Nano-scale Composite Hetero-structures: Novel High Capacity Reversible Anodes for Lithium-ion Batteries

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Overview

• **Timeline**
  – Start: Sept 2007
  – Finish: August 2009
  – 100% complete

• **Budget**
  – Total project funding
    • $515K
  – Funding received in FY09
    • $250K
  – Funding for FY10
    • $265K

• **Barriers**
  – Low available energy density
  – Poor cycle life
  – Poor rate capability

• **Targets for PHEV (2015)**
  ➢ Available Energy: 3.5-11.6 kWh
  ➢ Cycle life: 3,000-5,000 deep discharge
  ➢ Recharge rate: 1.4-2.8 kW

• **Partners/Collaborators/Students**
  • **Industries**
    • Ford Motor Company
    • PPG, Pittsburgh
  • **National Laboratory**
    • Dr. Robert Kostecki, LBNL
    • Dr. Vincent Battaglia, LBNL
  • **Other Universities**
    • Dr. Nikhil Koratkar, Rensselaer Polytechnic Institute
  • **Research Faculty/Students**
    • Dr. Moni Kanchan Datta, Univ. of Pittsburgh
    • Rigved Epur, Univ. of Pittsburgh
    • Prashant J. Hanumantha, Univ. of Pittsburgh
Objectives of this Study
May 2009-May 2010

- Identify new alternative anode materials to replace synthetic graphite that will provide higher gravimetric and volumetric energy density
- Similar or lower irreversible loss in comparison to synthetic graphite
- Similar or better cyclability and calendar life in comparison to synthetic graphite
- Investigate Nano-structured ($nc$-Si) and amorphous Si ($a$-Si) based composite anodes
- Improve the specific capacity, available energy density, rate capability and cycle life of nano-structured and amorphous Si based anode materials
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones or Go/No-Go Decision</th>
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<tbody>
<tr>
<td>July 2009</td>
<td><strong>Milestone:</strong> Synthesize nano-structured and amorphous Si based anodes using cost effective processing methods</td>
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<td>August 2009</td>
<td><strong>Milestone:</strong> Achieve stable reversible capacity higher than (~1000\text{mAh/g})</td>
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<td>November 2009</td>
<td><strong>Milestone:</strong> Reduce Irreversible loss to <strong>less then</strong> (\sim 20%)</td>
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<td>January 2010</td>
<td><strong>Milestone:</strong> Characterize the hetero-structures for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM</td>
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<td>March 2010</td>
<td><strong>Milestone:</strong> Investigate the origin and characterize the solid electrolyte interphase (SEI) layers</td>
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Approach

• **Explore Si and carbon based nano-composite electrodes**
  
  - Explore novel low cost approaches to generate nano-scale hetero-structures comprising nanocrystalline or amorphous Si and a variety of carbon precursors
  
    1. **Chemical Vapor Deposition (CVD)**
       
      - 1(a) Thermal cracking of Si based precursors
      
      - 1(b) Two step liquid injection CVD techniques

    2. **RF magnetron Sputtering**

    3. **Mechanochemical reduction** of Si based compounds using high energy mechanical milling (HEMM)

• **Characterization of structure and composition**
  
  - High Resolution XRD (HRXRD)
  
  - High Resolution SEM (HRSEM)
  
  - High Resolution TEM (HRTEM)
  
  - **In-situ Raman and FTIR** in collaboration with Robert Kostecki (LBNL) and Ford Motor Company

• **Electrochemical Characterization**
  
  - Electrodes evaluated in half cells against metallic Lithium as a counter electrode and comparisons have been made to graphite
  
  - Two electrode **2016 coin cell**
  
  - **Full cell testing using pouch cell** configuration in collaboration with Dr. Vincent Battaglia (LBNL) and Ford Motor Company
Technical Accomplishments (FY-09)

