Synthesis and Characterization of Structured Si-Carbon Nanocomposite Anodes and Functional Polymer Binders

Donghai Wang[1] and Michael Hickner[2]
[1]Department of Mechanical and Nuclear Engineering
[2]Department of Materials Science and Engineering

The Pennsylvania State University
May 14, 2012

Project# **ES147**

OVERVIEW

Timeline

Project Starts: Jan. 2011

Project Ends: Oct. 2014

Percent Completed: 20%

Barriers Addressed

- Power and energy density
- Cycle and calendar life
- Safety

Budget

- Total funding: $800K
- FY 2011: $200K
- FY 2012: $200K

Partners

- Ji-Guang Zhang and Jun Liu (PNNL)
- PA Nanomaterials Commercialization Center

OBJECTIVES

Design **Si-based nanocomposite anodes** with high volume change tolerance, fast kinetics, and low irreversible capacity loss.

- Design new structured Si-carbon nanocomposites to achieve high capacity and good cycling stability.
- Develop new functional polymer binders for Si-based anodes to improve cycling stability.

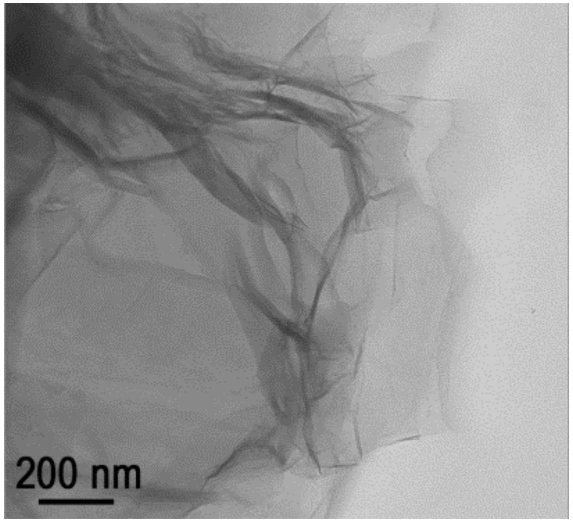
Milestones

- Prepared Si nanoparticles with controlled size and synthesized Si-carbon composites, including Si-graphene and Si@hollow carbon.
- Synthesized new polymer binders for Si-based anodes.
- Characterized electrochemical properties of Si, Si-carbon nanocomposites, and polymer binders in lithium cells up to 200 cycles.
- Achieved improved capacity retention with commercial Si-based anodes.
- Achieved 40% first cycle capacity and 90% coulombic efficiency thereafter.

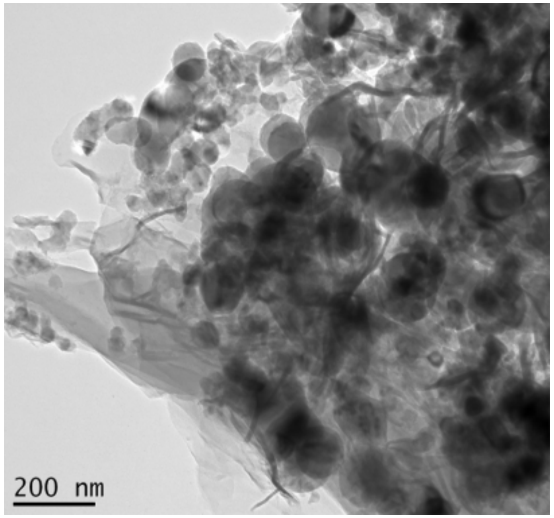
Approach

- **Develop Si-graphene composites** with good electrical contact and electrode conductivity.
- **Develop Si@hollow carbon nanocomposite** to tolerate volume change of Si and improve cycling stability of Si-based anodes.
- **Develop new polymer binders** with controlled elastic properties, ion-conductive moieties, and Si surface binding functionality to stabilize and bridge Si particles.

