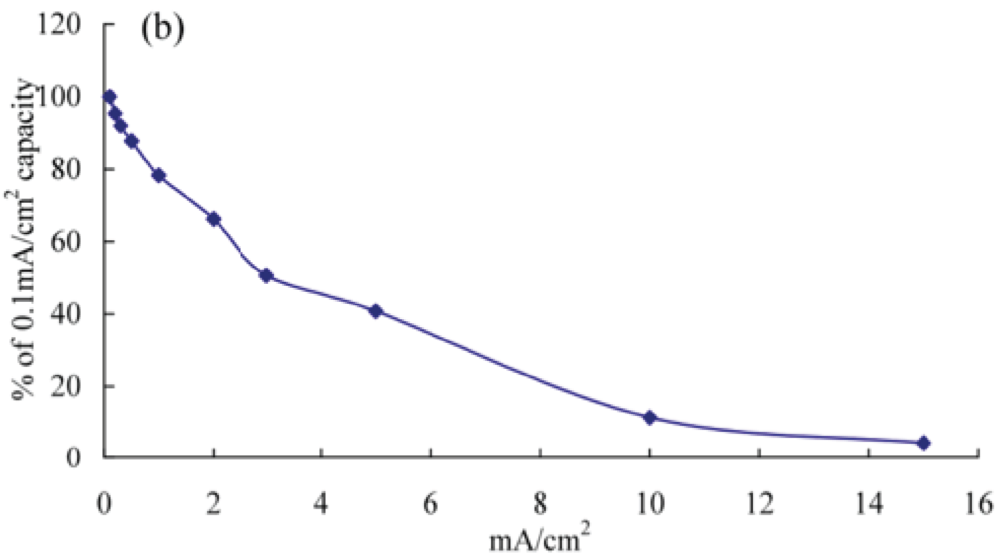
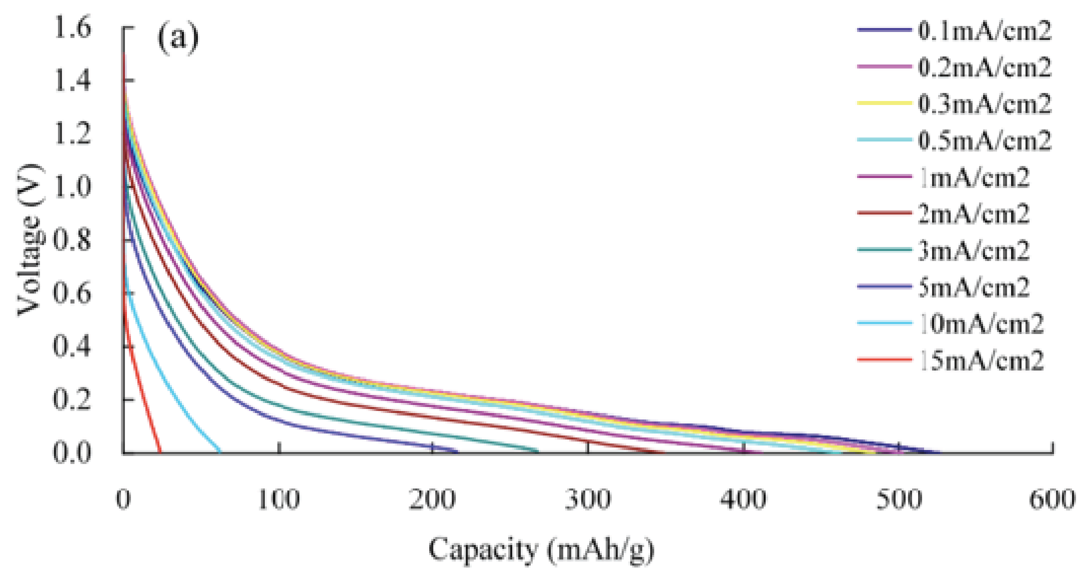
Nano-amorphous tin shows:

- Low lithium insertion rate
  - Only 50% of capacity at 3 mA/cm^2
- Results in low charging rates when used as anode





Milestone: What Conclusions can be drawn from Sn-Co? BATT effort completed March 2010

