Development of Si-based High Capacity Anodes

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Project ID#: ES144

Overview

Timeline

- Start date: Oct. 2010
- End date: Sept. 2014
- Percent complete:40%

Barriers addressed

- Low energy density
- High cost
- Limited cycle life

Budget

Project funding (DOE):

- FY11: $300k
- FY12: $300k

Partners

- Princeton University
- University of Rhode Island
- Vorbeck Inc.
- Vesta Si LLC.
- North Dakota State University

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Objectives

- Develop Si-based anodes with high capacity and good rate capability to replace graphite in Li-ion batteries.

- Develop new additive to improve the cycling stability of Si-based anode.

- Develop low cost scalable production methods for high capacity and stable Si-based anode.

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Milestones

- Understand the effect of the pore size of porous Si on its electrochemical performance. *− completed*
- Synthesize and characterize core shell structured porous Si-C nano-composite as anode for Li-ion batteries. *− on going*
- Synthesize and characterize conductive rigid skeleton supported Si as an anode for Li-ion batteries. *− on going*

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Approach

- Analyze the effect of the particle size and carbon coating thickness on the performance of Si based anode.
- Manipulate nano-structure and porosity of Si to improve its mechanical and electrical stability.
- Using template method to prepare core shell structured porous Si-C nanocomposite.
- Using ball milling method to prepare Si anode supported on a conductive rigid skeleton.

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Technical Accomplishments:
Understand the Failure Mechanism and Possible Solutions for Si Based Anode

Failure mechanism I

Mechanical instability:
Cracking and pulverization of Si particles

→

Solution I

Nano structures:
Use nano-structured silicon with a typical dimension < 200 nm

Failure mechanism II

Electrical instability:
Loss of electrical contacts among particles/substrate

→

Solution II

Conductive Additives:
Develop stable conductive additive/coating

Failure mechanism III

Electrochemical instability:
Breakdown of SEI layer and consumption of electrolyte

→

Solution III

New Electrolyte and Additives:
Form stable/flexible SEI layer

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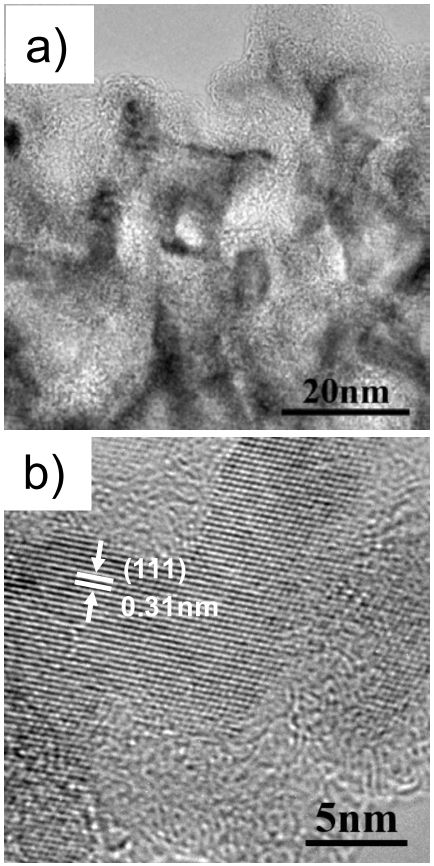
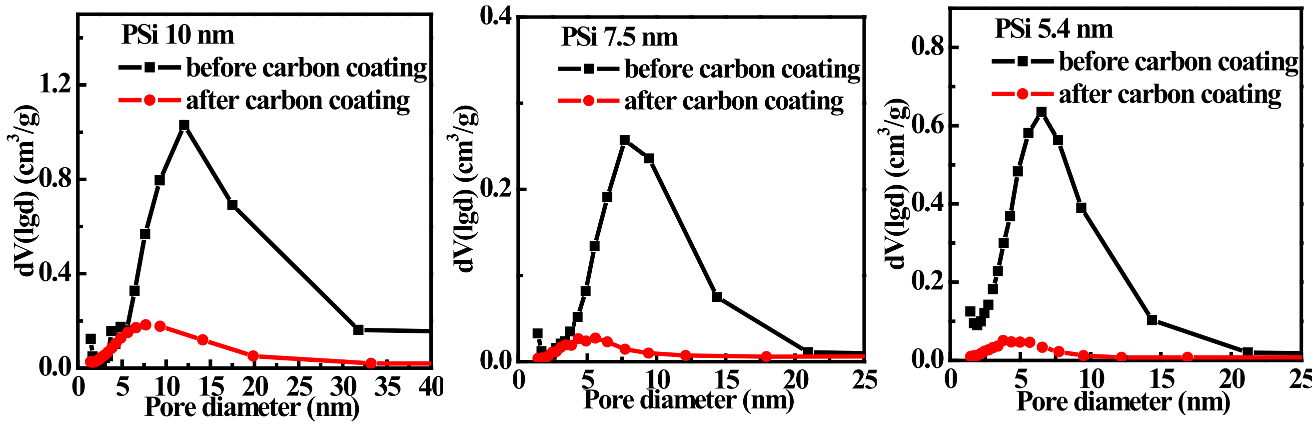
Technical Accomplishments:
Characterization of Pore Structure of Porous Si





	Surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
PSi-10 nm	139.4	0.5	12.1
PSi-7.5nm	41.2	0.12	7.7
PSi-5.4 nm	166.8	0.31	6.4
PSi-10 nm @ C	62.3	0.15	7.6
PSi-7.5 nm @ C	9.9	0.04	4.9
PSi-5.4 nm @ C	20.7	0.06	3.8

- Porous Si with pore sizes from ~5 nm to ~10 nm
- Thin carbon coating (~4 nm) on the interior and surface of Si nanoparticles.

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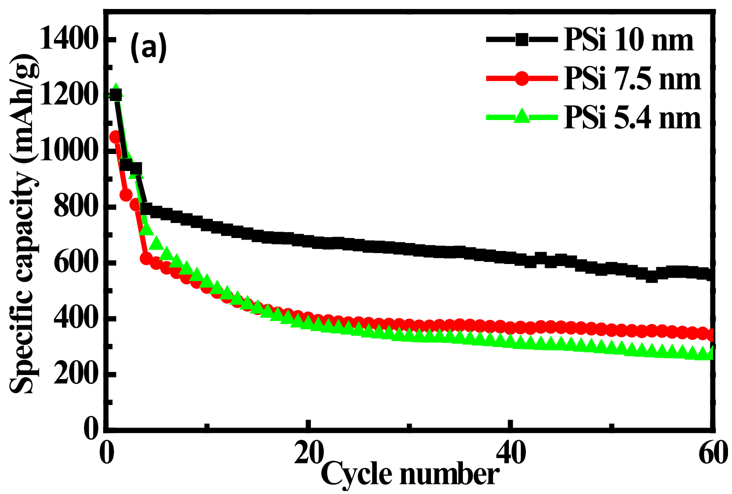
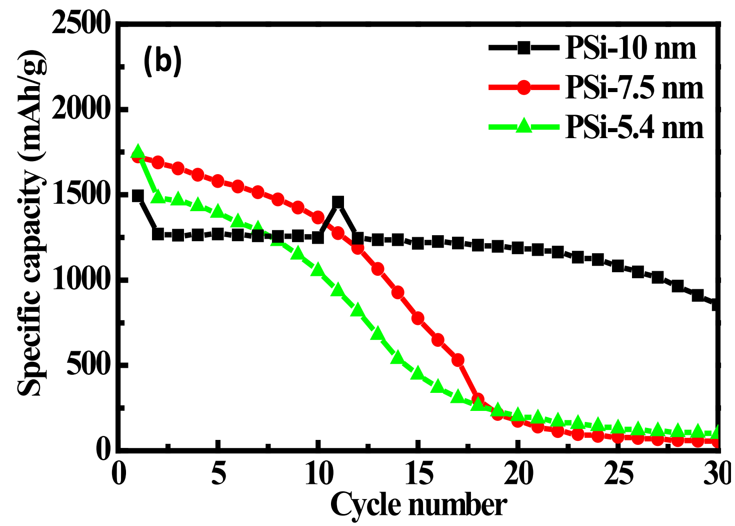
Technical Accomplishments: Effect of Pore Size on the Cycling Stability of Si Based Anodes





- Porous Si with larger pore sizes (~10 nm) has better cycling stability.
- A capacity of ~800 mAh/g (based on the entire electrode weight) can be obtained with capacity retention of ~650 mAh/g over 60 cycles at 1 A/g current density.

