Metal-Based High Capacity Li-Ion Anodes

M. Stanley Whittingham
State University of New York at Binghamton

May 14th, 2012

Project ID #
ES063

Overview

Stan Whittingham
SUNY at Binghamton

Timeline

- Project start date: 01-01-2011
- Project end date: 12-31-2014
- Percent complete: 25%

Budget

- Total project funding
  - DOE $724,626
  - Contractor share: Personnel
- Funding received
  - FY11: 172k$
  - FT12: 172k$

Barriers

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

Partners

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

Objectives and Relevance of Work

Stan Whittingham
SUNY at Binghamton

- **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:**
  - Increasing the volumetric capacity of the anode by a factor of two will increase the cell energy density by up to 50%.
  - Will lower the cost of tomorrow's batteries

Relevance: Milestones

Stan Whittingham
SUNY at Binghamton

a) Synthesize nano-size tin materials by at least two different methods (Dec. 11)

- **Completed.**

b) Have the nano-size tin meet the gravimetric capacity of the Sn-Co-C electrode and exceed the volumetric capacity of the Conoco Philips CPG-8 graphite (Mar. 12)

- **Completed. The nano-size tin meets the gravimetric capacity of the Sn-Co-C electrode and exceeds the volumetric capacity of carbon.**

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

- **Ongoing.**

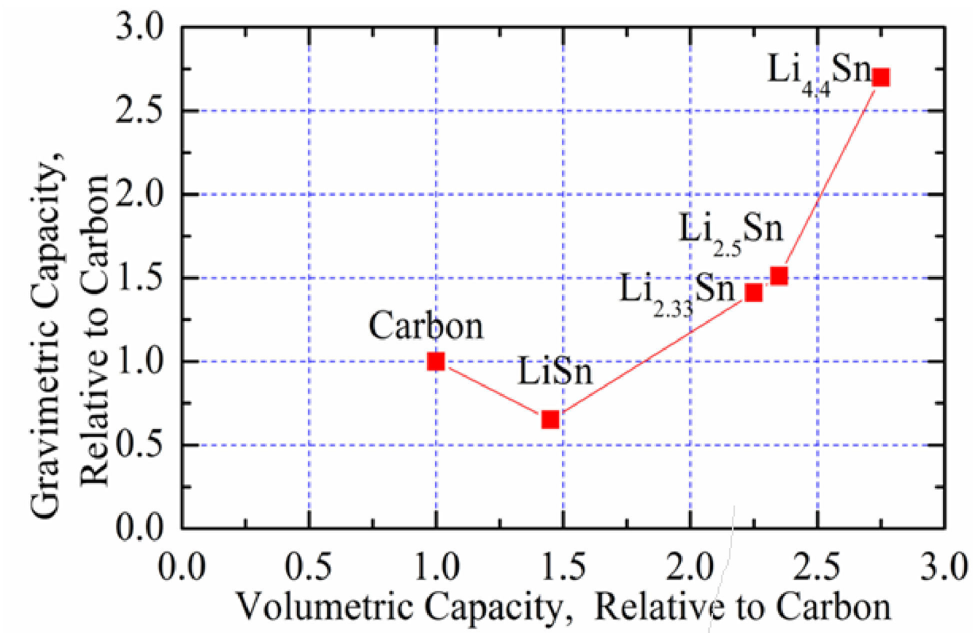
d) Determine the electrochemistry of a new synthetic nano-silicon material. (Sep. 12)

- **Ongoing.**

Approach and Strategy: Improved Anodes

Stan Whittingham
SUNY at Binghamton

- 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

Stan Whittingham
SUNY at Binghamton

- **High Cost**
  - Find a replacement tin anode for the expensive commercial SnCo-C
    - Low cost materials
    - Low cost manufacturing method

