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

Prashant N. Kumta
Swanson School of Engineering
University of Pittsburgh

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Project ID #: ES061

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

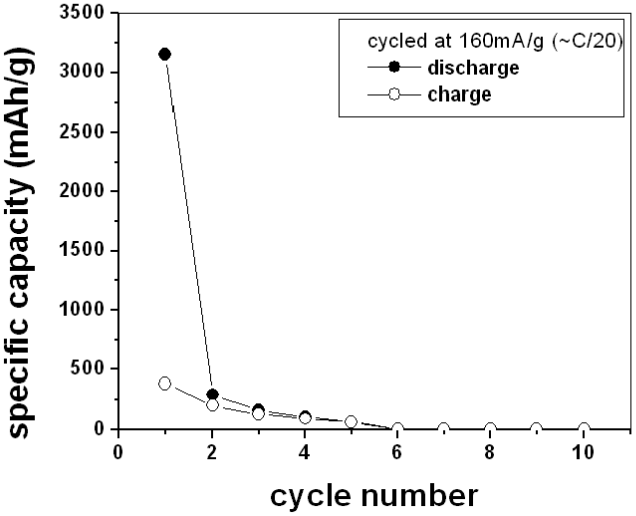
Month/Year	Milestones or Go/No-Go Decision
July 2009	Milestone: Synthesize **nano-structured and amorphous Si based** anodes using **cost effective processing** **methods**
August 2009	Milestone: Achieve stable reversible capacity higher than **~1000mAh/g**
November 2009	Milestone: Reduce Irreversible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

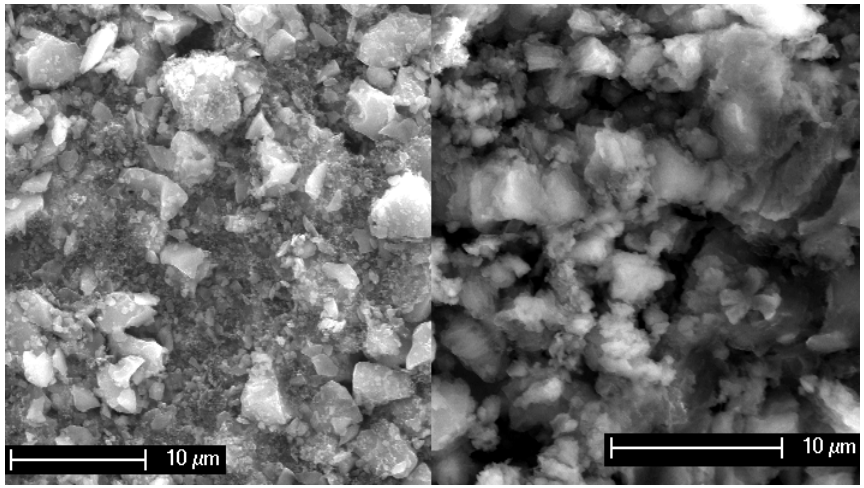
Approach

- ***Explore Si and carbon based nano-composite electrodes***
  - Explore novel low cost approaches to generate nano-scale 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)

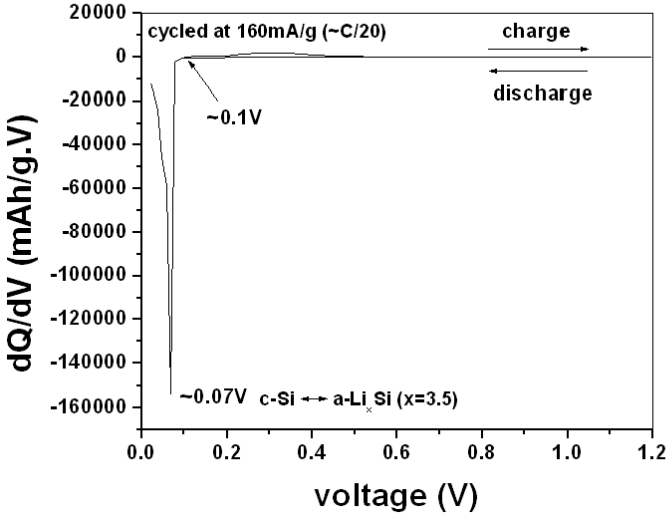
Problems with pure microcrystalline Si





Before cycling

After 10th cycle

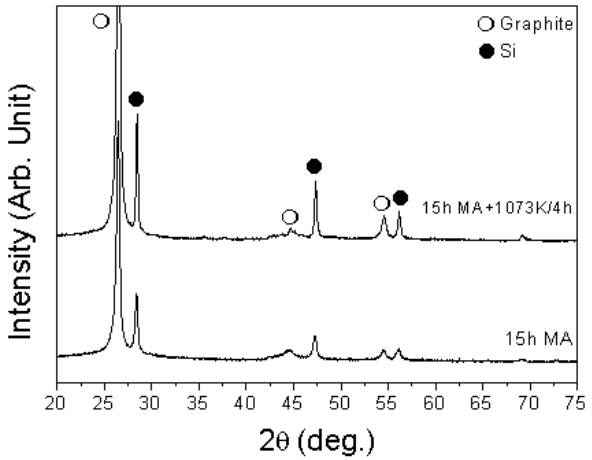


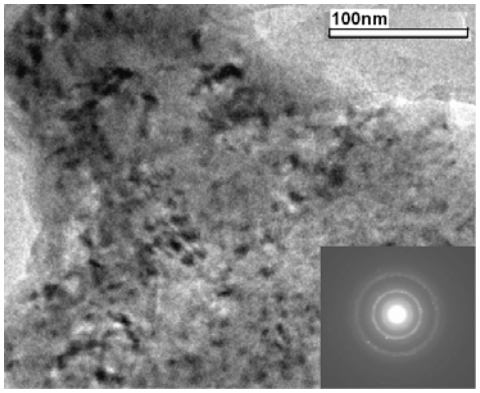
- **Pure microcrystalline Si (*c*-Si) (<44μm)**
  - Structural failure within few cycles
  - Large irreversible loss
- **Major challenge/Target**
  - Improve the mechanical properties
  - Improve the stability and cycle life
  - Decrease the volume expansion/contraction
  - Irreversible loss reduction
- **Active/Inactive nanocomposite concepts**
  - Improved mechanical properties
  - Improved electronic conductivity

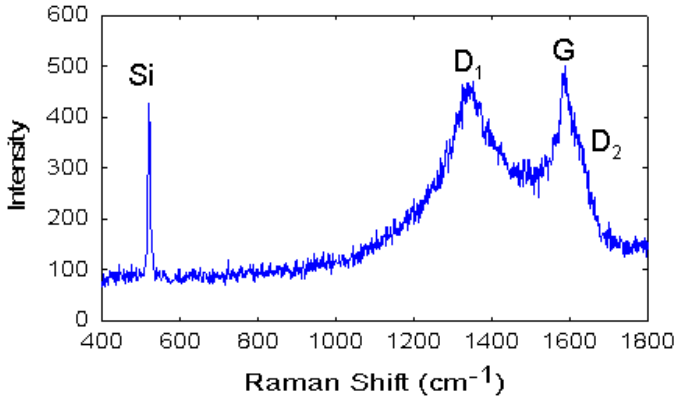
Technical Accomplishments (FY-09)