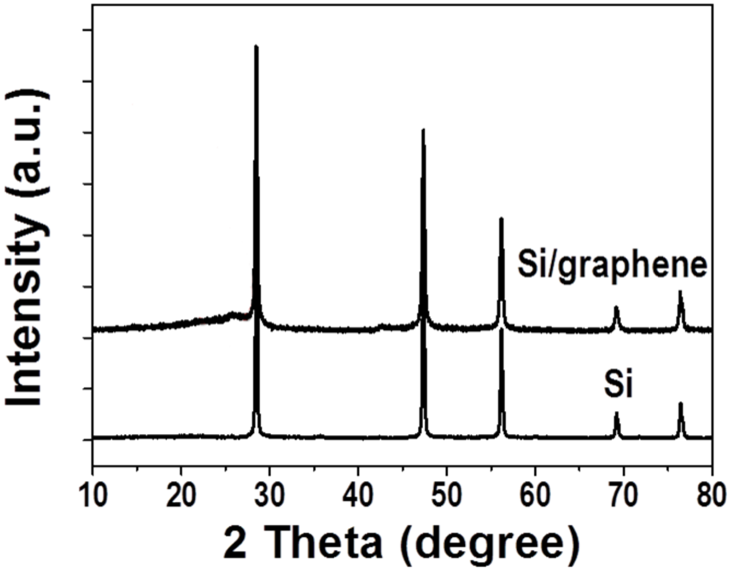
Si-Graphene Nanocomposites



Graphene Sheets



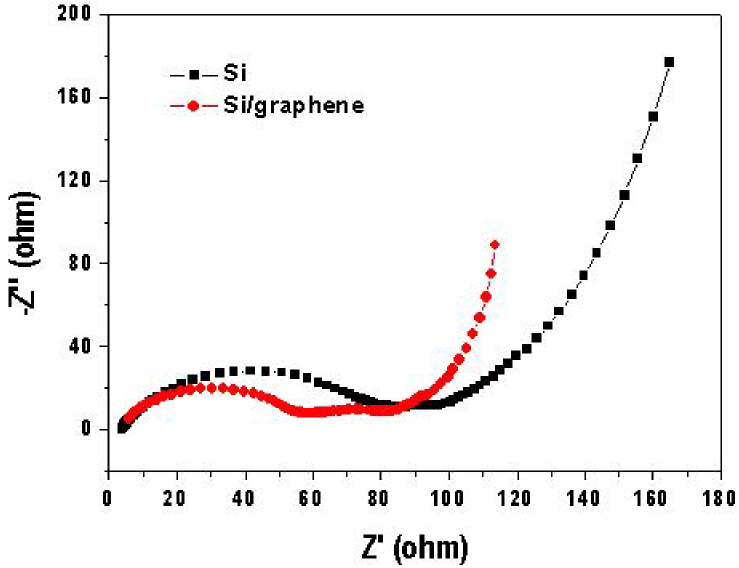
Si-Graphene



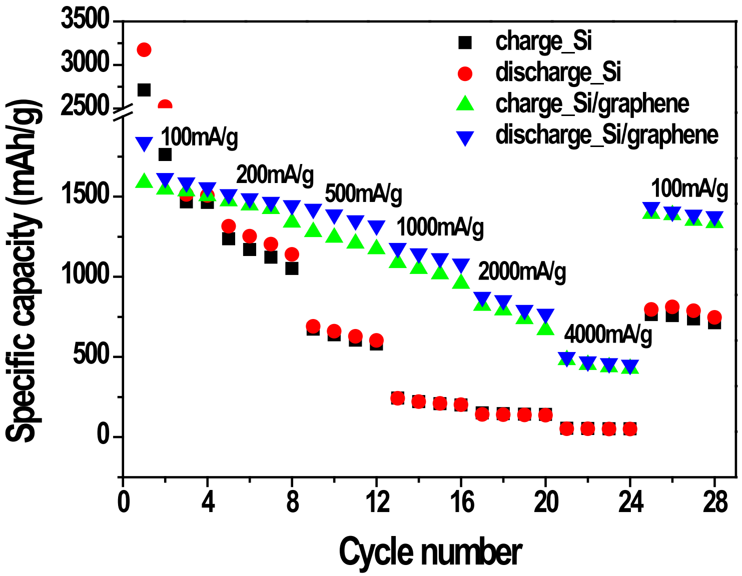
XRD of Si and Si-Graphene

- Si particles (<200nm) synthesized by magnesiothermic reduction.
- Si particles coated onto graphene sheets.

Graphene Improves Conductivity and Cycling Stability



Impedance Analysis of Electrodes



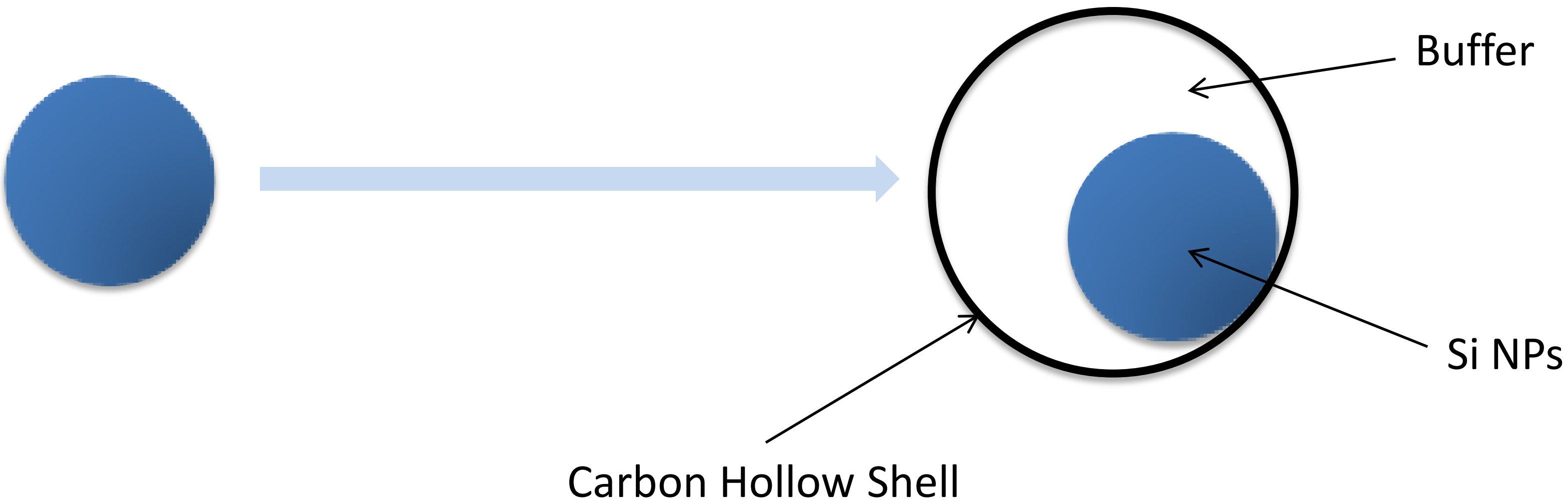
Rate Performance Comparison

- The Si-graphene nanocomposite shows increased electrode conductivity.
- Incorporating graphene improves the cycling stability of Si anodes, possibly due to the good electric contact between Si and graphene sheets.

