Metal-Based High Capacity Li-Ion Anodes

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Project ID #
ES063

Overview

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Timeline

- Project start date: 01-01-2011
- Project end date: 12-31-2014
- Percent complete: 50%

Barriers

- Barriers addressed
  - Lower-cost
  - Higher volumetric capacity and
  - Abuse-tolerant safer anodes

Budget

- Total project funding
  - DOE $724,626
  - Contractor share: Personnel
- Funding received
  - FY12: 172k$
  - FY13: 172k$

Partners

- National Laboratories
  - Brookhaven; Argonne; Lawrence Berkeley
- Local Industry
  - Primet
- Academia
  - Other Anode Partners

Relevance and Objectives of Work

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- **The primary objectives of our work are to:**
  - Increase the volumetric capacity of the anode by a factor of two over today's carbons
    - 1.6 Ah/cc
  - Increase the gravimetric capacity of the anode
    - $\geq$ 500 Ah/kg
  - Lower the cost of materials and approaches
  - Be compatible with low cost layered oxide and phosphate cathodes and the associated electrolyte
- **The relevance of our work is:**
  - Achieving the above objectives
    - Will increase the cell energy density by up to 50%.
    - Will lower the cost of tomorrow's batteries

Relevance: Milestones

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a) Determine the limitations to the electrochemical behavior of mechanochemical tin. Characterize these materials and determine their electrochemical behavior. (Sep. 12)

- **Completed. The nano-size tin meets the gravimetric capacity of the Sn-Co-C electrode. Ti reductant is superior to Al**

b) Determine the electrochemistry of a new synthetic nano-silicon material. (Sep. 12)

- **Completed**

c) Determine the reaction mechanism of the nano-Sn-Fe-C system. (May 13)

- **Ongoing. Carbon is an active element**

d) Identify an anode candidate having an energy density of 2 Ah/cc for at least 100 cycles. (Sept. 2013)

- **Ongoing**

Approach and Strategy: Improved Anodes

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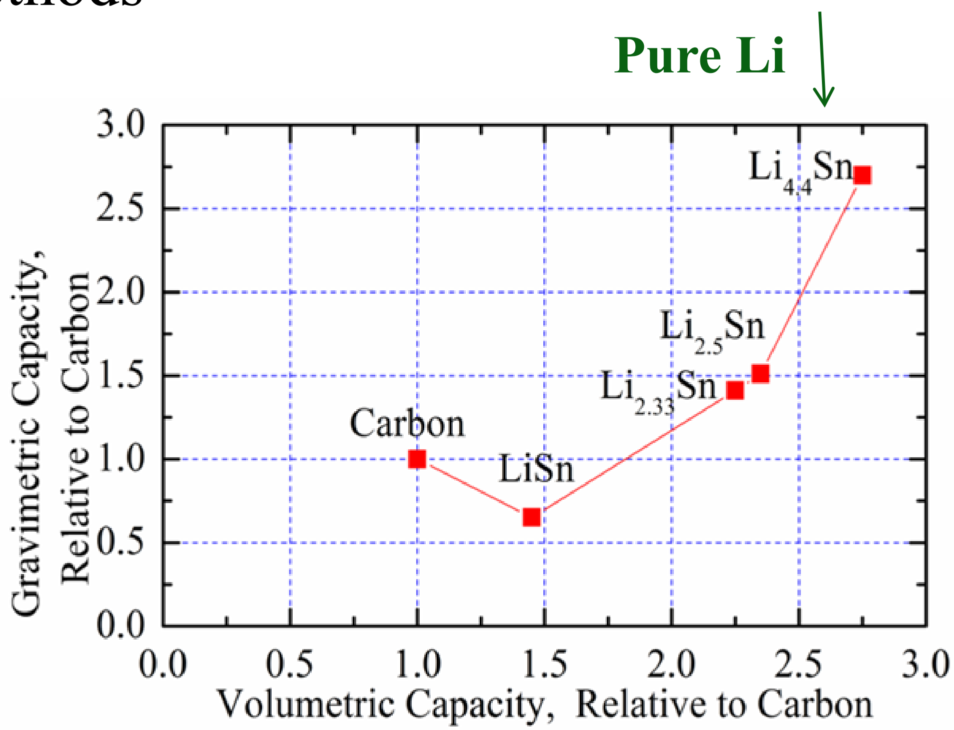
- Place emphasis on low cost materials, tin and silicon
  - Study modified tin initially
    - Safer than silicon
  - 2 Li/Sn doubles capacity
  - Find several simple synthesis methods
    - Nano-amorphous tin
    - Need low cost components
  - Protect the nano-tin
    - From side reactions



Technical Accomplishments: Barriers being Addressed

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- **High Cost**
  - Find a tin-based anode, that does not contain cobalt
    - Low cost materials
    - Low cost manufacturing method
- **Low Volumetric Capacity of Li-ion batteries**
  - Volumetric capacity of Li-ion batteries limited by carbon anode
  - Find a material with double the volumetric capacity
- **Low Safety and Abuse-tolerance**
  - Find an anode that reacts with lithium faster
    - Minimizes risk of dendrite formation
  - Find an anode that reacts with lithium at 300-500 mV vs Li
    - **Minimizes risk** of dendrite formation
    - Allows for higher rate charging