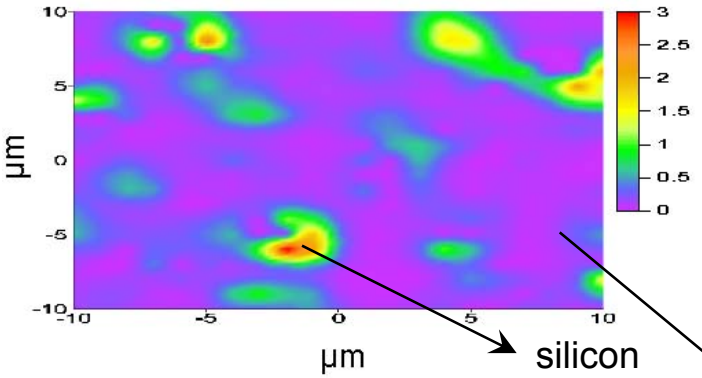
Synthesis of Si/C composite by HEMM

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









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

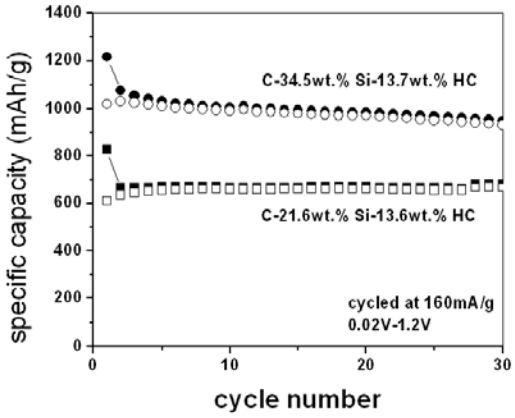
➢Shows ***homogeneous distribution of crystalline Si on graphite matrix***

➢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: 520cm^{-1}, Graphite: 1580cm^{-1}, Amorphous hard carbon: 1360 and 1620cm-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



Composition (wt.%)	Specific capacity (mAh/g)		Irreversible loss (%)	Loss per cycle (%)
	1st discharge	1st charge		
C-21.6 Si-13.7 HC	825	610	26	~0.08
C-34.5 Si-13.7 HC	1215	1019	16	~0.34

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.**

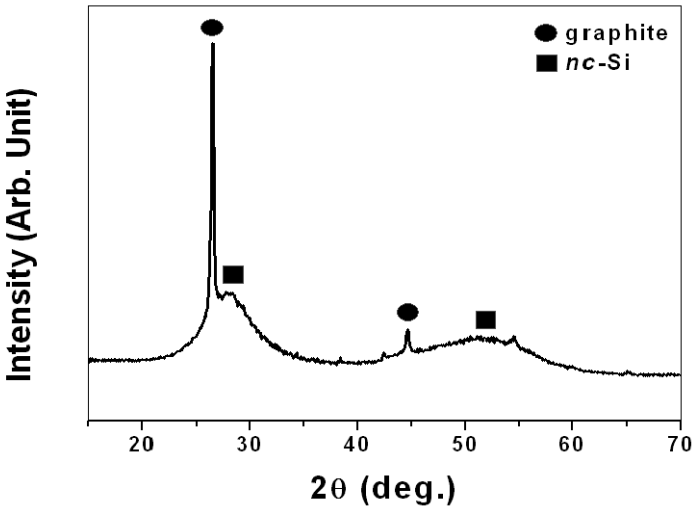
Major challenge for FY10

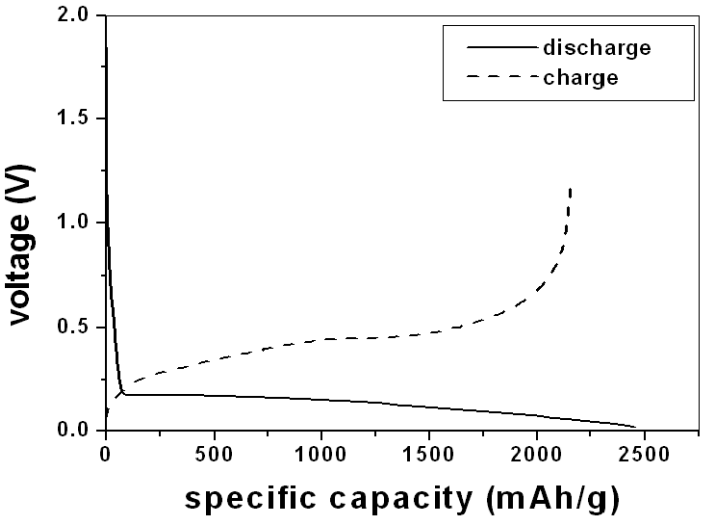
- **Improve the structural stability of higher composition Si based composite anode in order to achieve excellent cyclability exhibit high specific capacity (~1000-2000mAh/g) and energy density (800-1000Wh/kg)**
- **Reduction in the volume expansion/contraction during alloying of Li ion with Si**

Target for FY10

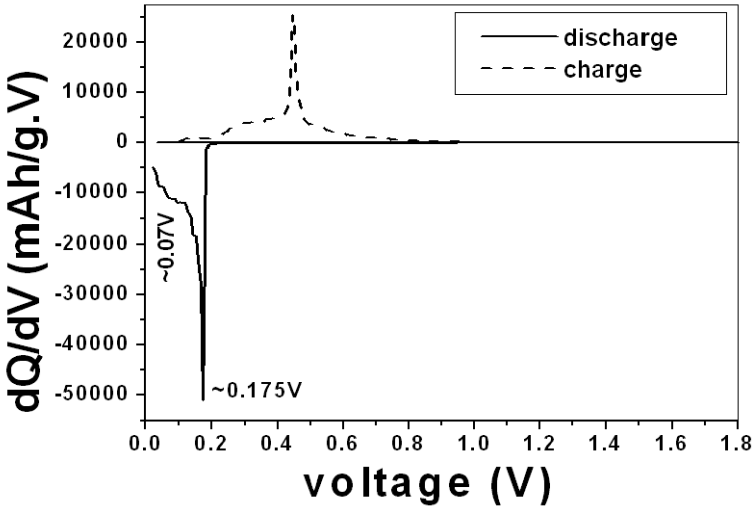
Synthesis of nanocrystalline (*nc*-Si)) or amorphous Si (*a*-Si) based hybrid nanostructured composite anode which is expected to undergo lower volume expansion and contraction as well as exhibit better mechanical properties compared to pure microcrystalline Si due to the presence of free volume

Technical Accomplishments (FY-10)
1 (a): Nano-crystalline Si synthesized by thermal cracking of Si based precursor





Cycled at C/7 rate



Nanocrystalline Si (*nc*-Si) synthesized by thermal cracking of Si based precursor on natural graphite

