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

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Project ID #: es_30_kumta

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/$LiPF_6$+EC:DEC/$LiNi_{1/3}Mn_{1/3}Co_{1/3}O_2$
  - Gr/$LiPF_6$+EC:DEC/$LiFePO_4$
- **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

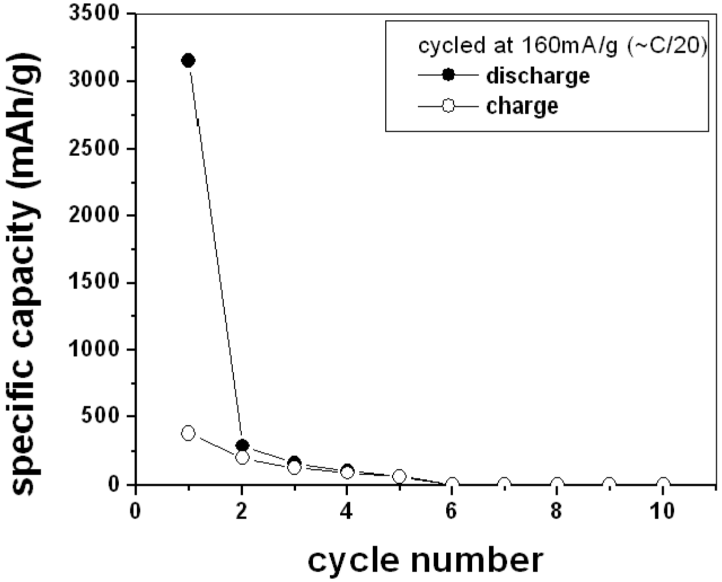
Milestones

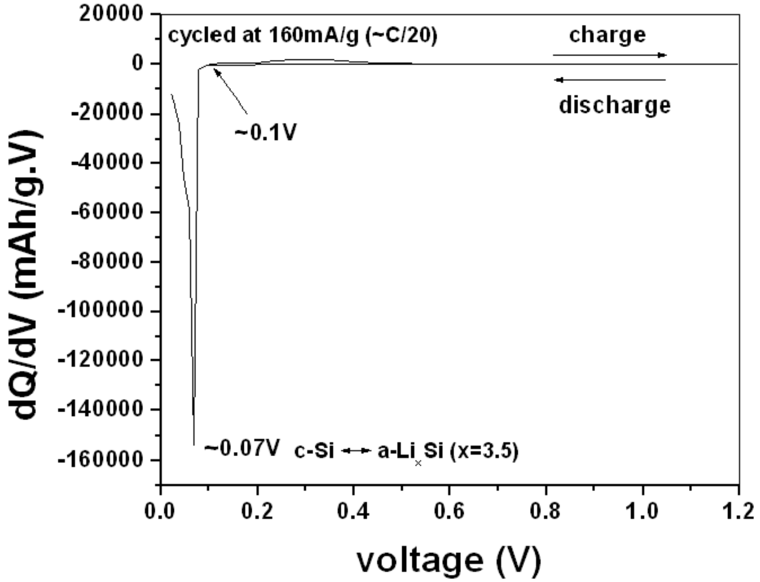
- Synthesize nano-structured Si based anodes using cost effective processing methods
- Achieve stable reversible capacity higher than ~700mAh/g
- Characterize the nano-scale hetero-structures for structure and composition using electron microscopy techniques such as, SEM, TEM and HREM
- Reduce Irreversible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

