Anodes-Nanoscale Heterostructures and Thermoplastic Resin Binders: Novel Li-ion Anode Systems

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Overview

• **Timeline**
  – Start: Jan 2011
  – Finish: December 2015
  – 100% complete

• **Budget**
  – Total project funding
    • $1,082.7K
  – Funding received in FY11
    • $310.3K
  – Funding for FY12
    • $330.8K

• **Barriers**
  – Low specific energy and energy density
  – Poor cycle life and coulombic efficiency
  – 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
  • **National Laboratory**
    • Dr. Robert Kostecki, LBNL
    • Dr. Vincent Battaglia, LBNL
  • **Other Universities**
    • Dr. Spandan Maiti, University of Pittsburgh
  • **Research Faculty/Students**
    • Dr. Moni Kanchan Datta, University of Pittsburgh
    • Rigved Epur, University of Pittsburgh
Objectives of this Study  
May 2011-May 2012

- Identify new alternative nanostructured anode materials to replace synthetic graphite that will provide higher gravimetric and volumetric energy density
- Similar or lower irreversible loss (≤15%) in comparison to synthetic graphite
- Similar or better coulombic efficiency (≥99.9%) in comparison to synthetic graphite
- Similar or better cyclability and calendar life in comparison to synthetic graphite
- Investigate microcrystalline (μm-Si), nano-crystalline (nc-Si), nanoparticle (np-Si) and amorphous Si (a-Si) based nanocomposite anodes
- Improve the specific capacity, available energy density, rate capability and cycle life of nano-structured and amorphous Si based anode materials
- Identify elastomeric thermoplastic binders capable of binding the active materials preventing de-lamination
## Milestones

<table>
<thead>
<tr>
<th>Month/Year</th>
<th>Milestones or Go/No-Go Decision</th>
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<tbody>
<tr>
<td>July 2011</td>
<td>Milestone: Reduce Irreversible loss to <strong>less then ~15%</strong> of Si/C and Si/CNT nanocomposite anodes using <strong>cost effective processing methods</strong></td>
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<tr>
<td>September 2011</td>
<td>Milestone: Improve the coulombic efficiency of Si/C and Si/CNT nanocomposite above 99.5%</td>
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<td>December 2011</td>
<td>Milestone: Achieve Si/C and CNT/Si composite exhibiting low irreversible loss, high coulombic efficiency, stable reversible capacity higher than ~1200mAh/g</td>
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<td>March 2011</td>
<td>Milestone: Characterize the hetero-structures for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM</td>
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<tr>
<td>May 2011</td>
<td>Milestone: <strong>Identify suitable elastomeric thermoplastic binders</strong> for anode materials</td>
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**Si**: Silicon, **C**: Graphite or Carbon, **CNT**: Carbon nanotube
Approach

- Explore **Si and carbon/CNT** based nanocomposite anode
  - Explore **novel low cost approaches** to generate Si/C and Si/CNT composite comprising microcrystalline (\(\mu\text{m-Si}\)), nanocrystalline (\(nc\text{-Si}\)), nanoparticle (\(np\text{-Si}\)) or amorphous Si (\(a\text{-Si}\)) and a variety of carbon precursors:
    - *High energy mechanical milling (HEMM)*
    - *Chemical reduction followed by HEMM*
    - *Chemical vapor deposition (CVD)*
    - *Pulsed laser deposition (PLD)*
    - *RF magnetron sputtering (RFMS)*
    - *Fluidized bed reactor (FBR)*
  - Explore **suitable surface control additives (SCA)**, interface control additives (ICA), and **surface electron conducting additives (SECA)** in Si/C and Si/CNT nanocomposite which will *reduce 1st cycle irreversible loss (IR) and improve the coulombic efficiency (CE)* in subsequent cycles
    - Use of selective microstructure of graphite (e.g. KS6, MCMB, SFG) as matrix exhibiting low (< 20%) first cycle irreversible loss.
    - *Coating of Si/C composite* with suitable element or compound surface control additives (SCA) *to improve CE and cycling stability.*
    - Use of highly conductive additives to improve CE.
- Explore high strength, high ductility **elastomeric thermoplastic binders** to bind the active materials
- Full cell and long cycling tests:
  - *Coin cell and pouch cell* configuration with suitable cathode
Technical Accomplishments (FY-11)