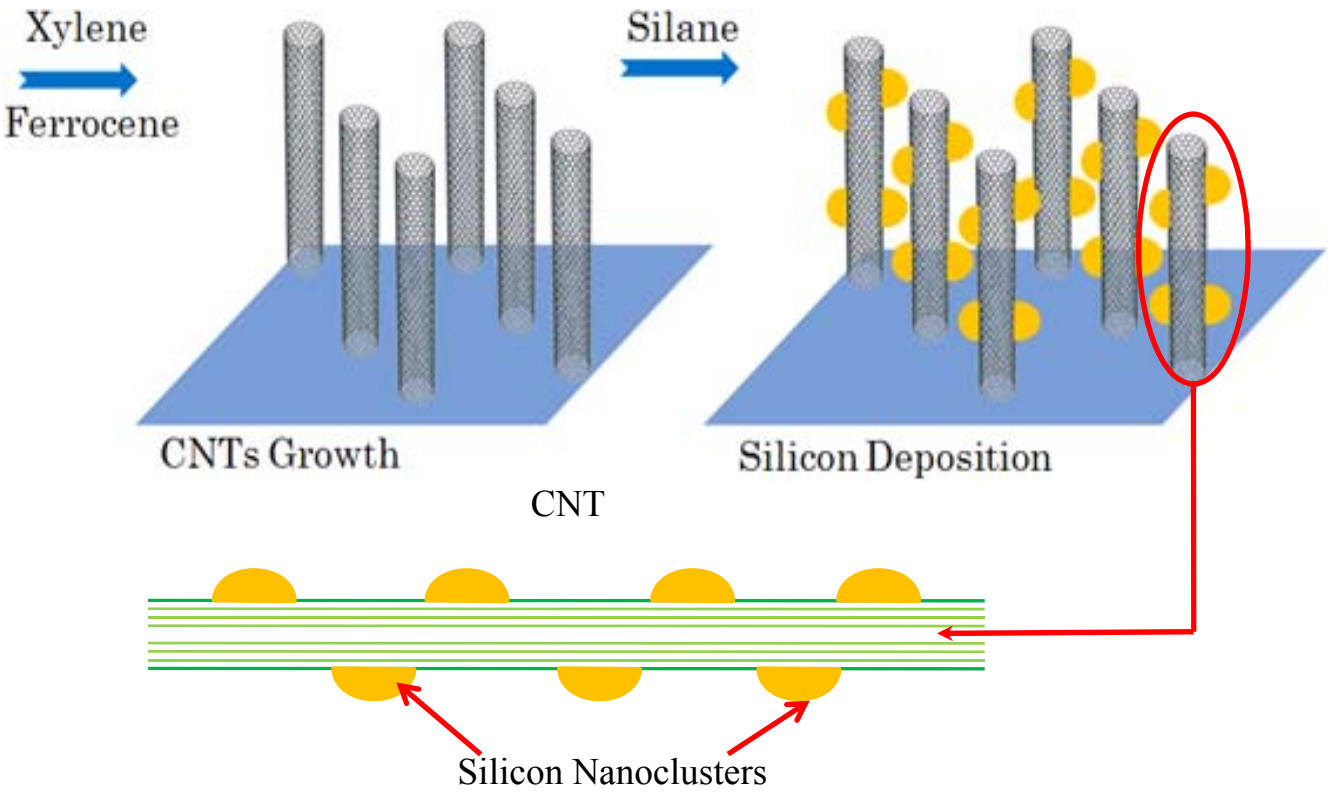
- Exhibit **high specific capacity** (~2400mAh/g)
- **Low first cycle irreversible loss (12%)**
- Alloying occurs at a peak potential of ~0.175V and ~0.07V
- *nc*-Si appears promising as an anode material

Target:

Synthesize *nc*-Si and carbon based composite anode

Technical accomplishments (FY-10)

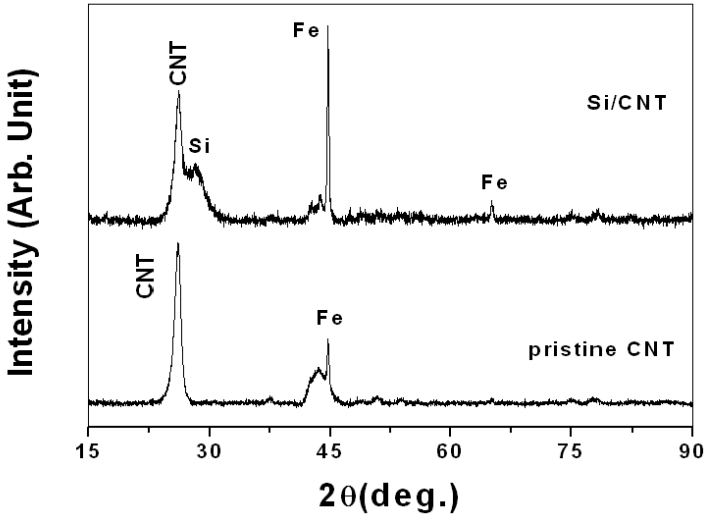
1 (b): Novel Synthesis of *nc*-Si/CNT composite anodes by simple two step CVD techniques



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 *nc*-Si/CNT composite anodes



XRD pattern shows the presence of *nc*-Si and CNT. Presence of ~5% Fe is CNT-catalyst