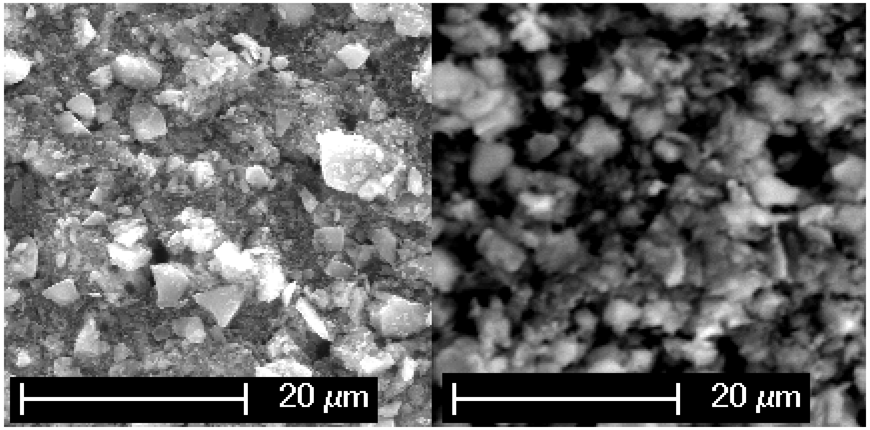
Approach

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





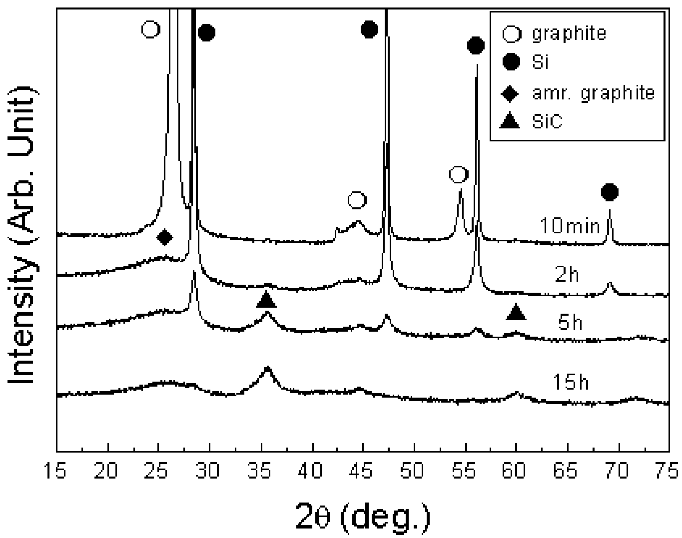


Before cycling After 10th cycle

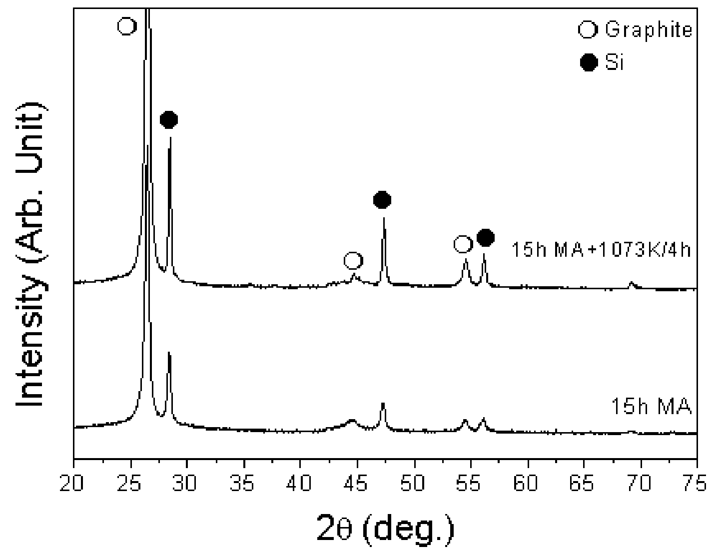
- **Pure microcrystalline Si (*c*-Si) (<44μm)**
  - Structural failure within few cycles
  - Formation of amorphous $Li_{3.5}Si$ at onset potential ~0.1V with a peak potential ~0.07V
  - Phase transformation of *c*-Si to *a*-$Li_{3.5}Si$ is associated with a large volume expansion (~300%)
- **Major challenge/Target**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