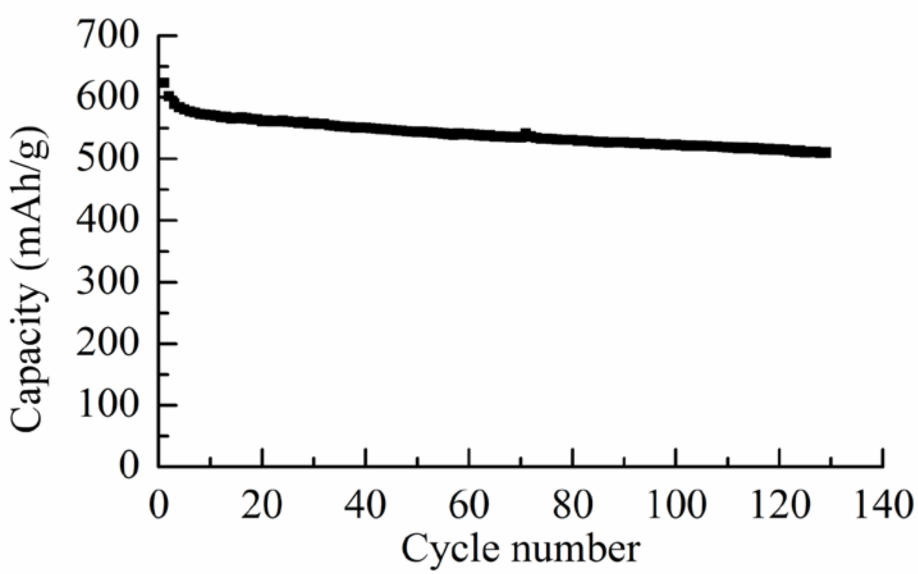
- **Low Volumetric Capacity of Li-ion batteries**
  - Volumetric capacity of Li-ion batteries limited by carbon anode
  - Find a material with double the volumetric capacity

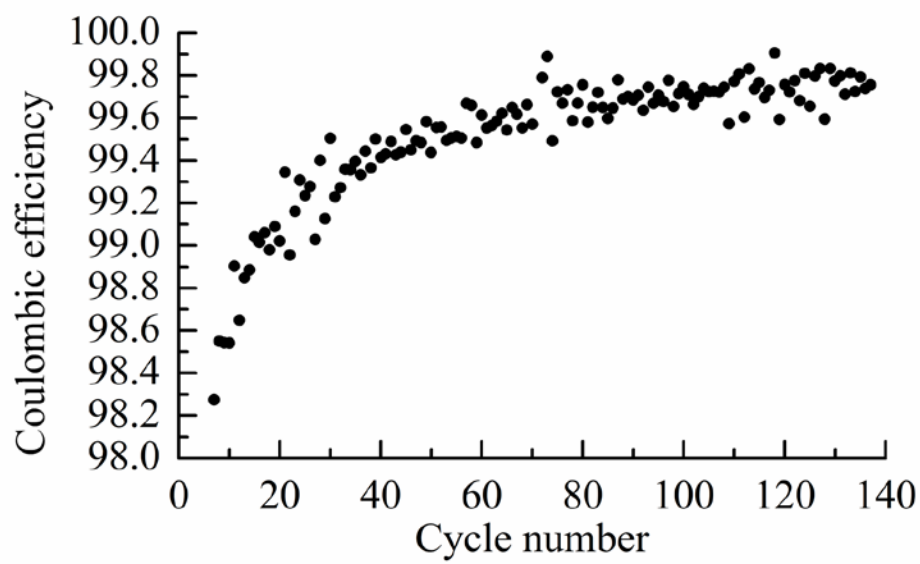
- **Low Safety and Abuse-tolerance**
  - Find an anode that reacts with lithium faster
    - Minimizes risk of dendrite formation
  - Find an anode that reacts with lithium at 300-500 mV vs Li
    - Minimizes risk of dendrite formation
    - Allows for higher rate charging

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

Stan Whittingham
SUNY at Binghamton

- **Method 1:**
  - SnO reduced by Ti (Al or Mg) and carbon by mechanochemical methods
    - Titanium found to be most effective reducing agent
    - Use of soft iron grinding media results in formation of Sn_2Fe/C composite
      - Material structurally characterized, 20-30 nm
    - Electrochemical behavior determined
      - Good electrochemistry found on un-optimized material, as shown below.