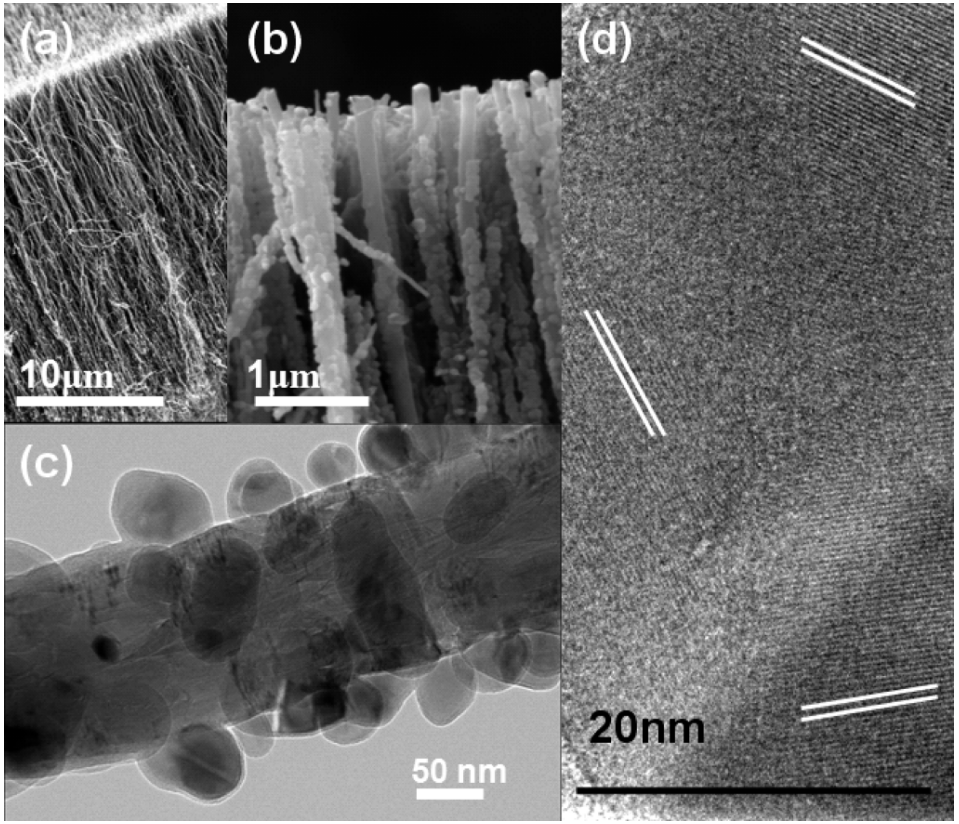
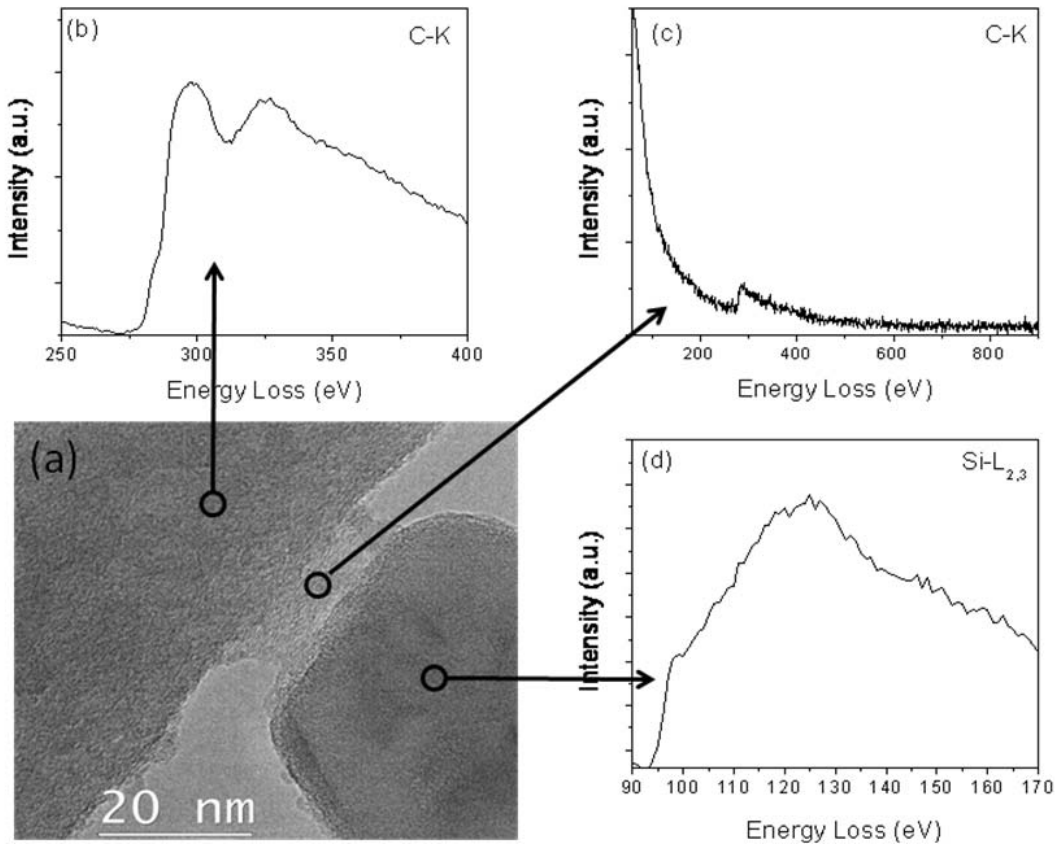


Fig. a: Vertically aligned CNT (VACNT) prior to Si deposition
Fig. b: SEM image showing **CNT (VACNT) covered with nanoscale (~40nm) Si droplets**
Fig. c: TEM image showing **CNT covered with *nc*-Si clusters** with defined spacing to each other
Fig. d: HR-TEM image of single Si nanoparticle showing lattice fringes of different orientation

Technical accomplishments (FY-10)

HRTEM studies on the interface of *nc*-Si/CNT

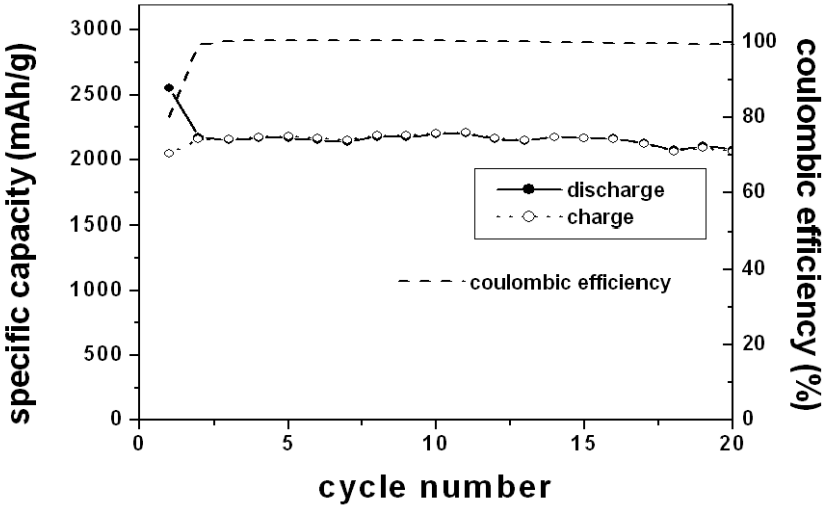


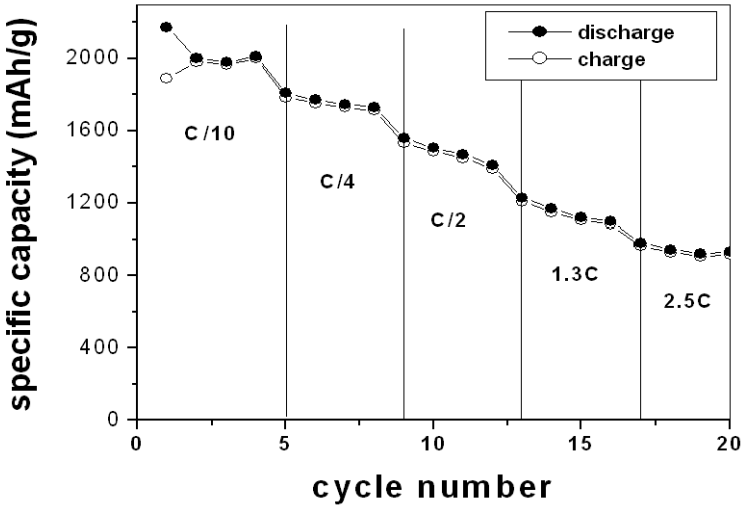
Note: Absence of SiC at the interface. Interface dynamics controlled by 10 nm amorphous C layer