Synthesis of Si/C nanocomposite by HEMM

Gr-25wt.% Si



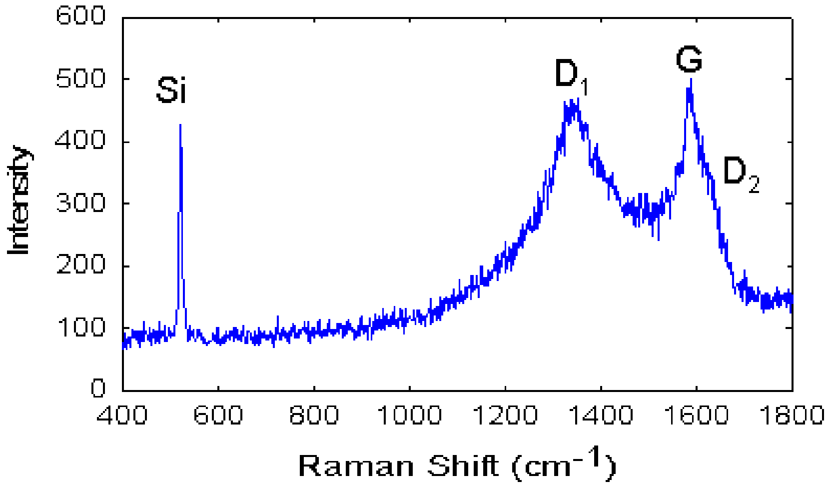
Gr-17.5wt.% Si-30wt.% PAN

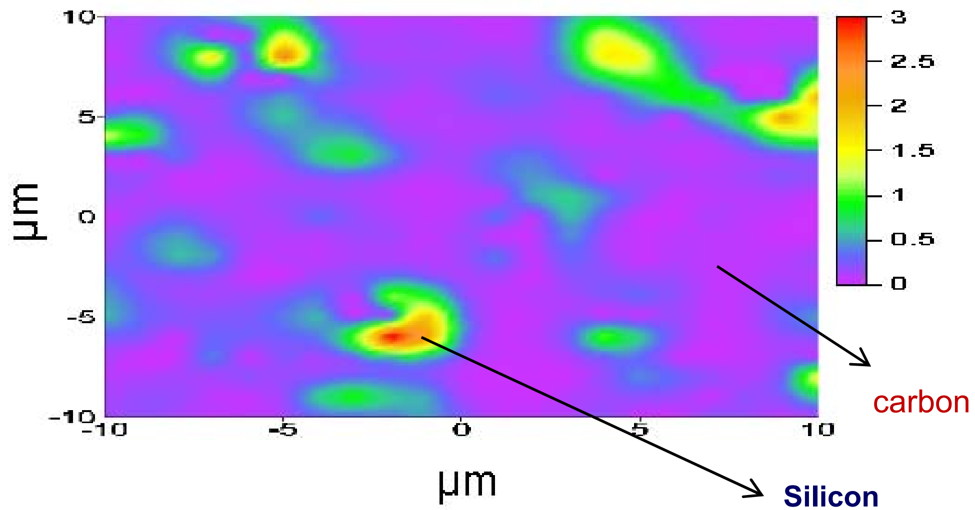


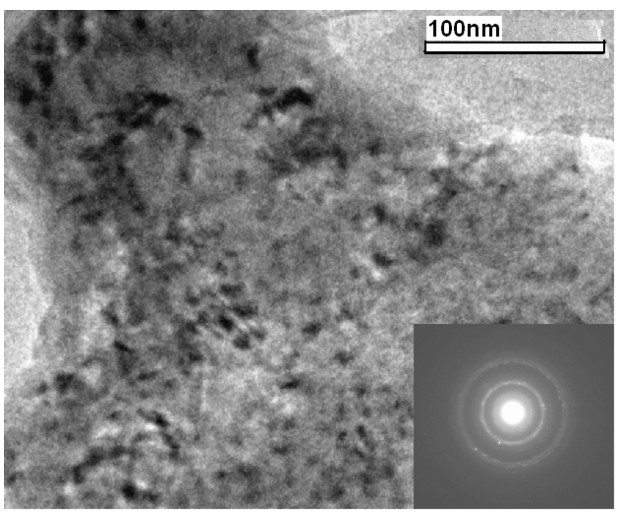
- Gr-25wt.% Si
  - Formation of SiC within 5h HEMM
  - The weight fraction of active Si decreases with increasing milling time
  - The specific capacity decreases with increasing milling time
  - Graphite transforms to amorphous structure
  - high irreversible loss

- 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
  - Graphite retains its graphitic structure
  - Polymer additive enhance 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





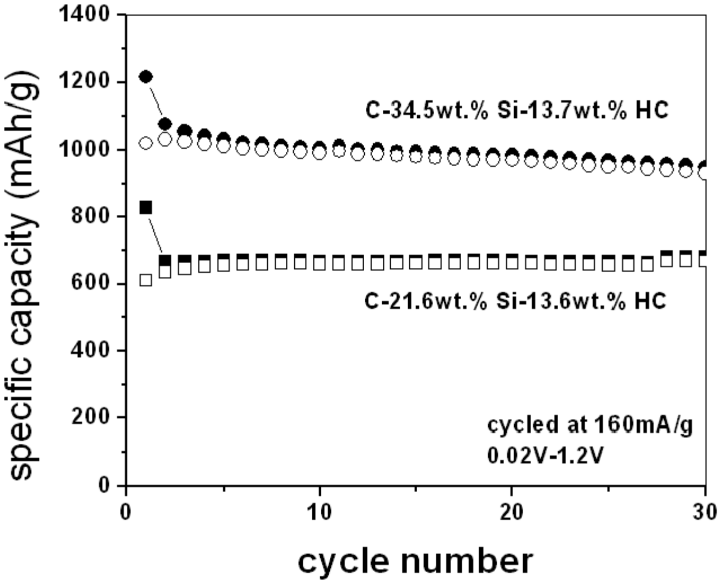


- **In-situ Raman spectroscopy**
  - Si band: 520cm^{-1}, Graphite: 1580cm^{-1}, Amorphous hard carbon: 1360 and 1620cm-1
  - Raman map shows that crystalline Si covered by graphite and amorphous hard carbon

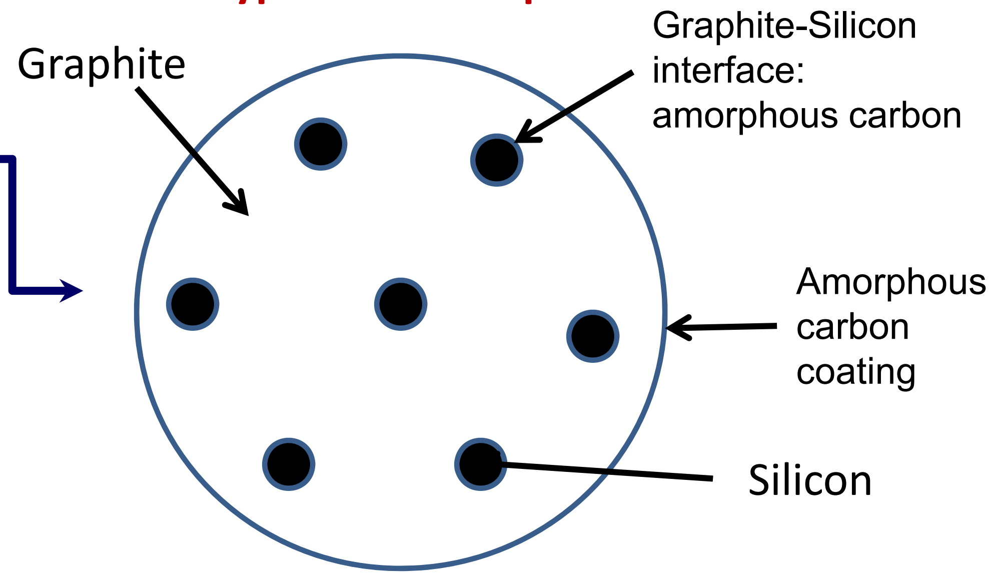
- **TEM and SEM investigation**
  - Shows homogeneous distribution of nanocrystalline Si (*nc*-Si) of particle size ~10nm on graphite matrix
  - Nanocrystalline Si likely to provide a strong interface bonding with graphite
  - Si/C nanocomposite likely enhances the mechanical properties in comparison to *c*-Si