Milestone (a) - Synthesis Approach:
Nano-size tin materials synthesized

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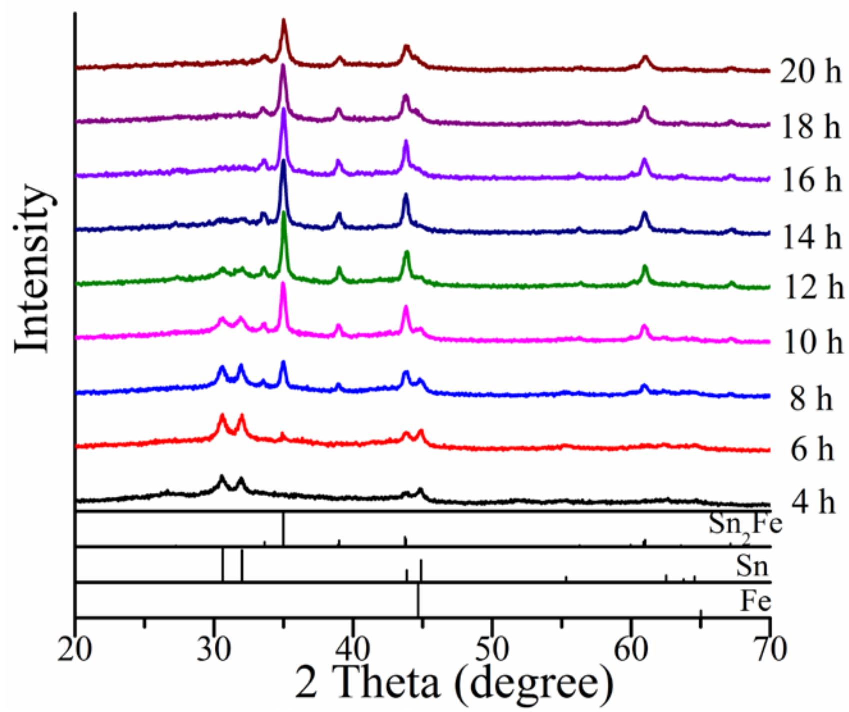
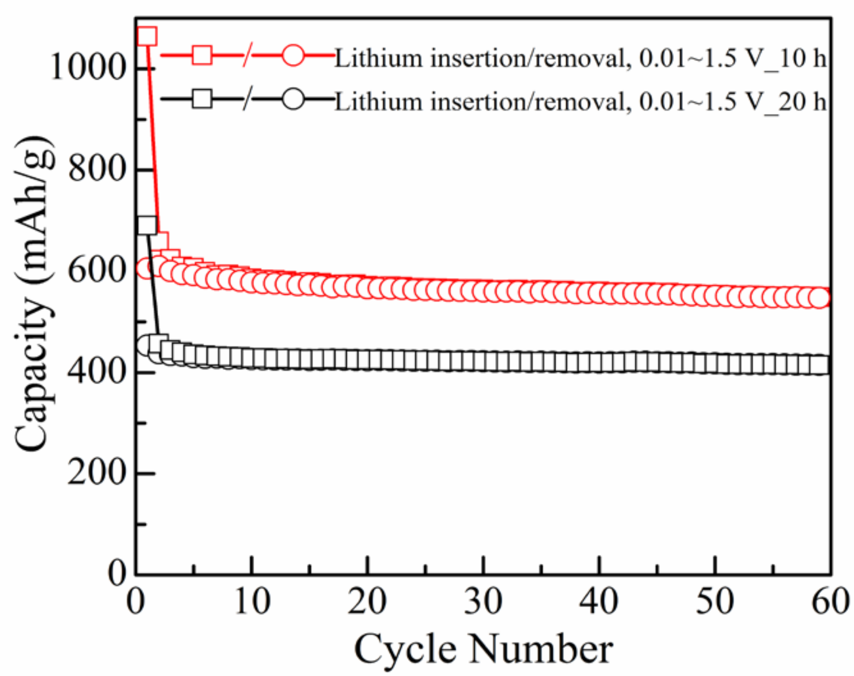
- **Method 1:**
  - SnO reduced by **<u>Ti</u>** and carbon with **<u>hard</u>** iron balls by mechanochemical methods
    - Use of iron grinding media results in formation of Sn_2Fe/C composite
      - As reaction time increases, tin phase becomes Sn_2Fe
      - If reaction too long, iron phase is gradually formed after all Sn is converted to Sn_2Fe
  - Electrochemical behavior determined
    - The capacity retention has been improved compared with our previous results.
    - Good electrochemistry associated with reaction time (e.g. 10 hours better than 20 hours).





Milestone (a) - Synthesis Approach:
Nano-size tin materials synthesized – Ti > Al

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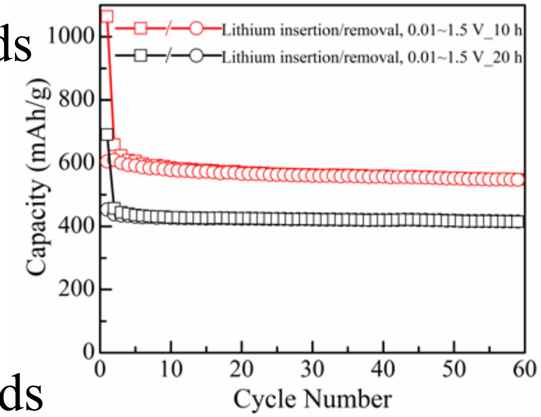
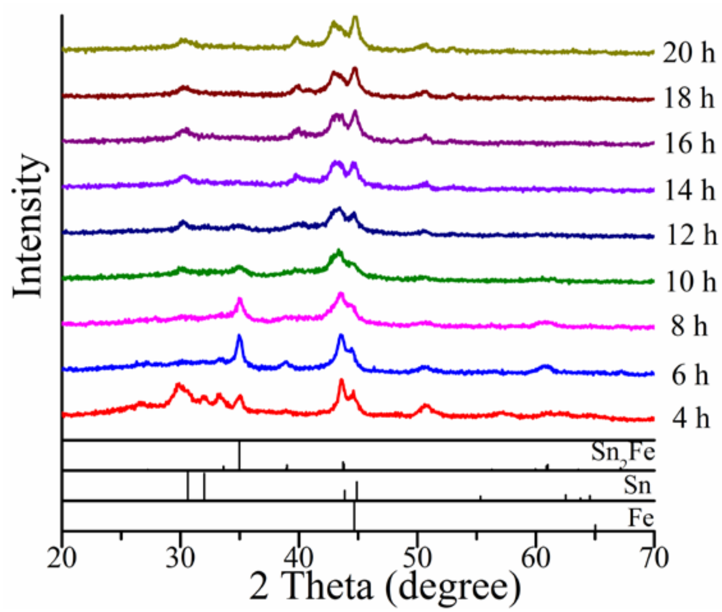
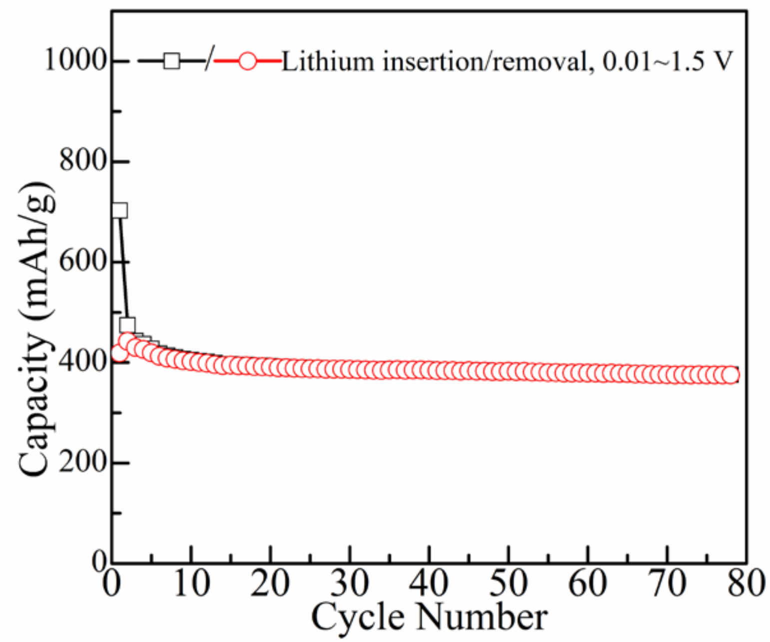
- **Method 1:**
  - **SnO reduced by Ti** and carbon by mechanochemical methods
    - Titanium found to be most effective reducing agent
    - Results in formation of Sn_2Fe/C composite
    - Good electrochemistry found