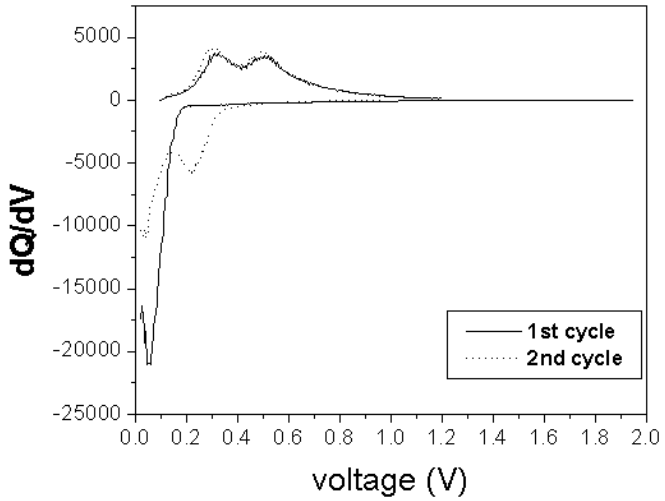
- Fig. a: **HRTEM image of CNT and *nc*-Si interface showing presence of Distinct Interfacial layer between CNT and *nc*-Si**
- Fig. b: EELS spectra showing presence of CNT
- Fig. c: EELS spectra at the interface is indicating presence of amorphous carbon
- Fig, d: Si nanocluster anchored to the CNT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

Technical accomplishments (FY-10)

Electrochemical behavior of *nc*-Si/CNT



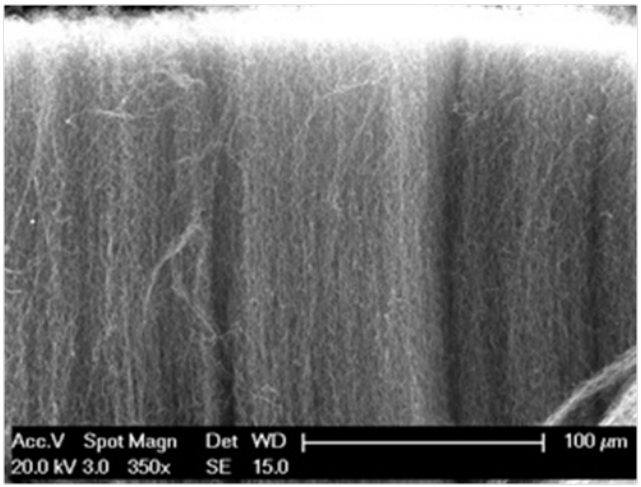




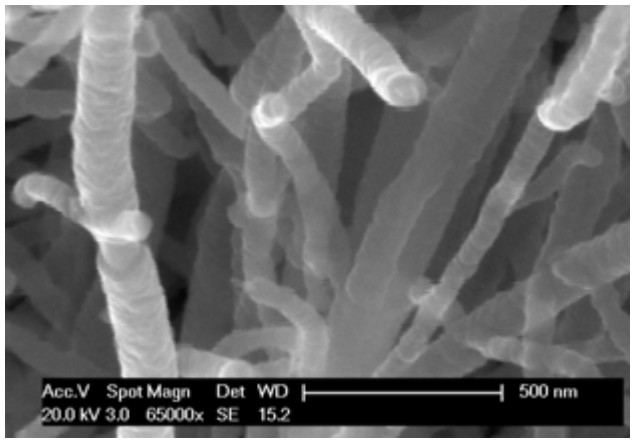
- 1st discharge specific capacity ~2552mAh/g
- 1st charge capacity **~2049mAh/g**
- Irreversible loss : **~18% and excellent coulombic efficiency (~99.9%)**
- Specific capacity at **2.5C rate ~1000mAh/g**
- The dQ/dV curve shows a significant alloying occurs at ~0.06V
- *Excellent electrochemical performance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

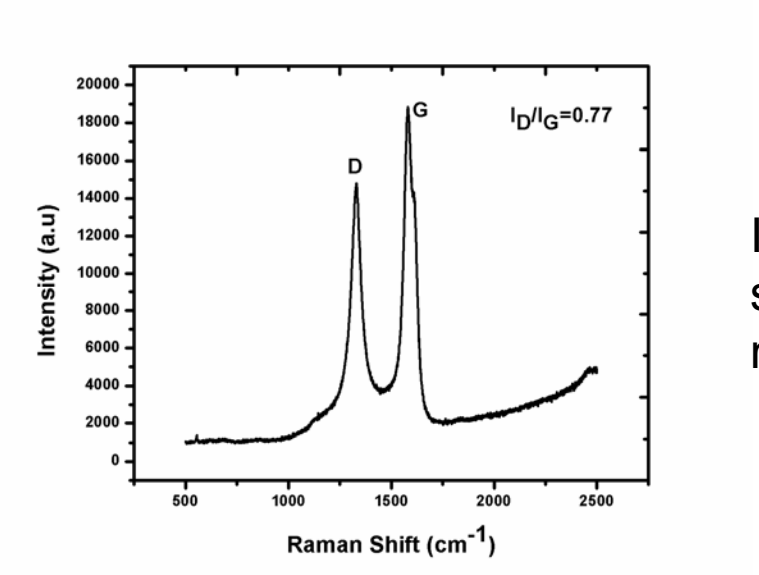
Core shell *nc*-Si/CNT structured



Vertically aligned CNT (VACNT)