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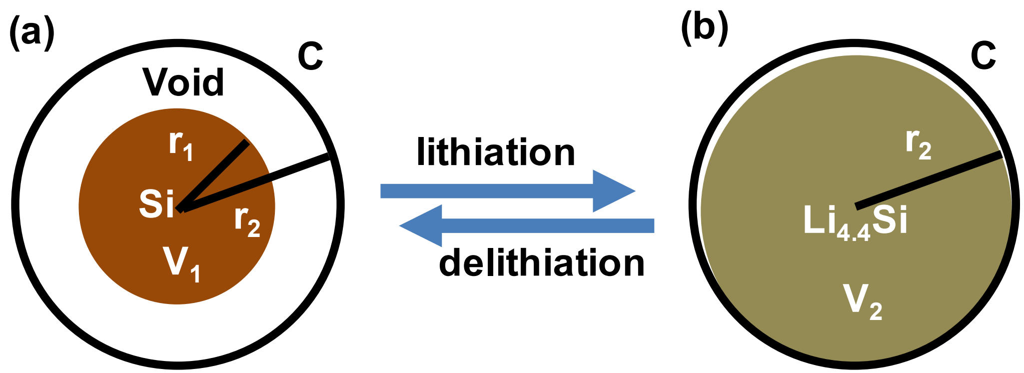
Technical Accomplishments:
Hollow Core-Shell Structured Si-C Nanocomposite



$$V_2/V_1 = (4/3\pi r_2^3)/(4/3\pi r_1^3)$$

$$V_2/V_1 = 400\%.$$
$$r_2/r_1 = 1.587.$$

- Porous Si
- Si has ~ 300% volume increase after lithiation
- ~80nm carbon shell is needed to keep the integrity of a 50nm Si core.

- Porous Si is one of the solutions to a practical Si-based anode
- It can improve the weight and volume energy density, cycling stability while keep a high capacity.

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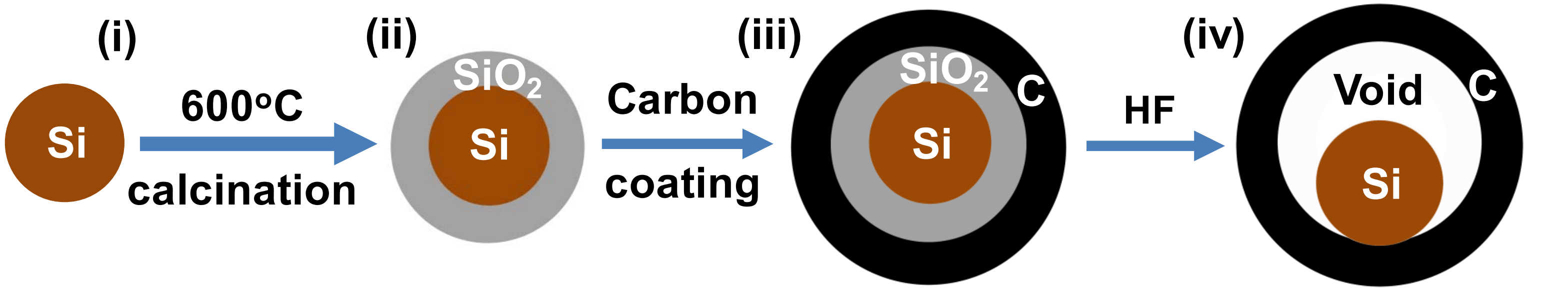
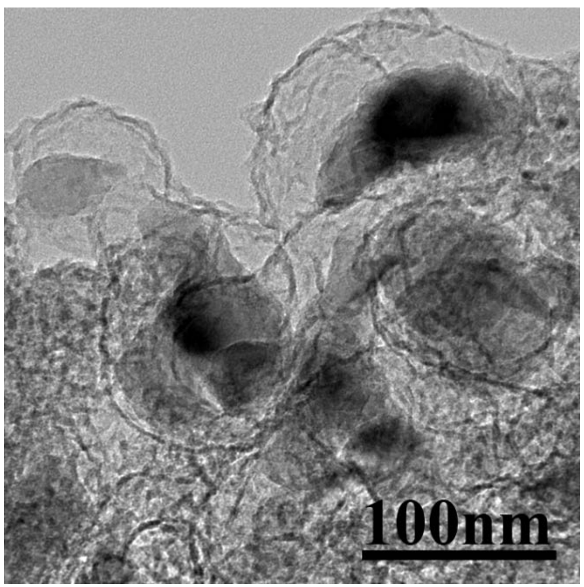
Technical Accomplishments: Synthesis of Hollow Core-Shell Structured Porous Si-C Nanocomposites