Problems with pure microcrystalline Si

- Pure microcrystalline Si (c-Si) (<44μm)
  - Structural failure within few cycles
  - Large irreversible loss

- Major challenge/Target
  - Improve the mechanical properties
  - Improve the stability and cycle life
  - Decrease the volume expansion/contraction
  - Irreversible loss reduction

- Active/Inactive nanocomposite concepts
  - Improved mechanical properties
  - Improved electronic conductivity
Technical Accomplishments (FY-09)
Synthesis of Si/C composite by HEMM

Gr-17.5wt.% Si-30wt.% PAN

- Si/C composite synthesized by HEMM in the presence of polymer additive polyacrylonitrile (PAN)
  - Polymer additive acts as an interfacial diffusion reaction barrier to form electrochemically inactive SiC during HEMM as well as during thermal treatment

- TEM investigation
  - Shows homogeneous distribution of crystalline Si on graphite matrix
  - Crystalline Si likely to provide a strong interface bonding with graphite due to presence of PAN derived carbon on the interface

- In-situ Raman spectroscopy
  - Si band: 520 cm\(^{-1}\), Graphite: 1580 cm\(^{-1}\), Amorphous hard carbon: 1360 and 1620 cm\(^{-1}\)
  - Raman map shows that crystalline Si covered by graphite and amorphous hard carbon
  - Homogeneous distribution of Si in graphite and amorphous carbon
Technical accomplishments (FY-09)

Cyclability of Si/C Composite anode

Improved cyclability of Si/C composite in comparison to pure c-Si arises due to

- Homogeneous dispersion and distribution of Si on graphite matrix
- Strong interface bonding between Si and graphite
- Compressive stress on Si/C composite due to coating with HC

Composites based on microcrystalline Si and C exhibit capacity more than ~1000mAh/g fades rapidly (more than 0.7% fade per cycle). **Need for improvement of the cycling stability of high capacity Si/C composite.**

**Major challenge for FY10**

- Improve the structural stability of higher composition Si based composite anode in order to achieve excellent cyclability exhibit high specific capacity (~1000-2000mAh/g) and energy density (800-1000Wh/kg)
- Reduction in the volume expansion/contraction during alloying of Li ion with Si

**Target for FY10**

Synthesis of nanocrystalline (nc-Si) or amorphous Si (a-Si) based hybrid nanostructured composite anode which is expected to undergo lower volume expansion and contraction as well as exhibit better mechanical properties compared to pure microcrystalline Si due to the presence of free volume
Technical Accomplishments (FY-10)

1 (a): Nano-crystalline Si synthesized by thermal cracking of Si based precursor

Nanocrystalline Si (nc-Si) synthesized by thermal cracking of Si based precursor on natural graphite
- Exhibit high specific capacity (~2400mAh/g)
- Low first cycle irreversible loss (12%)
- Alloying occurs at a peak potential of ~0.175V and ~0.07V
- nc-Si appears promising as an anode material

Target:
Synthesize nc-Si and carbon based composite anode
1 (b): Novel Synthesis of nc-Si/CNT composite anodes by simple two step CVD techniques

Schematic diagram showing the fabrication of nc-Si and carbon nanotube (CNT) hybrid nanostructures using simple two step liquid injection CVD techniques
Technical accomplishments (FY-10)
Structural analysis of \textit{nc-Si}/CNT composite anodes

XRD pattern shows the presence of \textit{nc-Si} and CNT. Presence of \textasciitilde5\% Fe is CNT-catalyst

Fig. a: Vertically aligned CNT (VACNT) prior to Si deposition
Fig. b: SEM image showing \textbf{CNT (VACNT) covered with nanoscale (\textasciitilde40\text{nm}) Si droplets}
Fig. c: TEM image showing \textbf{CNT covered with \textit{nc-Si} clusters} with defined spacing to each other
Fig. d: HR-TEM image of single Si nanoparticle showing lattice fringes of different orientation
Technical accomplishments (FY-10)

