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 2008
  – 100% complete

• **Budget**
  – Total project funding
    • $310K
  – Funding received in FY07
    • $150K
  – Funding for FY08
    • $160K

• **Present Systems**
  - Gr/LiPF₆+EC:DEC/LiNi₁/₃Mn₁/₃Co₁/₃O₂
  - Gr/LiPF₆+EC:DEC/LiFePO₄

• **Barriers**
  - Low energy density
  - Low specific capacity of graphite anode
  - Large irreversible loss
  - Poor cycle life

• **Targets**
  - Improve the specific capacity of anode
  - Low irreversible loss
  - Improve the cycle life

• **Partners/Collaborators/Students**
  - Dr. Jagjit Nanda, Ford Motor Company
  - Dr. Robert Kostecki, LBNL
  - Dr. Monikanchan Datta, Univ. of Pittsburgh
  - Wei Wang, Univ. of Pittsburgh
Objectives

- 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 in comparison to synthetic graphite
- Investigate Nano-structured Si based composite anodes
- Improve the specific capacity, rate capability and cycle life of nano-structured Si based anode materials
Milestones

• Synthesize **nano-structured Si based** anodes using **cost effective processing** methods
• Achieve stable reversible capacity higher than ~700mAh/g
• **Characterize the nano-scale hetero-structures** for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM
• Reduce Irreversible loss to less then ~20%
• **Investigate the origin and characterize** the solid electrolyte interphase (SEI) layers
Approach

- **Explore Si and carbon based nano-composite electrodes**
  - Explore novel low cost approaches to generate nano-scale heterostructures comprising crystalline Si and a variety of carbon precursors
    - High Energy Mechanical Milling (HEMM)
    - Chemical Vapor Deposition (CVD)
    - Pyrolysis of organic precursors

- **Characterization of structure and composition**
  - High Resolution XRD (HRXRD)
  - High Resolution SEM (HRSEM)
  - High Resolution TEM (HRTEM)
  - *In-situ* Raman

- **Electrochemical Characterization**
  - Electrodes evaluated in half cells against metallic Lithium as a counter electrode and comparisons have been made to graphite
  - Three electrode hockey puck cell
  - 2016 coin cell
Technical Accomplishments

Problems with pure microcrystalline Si

• Pure microcrystalline Si (c-Si) (<44μm)
  – Structural failure within few cycles
  – Formation of amorphous Li$_{3.5}$Si at onset potential ~0.1V with a peak potential ~0.07V
  – Phase transformation of c-Si to a-Li$_{3.5}$Si is associated with a large volume expansion (~300%)

• 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

Synthesis of Si/C nanocomposite by HEMM

Gr-25wt.% Si

- Formation of SiC within 5h HEMM
- The weight fraction of active Si decreases with increasing milling time
- The specific capacity decreases with increasing milling time
- Graphite transforms to amorphous structure
- High irreversible loss

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
  - Graphite retains its graphitic structure
  - Polymer additive enhances the wettability between Si and graphite
  - Composition after thermal treatment at 1073K: Gr-21.6wt.% Si-13.6wt.% HC
**Technical Accomplishments**

**Raman Spectroscopy and TEM of Si/C Nanocomposite**

- **In-situ Raman spectroscopy**
  - Si band: $520\text{cm}^{-1}$, Graphite: $1580\text{cm}^{-1}$, Amorphous hard carbon: $1360$ and $1620\text{cm}^{-1}$
  - Raman map shows that crystalline Si covered by graphite and amorphous hard carbon

- **TEM and SEM investigation**
  - Shows homogeneous distribution of nanocrystalline Si ($\text{nc-Si}$) of particle size $\sim10\text{nm}$ on graphite matrix
  - Nanocrystalline Si likely to provide a strong interface bonding with graphite
  - Si/C nanocomposite likely enhances the mechanical properties in comparison to $\text{c-Si}$
Technical accomplishments