  - **SnO reduced by Al** and carbon by mechanochemical methods
    - Use of iron grinding media results in formation of Sn_2Fe/C composite
    - Capacity retention is as good as in Ti-reduction, but the capacity is lower (~390 mAh/g).





Increasing tin content reduces capacity and retention

Electrochemical studies of Sn_5Fe compound

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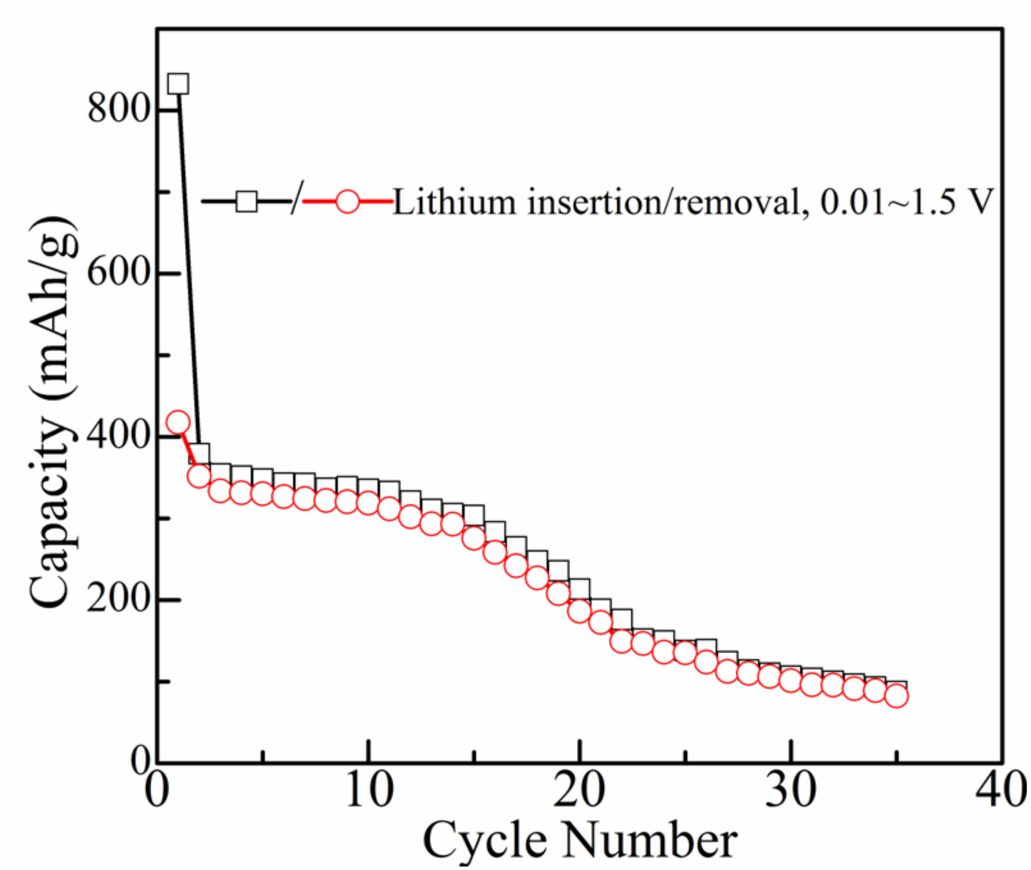