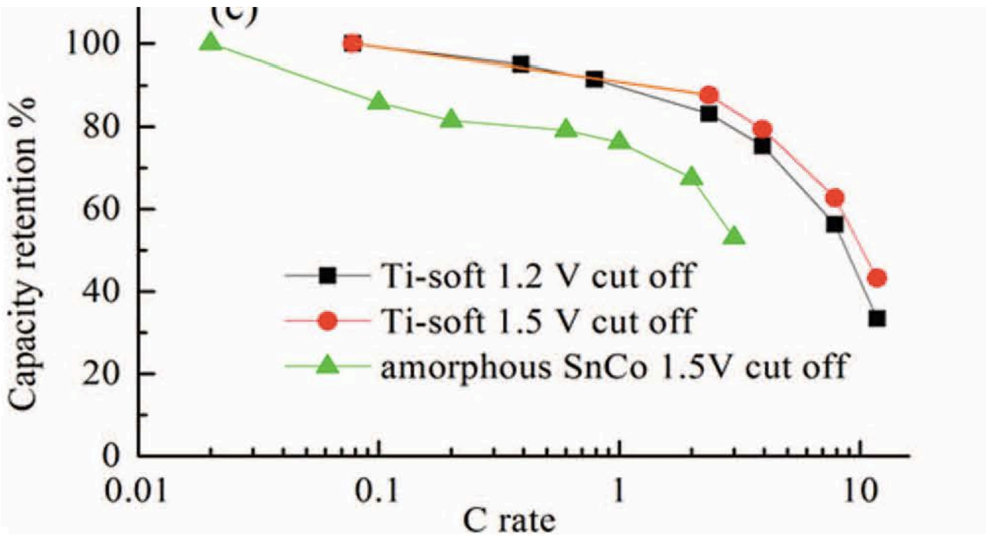




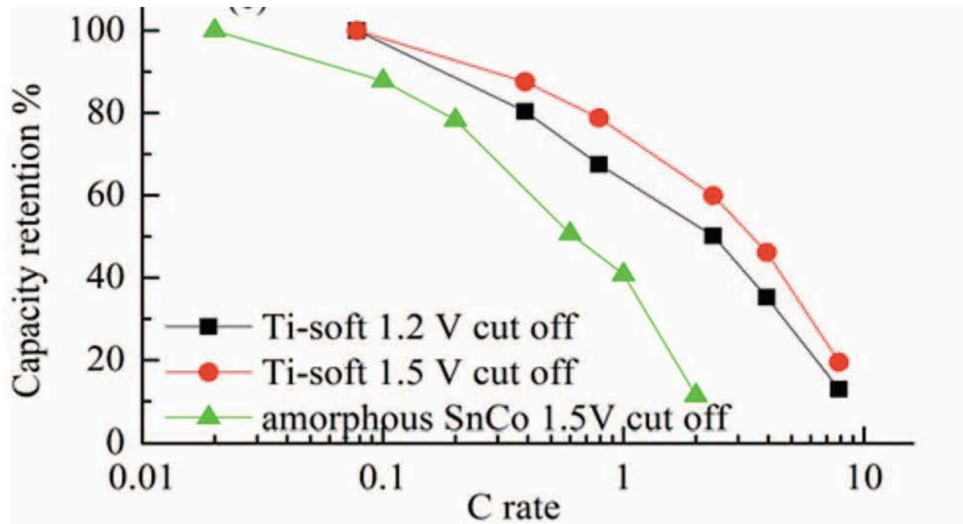
Milestone (b) achieved using method 1: Tin-carbon electrode + Fe as Sn_2Fe