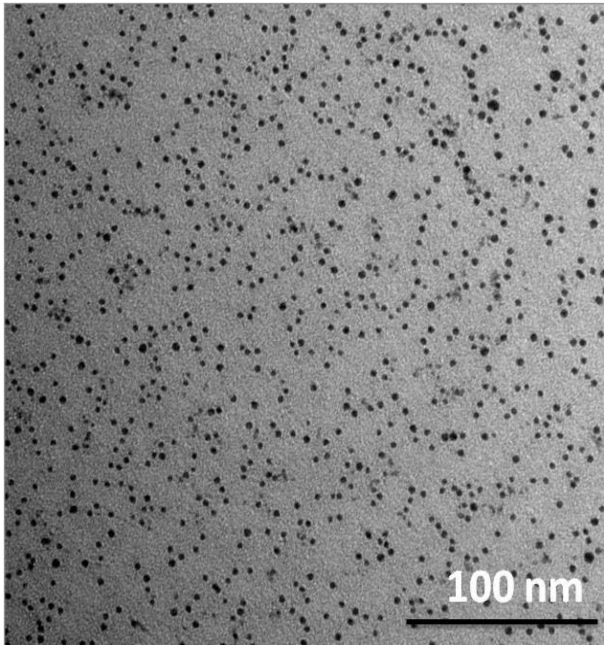
Methods to Further Improve Stability of Si-Carbon Composites