Technical accomplishments

Cyclability of Si/C Nanocomposite



Intra type Nano-composite -ITN



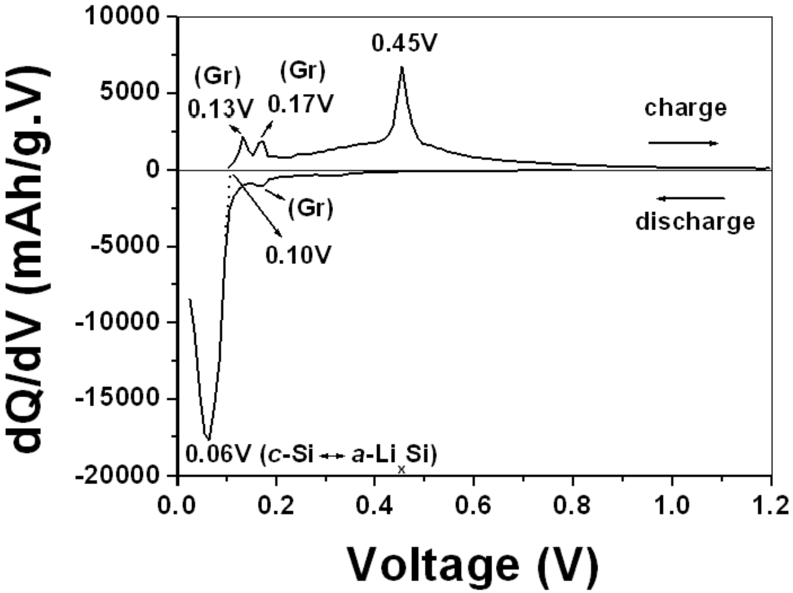
Composition (wt.%)	Specific capacity (mAh/g)		Irreversible loss (%)	Loss per cycle (%)
	1st discharge	1st charge		
C-21.6 Si-13.7 HC	825	610	26	~0.08
C-34.5 Si-13.7 HC	1215	1019	16	~0.34

- **Improved cyclability of Si/C 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**