Stan Whittingham
SUNY at Binghamton

1. SnFe Capacity/Rate Capability surpasses SnCo-C



Lithium removal – discharge of cell



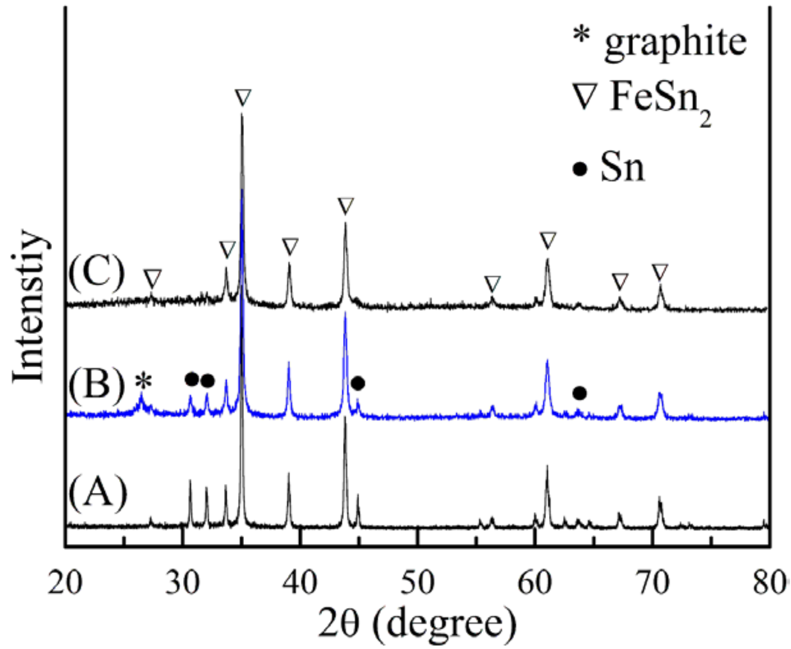
Lithium insertion – charging of cell

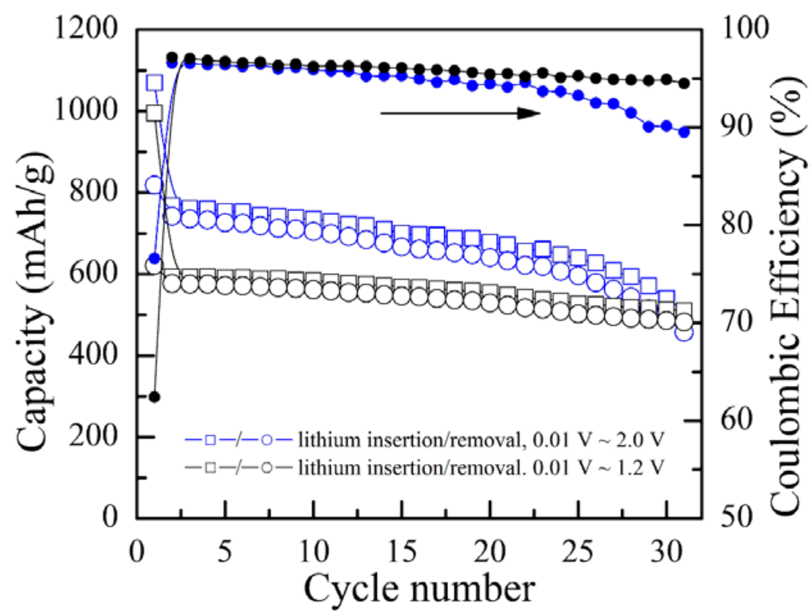
2. Volumetric capacity exceeds that of carbon: 2.2 Ah/cc vs < 1.0 Ah/cc

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

Stan Whittingham
SUNY at Binghamton

- **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
      - Grinding with carbon improves efficiency, but capacity drops to 500 (expts underway)