HRTEM studies on the interface of nc-Si/CNT

- **Fig. a:** HRTEM image of CNT and nc-Si interface showing presence of Distinct Interfacial layer between CNT and nc-Si
- **Fig. b:** EELS spectra showing presence of CNT
- **Fig. c:** EELS spectra at the interface is indicating presence of amorphous carbon
- **Fig. d:** Si nanocluster anchored to the CNT by the amorphous carbon interface layer

Note: Absence of SiC at the interface. Interface dynamics controlled by 10 nm amorphous C layer
Technical accomplishments (FY-10)

Electrochemical behavior of nc-Si/CNT

- 1st discharge specific capacity ~2552mAh/g
- 1st charge capacity ~2049mAh/g
- Irreversible loss: ~18% and excellent coulombic efficiency (~99.9%)
- Specific capacity at 2.5C rate ~1000mAh/g
- The dQ/dV curve shows a significant alloying occurs at ~0.06V

Excellent electrochemical performance of the Si/CNT hybrid structure. The approach appears promising for the fabrication of next generation anodes exhibiting high energy density and extended cycle life.
Technical accomplishments (FY-10)

**Core shell $nc$-Si/CNT structured**

Vertically aligned CNT (VACNT)

**Core shell structure** where VACNT is fully covered with $nc$-Si

$I_G/I_D$ ratio on the Raman spectroscopy indicates high purity multi-walled CNT (MWCNT)
Technical Accomplishments (FY-10)

Electrochemical performance of \textit{nc}-Si/CNT core shell structured anode

- \textit{nc}-Si/CNT core shell structured anode shows
  - High specific capacity (1\textsuperscript{st} discharge: 2720mAh/gm and 1\textsuperscript{st} charge capacity: 2491mAh/g)
  - 0.2\% loss per cycle up to 20 cycles
  - Low irreversible loss (8\%) and excellent columbic efficiency (close to 99.9\%)
  - Alloying occurs at a peak potential of \(~0.16\text{V}\) and \(~0.078\text{V}\)

Cycled at C/27 rate

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure}
\caption{Discharge capacity and coulombic efficiency vs. cycle number.}
\end{figure}
Technical Accomplishments (FY-10)
Synthesis of Si Nanowire/Nanorod using Vapor and Etching Techniques

- Optimization of Si-Nanowire/Nanorod morphology
- Generation of hybrid nanocomposite based on Si nanowire/nanorod and carbon (CNT) is on going
Technical Accomplishments (FY-10)

2. Synthesis of amorphous Si film by RF Magnetron Sputtering

Amorphous Si deposited by RF magnetron sputtering

- EDAX shows the presence of Si
- Raman spectroscopy confirms the presence of amorphous Si (Si band: 475cm\(^{-1}\))
Technical accomplishments (FY-10)

Thin film amorphous Si

- Thin film $a$-Si film
  - Synthesized by RF magnetron sputtering
  - Cycled at C/2.5 (0.02V-1.2V)
  - Low irreversible loss ($\sim$20%)
  - Excellent cyclability ($0.11\%$ loss per cycle) and columbic efficiency ($\sim$100%) up to 30 cycles
- $a$-Si based anodes show promise for Li ion batteries
- Need for improved cycling stability beyond 30 cycles suggesting the desired improvements in interface stability
Technical accomplishments (FY-10)

Thin film amorphous Si/C composites

- Thin film a-Si/C composite film
  - Synthesized by RF magnetron sputtering
  - Cycled at C/2.3 (0.02V-1.2V)
  - Excellent cyclability (0.09% loss per cycle) and cumbic efficiency (~100%), and low irreversible loss (20%) up to 50 cycles

- a-Si/C based composite anodes show promise for Li ion batteries
  - Major challenge and target: Large scale synthesis of a-Si/C based composites