Cyclability of Si/C Nanocomposite

**Intra type Nano-composite - ITN**

- Improved cyclability of Si/C nano-composite in comparison to pure c-Si arises due to:
  - Homogeneous dispersion and distribution of nc-Si on graphite matrix
  - Strong interface bonding between Si and graphite
  - Compressive stress on Si/C composite due to coating with HC

- Major challenge:
  - Improve the cyclability of higher composition of Si based composite (higher specific capacity) anode
  - Reduction in the volume expansion/contraction during alloying of Li ion with Si

- Target:
  - Synthesis of Li-Si based alloy which will undergo lower volume expansion and contraction compared to pure Si as an anode

### Composition (wt.%) and Specific Capacity (mAh/g)

<table>
<thead>
<tr>
<th>Composition (wt.%)</th>
<th>Specific capacity (mAh/g)</th>
<th>Irreversible loss (%)</th>
<th>Loss per cycle (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C-21.6 Si-13.7 HC</td>
<td>825</td>
<td>610</td>
<td>26</td>
</tr>
<tr>
<td>C-34.5 Si-13.7 HC</td>
<td>1215</td>
<td>1019</td>
<td>16</td>
</tr>
</tbody>
</table>
Technical accomplishment
Phase formation during alloying/dealloying of Li with Si

First Cycle

- 1st discharge and charge of Gr-21.6wt.% Si-13.6wt.% HC
  - cycled at ~160mA/g (~C/6)
  - 0.02V-1.2V
  - a-Li$_{3.5}$Si after 1st discharge (~0.06V)
  - Amorphous Si (a-Si) after 1st charge (~1.2V)
  - Both Si and graphite are active

Second discharge profile

- 2nd discharge of Gr-21.6wt.% Si-13.6wt.% HC
- a-Si transforms to P-I, P-II and P-III phases during electrochemical reaction with Li$^+$
- Calculated composition from electrochemical reaction
  - P-I: Li-50at.% Si (LiSi)
  - P-II: Li-30at.% Si (Li$_7$Si$_3$)
  - P-III: Li-24at.% Si (Li$_{13}$Si$_4$)
Technical accomplishment

Alloying/dealloying behavior of Li with Si

- **2nd charge**
  - 0.6V: P-I (Li-50at.% Si (LiSi))
  - 0.4V: P-II (Li-30at.% Si(Li\textsubscript{7}Si\textsubscript{3}))
  - 0.5V: P-I+P-II (Li-40at.% Si)

<table>
<thead>
<tr>
<th>Phase transformation</th>
<th>Volume expansion (%)</th>
<th>Theoretical specific capacity (mAh/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P-I→P-III</td>
<td>114</td>
<td>2154</td>
</tr>
<tr>
<td>P-II→P-III</td>
<td>31</td>
<td>877</td>
</tr>
<tr>
<td>Si→P-III</td>
<td>236</td>
<td>3100</td>
</tr>
</tbody>
</table>
Technical accomplishments
Li-Si/C composite anode

- Li-Si/C composite generated by electrochemical reaction in situ
  - Synthesized by controlled electrochemical reaction of Li with a-Si
  - Charging reaction was terminated at ~0.6V, ~0.5V and ~0.4V
  - Cycled at 160mA/g within their stable potential window
  - Transformation of a-Si ↔ P-I phase is bypassed
  - Calculations based on electrochemical testing of Li-Si/C composite of composition C-21.6at.% Li-14.4at.% Si indicate a higher energy density with suitable cathode in comparison to pure HEMM derived Si/C composite.

<table>
<thead>
<tr>
<th>Alloy</th>
<th>Composition</th>
<th>Specific capacity (mAh/g)</th>
<th>Capacity Loss per cycle (%)</th>
<th>Energy density (Wh/kg)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/C</td>
<td>C-18.4at.% Si</td>
<td>~1000</td>
<td>~0.34</td>
<td>~369</td>
</tr>
<tr>
<td>Li-Si-C (0.02-0.6V)</td>
<td>C-15.5at.% Li-15.5at.% Si</td>
<td>~800</td>
<td>~0.21</td>
<td>~429</td>
</tr>
<tr>
<td>Li-Si-C (0.02-0.5V)</td>
<td>C-21.6at.% Li-14.4at.% Si</td>
<td>~700</td>
<td>~0.13</td>
<td>~432</td>
</tr>
</tbody>
</table>
Technical Accomplishments