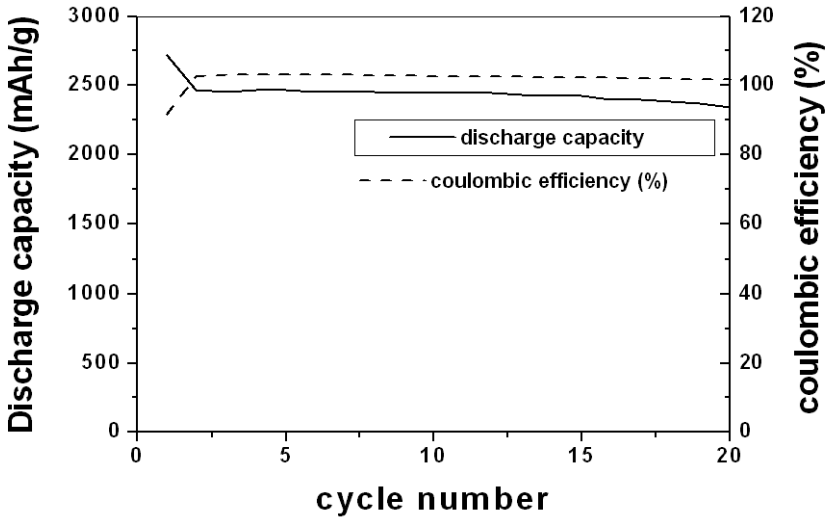


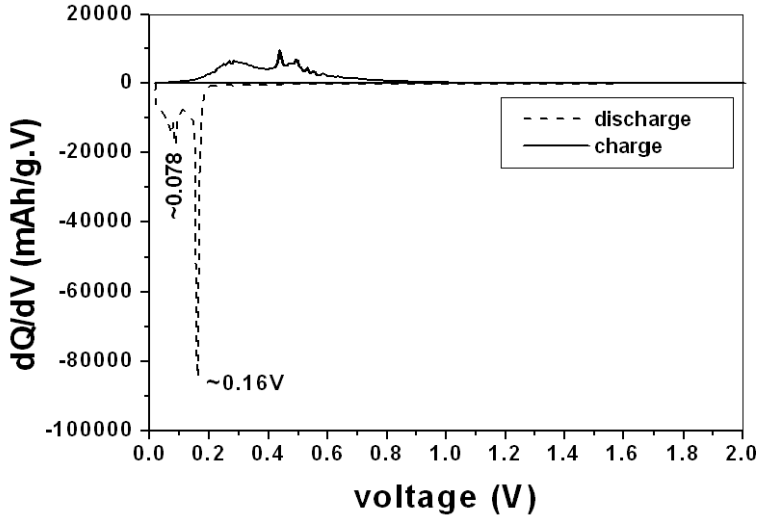
Core shell structure where VACNT is fully covered with *nc*-Si



I_G/I_D ratio on the Raman spectroscopy indicates high purity multi-walled CNT (MWCNT)

Technical Accomplishments (FY-10)
Electrochemical performance of *nc*-Si/CNT core shell structured anode

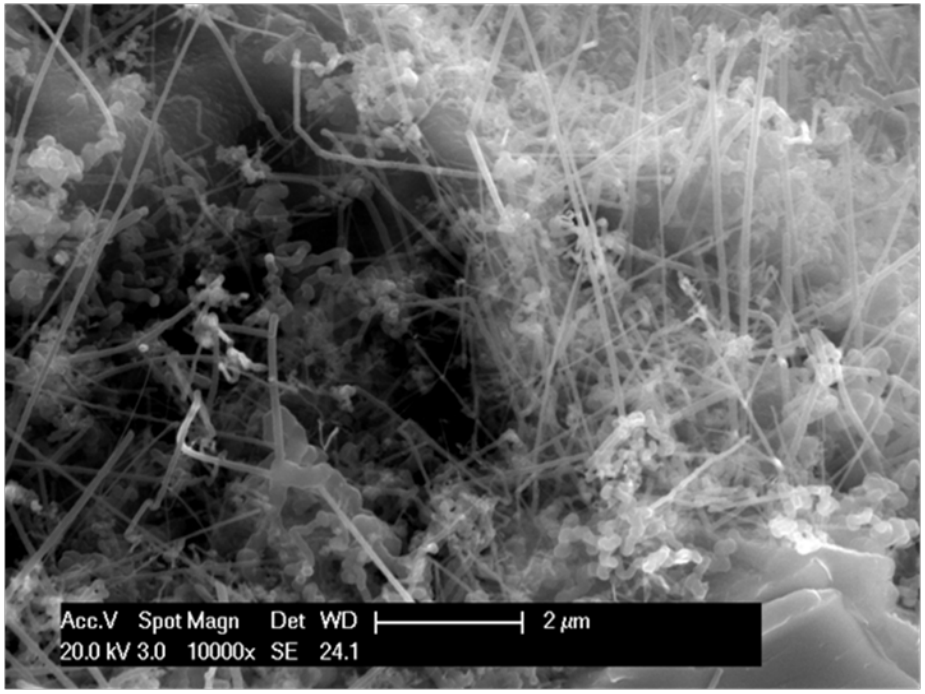


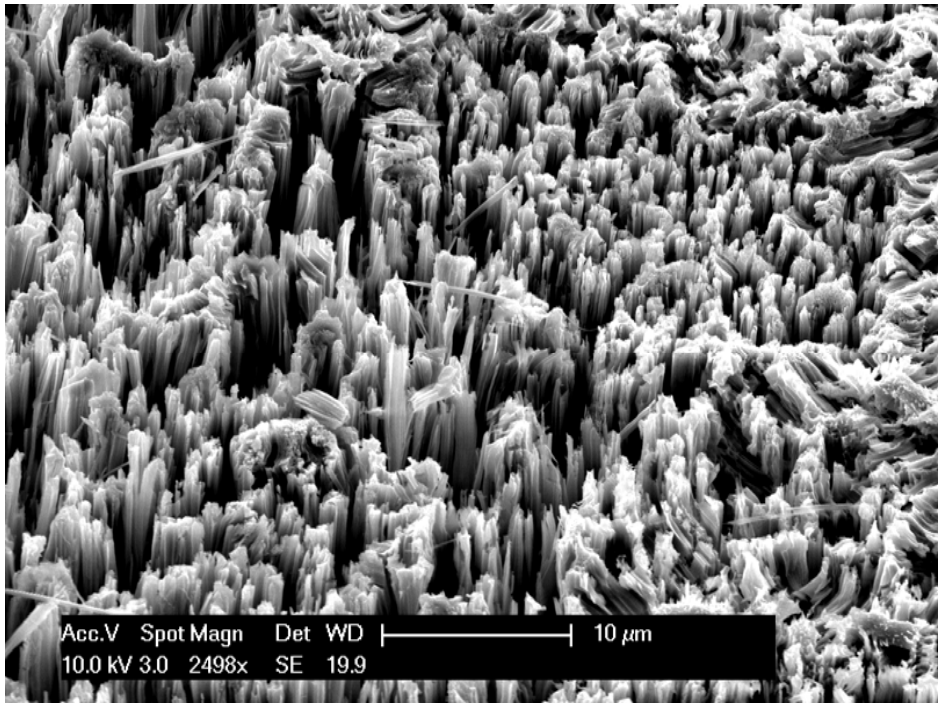


Cycled at C/27 rate

- *nc*-Si/CNT core shell structured anode shows
  - High specific capacity (**1st discharge: 2720mAh/gm** and **1st 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 ~0.16V and ~0.078V

Technical Accomplishments (FY-10)
Synthesis of Si Nanowire/Nanorod using Vapor and Etching Techniques