- Hollow core-shell structured Si-C nanocomposite is synthesized.
- Void space between the Si core and the carbon shell is up to tens of nanometers to accommodate the volume change of Si during repeated cycling.

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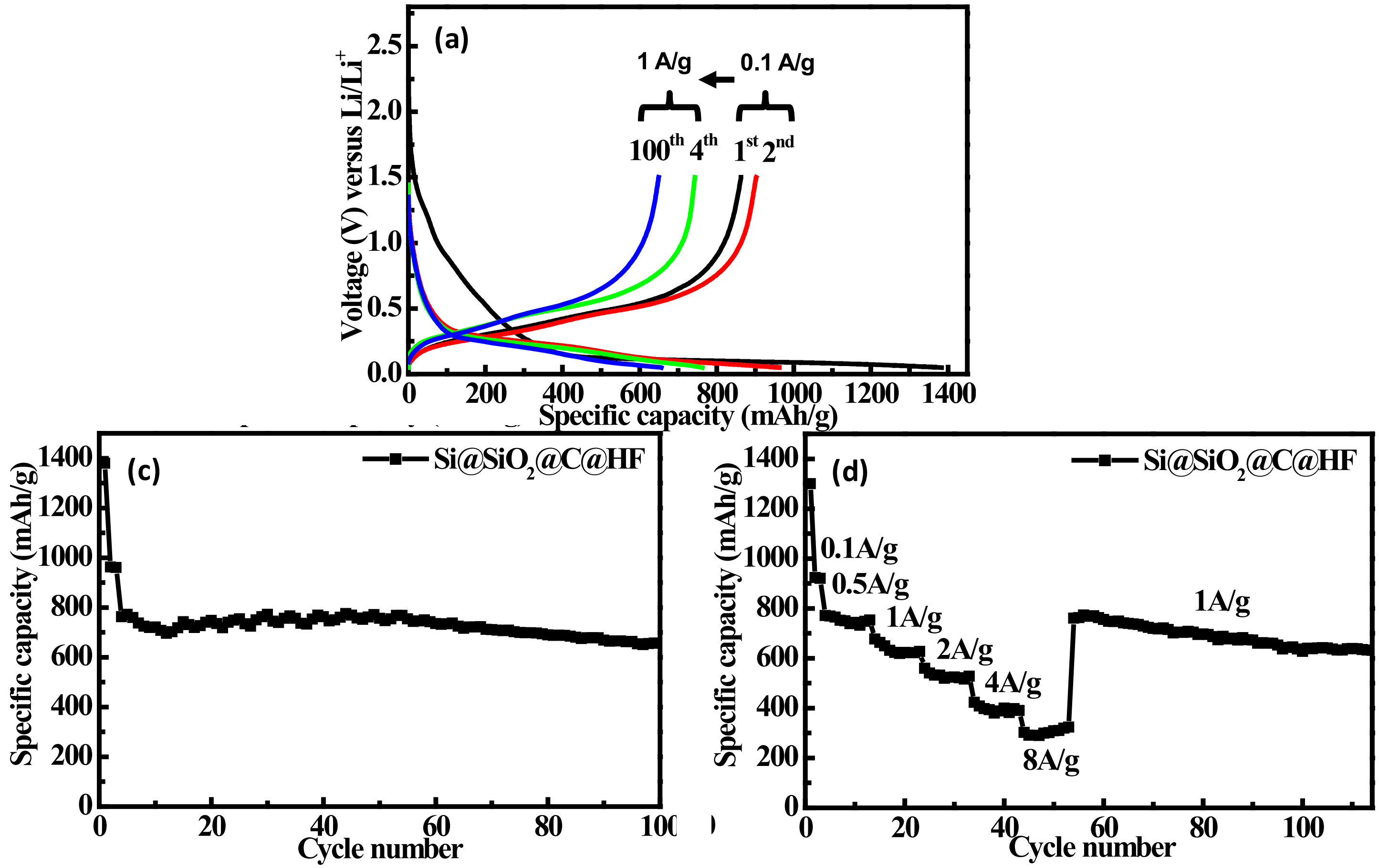
Technical Accomplishments