Effect of phase formation on the structural stability of Si/C composite

- Effect of formation of $\alpha$-Li$_{3.5}$Si on the stability of the Si/C composite
  - Cycled the electrode between 0.07V-1.2V to prevent the formation of $\alpha$-Li$_{3.5}$Si
  - Capacity retention has been improved (0.14% loss per cycle)

- Target
  - Design a Si based alloy which can prevent the formation of $\alpha$-Li$_{3.5}$Si during discharge up to 0.02V
  - Synthesis of different structural morphologies of Si (amorphous, nano-crystalline, nano-wires, nano-rods) and composite hetero-structures
Technical accomplishments
Thin film amorphous Si/C composites

• Thin film a-Si/C composite
  – Synthesized by RF magnetron sputtering
  – Cycled at C/2.5 (0.02V-1.2V)
  – Excellent cyclability (0.07% loss per cycle) and low irreversible loss (25%)
  – Formation of high Li content a-Li$_{3.5}$Si or Li$_{3.75}$Si is by-passed
• a-Si based composite anodes show promise for Li ion batteries
  – Major challenge: Large scale synthesis of a-Si based composites
Technical accomplishments

Novel Synthesis of $a$-Si and $nc$-Si based composite anodes

- Large Scale Synthesis of $a$-Si and $nc$-Si based composite anodes achieved by HEMM

Calculated crystallite size of Si $\sim 15$nm
Technical accomplishments

Novel Synthesis of a-Si/C composite anodes

- $a$-Si nano-particles coated on carbon nano-tubes (CNT)
  - Controlled synthesis of $a$-Si particles of varying size on CNT
  - Generation of controlled thicknesses of $a$-Si particles/films on CNT
Technical accomplishments
Novel Synthesis of $a$-Si/C composite anode

- $a$-Si /CNT core shell nanostructures
- CNTs re-enforced Si hetero-structures
Activities for next fiscal year

- Activities for next fiscal year (Phase 2)
- Synthesis of high specific capacity anode
  - Novel Materials Synthesis
    - bulk crystalline Si, Nanocrystalline Si, Amorphous Si with carbon as a matrix
    - Nanorods, Nanowire or amorphous Si on carbon nanotube.
  - Synthesis Techniques that will be further explored
    - High energy mechanical milling
    - Novel mechanochemical processes
    - High through-put chemical vapor deposition (CVD)
- Reducing irreversible loss
  - Reducing the irreversible reaction of Li ion with Si based nano-composite (ITN)
    - Improve the kinetics of Li ion alloying/dealloying processes
    - Coating of Li ion conducting oxide
  - Understand the origin of the SEI layer
    - Raman Spectroscopy, FTIR
    - SEM analysis of post cycled structures
Summary

• Si/C nano-composite synthesized by HEMM in presence of polymer additives

• Usefulness of Polymer Additives
  – To prevent the formation of electrochemically inactive SiC
  – Reduce the kinetics of amorphisation of graphite

• Si/C nanocomposite shows
  – excellent cyclability (~0.1% loss per cycle) with a specific capacity up to ~700mAh/g
  – low irreversible loss (~15-30%)

• Li-Si/C composite synthesized by *in-situ* controlled electrochemical reaction
  – Identification of suitable phase composition and phase fields exhibiting excellent cyclability with high reversible capacity
  – Shows better stability than pure Si/C composite
  – High energy density compared to pure Si/C composite anode

• Synthesize Si based nano-composites of different morphologies such as amorphous, nano-crystalline, nano-wires and nano-rods.
  – Large scale synthesis of *a*-Si and *nc*-Si based composite using cost effective methods
  – Thin film *a*-Si/C nanocomposite show promising response as an anode for Li ion batteries
  – *a*-Si particles and films on CNT have been successfully synthesized by cost effective techniques