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- Amorphous nano-tin probably meets technical needs of PHEV and EV
  - \+ Has excellent capacity retention on cycling
    - \+ Releases lithium at high rate
  - – However, fails to meet cost and materials availability targets
    - – Essentially SnCo alloy
    - – Fails to meet charging rate capability
    - – Also questions about cost of large-scale manufacturing
- What is next?
  - – Effort shifted to cobalt-free nano tin materials
  - – Reaction mechanism still not known
    - – Will be studied under BES – EFRC
      - – Intercalation followed by conversion (ejection of magnetic cobalt)

Milestone - Other Alloy Anodes: Mixed Aluminum Based Anode

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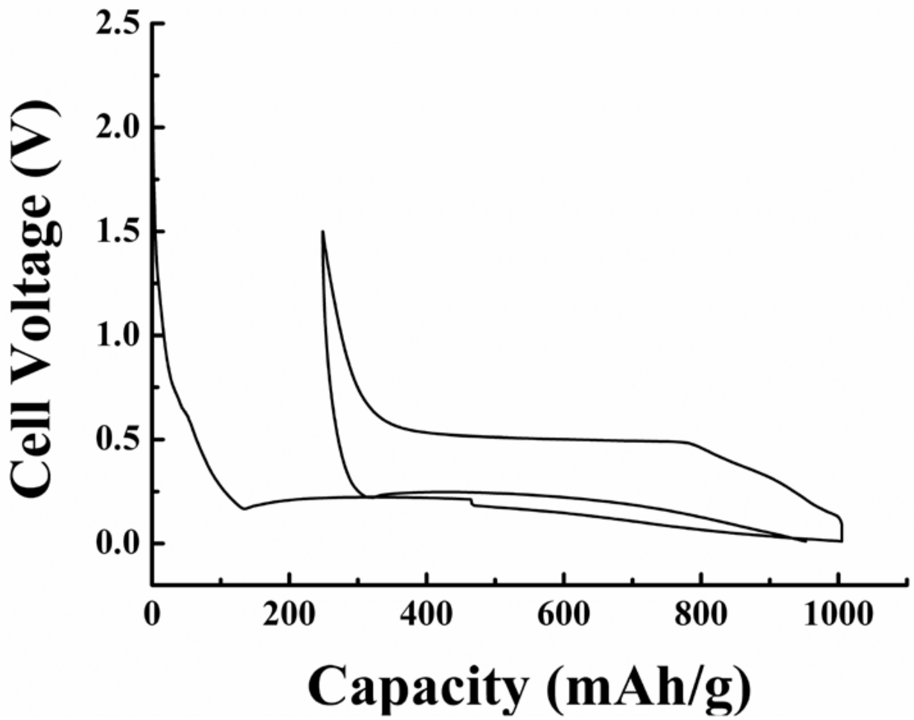
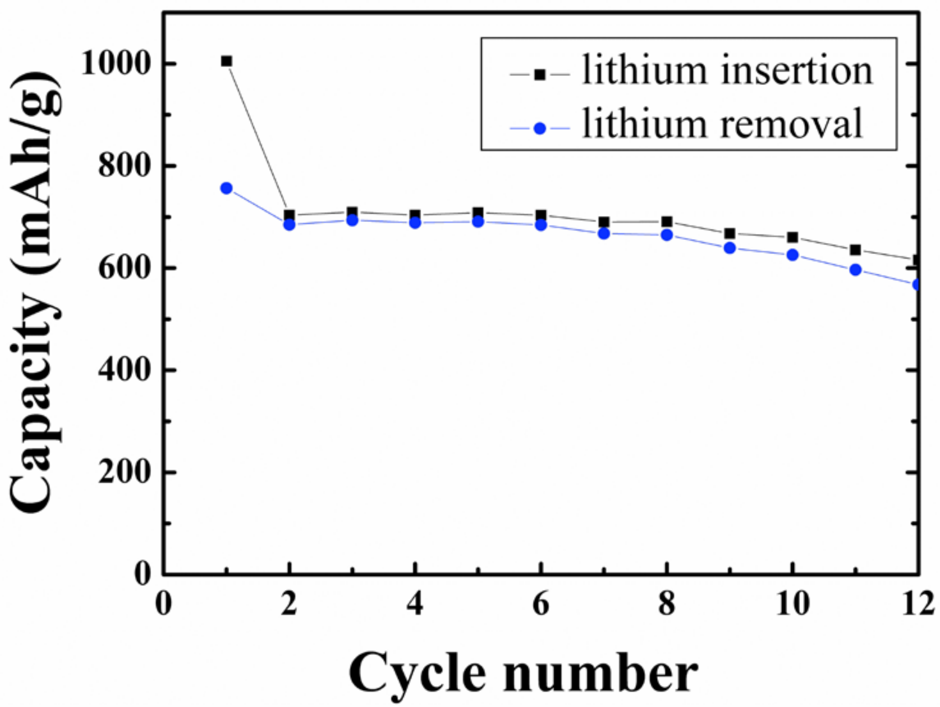
- Work continuing on silicon-based anodes
- Successfully formed an aluminum based anode
  - Cycles much better than pure aluminum in carbonates
    - A clue that aluminum may yet work