High Performance of the Hollow Core-Shell Structured Porous Si-C Nanocomposites



- Good cycling stability: ~760 mAh/g at 1 A/g current density (based on the total electrode weight, including binder and conductive carbon)
- Excellent cycling stability: ~ 500 mAh/g in 100 cycles (2 A/g).

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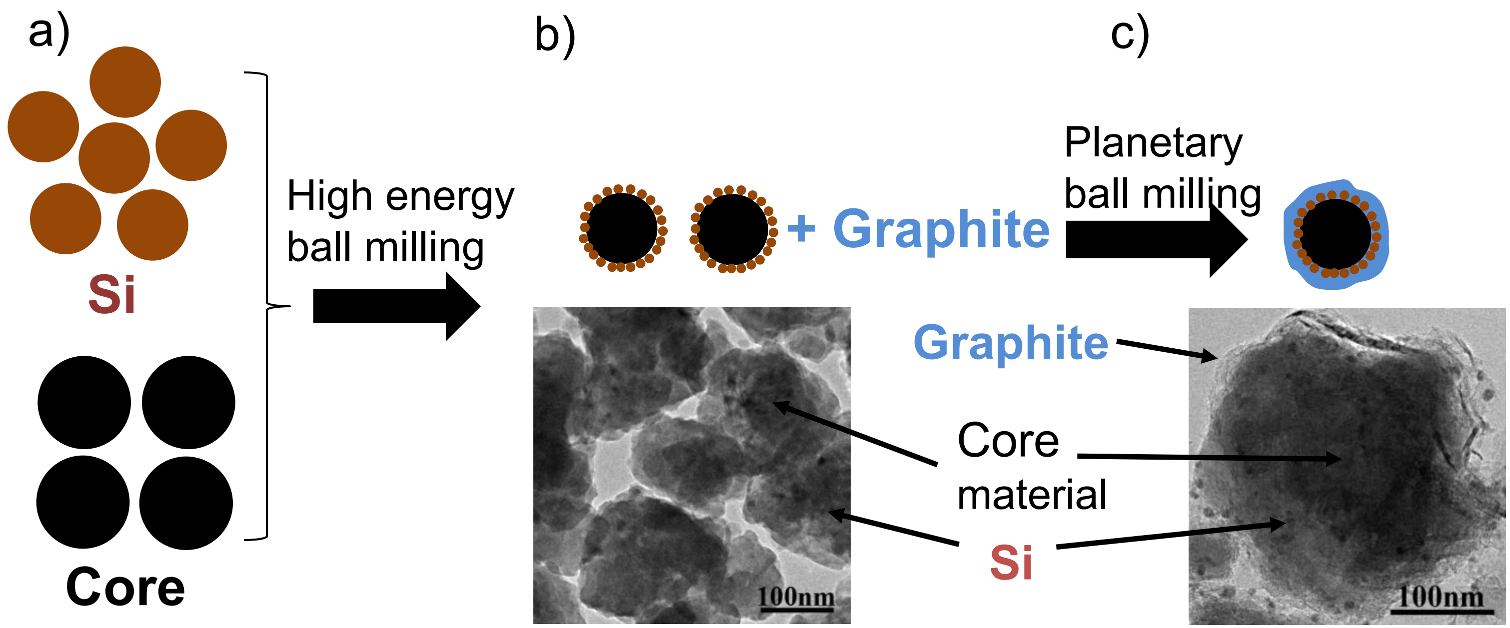
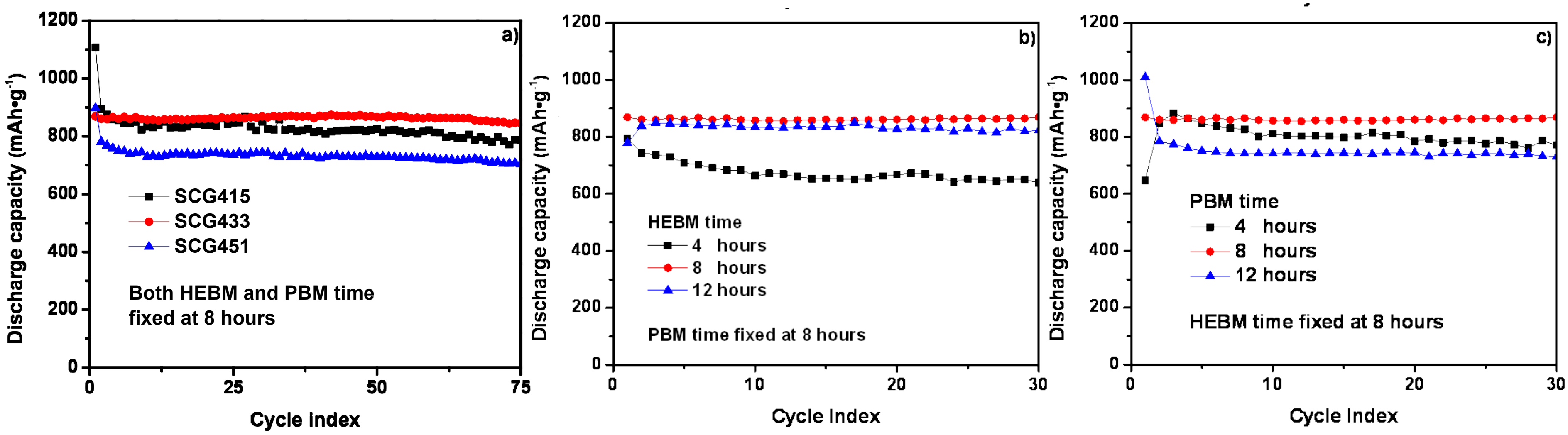
Technical Accomplishments: Conductive Rigid Skeleton Supported Silicon as High-Performance Li-ion Battery Anodes