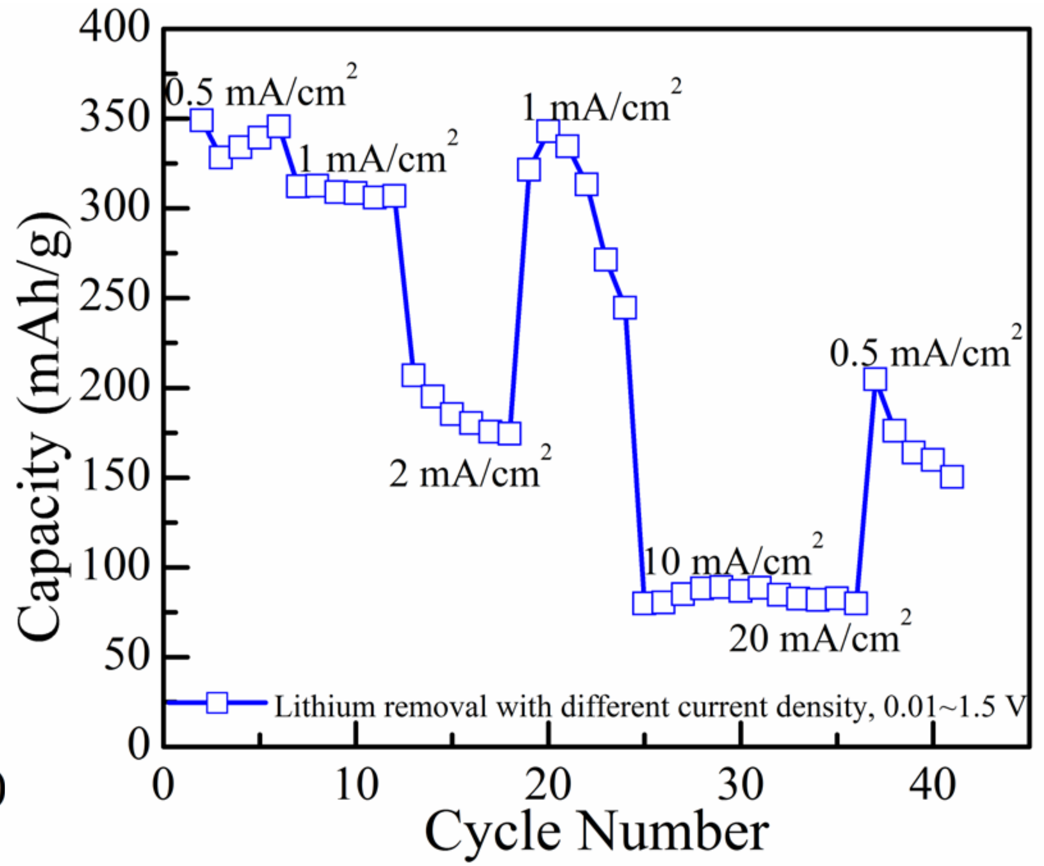

Collaboration with CNF at Brookhaven National Laboratory

Milestone (a) achieved using method 1:
Tin-carbon electrode + Fe as Sn_2Fe

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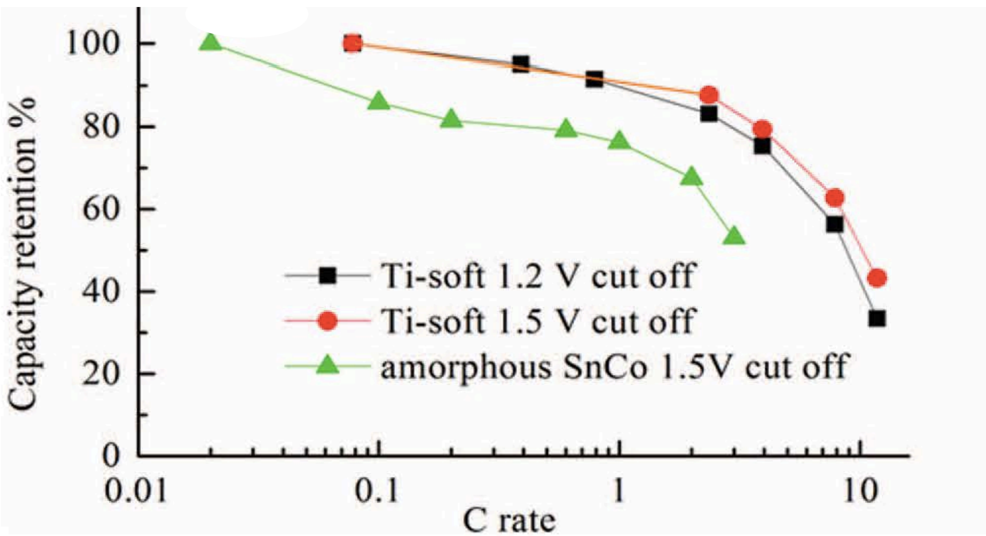
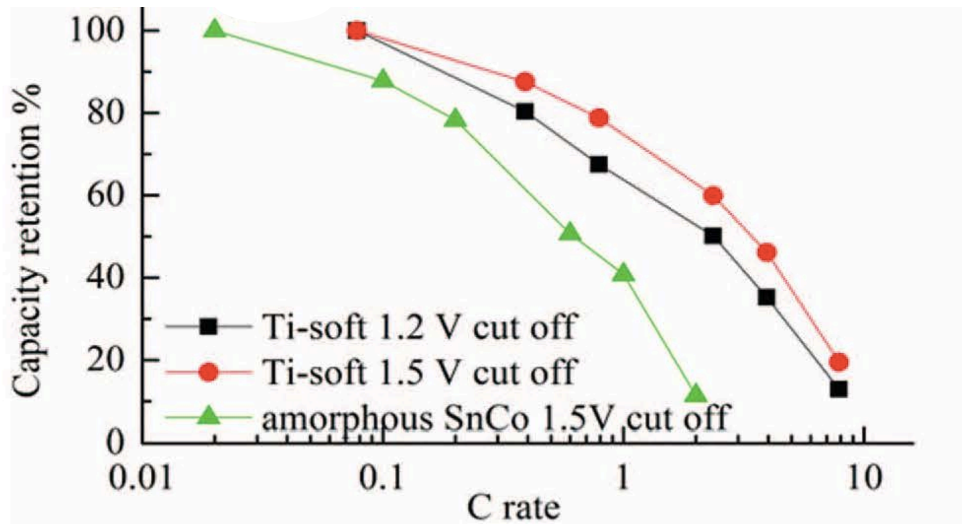
SnFe Capacity/Rate Capability surpasses present commercial SnCo-C





Lithium removal – discharge of cell

Lithium insertion – charging of cell

Milestone (c) underway:
Reaction mechanism of nano-Sn-Fe-C

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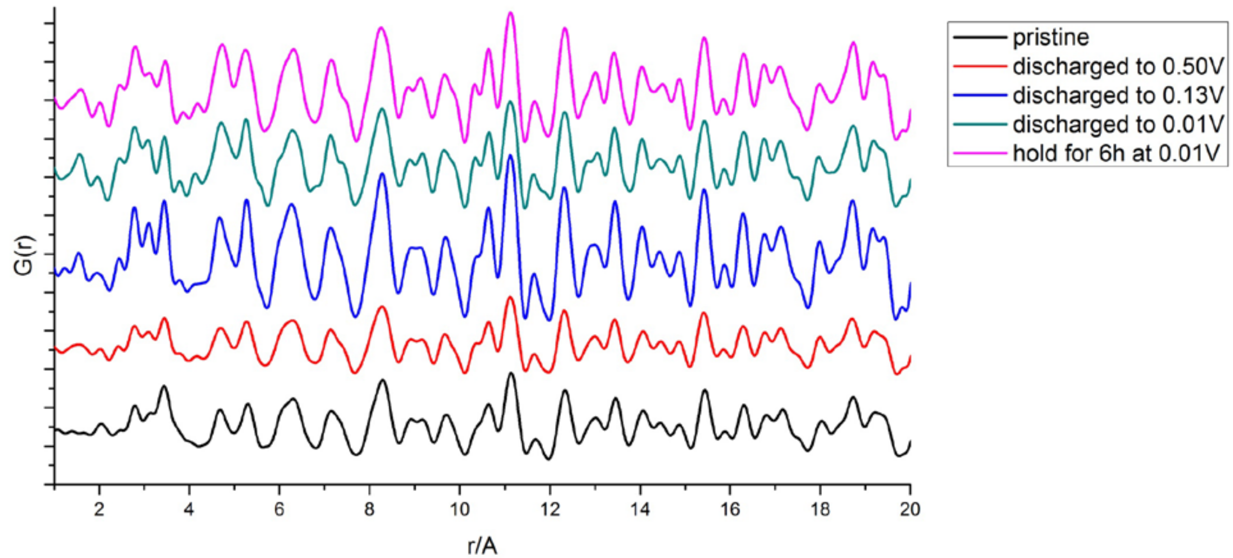
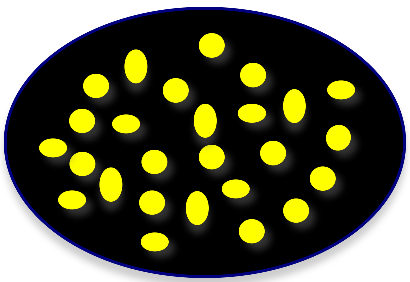
PDF analysis identifies phases formed