First cycle of Al-M-C material



Cycling capacity of Al-M-C material.

Aluminum-Silicon Alloys

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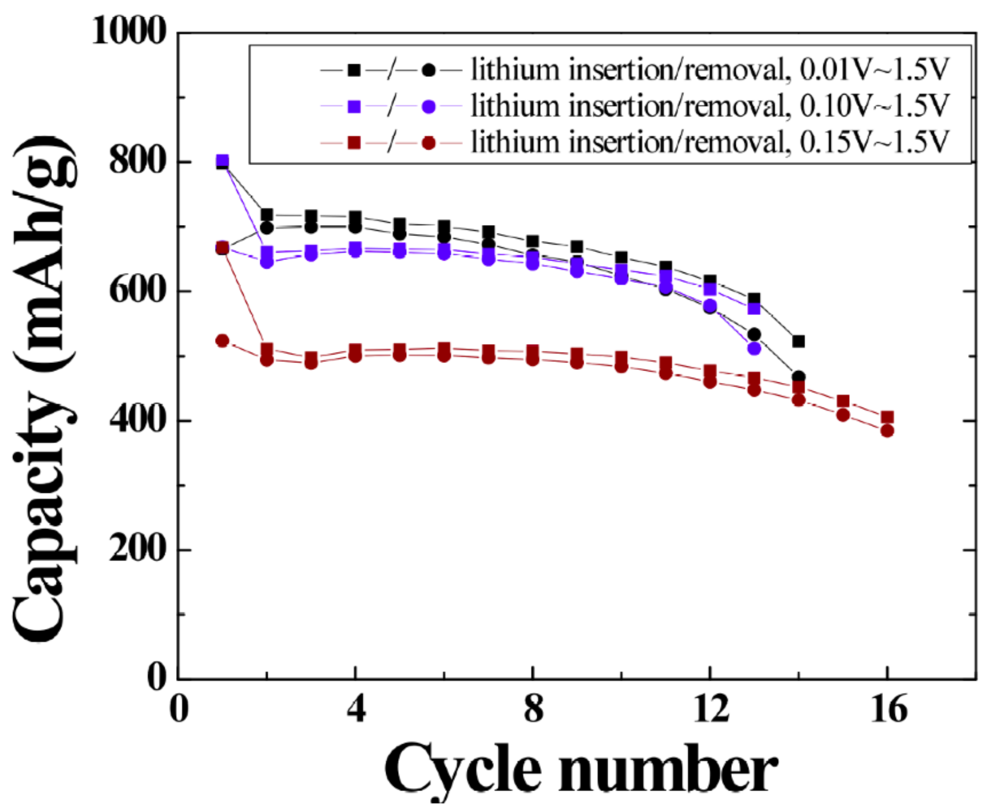
- Aluminum-silicon alloy mixed with carbon
- Evaluated as function of discharge cut-off voltage
  - Capacity fades in all cases
  - Less than 100% efficiency
    - In contrast, tin cycles with close to 100% efficiency