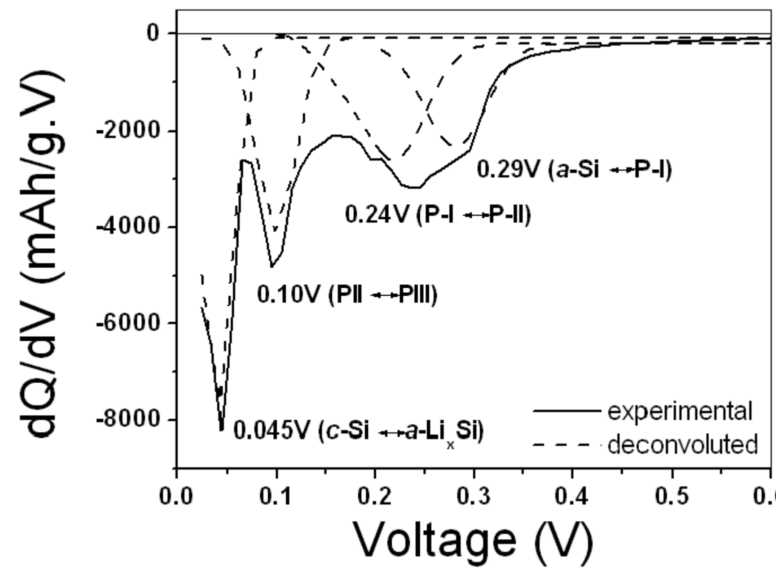
Technical accomplishment

Phase formation during alloying/dealloying of Li with Si

First Cycle



Second discharge profile

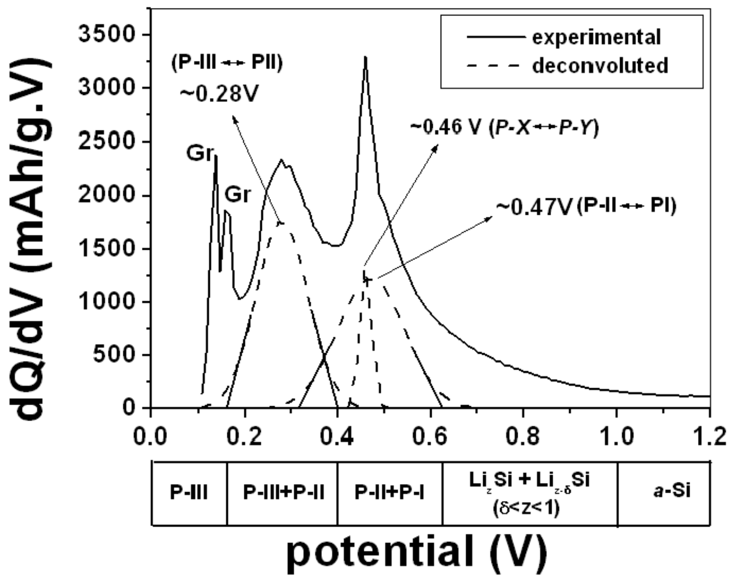


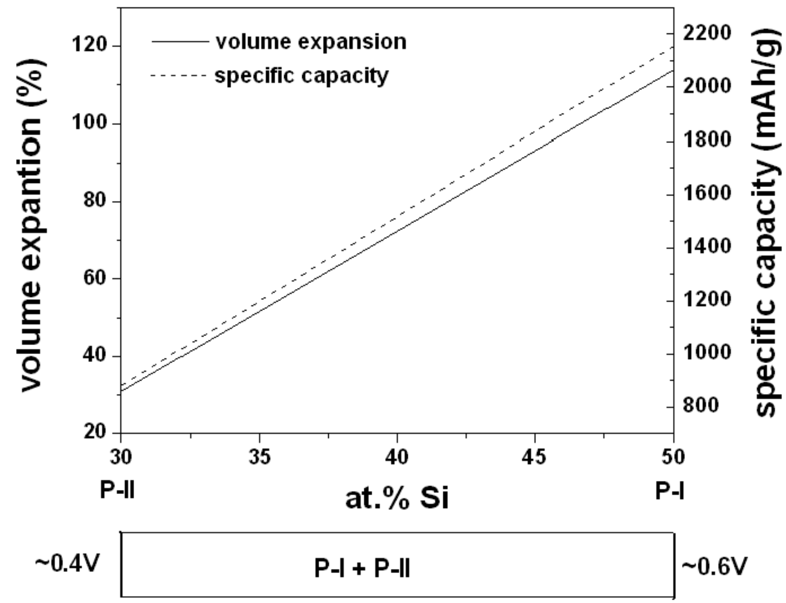
- 1st discharge and charge of Gr-21.6wt.% Si-13.6wt.% HC
  - cycled at ~160mA/g (~C/6)
  - 0.02V-1.2V
  - ***a*-$Li_{3.5}$Si after 1st discharge (~0.06V)**
  - Amorphous Si (*a*-Si) after 1st charge (~1.2V)
  - Both Si and graphite are active

- **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_7Si_3)**
  - **P-III: Li-24at.% Si ($Li_{13}Si_4$)**

Technical accomplishment

Alloying/dealloying behavior of Li with Si



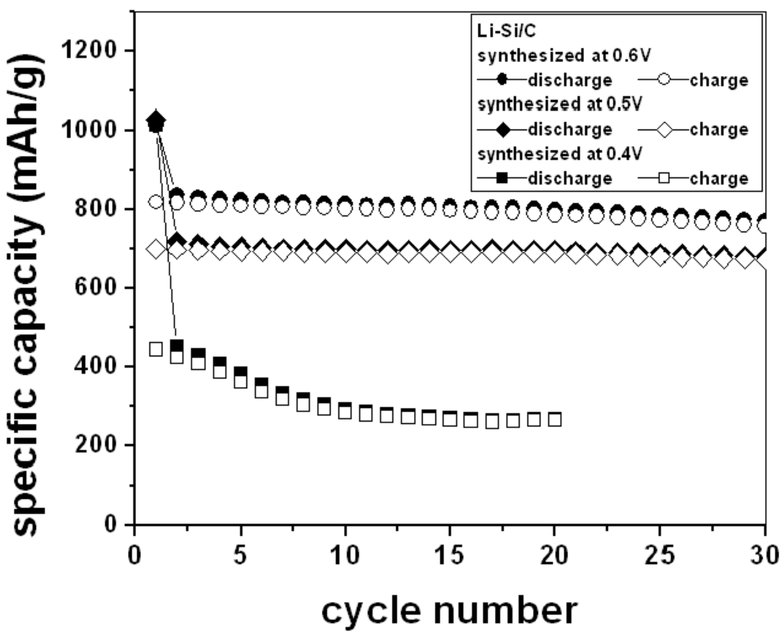


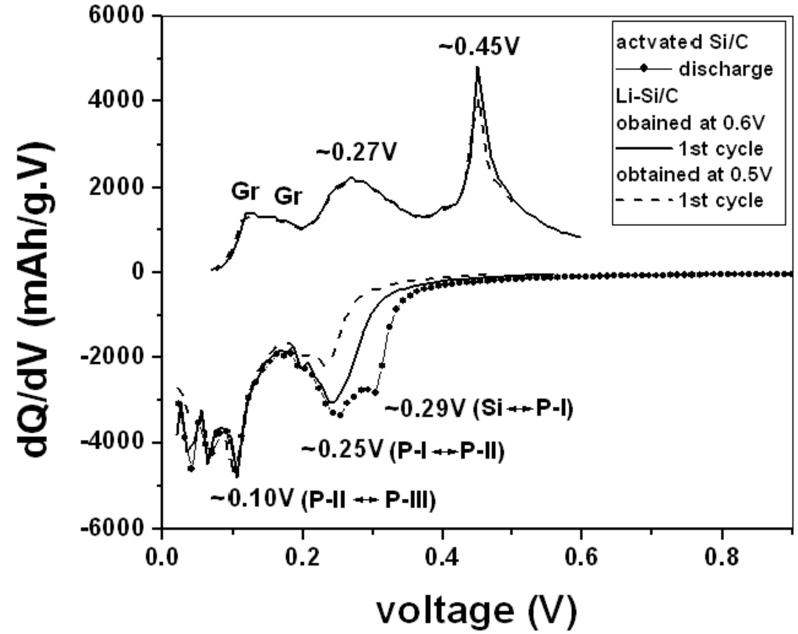
- **2nd charge**
  - 0.6V: P-I (Li-50at.% Si (LiSi))
  - 0.4V: P-II (Li-30at.% Si(Li_7Si_3))
  - 0.5V: P-I+P-II (Li-40at.% Si)