SEM after 75\textsuperscript{th} cycle: C/2.3 rate - No noticeable significant crack formation
Technical Accomplishments (FY-10)

3. Formation of amorphous Si (a-Si) by direct mechanochemical reduction (DMCR) of SiO

- Pure SiO shows significant alloying at ~0.23V due to the reduction of SiO by Li forming a-Si
- a-Si+Li₂O synthesized by electrochemical reaction between SiO and Li shows alloying occurs at ~0.08V
- dQ/dV plot of a-Si composite also showing significant alloying at ~0.08V confirming the formation of a-Si during direct mechanochemical reduction of SiO

Successful generation of amorphous Si (a-Si) by direct mechanochemical reduction of SiO.

Optimization of the synthesis and study of the electrochemical properties of a-Si based composite anode is currently on going.
Collaborations

**Industry**
- **Ford Motor company**: collaboration on the materials characterization (Raman spectroscopy) during alloying and dealloying reaction of the electrode with Li ion, and full cell testing using pouch cell configuration.

**National Laboratory**
- **Robert Kostecki (LBNL)**: Collaborated to investigate the origin and characterize the soild electrolyte interphase (SEI) in HEMM derived Si/C composite.
- **Vincent Battaglia (LBNL)**: Collaboration on-going to conduct full cell test using pouch cell configuration

**University**
- **Nikhil Koratkar (RPI)**: On-going collaboration to grow Si of different morphologies.

*Collaborators within the VT Program*
Activities for next fiscal year (FY 2011)

- Synthesis of high specific capacity and high energy density anode
  - Novel Materials Synthesis
    - Nanocomposite based on Nanocrystalline Si and Amorphous Si, generated from mechanochemical reduction, with carbon as a matrix
    - Nanorods, Nanowire or amorphous Si on carbon nanotube.
    - Control of Si/C interface chemistry
  - Synthesis Techniques that will be further explored
    - High through-put liquid injection chemical vapor deposition (HT-LICVD)
    - High energy mechanical alloying (HEMM)
    - Direct Mechanochemical Reduction (DMCR)
    - Thermal Cracking of Si Precursors
- Reducing irreversible loss, improve coulombic efficiency and improve recharge rate
  - Reducing the irreversible reaction of Li ion with Si based Intra type nano-composite (ITN)
    - Improve the kinetics of Li ion alloying/dealloying processes
    - Coating of Li ion conducting oxide
    - Improve the electronic conductivity of Si with doping to improve rate capability
  - Understand the origin of the SEI layer
    - Raman Spectroscopy, FTIR
    - SEM analysis of post cycled structures
- Full cell testing:
  - Coin cell and pouch cell configuration with suitable cathode
Summary

- **Synthesize Si based nano-composites of different morphologies such as amorphous, nano-crystalline, nano-wires and nano-tube.**
  - Demonstrated successful synthesis of **a-Si** and **nc-Si** based composite using cost effective methods in FY-10 that are amenable for scale up
  - **nc-Si** particles and **films on CNT** have been successfully synthesized by cost effective techniques
  - nc-Si/CNT hybrid nanostructures developed in FY-10 show promising response of ~2000 mAh/g as an anode for next generation high energy density anode materials compared to Si/C composites developed in FY-09
  - Thin film **a-Si/C nanocomposite** developed in FY-10 show promising response of a-Si as an anode for Li ion batteries
  - Si/C nano-composite synthesized by HEMM in the presence of polymer additives

- **Usefulness of Polymer Additives**
  - To prevent the formation of electrochemically inactive SiC
  - Reduce the kinetics of amorphization of graphite

- **nc-Si/CNT nanocomposite developed in FY-10 shows**
  - excellent cyclability (~0.1% loss per cycle) with a specific capacity above ~1000mAh/g compared to ~700 mAh/g achieved in FY-09
  - low irreversible loss (~5-20%) compared to 25% in FY-09
  - Excellent coulombic efficiency (~99.9%)