Nanosized Sn_2Fe embedded in carbon



Sn_2Fe-C $\xrightarrow{+\,Li}$ $Li_{4.4}Sn$ + Fe + Sn_2Fe (unreacted) + $Li_{0.5}C$

$Li_{4.4}Sn$ + Fe $\xrightarrow{-\,Li}$ Sn_2Fe

$Li_{0.5}C$ $\xrightarrow{-\,Li}$ C

Milestone (c) being achieved using method 1:
Volumetric energy density exceeds carbon

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- **Gravimetric capacity:**
  - **Measured reversible capacity of 600 Ah/kg of total composite**
  - **Sn_2Fe contributes 804 Ah/kg of Sn_2Fe**
  - Remainder contributed by carbon
    - Must be C_2Li
      - 1100 Ah/kg
      - Theoretical capacity of 760 Ah/kg for total composite
    - If C_6Li then theoretical capacity is 490 Ah/kg
- **Volumetric capacity:**
  - **Approaches 1.5 Ah/cc, based on above value of 600 Ah/kg**

Milestone (a) completed:
Nano-size tin materials synthesized

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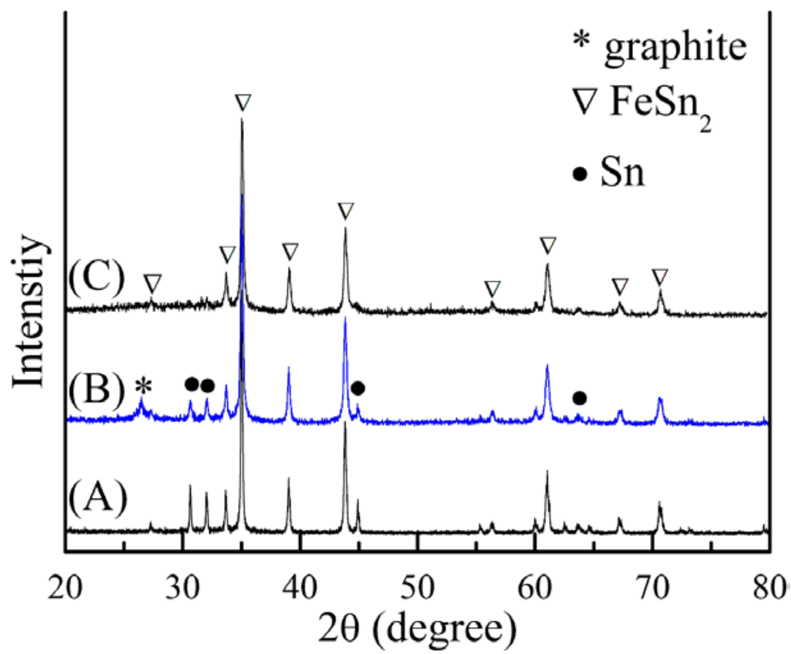
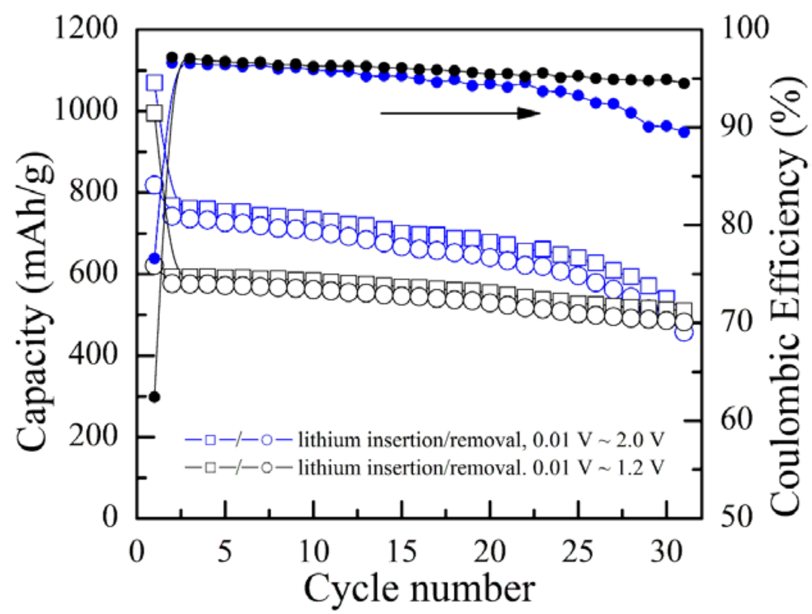
- **Method 2:**
  - $FeCl_3$ and $SnCl_2$ reacted with $NaBH_4$ by solvothermal treatment at 200 ºC
    - Product is Sn_2Fe with particle size less than 100 nm
    - Trace amounts of Sn remaining lead to capacity fade as in pure tin





(left) XRD patterns of (A) Solvothermally formed Fe-Sn; (B) Planetary ball-milled (pBM) Sn-Fe-C composite; (C) High-energy ball-milled (HEBM) Sn-Fe-C composite. Sn metal phase in the solvothermally formed material disappears after high-energy milling with graphite. (right) Electrochemical cycling of this Sn-Fe alloy in two voltage windows; no grinding with carbon. The current was 0.3 mA/cm^2 in the 1st cycle and then changed to 0.5 mA/cm^2 thereafter.