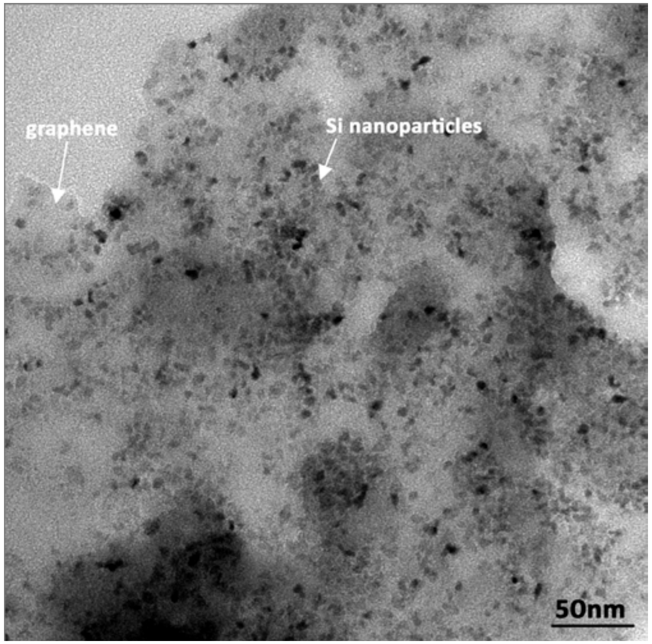
1. Decrease Si nanoparticle size

2. Provide built-in buffer volume for Si expansion



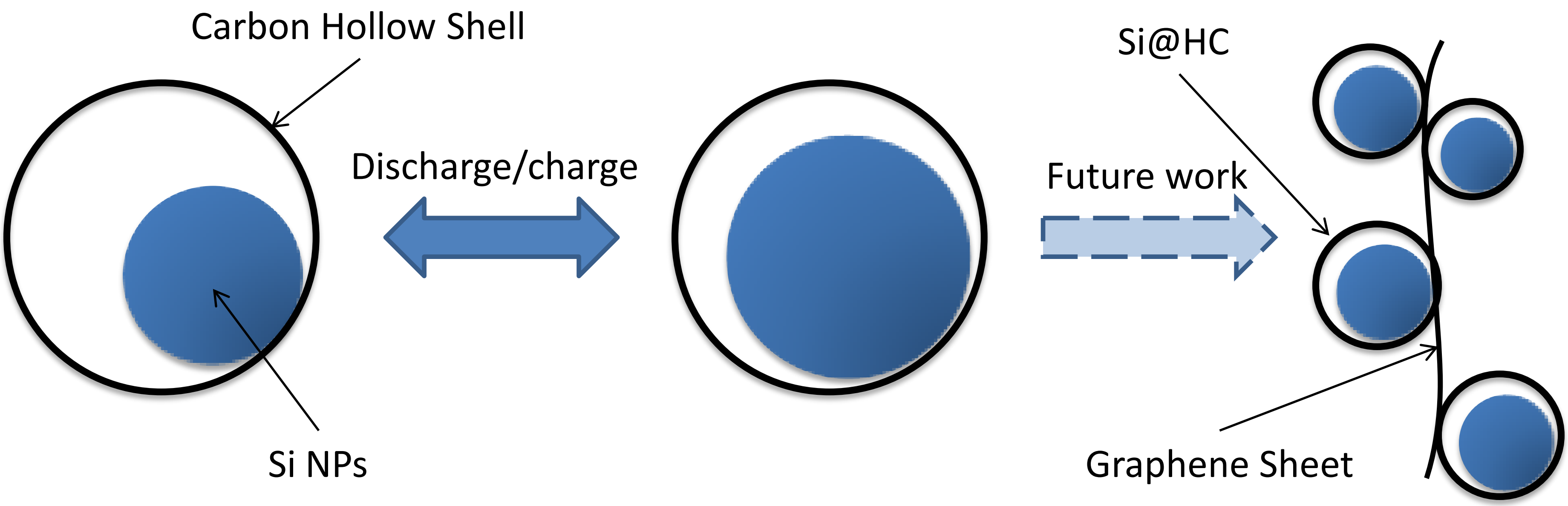
Si Nanoparticles and Si-Graphene Hybrid





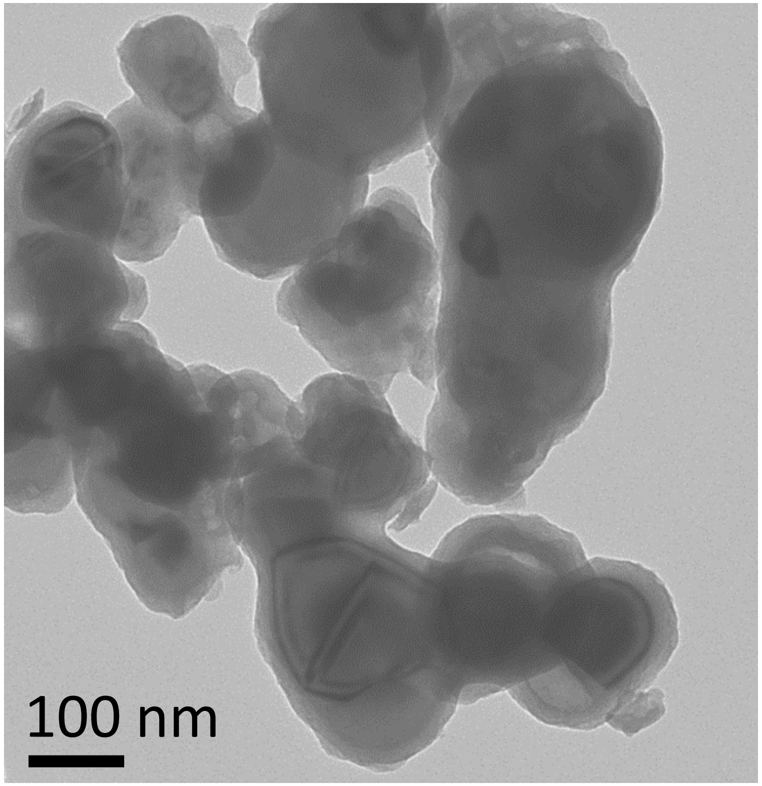
- Synthesized Si nanoparticles with diameter of 5-10 nm.
- Synthesized Si-graphene nanocomposites with well-dispersed Si nanoparticles, providing Si with buffer space for superior volume change tolerance.
- Performance testing in battery cells underway.

Si@Hollow Carbon With Controlled Buffer Volume

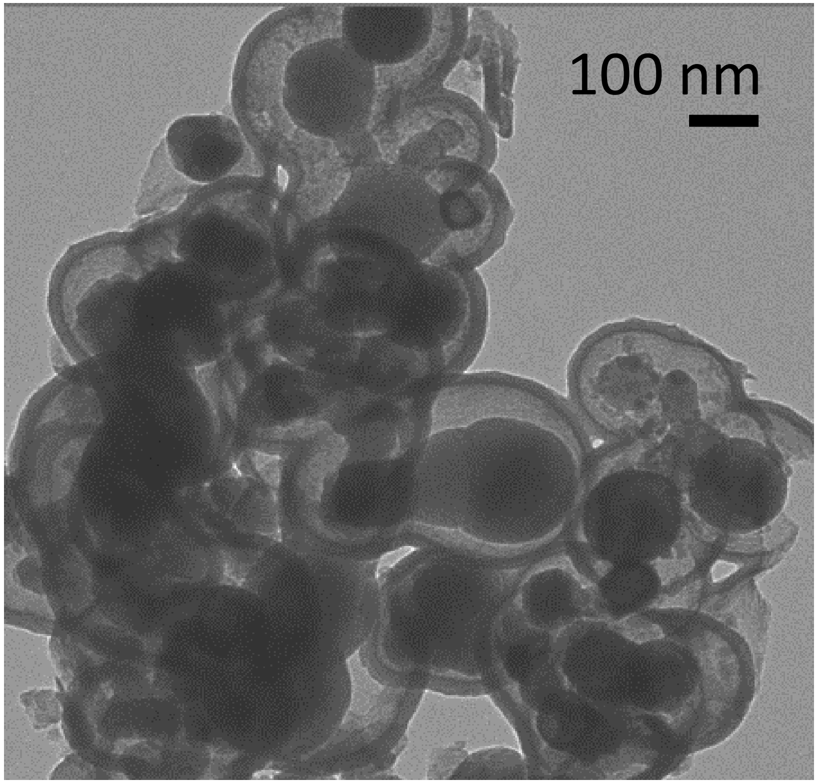


- Synthesized Si@hollow carbon nanocomposites – commercial Si nanoparticles inside hollow carbon spheres.
- Structure allows Si to expand/contract freely inside carbon support structure.

