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

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Project ID : ES147

Overview

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Timeline

Project Starts: Jan. 2011

Project Ends: Dec. 2014

Percent Completed: 60%

Barriers

- Power and energy density
- Cycle life

Budget

- Total funding: $826K
  - FY 2011: $205K
  - FY 2012: $205K

Partners

- Jason Zhang and Jun Liu (PNNL), and Gao Liu (LBNL)
- Johnson Control and PA Nanomaterials Commercialization Center.
- In discussion with Nissan Tech Center (USA) for sample test.

Objectives

- ❑ Achieve high performance Si anode materials by developing novel structured Si-carbon nanocomposites and polymer binders.

- ❑ Improve management of volume change and pulverization characteristics of Si-C anodes.

- ❑ Decrease initial irreversible capacity loss and increase coulombic efficiency of Si-C anodes.

- ❑ Improve both gravimetric and volumetric capacity, electrode kinetics and cycling life of Si-C anodes.

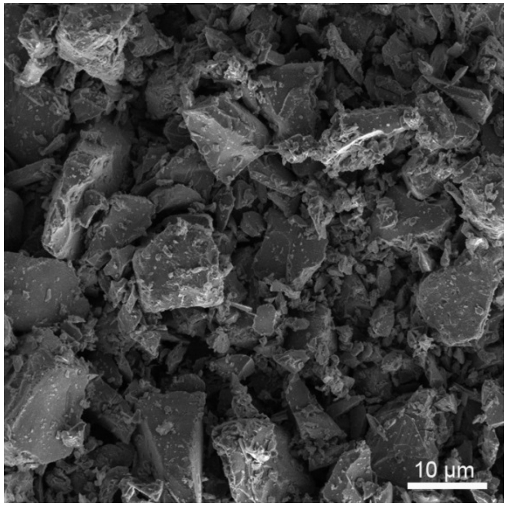
Technical Approach

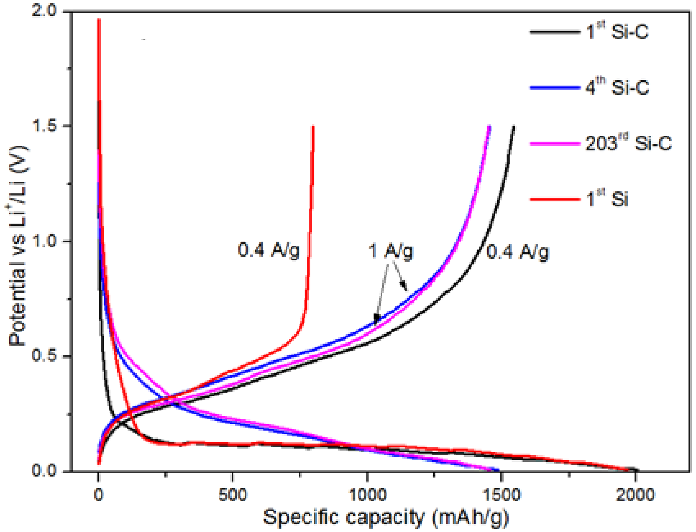
- Synthesize Si-C nanocomposites with controlled nanostructures and composition to improve kinetics and cycling stability upon lithiation/delithiation and illuminate structure-property relationship.

- Design mechanically stiff polymers with varying functional groups composition to test structure-property relationships. Understand the function of binders in Si anodes and uncover the key design features for new materials.