Phase transformation	Volume expansion (%)	Theoretical specific capacity (mAh/g)
P-I↔P-III	114	2154
P-II↔P-III	31	877
Si↔P-III	236	3100

Technical accomplishments

Li-Si/C composite anode



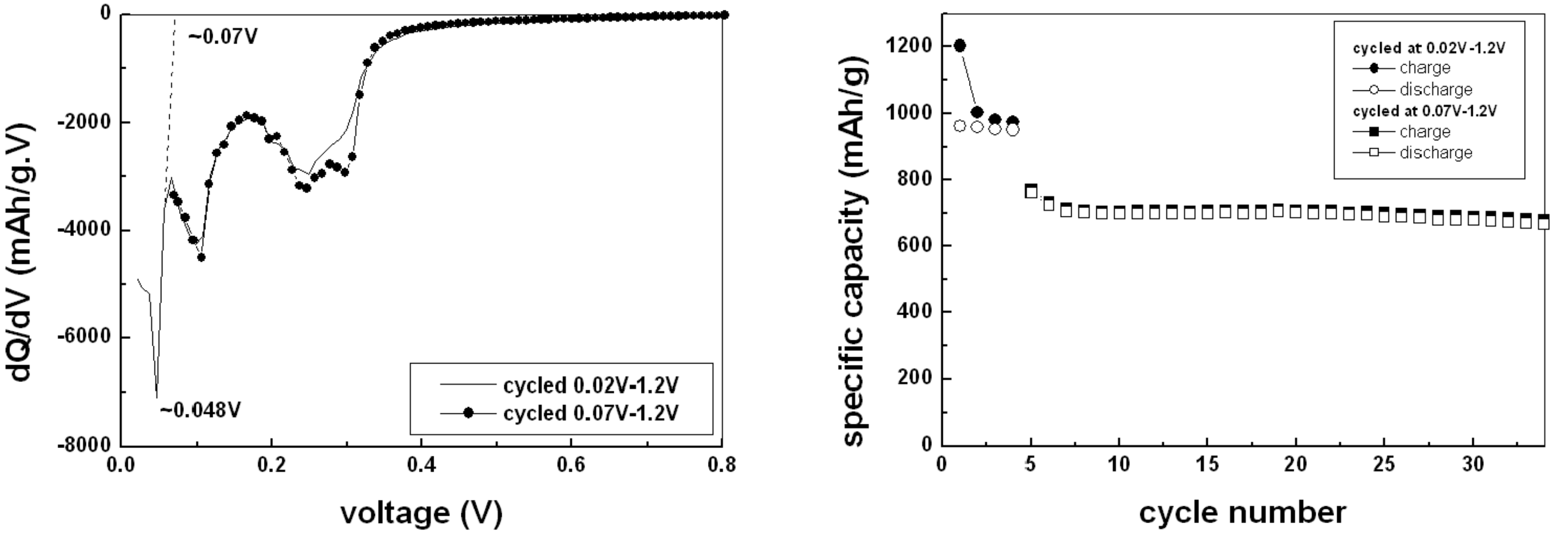


- **Li-Si/C composite generated by electrochemical reaction *in situ***
  - Synthesized by controlled electrochemical reaction of Li with ***a*-Si**
  - **Charging reaction was terminated at ~0.6V, ~0.5V and ~0.4V**
  - Cycled at 160mA/g within their stable potential window
  - **Transformation of *a*-Si↔P-I 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.

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

Technical Accomplishments

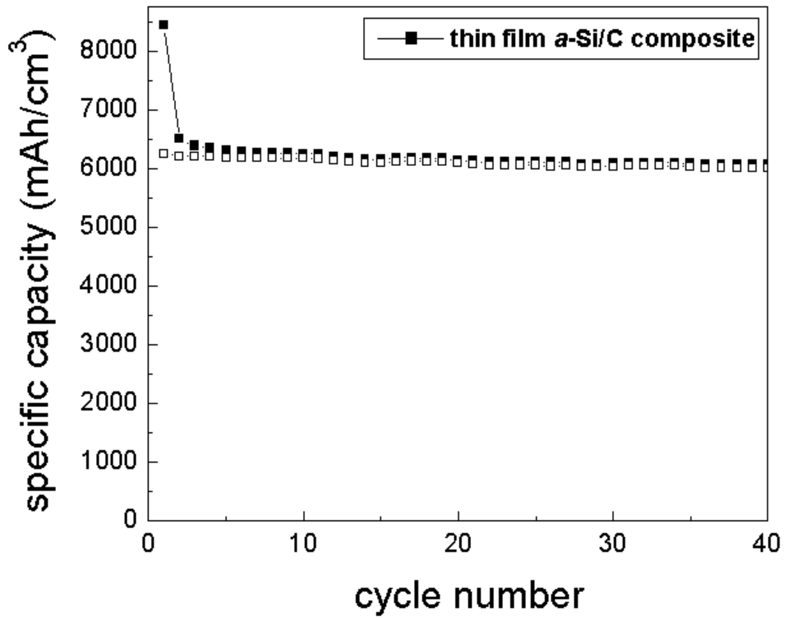
Effect of phase formation on the structural stability of Si/C composite