- Use conductive, hard material as nano-/micro- millers to synthesize nano Si (< 10 nm).
- Use rigid skeleton to support in-situ generated nano-Si.
- Use conductive carbon to coat the rigid skeleton supported silicon to form Si/Core/graphite (SCG) which can improve the structural integrity and conductivity of silicon anode.

Technical Accomplishments:
Effects of Composition and Synthesis Condition on the Electrochemical Performances of Si Anodes



- The ratio of Si, Core material and graphite are important to the electrochemical performance. **Si:Core:graphite = 4:3:3 is the optimized ratio.**
- Ball milling time is also important to the electrochemical performance. 8 hr milling is good for HEBM and PBM.

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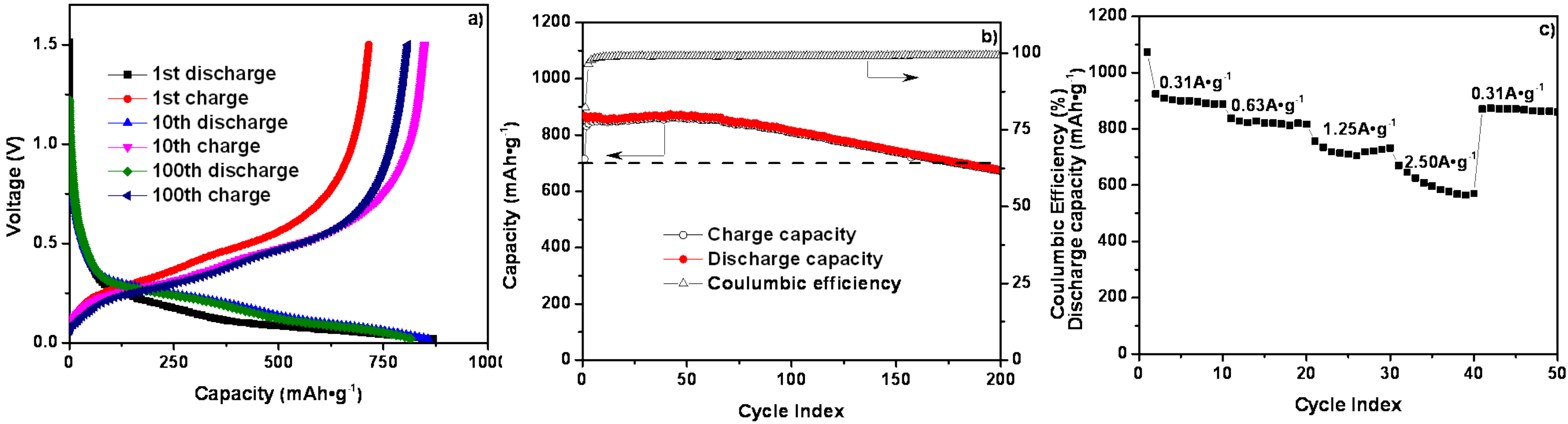
Technical Accomplishments:
SCG Composite Demonstrated Improved Cyclability and Rate Performance