Si@Carbon and Si@Hollow Carbon Nanocomposites



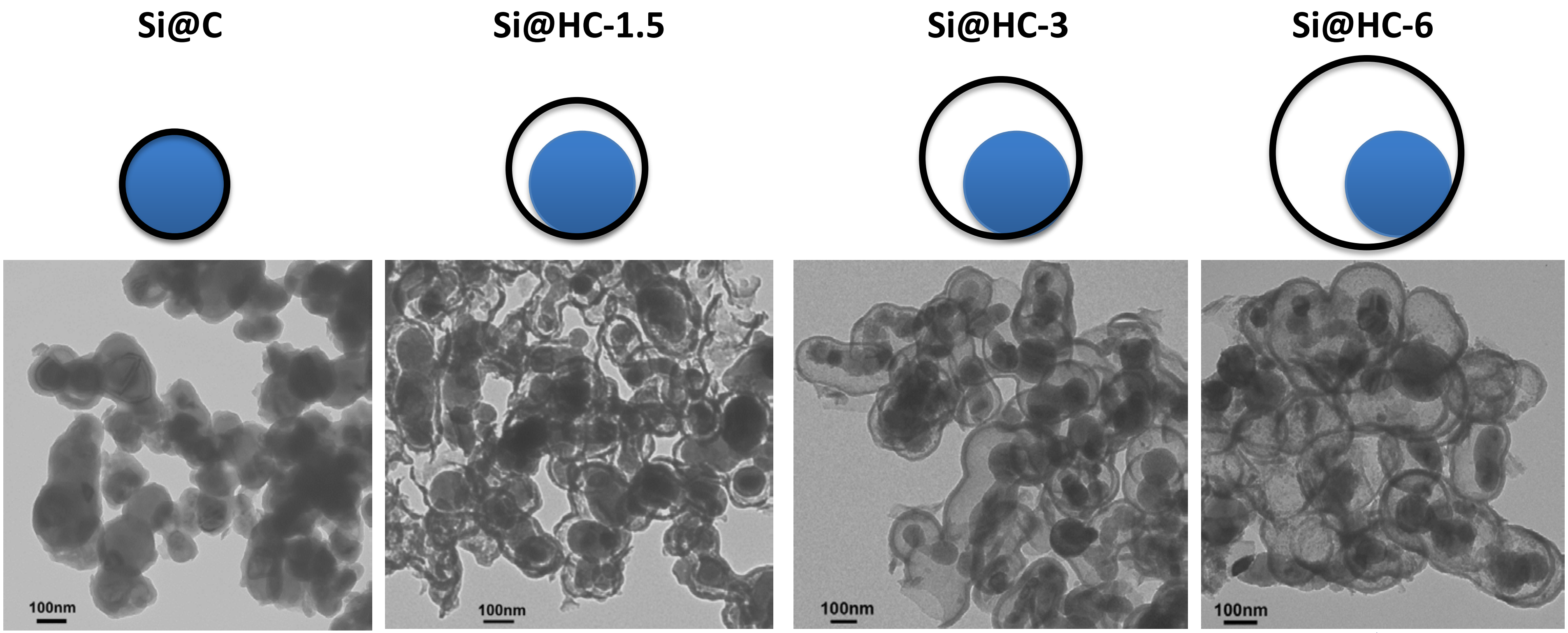
Si@carbon nanocomposite



Si@hollow carbon nanocomposite

- Used commercial Si nanoparticles.
- Synthesized Si@C and Si@HC nanocomposites.

Si@Hollow Carbon Nanocomposites With Controlled Buffer Volume

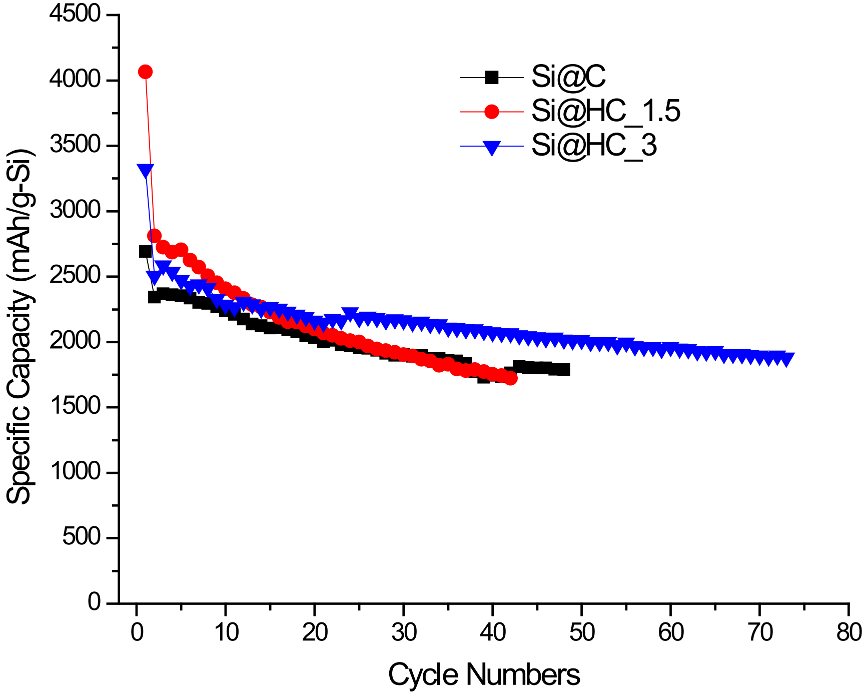


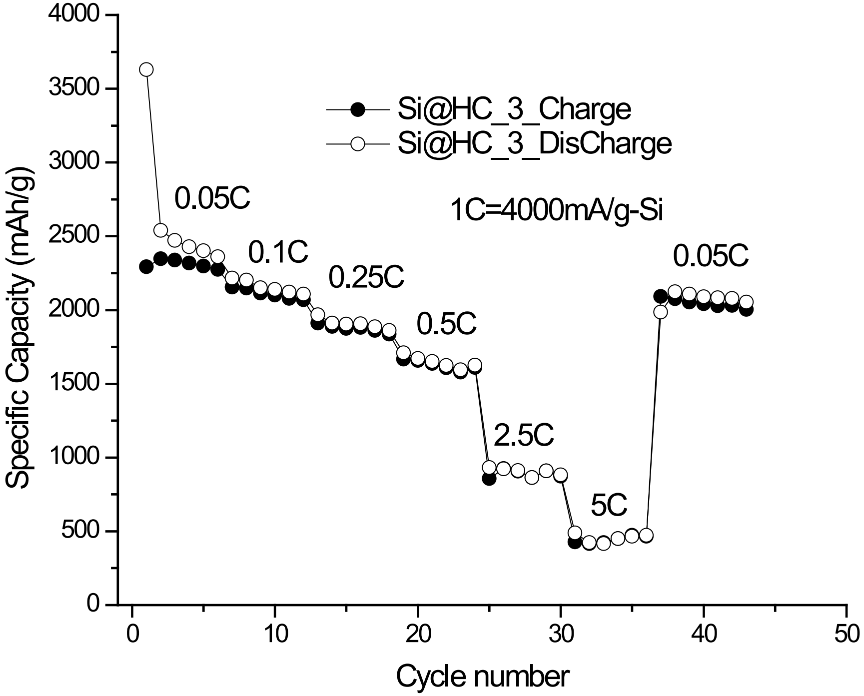
Buffer to Si Volume Ratio = 0, 1.5, 3 and 6.