Silicon holds Capacity better than Al-Si

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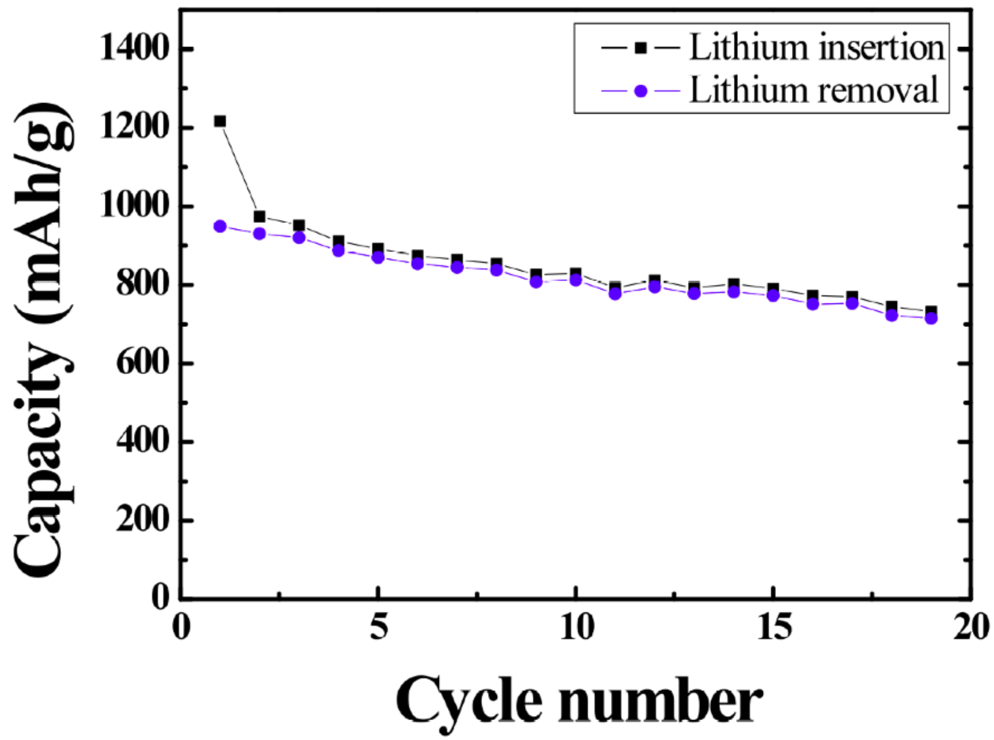
- Silicon formed by ball-milling and high temperature anneal
  - Cycled at 0.5 mA/cm^2
  - Less than 100% efficiency
    - In contrast, tin cycles with close to 100% efficiency
- Aluminum based systems are a Nogo