- Capacity based on whole electrode is ~822 mAh/g and the capacity retention is ~94% after 100 cycles.
- Good rate performance is obtained. A capacity of ~600 mAh/g is obtained at a current density of 2.5 A/g

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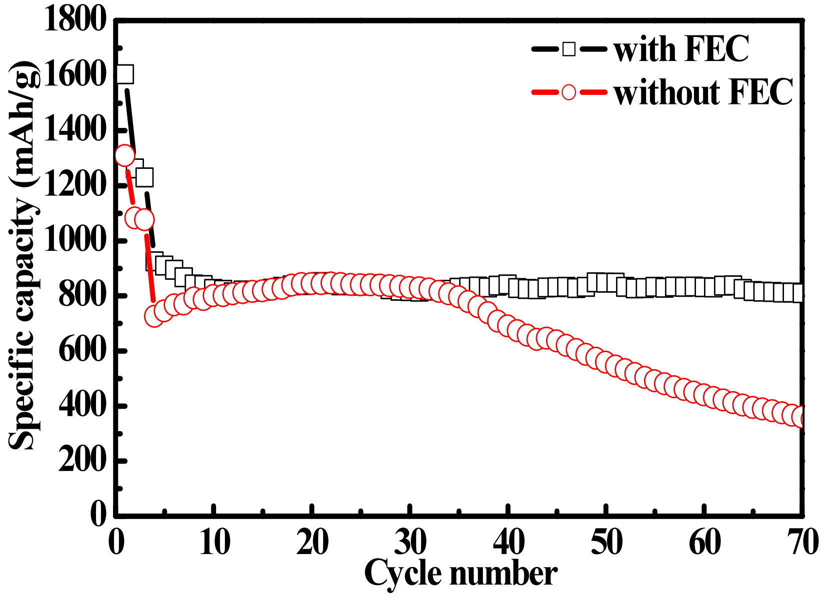
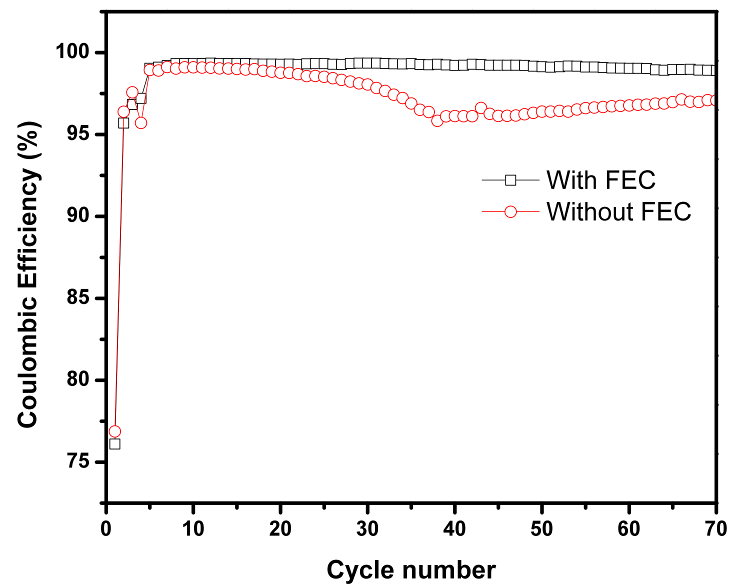
Technical Accomplishments: Understand the Electrolyte Additive Effect





- The cycling stability of Si anode was significantly improved with 10% weight of FEC added in EC:DMC (1:2) electrolyte.
- Almost no capacity fade over 70 cycles with the addition of FEC.
- A capacity fade of ~50% was observed after 70 cycles with no FEC additive exhibited