Increasing buffer volume

- Si@carbon and Si@hollow carbon nanocomposites with controlled buffer volume were developed.
- Si content is currently 48-62 wt %.

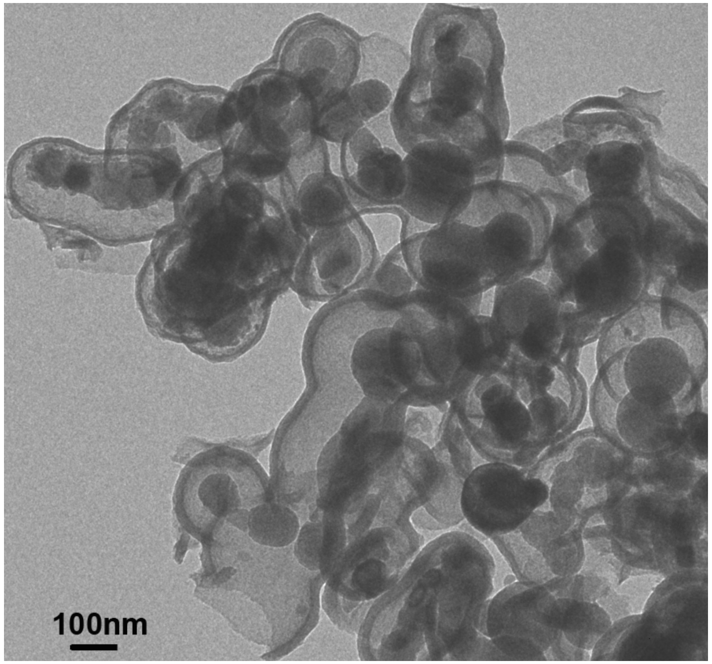
Cycling Performance of Si@C and Si@HC Nanocomposites



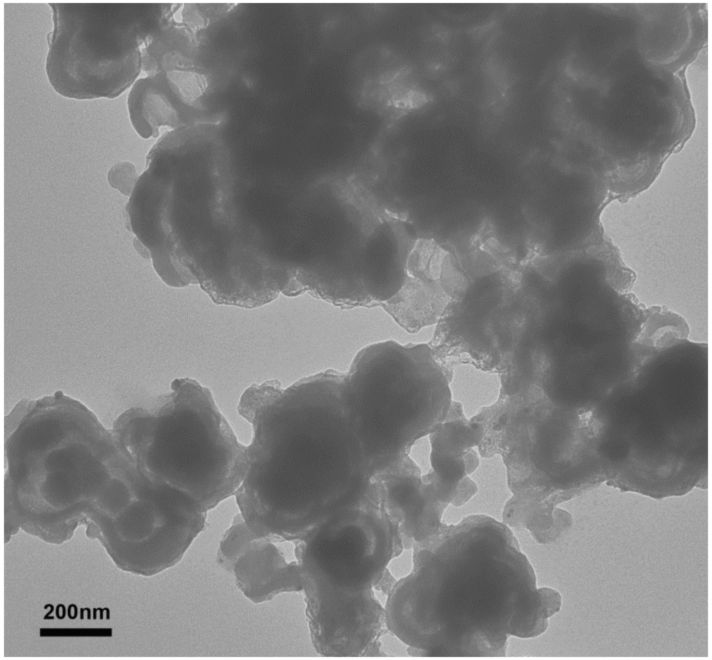


- Si@HC with buffer/Si volume ratio of 3 has the best capacity retention among the Si@C and Si@HC nanocomposites.
- 1st cycle capacity: 2250 mAh/g of Si at 400 mA/g.
- Capacity above 1000 mAh/g of Si@HC after 50 cycles.

Si Nanoparticles Remain in Hollow Carbon Structures



Fresh Si@HC

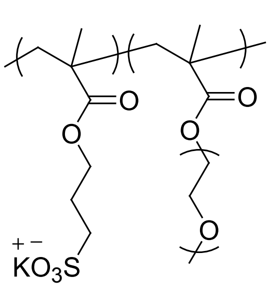
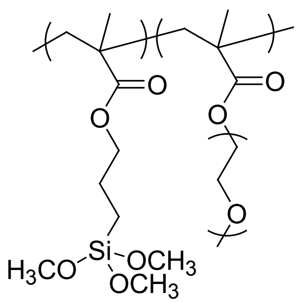
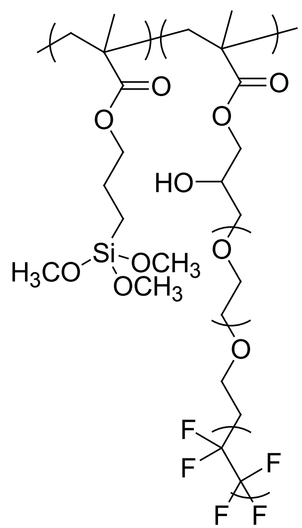
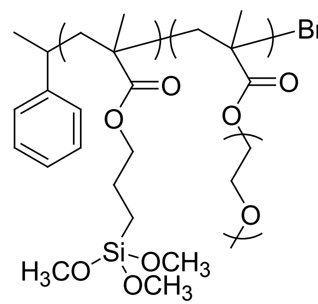
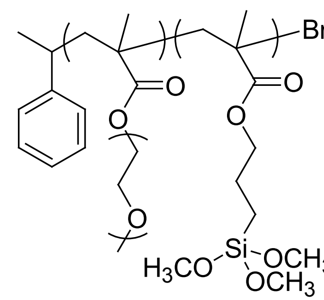