Problems with Si/Graphite Nanocomposite

1st cycle Irreversible loss and Coulombic efficiency

In FY-10, Si/C nanocomposite synthesized by HEMM using PAN as interface reaction barrier

Si microstructures used in FY-10:
- microcrystalline (≤44μm)
- amorphous (a-Si)
- nanocrystalline (nc-Si) (~10-20nm)
- nanoparticles (np-Si) (~50-100nm)

Carbon source used in FY-10:
- Graphite flake (1-2µm, Aldrich)
- PAN based carbon

Si/C composite with µm-Si and graphite flake

Cycled at 160mA/g (C/6), 0.02V-1.2V
Loss per cycle: 0.09%, CE: 99.2%, IR: 37%

Si/C nanocomposite synthesized by HEMM, studied in FY-10, within a wide range of composition shows:

**Advantage:**
- High reversible capacity: 700-1200mAh/g
- Excellent cyclability: 0.01-0.2% loss per cycle

**Disadvantage:**
- Large irreversible loss: ≥30%
- Low coulombic efficiency: ≤99.5%
Technical Accomplishments (FY-11)
Probable cause of 1st cycle irreversible loss of Si/C Nanocomposite

Electrochemical properties of 
Graphite flake (Aldrich) used in FY-10

- Si/Graphite flake nanocomposite studied in FY10
  - Large first cycle irreversible loss (>30%)
  - Low coulombic efficiency (<99.5%)
- Major challenge/Target
  - Irreversible loss reduction (≤15%)
  - Improve the coulombic efficiency (≥99.9%)
- Concepts
  - Reduce the SEI layer formation which may arise due to the presence of graphite flake and PAN-C
  - Increase electronic conductivity to improve the coulombic efficiency using (SECA)
  - Improve the IR, CE and stability of Si/C composite using SCA

Drawback:
- Large IR loss: ~28-35%

Cycled at 100mA/g (C/3.2), 0.02V-1.2V

Cycled at 160mA/g, C/15, 0.02V-1.2V

\( \text{a-Si, np-Si, nc-Si} \) synthesized by thermal cracking of Si based precursor

- Irreversible loss: 12%
- \( \text{a-Si, nc-Si and np-Si} \) shows: ~5-15% irreversible loss (supplemental slides)
Technical Accomplishments (FY-11)
Reduction of 1st cycle irreversible loss of Si/C composite

Use of *low first cycle irreversible loss based synthetic graphite as matrix*

Electrochemical properties of synthetic graphite (MCMB, KS6)

- **Target:** synthesis of Si/C composite using KS6/MCMB graphite as a matrix
  - Cycled at 100mA/g (C/3.2), 0.02V-1.2V
    - Excellent coulombic efficiency and stability
    - **Low first cycle irreversible loss: 15-20%**

- Major challenge: improve the coulombic efficiency of KS6/Si above 99.9%

KS6/np-Si nanocomposite synthesized by HEMM

- Cycled at 160mA/g, 0.02V-1.2V
  - Low first cycle irreversible loss: 20%
  - Low irreversible loss due to presence of KS6 graphite as matrix
  - Couloumbic efficiency: ~99.2%
  - Excellent stability: 0.01% loss per cycle
Technical Accomplishments (FY-11)
Improve the coulombic efficiency of Si/C nanocomposite using surface electron conducting additives (SECA)

\[ \mu\text{m-Si/KS6/SECA} \] nanocomposite with microcrystalline Si:
Cycled at 160mA/g, 0.02V-1.2V
- Irreversible loss: 14%
- Coulombic efficiency: 99.8%
- Loss per cycle: 0.3%
- KS6/Si/SCA improve the coulombic efficiency while maintaining low 1\text{st} cycle irreversible loss

**Target:** improve the cyclability while maintaining low first cycle irreversible loss and high coulombic efficiency using a-Si or np-Si

\[ a\text{-Si/KS6/SECA} \] based composite
Cycled at 160 mA/g, C/6.5, 0.02V-1.2V
- Reversible capacity: \( \sim 1050 \text{mAh/g} \)
- Fade in capacity: 0.04% per cycle
- First cycle Irreversible loss: \( \sim 17\% \)
- Coulombic efficiency: 99.8%