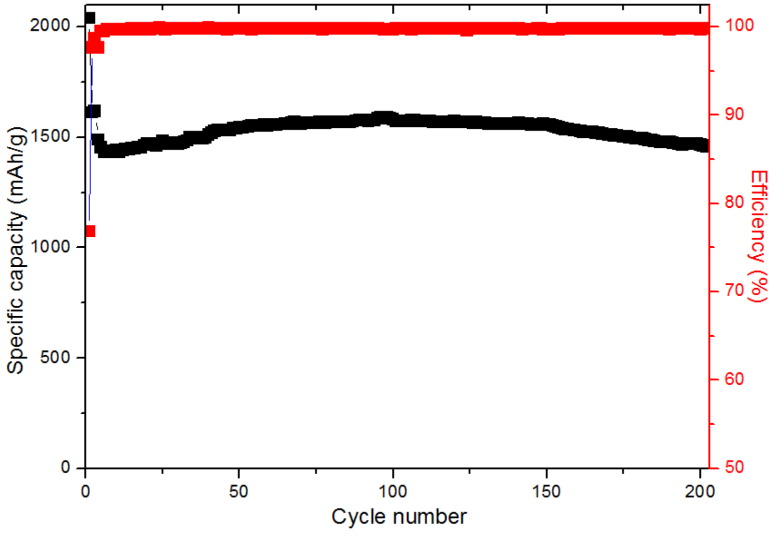
Technical Accomplishments

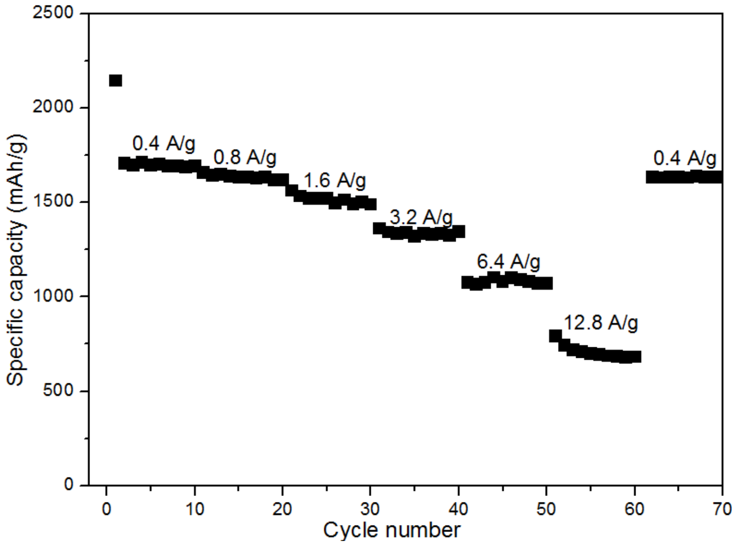
I. Micro-sized Si-C Composite with Interconnected Nanoscale Building Blocks



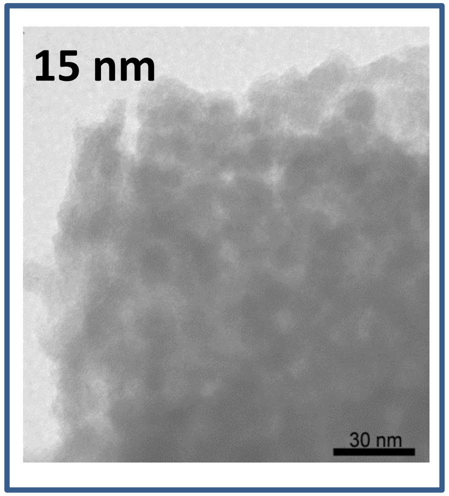


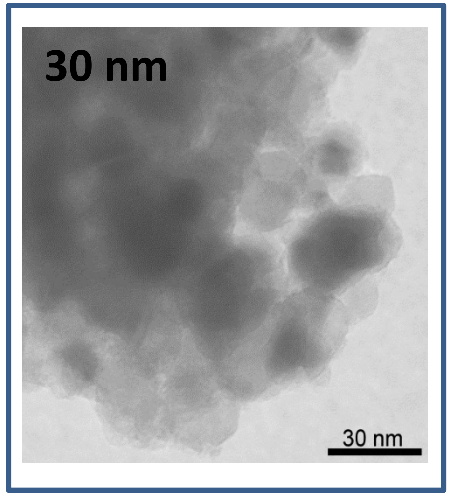
The composite composed of interconnected 10-nm Si nanoparticles coated with carbon (20 wt%)