Si@HC after 20 cycles of discharge/charge

- TEM investigation shows Si nanoparticles confined within the hollow carbon shells after repeated discharge/charge.
- SEI coatings were observed on Si@HC particles.

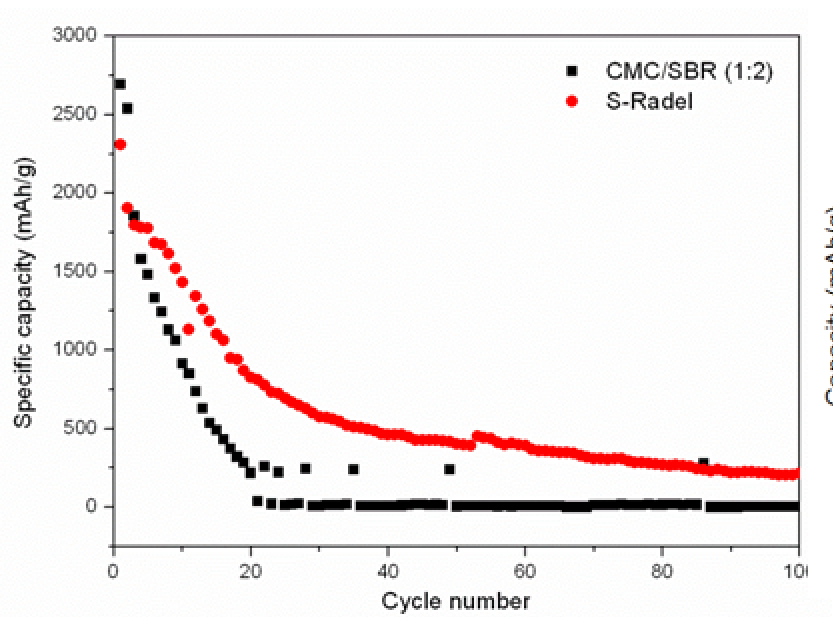
Li-conducting Block Copolymer Binders

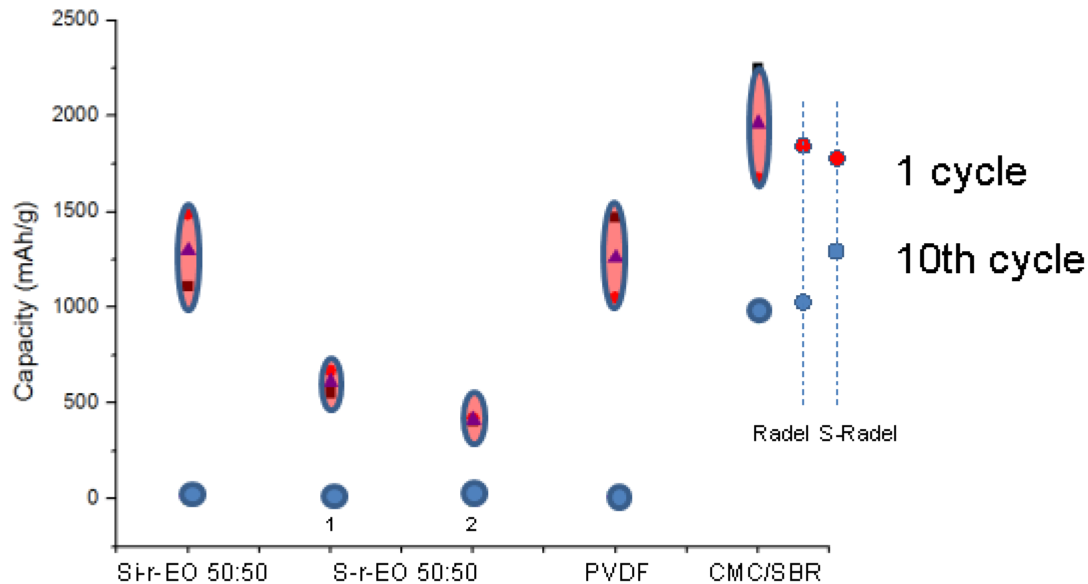
Random and block copolymers were designed to have Li-conducting EO segments and Si NP surface binding groups. Modular synthesis was used to substitute various functional groups easily without drastically modifying synthetic methodology.

Random Copolymers	Block Copolymers
 S-r-EO 50:50  Si-r-EO 50:50  Si-r-Z 50:50	  Segregating Si-binding block from Li-conducting block may improve binding to nanoparticles. Testing underway.

Initial Binder Cycling Tests

- Symbols show 1st cycle and 10th cycle capacity of Si NP-based anodes with various binders.
- EOrandom polymers had poor cycling performance. Investigating blocks now.
- Radel® samples have similar initial capacity retention to CMC/SBR.