Silicon cycles well when Capacity Limited

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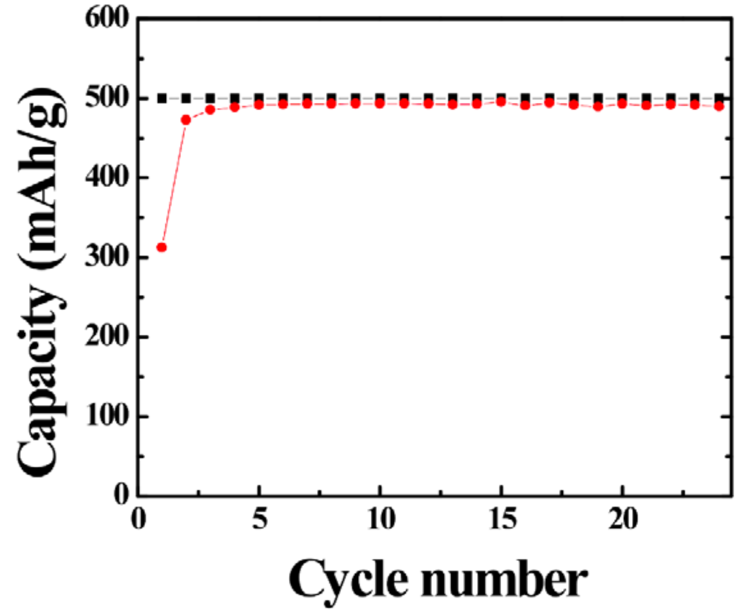
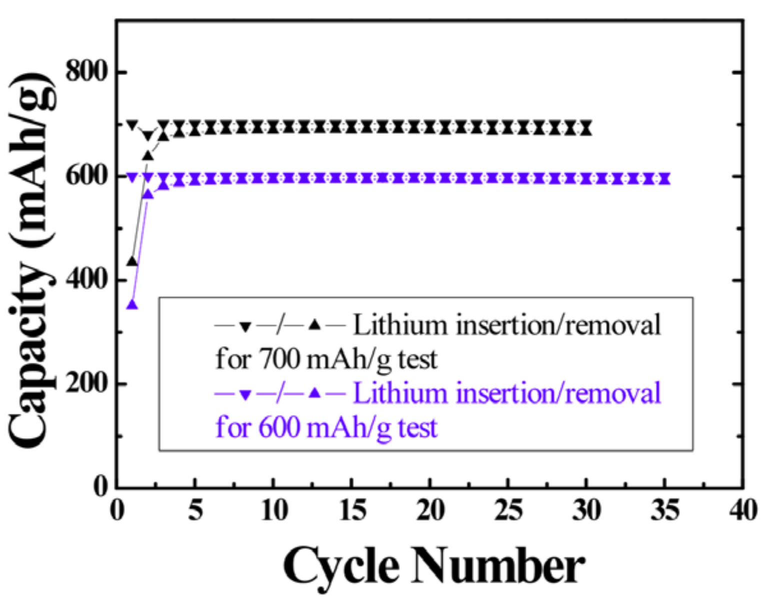
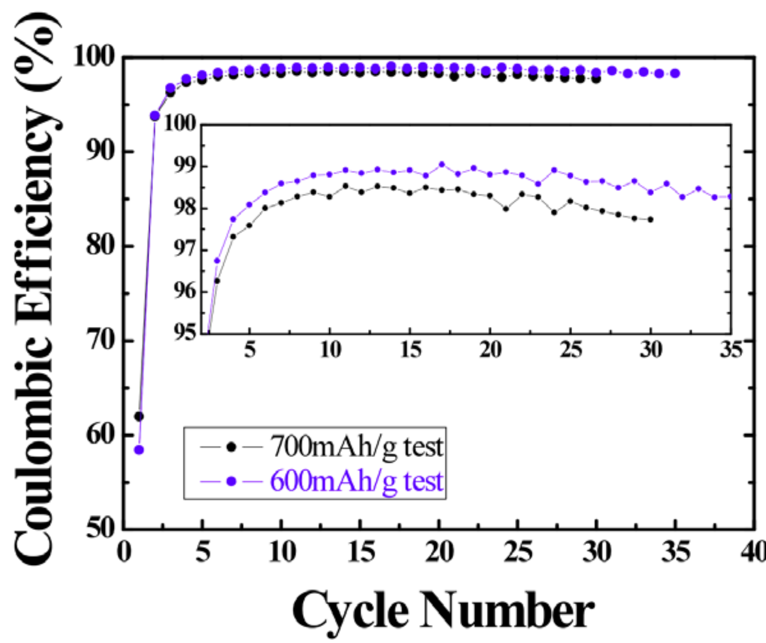
- Silicon formed by ball-milling and high temperature anneal
  - Cycled at 0.5 mA/cm^2
  - Charged only to 0.9 volts 500 mAh/g ←
  - Charged to 1.5 volts – 600/700 mAh/g ↓
    - Still less than 100% efficiency







Collaboration and Coordination with other Institutions

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- **Collaborations with National Labs**
  - LBNL – Robert Kostecki on changes of tin surfaces on cycling
  - ANL – Peter Chupas on structure of amorphous materials
  - BNL – Expansion of particles on lithium reaction, and oxidation state
  - NREL – Transferred Electro-spinning technology with personnel
- **Industry**
  - Working with Primet on novel nano-anode materials
  - Contract underway with Advanced Materials & Primet on advanced anode/cathode materials and electrode manufacturing
- **New York State Battery Consortium**
  - Building collaborations between Industry, Academia, and Government (NYBEST-NYSERDA)

Future Work

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- Emphasize tin nanostructures
  - Tin shows high rate capabilities
- Synthesize nano-tin by a range of techniques
  - Solvothermal, electrospinning and mechanochemical
- Protect these nanoparticles from reaction with the electrolyte by a protective layer
- Substitute part of the main metal, tin, to raise the redox potential and thus the safety
- Identify the structural and surface changes of tin anodes during cycling working collaboratively with LBNL.
- Continue to explore new anode host materials.

Summary

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- Concluded study on nano-amorphous tin – Concept - **Go**
  - Rate Capability
    - High lithium release rate
    - Low lithium insertion rate
  - Capacity maintained on cycling at all depths of discharge
  - Meets most technical targets for PHEV
    - Higher capacity than carbon anodes, both volumetric and gravimetric
    - Recent reports by the Army Research Lab support excellent technical attributes of this material; recommended for military use
- Above material now needs mimicking using low cost additives
  - Tin shows higher efficiency on cycling than silicon
- Aluminum-based anodes are not effective, and work on them will be discontinued