Identify and engineer a Si/C nanocomposite structure which shows high specific capacity with low IR, high CE and excellent cyclability

**Target for FY-12:** Long cycle life \( \geq 300 \text{ cy.} \) and tested in full cell configuration
Technical Accomplishments (FY-11)
Improve the CE, IR and stability of Si/C nanocomposite using surface control additives (SCA)

Target:
Improve the stability of μm-Si/KS6 composite using surface control additives (SCA)

μm-Si/KS6 nanocomposite without SCA
Cycled at 160mA/g, 0.02V-1.2V
1st discharge: ~1317mAh/g, 1st charge: ~1131mAh/g
➢ Irreversible loss: 14%
➢ Coulombic efficiency: 99.1%
➢ Loss per cycle: 1%

μm-Si/KS6 nanocomposite with SCA
Cycled at 160mA/g, C/5, 0.02V-1.2V
1st discharge: ~923mAh/g, 1st charge: ~798mAh/g
➢ Irreversible loss: 13.5%
➢ Coulombic efficiency: 99.8%
➢ Loss per cycle: 0.1%

Surface control additive improve the stability while maintaining the IR and CE

Target for FY-12: Proper design and precise surface control to achieve high specific capacity with low IR and CE
Technical Accomplishments (FY-11)
Formation of amorphous or nanocrystalline Si (a-Si/nc-Si) by chemical reduction of silicon precursors

\[ \text{SiX}_4 + 4 \text{Li} \rightarrow \text{Si} + 4 \text{LiX} \]

- Heat Li metal to 150°C in solvent with flowing Ar gas
- Add required amount of Si-precursors in controlled fashion
- Product is centrifuged in anhydrous methanol to remove Li-complex and vacuum dried to give mix of a-Si & nc-Si
- The above product is milled with graphite (Aldrich) +PAN and decomposed at 500°C to form a-Si/nc-Si/G/PAN-C composite

- XRD analysis showing effect of solvent on crystallinity of Si
- Raman spectra obtained at 2 different regions of the obtained Silicon product confirming a-Si and nc-Si.
Technical Accomplishments (FY-11)

a-Si/nc-Si by chemical reduction of silicon precursors

(a) SEM (b) EDAX & (c) TEM image of the nc/a-Si obtained after vacuum drying. EDAX shows presence of Si and O.
Cycled at: 100 mA/g, Voltage: 0.02 – 1.2 V vs. Li+/Li

- First discharge capacity ~ 1180 mAh/g
- First cycle irreversible loss: ~ 38%
- Possible reasons for IR loss:
  - Surface oxide (SiOₓ)
  - SEI layer formation

Technical Accomplishments (FY-11)

(a-Si/nc-Si/G-PAN-C) composite synthesized by chemical reduction of silicon precursors followed by HEMM

Composition:
PI: Li-50at.% Si (LiSi), PII: Li-30at.% Si (Li₇Si₃), PIII: Li-24at.% Si (Li₃.16Si)

Target at FY-12: Reduce the IR ≤15% and CE ≥99.9%

Wang et al., 2011, Elec. Comm , 13, 429
Datta et al., 2009, J. Power Sources, 194, 1043
Technical accomplishments (FY-11)
Novel Synthesis of $nc$-Si/CNT composite anodes using Interface Control Additives (ICA)
Technical accomplishments (FY-11)
Structural analysis of \textit{nc-Si}/CNT Heterostructures by CVD

- Silicon coated as uniform film on CNTs
  - Higher partial pressure of SiH$_4$ (SiH$_4$:Ar=1:10)
- Silicon coated as film droplets at uniform spacing on CNTs
  - Lower partial pressure of SiH$_4$ (SiH$_4$:Ar=1:30)
  - Size of silicon droplets: 40-60 µm

\textit{Wang et al.}, 2010, \textit{ACS Nano}, 4, 2233
Technical accomplishments (FY-11)
Electrochemical behavior of different morphologies of Si on MWCNTs (grown on Inconel 600 alloy)

- Cycled at 100mA/g, 0.02V-1.2V
  - 1st discharge specific capacity $\sim 2078 \text{mAh/g}$
  - 1st charge capacity $\sim 1958 \text{mAh/g}$
  - Irreversible loss: $\sim 6\%$ and excellent coulombic efficiency ($\sim 99.5\%$)