(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 (c) underway:
Electrochemical behavior of nano-tin

Stan Whittingham
SUNY at Binghamton

- Determine the limitations to the electrochemical behavior of the mechanochemical tin.
  - Tin reductant gave superior electrochemistry
    - Superior to Mg and Al
  - First cycle loss identified as an issue
    - Loss increases with tin metal content,
    - Loss also associated with carbon content
      - Plan to study various carbon contents
        - Determine minimum content

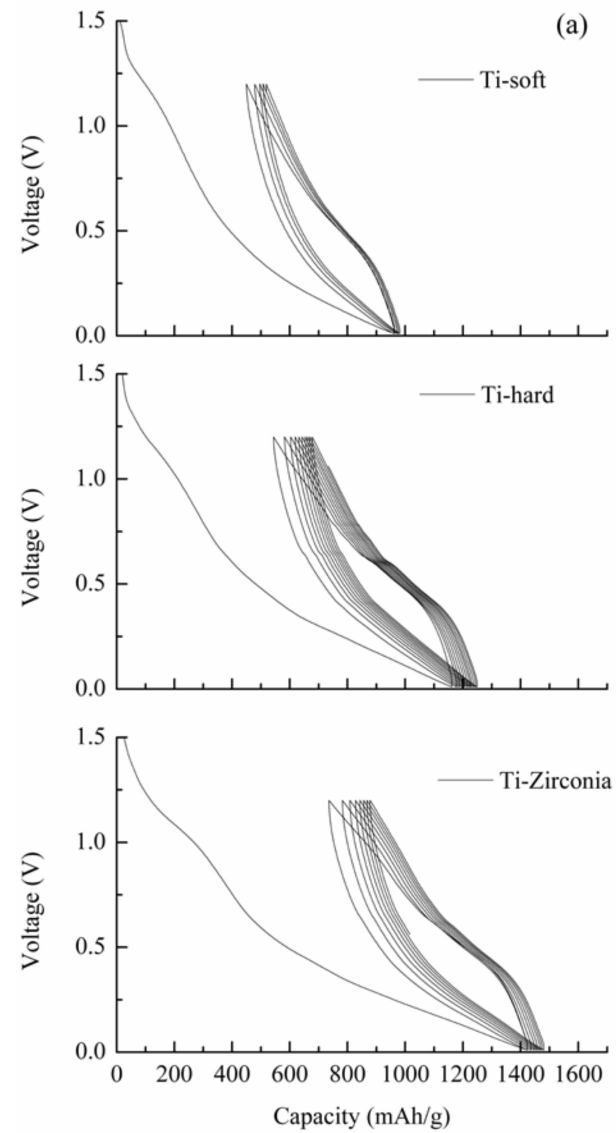
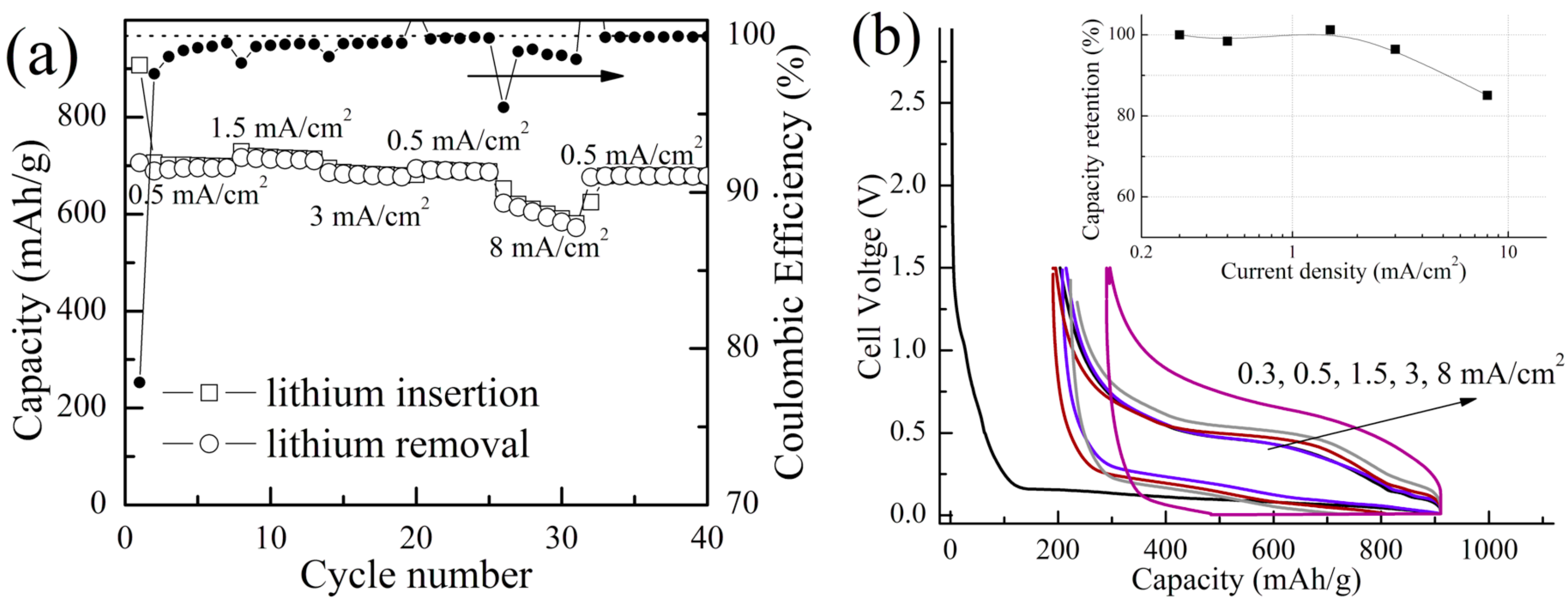