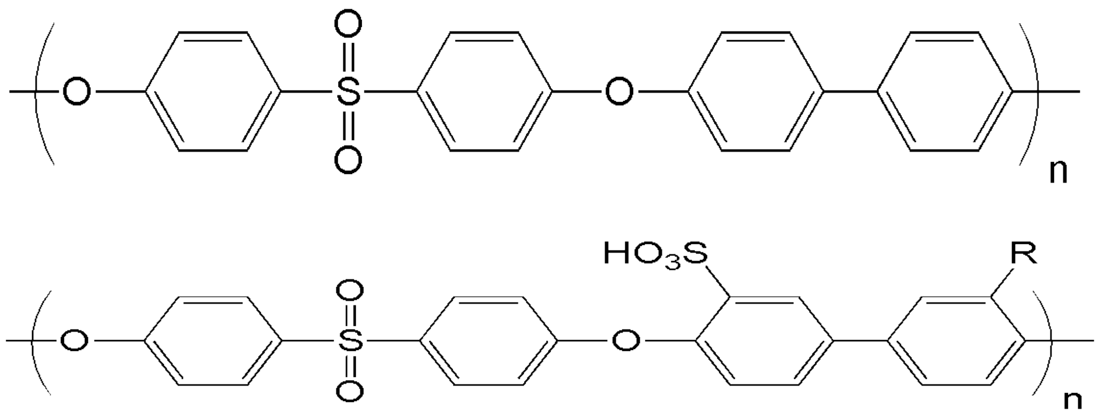


Stiff-Backboned Polymer Binders

- Radel poly(sulfone)-based polymers not as prone to swelling in liquid Li-ion battery electrolytes compared to EO samples.
- Investigate how mechanical properties influence Si-binder anode performance.

Radel

S-Radel



$R = H$ or $-SO_3H$

Moduli

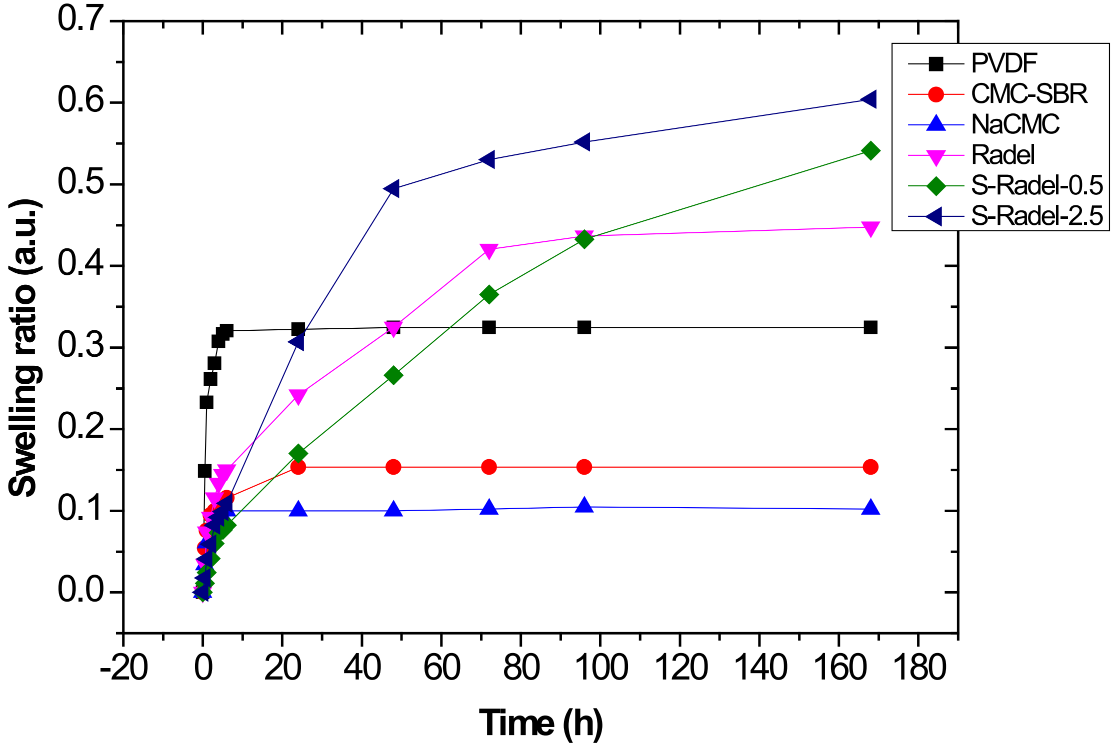
Radel: 2 GPa

PVDF: 200 MPa

PEO: 20 MPa

Polymer Binder Swelling Study

Swelling experiments performed in electrolyte mixtures to determine rate and extent of binder dissolution



Key information relating the swelling profile to the cell performance. Next iteration of polymers will incorporate crosslinkable groups to limit the swelling in electrolyte.

Future Work

- Study of SEI formation on Si-graphene and Si@HC nanocomposites.
- Synthesis, characterization, and testing of amorphous Si-carbon nanocomposite.
- Continued investigation of binder failure mechanisms.
- Design of low-swelling binders.

Summary

- Synthesized Si-graphene, Si NP-graphene, Si@C, and Si@HC nanocomposites.
- Characterized and tested the electrochemical performance of our new composites. Found performance improvements over conventional Si-based materials.
- Developed new binders for Si-based anodes.
- Tested several promising binders and elucidated potential failure mechanisms to direct further work.

Acknowledgment

Support for this work from DOE-EERE, Office of Vehicle Technologies is gratefully acknowledged – Tien Duong and David Howell