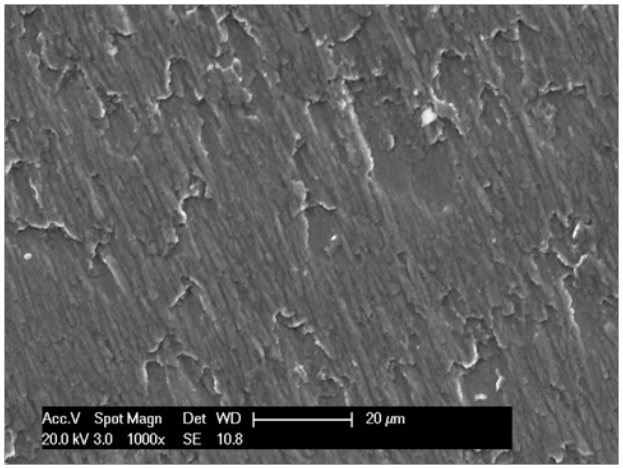


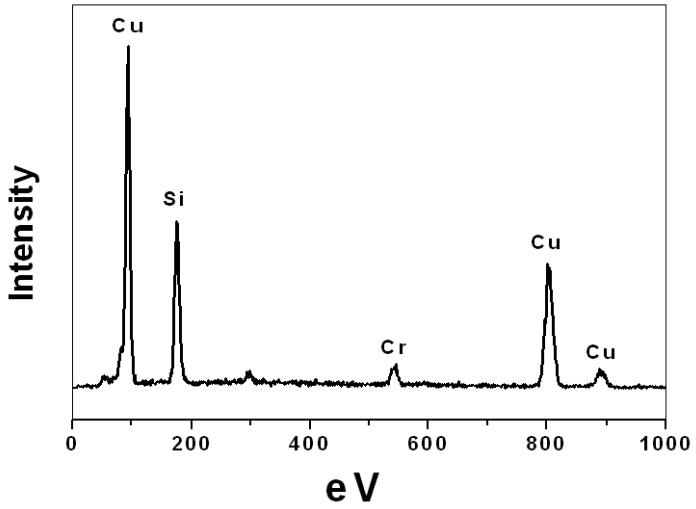


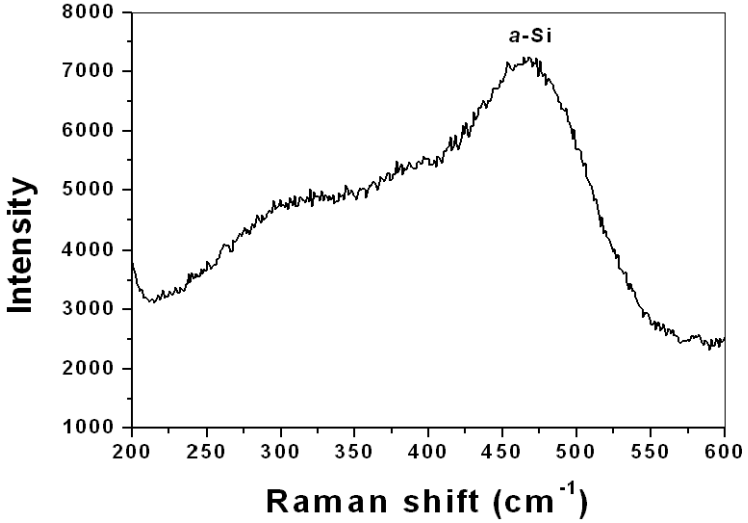
- Optimization of Si-Nanowire/Nanorod morphology
- Generation of hybrid nanocomposite based on Si nanowire/nanorod and carbon (CNT) is on going

Technical Accomplishments (FY-10)

2. Synthesis of amorphous Si film by RF Magnetron Sputtering





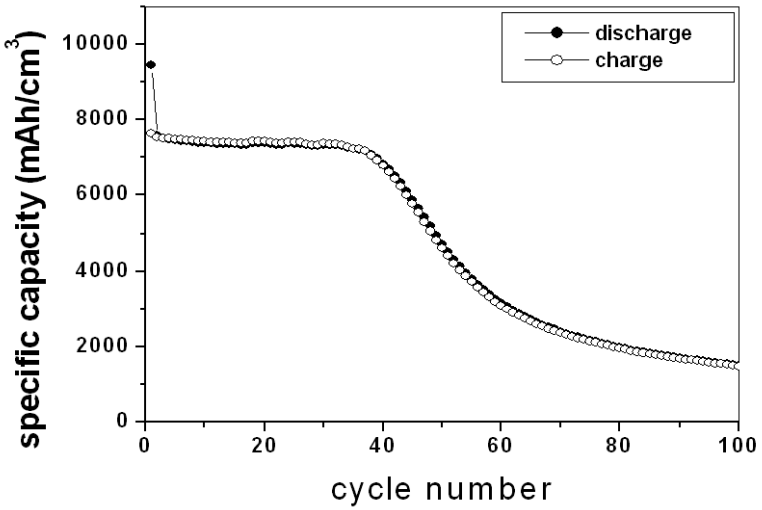


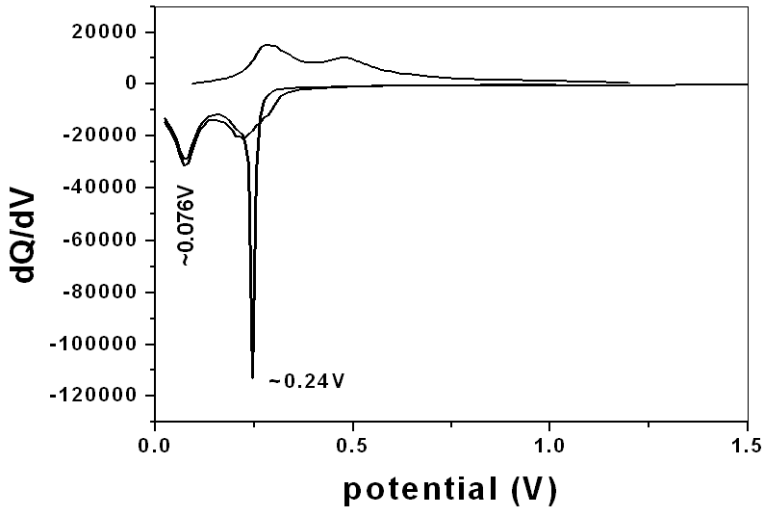
Amorphous Si deposited by RF magnetron sputtering

- EDAX shows the presence of Si
- Raman spectroscopy **confirms the presence of amorphous Si (Si band: 475cm^{-1})**

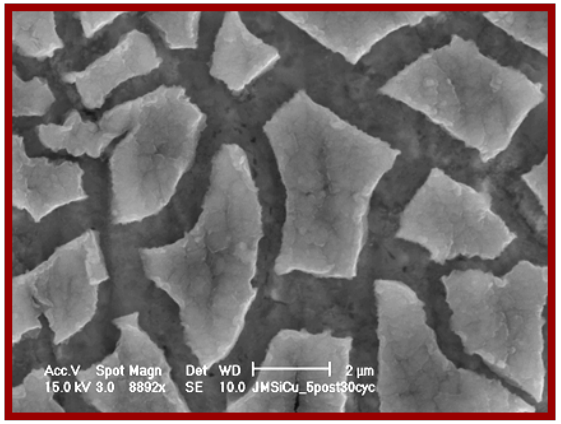
Technical accomplishments (FY-10)