- Lithiation (1st cycle):
  - 0.20V: Lithiation of a-Si to form Li$_x$Si alloys
  - 0.08V: P(II) $\rightarrow$ P(III)

- Lithiation (2nd, 5th and 20th cycles):
  - 0.28V: P(I) $\rightarrow$ P(II)
  - 0.08V: P(II) $\rightarrow$ P(III)

- Delithiation
  - 0.3V: P(III) $\rightarrow$ P(II)
  - 0.45V: P(II) $\rightarrow$ P(I) for all cycles

- No need of conductive polymer additive in the preparation process: “Binder-Free” approach

Composition:
- PI: Li-50at.% Si (LiSi), PII: Li-30at.% Si (Li$_7$Si$_3$), PIII: Li-24at.% Si (Li$_{3.16}$Si)

Datta et al., 2009, J. Power sources, 194, 1043
Wang et al., 2011, Elec. Comm, 13, 429
Wang et al., 2010, ACS Nano, 4, 2233
Technical accomplishments (FY-11)
CNT/Si/ICA – Interface Control

ICA – Interface control additives

CNTs by CVD of m-xylene on quartz

ICA deposition by eBeam

Si by CVD of SiH$_4$
Technical accomplishments (FY-11)
CNT/Si/ICA heterostructures

SEM images of
(a) pure CNTs
(b) ICA (10nm) on CNTs
(c) Si (~50nm) on CNT/ICA
Technical Accomplishments (FY-11)
Synthesis of CNT/Si by Pulsed laser deposition

- $E = 10$ to $150 \text{ eV}$
- KrF excimer laser operating at 248 nm with pulse duration of 25 ns, 600 mJ/pulse, and maximum 50 Hz repetition rate
- Non steady-state atom concentrations

Silicon thickness: 15-20 nm
Technical Accomplishments (FY-11)
CNT/Si by Pulsed laser deposition

- Raman spectra shows the presence of CNTs (D’ band) with $I_g/I_d \approx 1$
- Presence of both amorphous and crystalline phases of Silicon
- Cycled at: 100 mA/g, Voltage: 0.02-1.2 V vs. Li⁺/Li
- Reversible capacity: ~1500 mAh/g with 99.8% CE
- Capacities calculated based on silicon weight of the composite

Target for FY-12: Optimize the process control to reduce the IR ≤15% and CE ≥99.9%
Technical Accomplishments (FY-11)
Synthesis of $a$-Si/C by RF magnetron sputtering

Thin film $a$-Si

Cycled at $100\mu A/cm^2$, C/2, 0.02V-1.2V
Specific capacity: **7080 mAh/cm$^3$** (~2820mAh/g)

Thin film $a$-C/Si

Cycled at $100\mu A/cm^2$, C/2.5, 0.02V-1.2V
Specific capacity: **6350 mAh/cm$^3$** (~2500mAh/g)

Thin film $a$-Si and $a$-Si/C film

*Synthesized by RFMS*

- Low irreversible loss (~20%)
- $a$-Si shows excellent cyclability (0.11% loss per cycle) and coulombic efficiency (~99.8%) up to 30 cycles
- Improve the stability of $a$-Si/C thin film in comparison to $a$-Si film beyond 30 cycle (0.09% loss per cycle)
- Excellent rate capability up to 3.5C

*Datta et. al., Elec. Acta., 2011, 56, 4717*
No crosslinking within polymer

No coupling of Si to polymer

Lower conductivity

PVDF

No crosslinking within polymer

Lower elasticity

Lower conductivity

Approach

Properties:

- Higher fracture strength of the binder
- Better elasticity and conductivity
- Crosslinking and coupling agents to enhance binding capacity
Effective Binder system

Improve degree of crosslinking

Use of adhesion promoters

Use of conductive polymers

Use of functionalized polymers for better binding

Chemical treatment of active material to promote adhesion

Effective Binder system

Direction of Approach

Cycled at 300mA/g, 0.02V-1.2V

- Better adhesion of Silicon with polymer
- High capacity retention (>1000mAh/g by 30 cycles)
- Better cyclability
- Loading of active materials: 2-3mg/cm²
- Preliminary results indicate promise of novel binder

Technical Accomplishments (FY-11)
Development of higher fracture strength thermoplastic binder