Milestone (a) completed:
Nano-size tin materials synthesized

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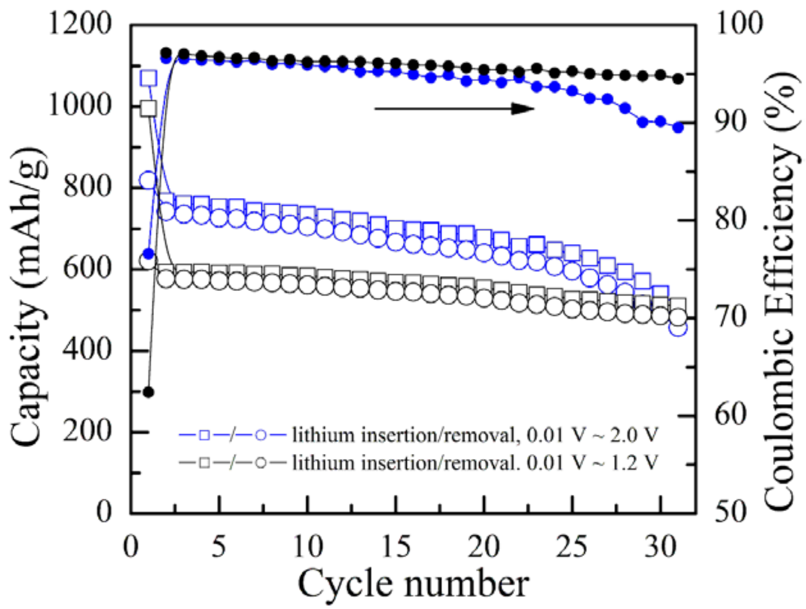
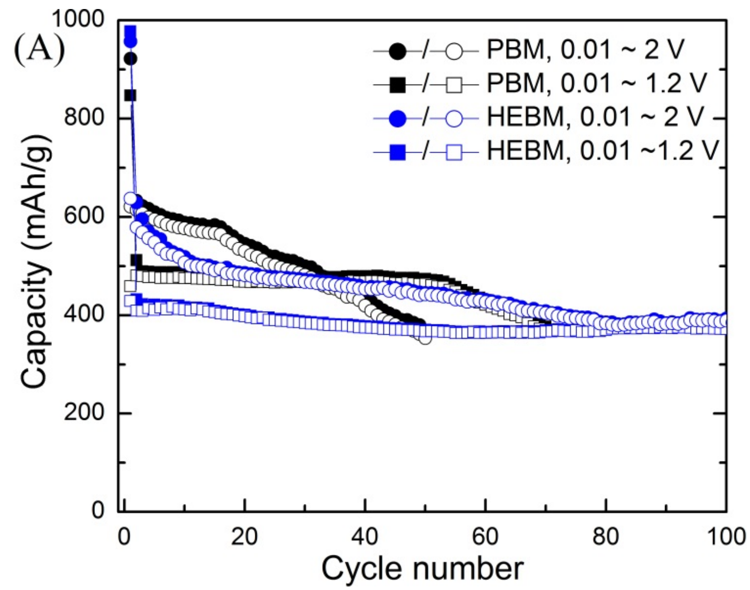
- **Method 2:**
  - $FeCl_3$ and $SnCl_2$ reacted with $NaBH_4$ by solvothermal treatment at 200 ºC
    - Product is Sn_2Fe with particle size less than 100 nm
    - Trace amounts of Sn remaining lead to capacity fade as in pure tin
      - Sn removed by grinding with carbon
      - Stable capacity can be obtained when high-energy ball-milling is utilized
      - But capacity drops to 400 mAh/g





(left) Original cycling of solvothermal Sn_2Fe, and (right) cycling of this Sn-Fe alloy after ball milling (planetary and high energy) in two voltage windows. The current was 0.3 mA/cm^2 in the 1st cycle and then changed to 0.5 mA/cm^2 thereafter.

Milestone (b) underway:
Nano-size silicon material synthesized

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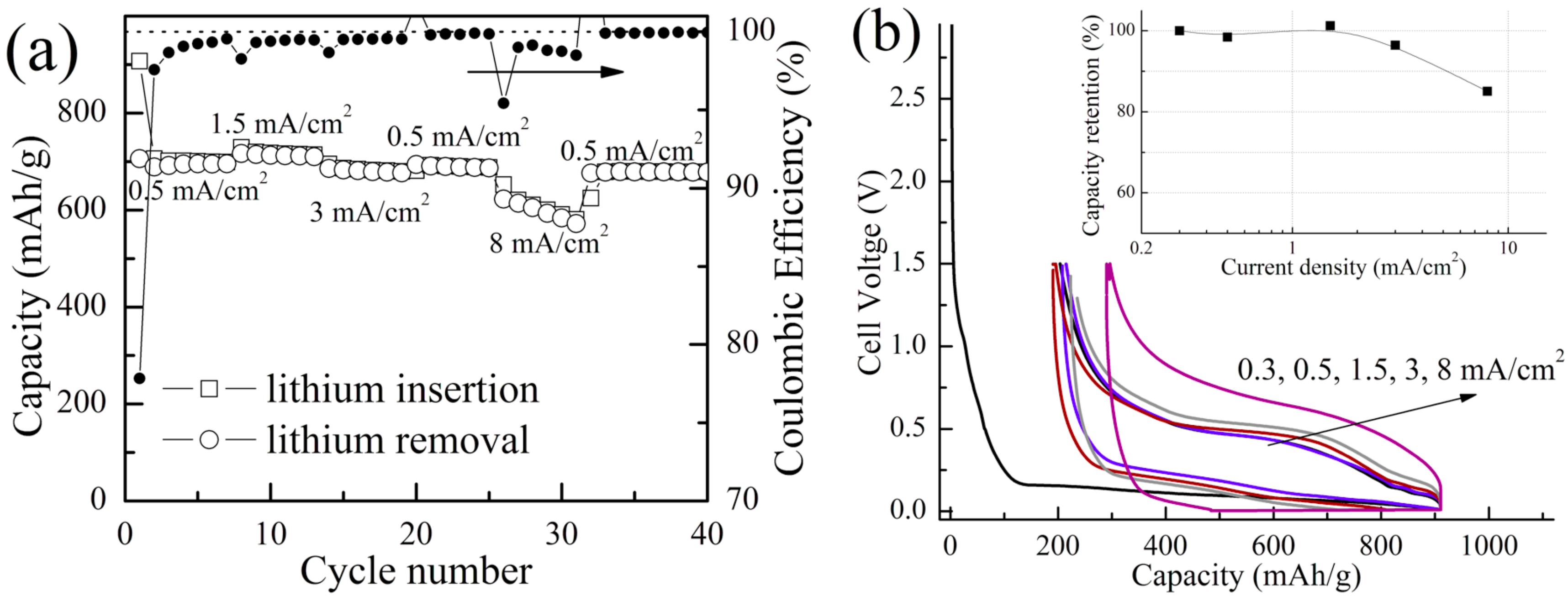
- **Method 1:**
  - Si/MgO/graphite (SMOG) composite was synthesized by a two-step process high energy ball-milling reduced by Mg and carbon by mechanochemical methods
    - First step: SiO reduced by Mg by high energy ball-milling
    - Second step: Product of 1st step high-energy ball milled with carbon
  - Electrochemical behavior determined



Rate capability of SMOG electrode between 0.01 V and 1.5 V. (a) capacity on cycling at different current densities; (b) cycling curves at different rates, and Ragone plot for Li insertion. 1 C rate = 2.8 mA/cm^2. The first cycle current density was 0.3 mA/cm^2.