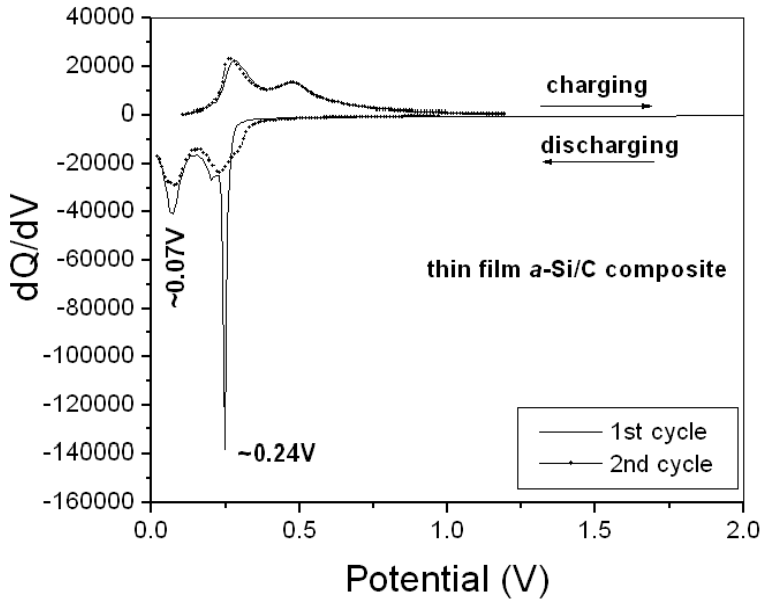


- **Effect of formation of *a*-$Li_{3.5}Si$ on the stability of the Si/C composite**
  - Cycled the electrode between 0.07V-1.2V to prevent the formation of ***a*-$Li_{3.5}Si$**
  - Capacity retention has been improved (0.14% loss per cycle)
- **Target**
  - **Design a Si based alloy which can prevent the formation of *a*-$Li_{3.5}Si$ 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

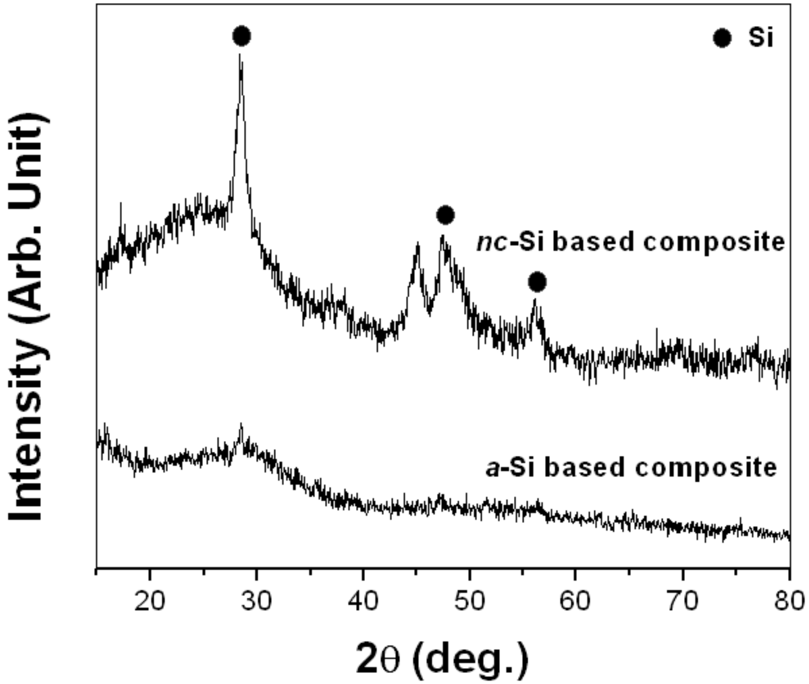




- **Thin film *a*-Si/C composite**
  - **Synthesized by RF magnetron sputtering**
  - Cycled at C/2.5 (0.02V-1.2V)
  - **Excellent cyclability (0.07% loss per cycle) and low irreversible loss (25%)**
  - **Formation of high Li content *a*-$Li_{3.5}Si$ or $Li_{3.75}Si$ is by-passed**
- ***a*-Si based 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

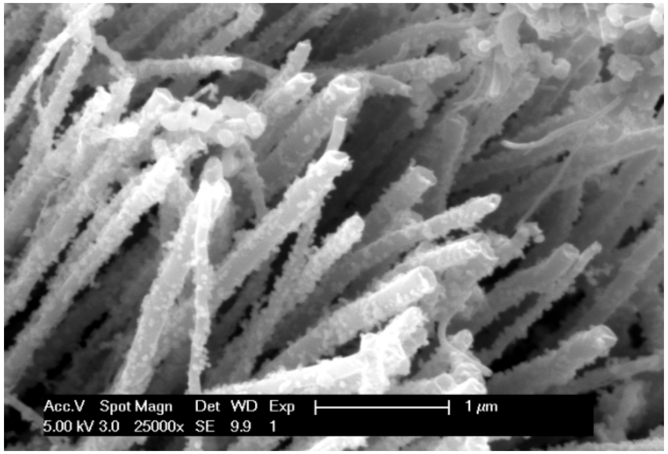


Calculated crystallite size of Si ~15nm

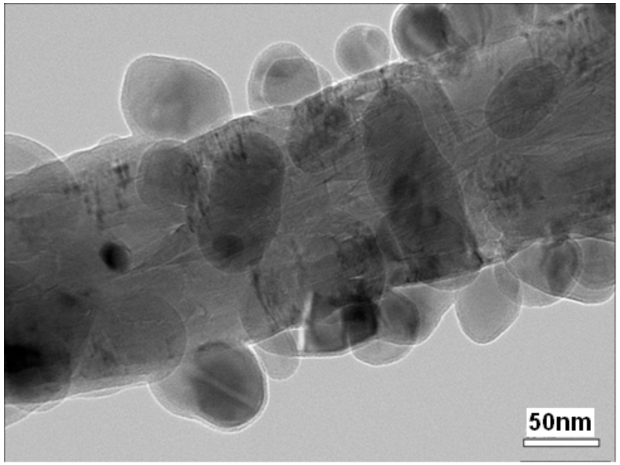
- **Large Scale Synthesis** of ***a*-Si** and ***nc*-Si** based composite anodes **achieved by HEMM**