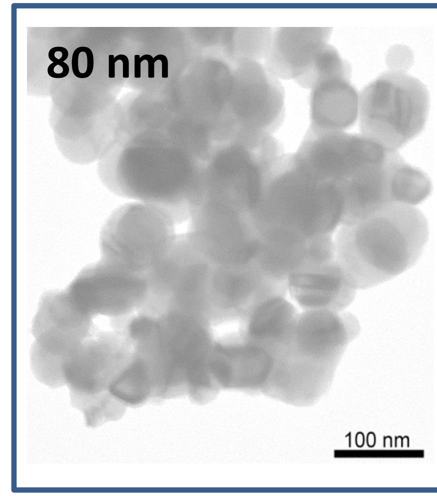




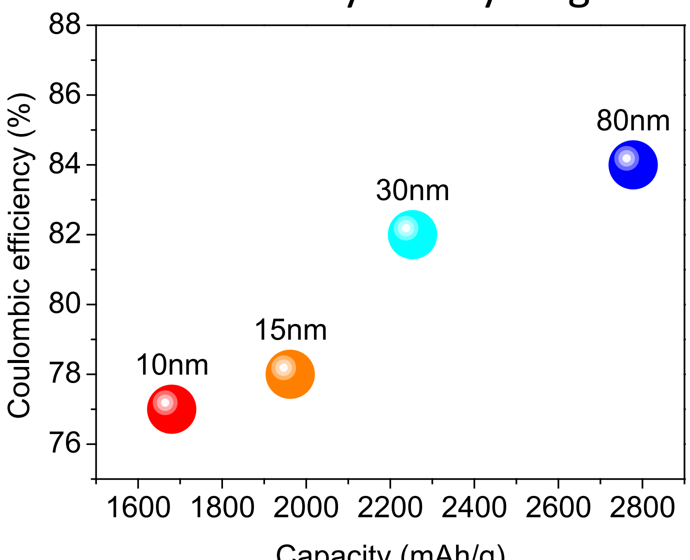
II. Primary Building Block Size Effect in Micro-sized Si-C Composites



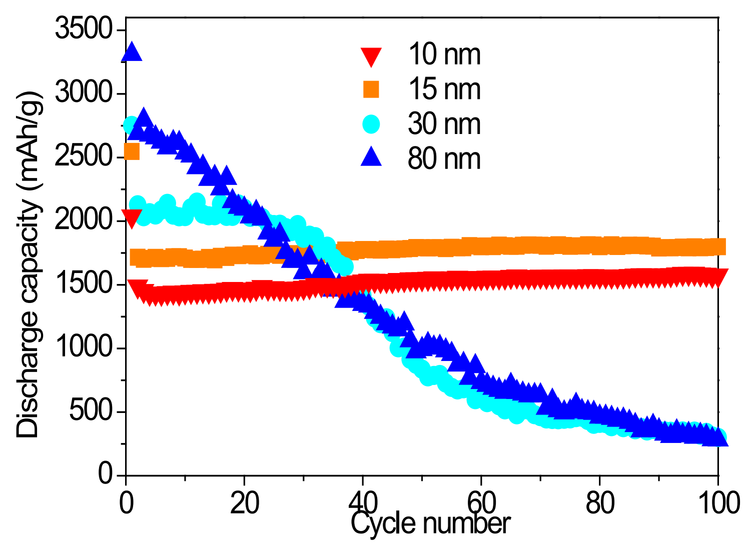




Si building block size of micro-sized Si-C composites significantly affects the first cycle coulombic efficiency and cycling stability.