Milestone (b) completed:
Nanosilicon synthesis and electrochemical behavior

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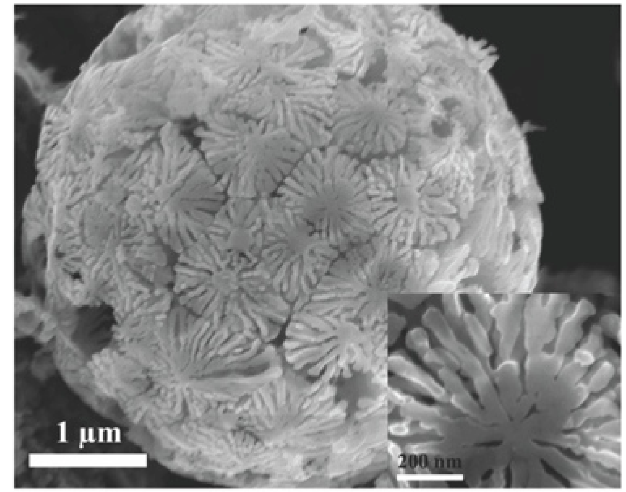
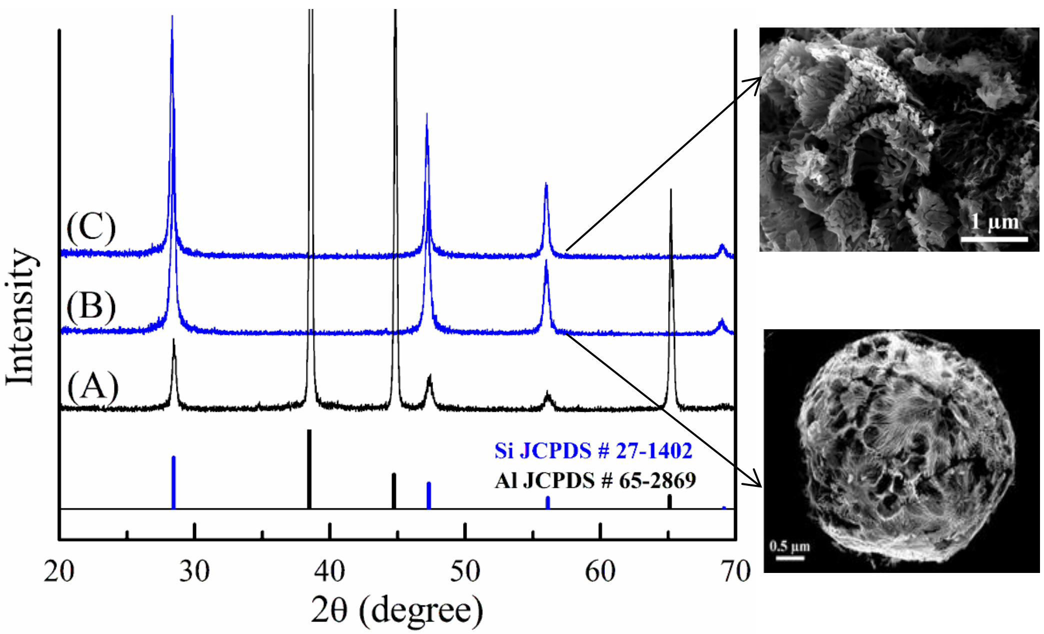
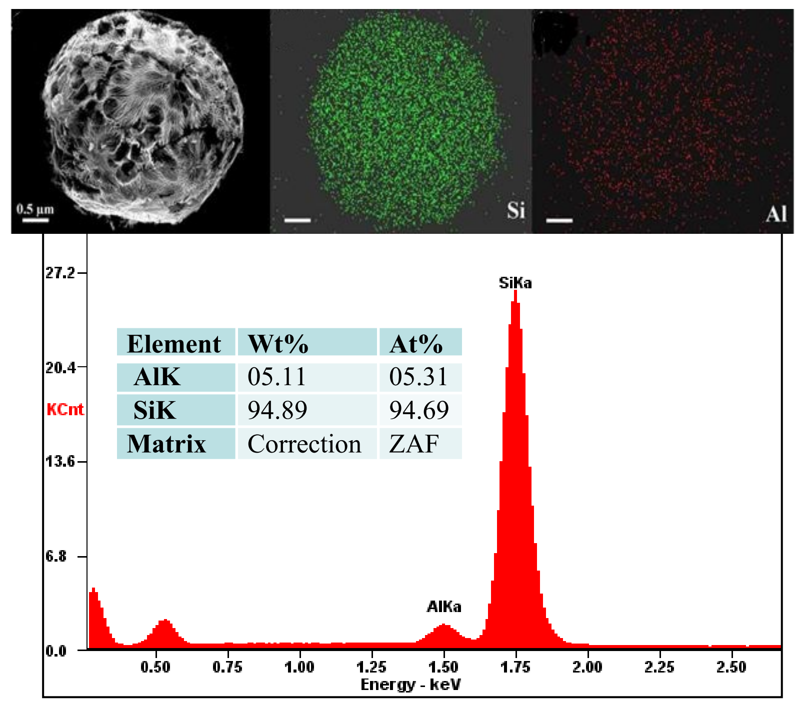
- **Method 2:**
  - Etching Al-Si alloy
    - Gives porous Si with 3D network
    - XRD data yields a lattice parameter larger than pure Si
    - EDS ~5 wt. % Al uniformly distributed in this material





(A) Al-Si, (B) Si spheres and (C) broken Si spheres.