Graph showing discharge capacity versus cycle number.
Collaborations

Industry
• Ford Motor company (A. Drews, T. Miller)

National Laboratory:
• LBNL (Vince Bhattaglia); ANL (Chris Johnson), NREL (Dillon); PNNL (J. Liu, C. Wang)

University*:
• University of Pittsburgh (S. Maiti)
• Pennsylvania State University (D. Wang)

*Collaborators within the VT Program
Activities for next fiscal year

- Synthesize nanostructured and amorphous Si based anode by cost effective methods and identify new binders to achieve stable *reversible capacity (~1200mAh/g)* with low *irreversible loss (≤ 15%)* and high *coulombic efficiency (≥99.9%)* in full cell configurations.

- Identify interface control additives (ICA) to minimize first cycle irreversible loss and improve coulombic efficiency in hierarchical nano-scale structures.

- Identify novel SECA and SCA to achieve IR of ~15% and CE ~99.9% in HEMM derived systems.

- **Novel thermoplastic binders** with better coupling to active material resulting in improved cyclability.

- Coin cell and pouch cell configuration with suitable cathode.
Summary

• Approaches to generate scaled up quantities of high performance amorphous Si (a-Si) and nanocrystalline Si (nc-Si) indicate promising electrochemical response.
  – Results on HEMM and CVD derived composites indicate capacities in the 1000 mAh/g – 2000 mAh/g range.
  – Low irreversible loss (~5-18%) have been achieved.
  – Excellent coulombic efficiency (~99.5-99.8%) has been attained.
  – Binderless concept of VASCNT exhibit capacities ~1400-2000 mAh/g.

• Use of ICA, SECA and SCA are useful for lowering first cycle irreversible loss, improving the coulombic efficiency and cyclability as well as rate capability.

• Project initiated on generation of novel thermoplastic binders.
  – Initial results indicate improvements compared to PVDF.
List of Publications and Presentations

**Publications**
- M. K. Datta and P. N. Kumta, “Alloying/dealloying behavior of Li-ion with Si during electrochemical reaction”, in preparation.
- M. K. Datta, P. N. Kumta, “Si/C composite anode with surface control agent”, J. Power Sources, Under preparation,

**Presentations**
- R. Epur, M. K. Datta, W. Wang, J. Maranchi, P. Jampani and P. N. Kumta, “Silicon/Carbon based nanocomposite anodes for lithium-ion batteries”, 218th ECS meeting at Las Vegas, NV, USA - Oral presentation
- R. Epur, W. Wang, M. K. Datta and P. N. Kumta, “Hybrid nanostructures of silicon and vertically aligned multiwalled carbon nanotubes: Reversible high capacity lithium ion anodes”, 218th ECS meeting, Las Vegas, NV, USA – Poster
- R. Epur, W. Wang and P. N. Kumta “Carbon nanotube and silicon based novel heterostructures as high capacity anodes for lithium ion batteries”, 15th IMLB meeting 2010, Montreal, Canada – Poster
- P.N. Kumta, “Nano-scale Engineered Electrochemically Active Silicon Based Heterostructures” MRS meeting, Boston (2011) – Oral presentation

**Patent**
TECHNICAL BACK – UP SLIDES
1st cycle irreversible loss of Nanoparticle Si used in the present study

Nanoparticle Si (MTI Corporation): spherical crystalline
Particle size: 100nm, surface area: 80m²/g,

Cycled at 160mA/g, 0.02V-1.2V
1st cycle discharge capacity ~1500mAh/g
and 1st cycle charge capacity ~1260mAh/g
with an irreversible loss of only ~16%
Cycled at 160mA/g, 0.02V-1.2V
1st cycle discharge capacity ~1400mAh/g and 1st cycle charge capacity ~1200mAh/g with an irreversible loss of only ~10%.
Fade in capacity: 0.19% per cycle upto 100 cycles
Vertically aligned CNTs by CVD
CNT/Si Heterostructures by CVD
Other low cost approaches for generating large area amorphous silicon
SEM/EDAX/Raman of a-Si derived by electrochemical reduction

(a) SEM (b) EDAX & (c) Raman results of the electrodeposited a-Si film on copper foil
Electrochemical characterization of a-Si films derived by electrochemical reduction