Thin film amorphous Si





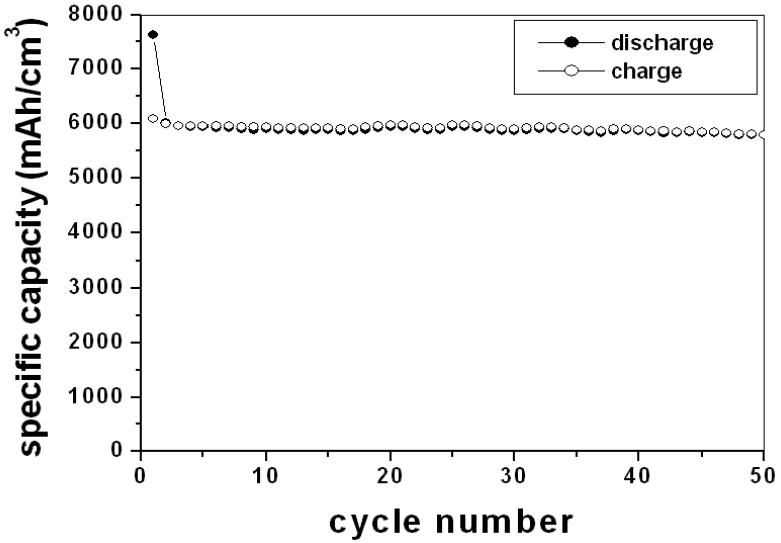
- **Thin film *a*-Si film**
  - **Synthesized by RF magnetron sputtering**
  - Cycled at C/2.5 (0.02V-1.2V)
  - Low irreversible loss **(~20%)**
  - **Excellent cyclability (0.11% loss per cycle) and columbic efficiency (~100%) up to 30 cycles**
- ***a*-Si based anodes show promise for Li ion batteries**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

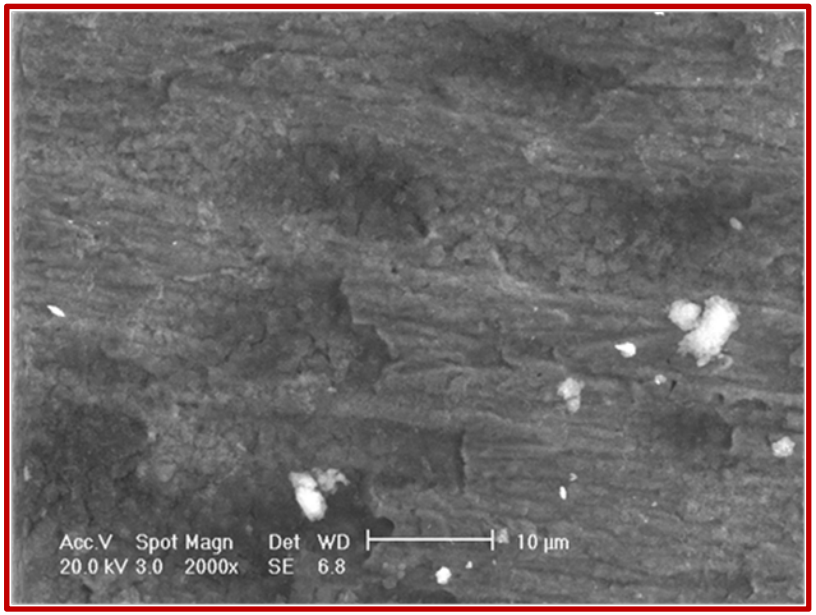


SEM : C/2.5 rate – 30 cycles

Technical accomplishments (FY-10)

Thin film amorphous Si/C composites



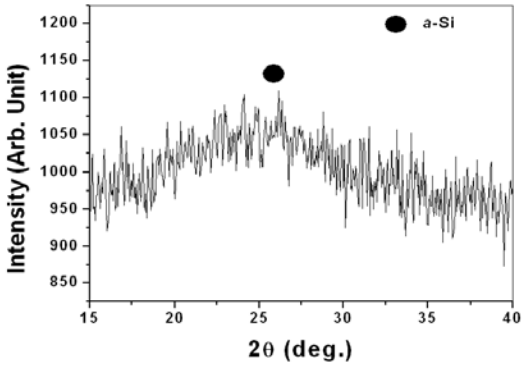


- **Thin film *a*-Si/C composite film**
  - **Synthesized by RF magnetron sputtering**
  - Cycled at C/2.3 (0.02V-1.2V)
  - **Excellent cyclability (0.09% loss per cycle) and columbic efficiency (~100%), and low irreversible loss (20%) up to 50 cycles**
- ***a*-Si/C based composite anodes show promise for Li ion batteries**
  - **Major challenge and target: Large scale synthesis of *a*-Si/C based composites**

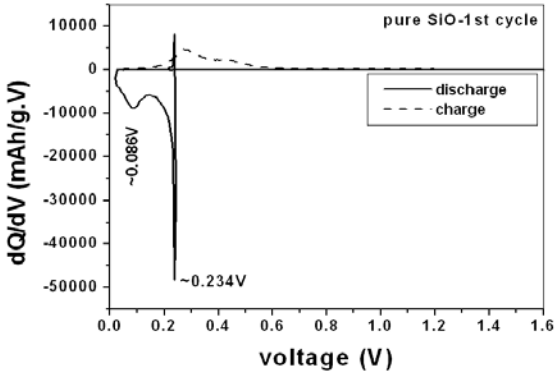
SEM after 75th cycle: C/2.3 rate - No noticeable significant crack formation

Technical Accomplishments (FY-10)
3. Formation of amorphous Si (*a*-Si) by direct mechanochemical reduction (DMCR) of SiO

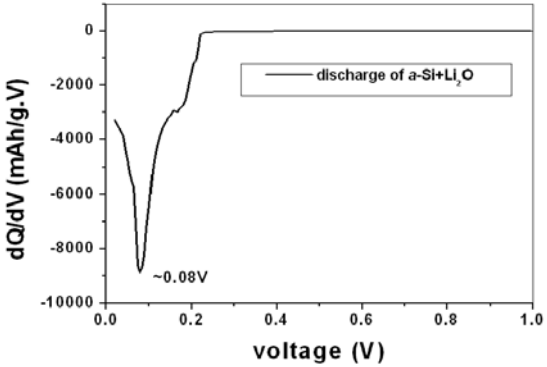
XRD



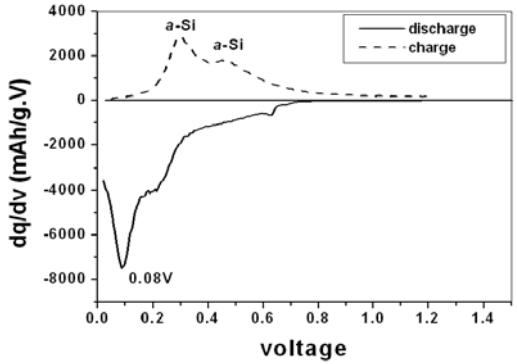
Pure SiO



Pure Si+L_2O



DMCR derived *a*-Si composite



- Pure SiO shows significant alloying at ~0.23V due to the reduction of SiO by Li forming *a*-Si
- *a*-Si+Li_2O 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%)