Element	Wt%	At%
AlK	05.11	05.31
SiK	94.89	94.69
Matrix	Correction	ZAF

Milestone (b) completed : Nanosilicon synthesis and electrochemical behavior

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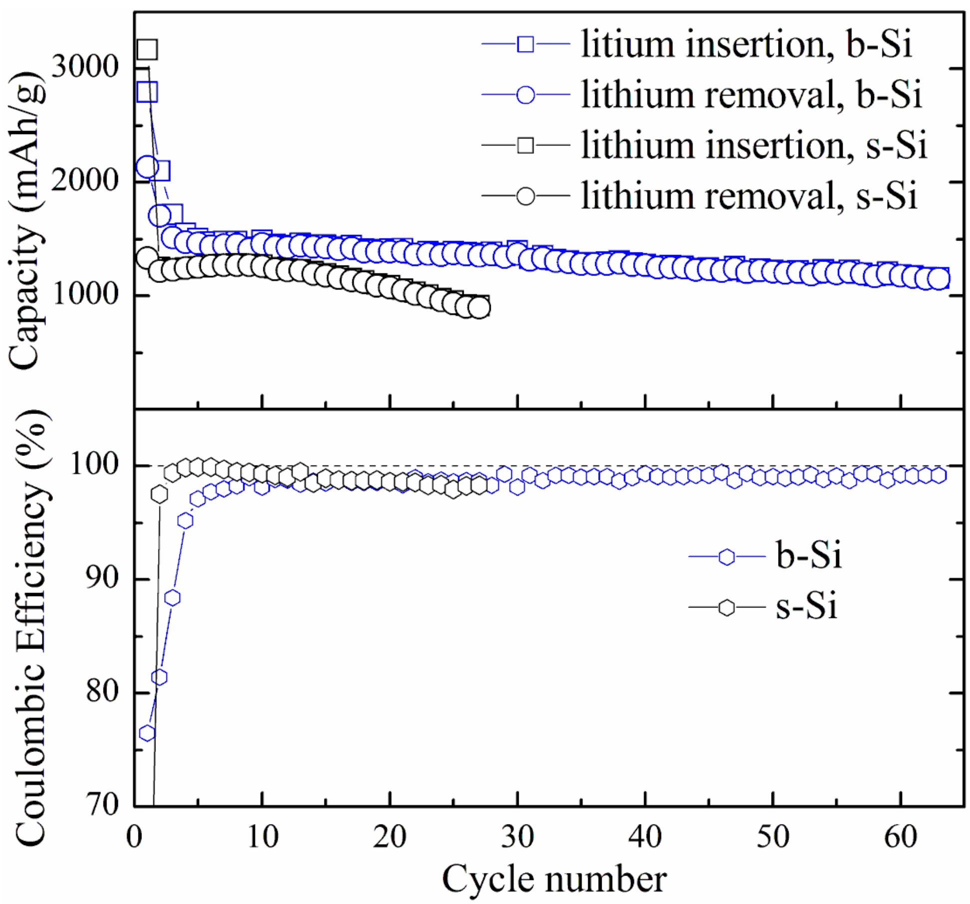
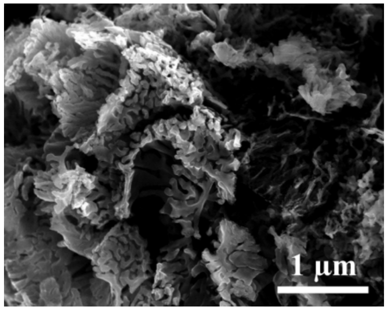
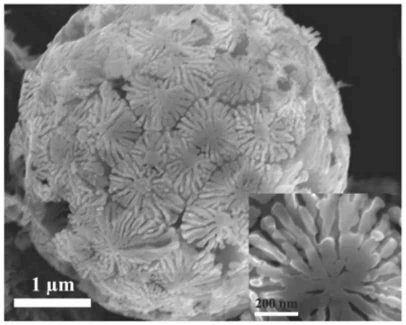
– Electrochemical behavior determined
  - This porous nanosilicon material shows high lithium capacity
  - Breaking the spheres enhances the contact between silicon and carbon, improving capacity retention





broken Si spheres (b-Si)



Si sphere (s-Si)

Electrochemical cycling of broken Si spheres (b-Si) and Si sphere (s-Si) materials at 0.5 mA/cm^2 between 0.01 V ~1.5 V. First cycle current density was 0.3 mA/cm^2. The electrodes were made of Si, carbon black additive and binder in a weight ratio of 70:20:10

Collaboration and Coordination with other Institutions

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- **Brookhaven National Laboratory**
  - Provided samples of the new Sn_5Fe compound
    - Electrochemical studies completed
  - Ex-situ and in-situ synchrotron X-ray diffraction, PDF (pair distribution function) and XAS (X-ray absorption) studies
- **Lawrence Berkeley National Laboratory**
  - Working with BATT anode team comparing tin and silicon materials
    - Similar challenges, such as 1st cycle loss, being addressed
  - Umicore nanograin Si material for Si baseline standard
- **Primet Precision (Ithaca Co)**
  - Collaboration underway on nanosizing materials (Nano-scissoring^{TM})
- **NYBEST** (New York Battery and Energy Storage Technology Consortium
  - Building collaborations between Industry, Academia, and Government

Future Work

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- **Nano-Sn_2Fe**
  - Optimize synthesis methods
    - Mechanochemical method
      - Find viable source of iron for scale-up, that maintains nano-size
    - Solvothermal method
      - Eliminate tin metal and oxide impurity
      - Increase capacity
      - Make GO/NOGO decision
  - Reduce first cycle loss
    - Find optimum carbon and titanium content
  - Fully understand the reaction mechanism

- **Nano-Si**
  - Investigate other reductants, such as titanium
  - Reduce 1^{st} cycle loss
  - Improve cycling performance

Summary

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- **Nano-tin**
  - Discovered the excellent electrochemical behavior of nano-Sn_2Fe
    - Equal to SONY SnCo-C anode in capacity and rate capability
      - GO for replacement of SnCo-C
    - Doubles the volumetric capacity of carbon
      - GO for replacement of carbon anode
      - Need to understand role of carbon – what is LiC_2?
  - Found two synthesis methods for nano-Sn_2Fe
    - Mechanochemical method – GO
      - Need to reduce first discharge excess capacity
    - Solvothermal method – needs improvement
- **Nano-silicon**
  - Formed by two different methods
    - Nano-silicon formed from Al-Si alloy
      - Unique morphology
      - Preliminary electrochemical results look promising - GO
    - Nano-silicon formed from SiO
      - Lower capacity