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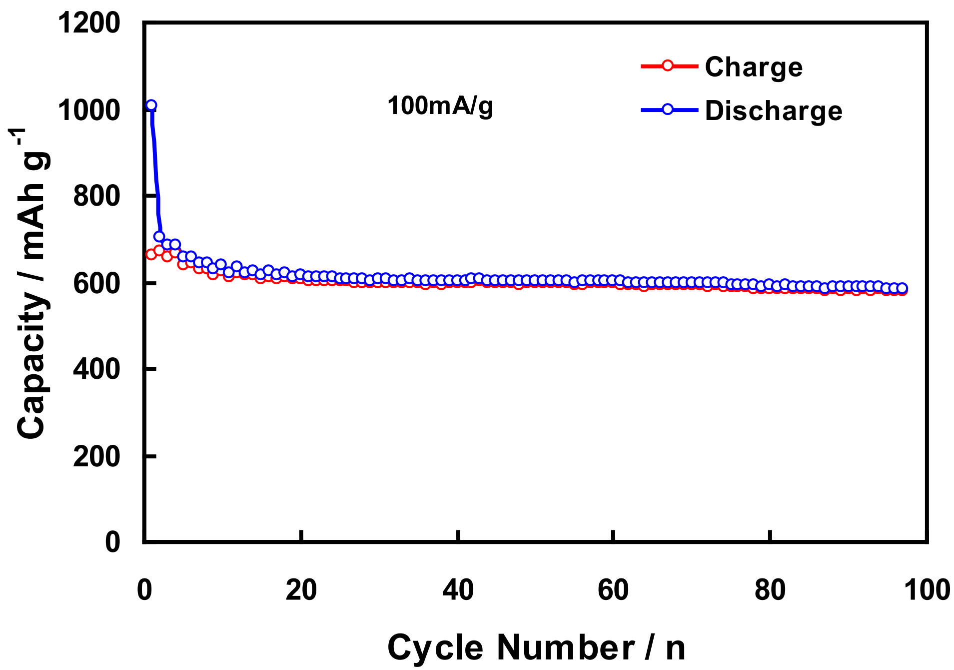
Technical Accomplishments: SiO_x-based Composite Demonstrated Improved Cyclability



- The conductive rigid skeleton supported structure is a general method for making electrodes
- Capacity based on whole electrode is ~600 mAh/g and the capacity retention is ~99% after 90 cycles.

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Collaboration and Coordination with Other Institutions

Partners:

•Princeton University: Preparation and characterization of graphene.

•University of Rhode Island: Tested electrolyte additive provided by Prof. Brett Lucht

•Vorbeck Inc.: Provider of graphene sheet.

•Vesta Si LLC: Provider of porous Si

•North Dakota State University: Collaboration on characterization of silicon nanowires prepared by electrospinning method.

Future Work

- Continue to improve the performance of silicon based anodes for Li-ion batteries.
  - Further improve the conductive rigid skeleton supported Si anode for better cycling stability.
  - Optimize the carbon layer thickness, void space and porosity in the core-shell structured porous Si-C nanocomposite to further improve the cycling stability.

- Investigate the formation and evolution of SEI layers on Si based anode.

- Develop new electrolyte additives and binders to improve the stability of SEI layer on Si based anode.

- Investigate the performance of nano-structured Si-based electrodes in full cells.

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Summary

High capacity Si anodes with excellent cycling stability have been developed for Li-ion batteries.

- Porous Si based electrode has a full electrode capacity of ~800 mAh/g and a capacity retention of ~650 mAh/g over 60 cycles.
- Hollow core-shell structured porous Si-C nanocomposite is developed. The full anode has a capacity of 760 mAh/g and a capacity retention of 650 mAh/g in 100 cycles.
- **Si electrode supported by a conductive, rigid skeleton has demonstrated highly stable cycling stability.**
  - ✓ The optimized composition is Si:Core:Graphite = 4:3:3.
  - ✓ The full electrode has a capacity of ~ 822 mAh/g and a capacity retention of ~ 94% in 100 cycles.
  - ✓ The preparation process only involves ball milling and can be scale up cost effectively.

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Acknowledgements

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✓ Team Members:
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