Technical accomplishments

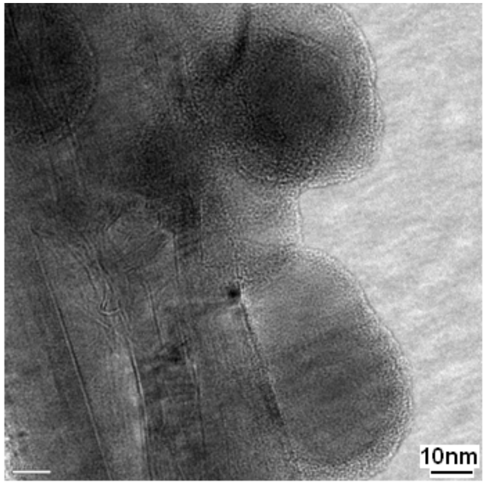
Novel Synthesis of *a*-Si/C composite anodes



HRSEM of nano-scale composite hetero-structures



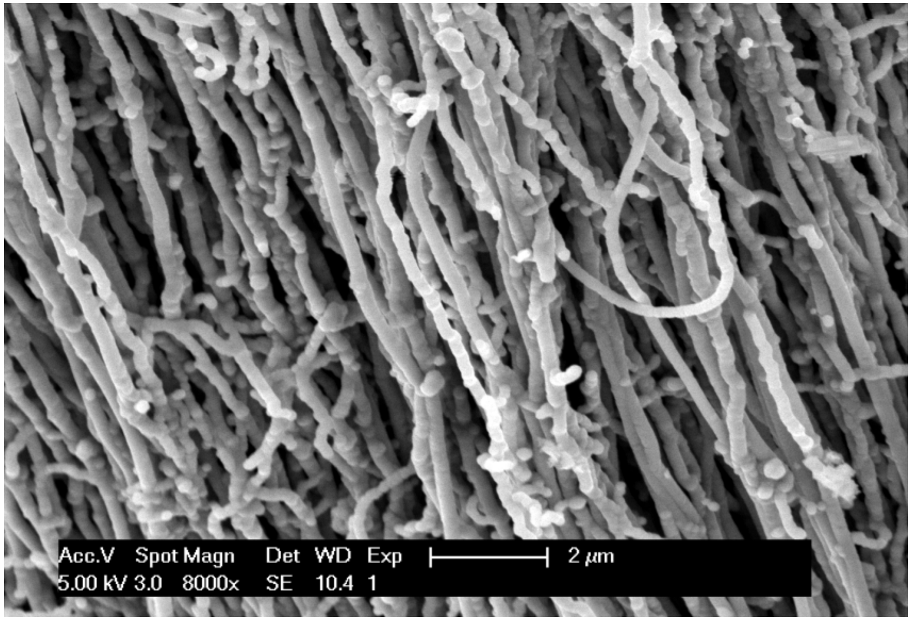
TEM of ***a*-Si** droplet coatings on **CNT**

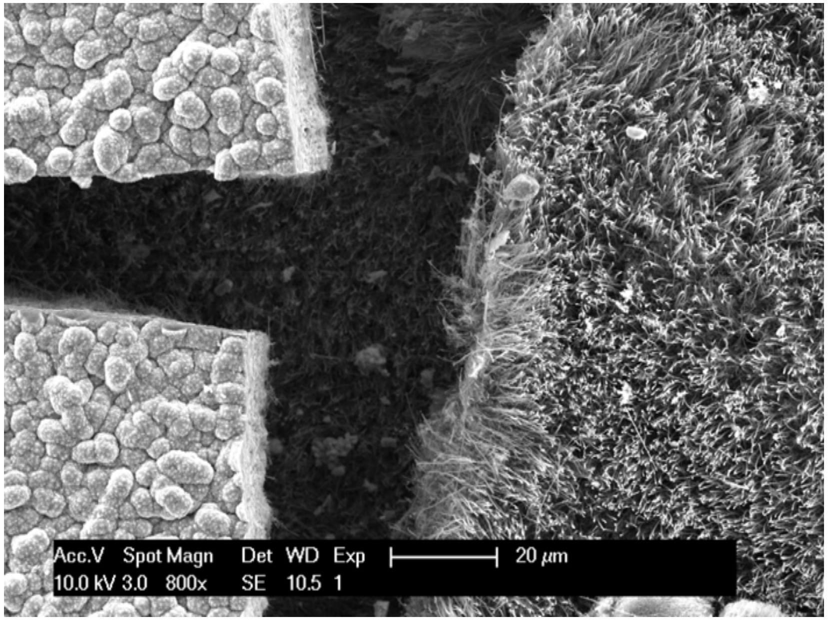


HRTEM of **single CNT** coated with ***a*-Si droplets**

- *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**