Metal-Based High Capacity Li-Ion Anodes

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ES063

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Overview

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
• 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
    • ≥ 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

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

- 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

- **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

**Method 1:**
- SnO reduced by Ti and carbon with hard iron balls by mechanochemical methods
  - Use of iron grinding media results in formation of Sn$_2$Fe/C composite
    - As reaction time increases, tin phase becomes Sn$_2$Fe
    - If reaction too long, iron phase is gradually formed after all Sn is converted to Sn$_2$Fe
- 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

- **Method 1:**
  - **SnO reduced by Ti** and carbon by mechanochemical methods
    - Titanium found to be most effective reducing agent
    - Results in formation of Sn$_2$Fe/C composite
    - Good electrochemistry found

  - **SnO reduced by Al** and carbon by mechanochemical methods
    - Use of iron grinding media results in formation of Sn$_2$Fe/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 Sn₅Fe compound

Collaboration with CNF at Brookhaven National Laboratory
Milestone (a) achieved using method 1:
Tin-carbon electrode + Fe as Sn$_2$Fe

SnFe Capacity/Rate Capability surpasses present commercial SnCo-C

Lithium removal – discharge of cell  
Lithium insertion – charging of cell
Nanosized Sn\textsubscript{2}Fe embedded in carbon

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

PDF analysis identifies phases formed

Sn\textsubscript{2}Fe-C + Li → Li\textsubscript{4.4}Sn + Fe + Sn\textsubscript{2}Fe (unreacted) + Li\textsubscript{0.5}C

C

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

- **Gravimetric capacity:**
  - Measured reversible capacity of 600 Ah/kg of total composite
  - $\text{Sn}_2\text{Fe}$ contributes 804 Ah/kg of $\text{Sn}_2\text{Fe}$
  - Remainder contributed by carbon
    - Must be $\text{C}_2\text{Li}$
      - 1100 Ah/kg
    - Theoretical capacity of 760 Ah/kg for total composite
    - If $\text{C}_6\text{Li}$ 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

- **Method 2:**
  - FeCl₃ and SnCl₂ reacted with NaBH₄ by solvothermal treatment at 200 ºC
    - Product is Sn₂Fe 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/cm² in the 1st cycle and then changed to 0.5 mA/cm² thereafter.
Milestone (a) completed: Nano-size tin materials synthesized

• **Method 2:**
  - FeCl₃ and SnCl₂ reacted with NaBH₄ by solvothermal treatment at 200 °C
    - Product is Sn₂Fe 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 Sn₂Fe, 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/cm² in the 1st cycle and then changed to 0.5 mA/cm² thereafter.
Milestone (b) underway: Nano-size silicon material synthesized

- **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

![Graph](image)

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/cm². The first cycle current density was 0.3 mA/cm².
Milestone (b) completed: Nanosilicon synthesis and electrochemical behavior

- **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
Milestone (b) completed: Nanosilicon synthesis and electrochemical behavior

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

Electrochemical cycling of broken Si spheres (b-Si) and Si sphere (s-Si) materials at 0.5 mA/cm² between 0.01 V ~1.5 V. First cycle current density was 0.3 mA/cm². 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

- **Brookhaven National Laboratory**
  - Provided samples of the new $\text{Sn}_5\text{Fe}$ 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™)

- **NYBEST (New York Battery and Energy Storage Technology Consortium)**
  - Building collaborations between Industry, Academia, and Government
Future Work

• **Nano-Sn$_2$Fe**
  – 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$^{\text{st}}$ cycle loss
  – Improve cycling performance
Summary

• **Nano-tin**
  – Discovered the excellent electrochemical behavior of nano-Sn$_2$Fe
    • 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$_2$Fe
    • 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