Figure: Cycling of nano-tin using Ti as reductant
Ti-soft used soft iron grinding media
Ti-hard used hard iron grinding media
Ti-zirconia used zirconia grinding media

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

Stan Whittingham
SUNY at Binghamton

- **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

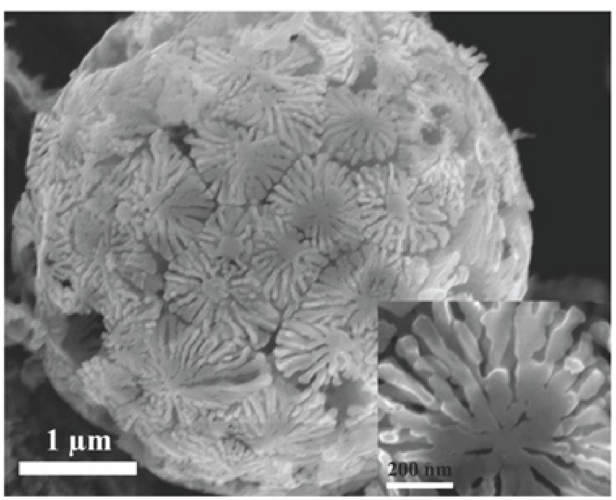


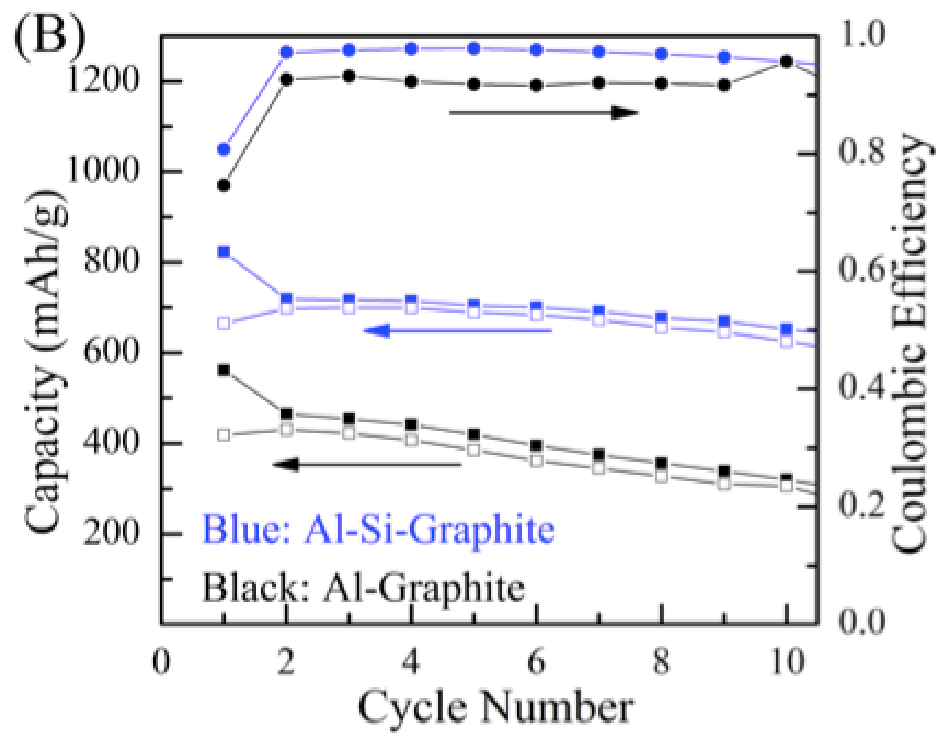
Rate capability of SMOG electrode between 0.01 V and 1.5 V. (a) capacity on cycling at different current densities; (b) cycling curves at different rates, and Ragone plot for Li insertion. 1 C rate = 2.8 mA/cm^2. The first cycle current density was 0.3 mA/cm^2.

Milestone (d) underway:
Nanosilicon synthesis from commercial alloy

Stan Whittingham
SUNY at Binghamton

- Using low cost engine-block Al-Si alloy
  - Determined the electrochemistry
- Nano-size changes properties and improves electrochemistry of Al:
  - Al dissolves silicon when nano-size (no solubility in bulk)
    - Increases capacity by > 50%
    - Improves capacity retention; loss reduced by a factor of 2
    - Coulombic efficiency improved
- Conclusion: Going nano helps
- Next step
  - Test nano-Si, after Al leached out





Collaboration and Coordination with other Institutions

Stan Whittingham
SUNY at Binghamton

- **Brookhaven National Laboratory**
  - Provided samples of the new Sn_5Fe compound
    - Electrochemical studies underway
- **Lawrence Berkeley National Laboratory**
  - Working with BATT anode team comparing tin and silicon materials
    - Similar challenges, such as 1st cycle loss, being addressed
- **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

Stan Whittingham
SUNY at Binghamton

- **Nano-Sn_2Fe**
  - Optimize synthesis methods
    - Mechanochemical method
      - Find viable source of iron for scale-up, that maintains nano-size
      - Determine optimum level of titanium reductant
    - Solvothermal method
      - Eliminate tin metal impurity
      - Increase capacity
  - Reduce first cycle loss
    - Find optimum carbon content

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

Summary

Stan Whittingham
SUNY at Binghamton

- **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
  - Found two synthesis methods for nano-Sn_2Fe
    - Mechanochemical method - GO
    - Solvothermal method – needs improvement
- **Nano-silicon**
  - Nano-silicon formed by Mg reduction of SiO in the presence of carbon
    - Preliminary electrochemical results look promising - GO
  - Common Al-Si engine-block alloy evaluated as nano-metal anode
    - Nano-Al, with Si doping, much superior to Si-free nano-Al
    - Nano-Si, after Al removal, shows unique morphology
      - Electrochemical behavior being evaluated