The 1st cycle efficiency



Cycling stability

III. Electrode Structure and Pulverization Tolerance in Micro-sized Si-C Composites

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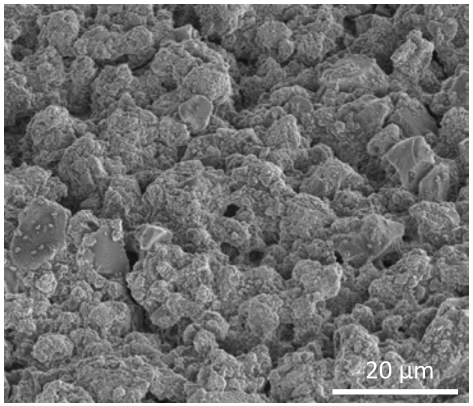
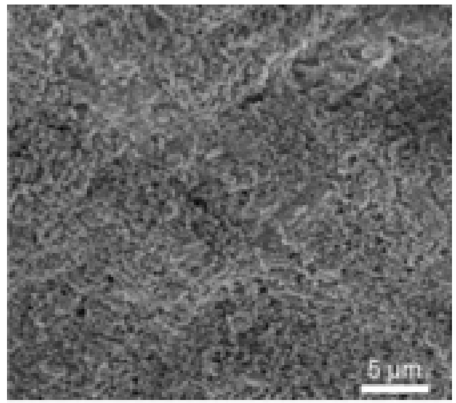
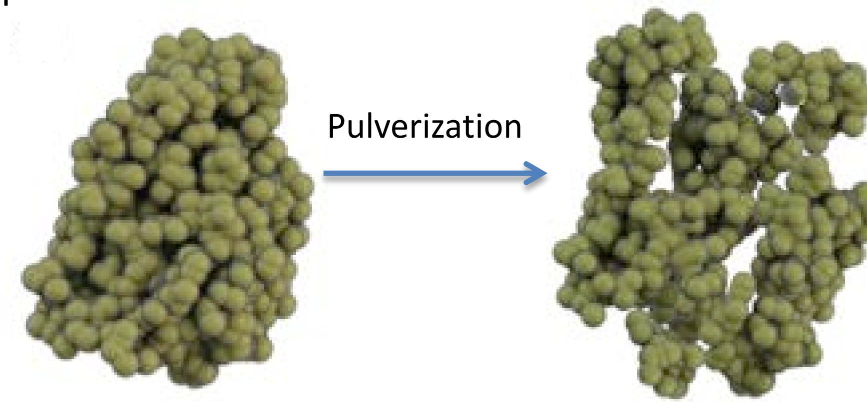
SEM images of Si-C electrodes of 10 nm Si building blocks

Before cycling

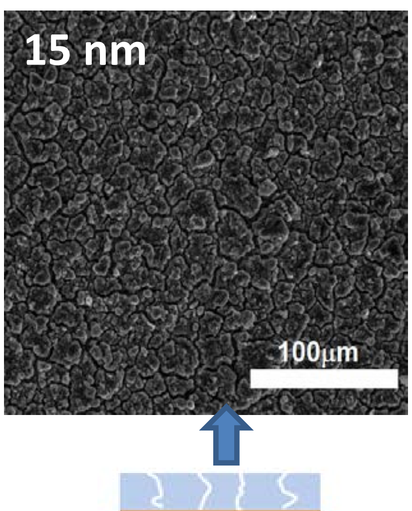


After 10 cycle without SEI layer

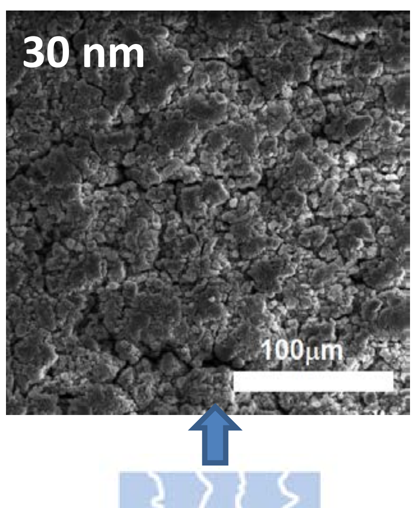




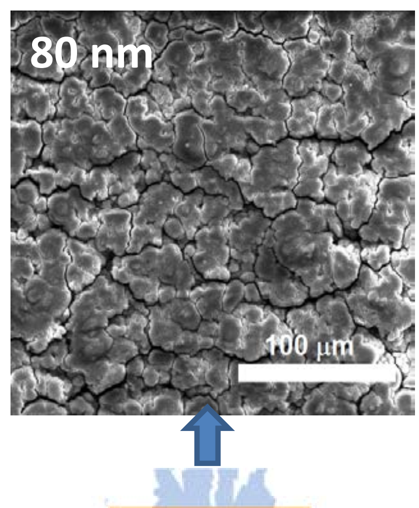
SEM image of electrodes with SEI layers after 100 cycles:



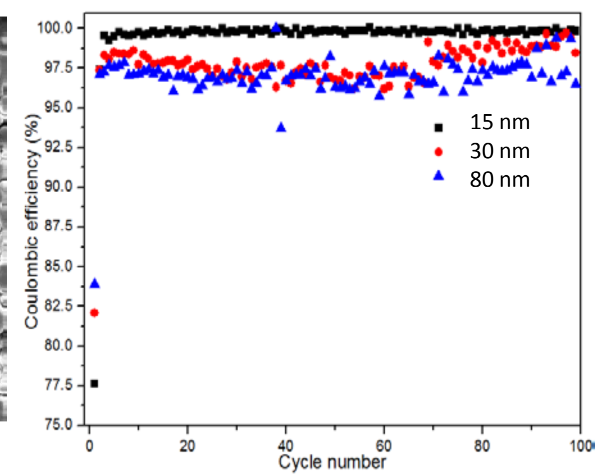
Slightly crack



Deep crack



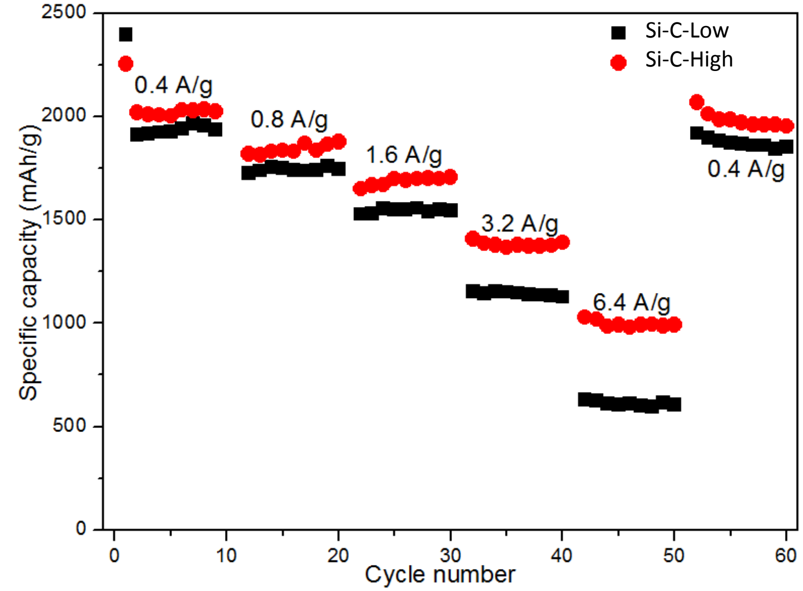
Peel off



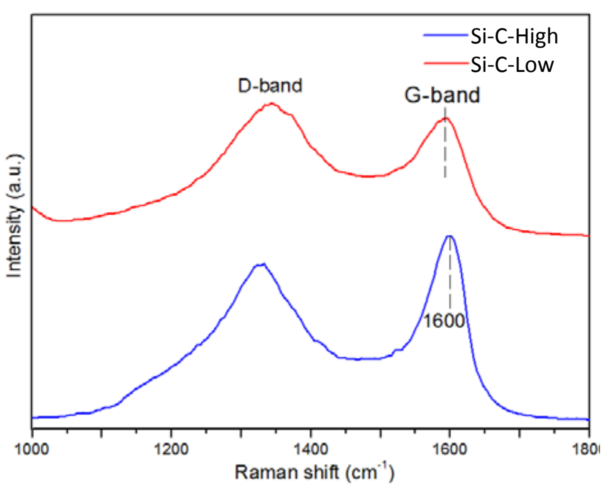
Cycling efficiency

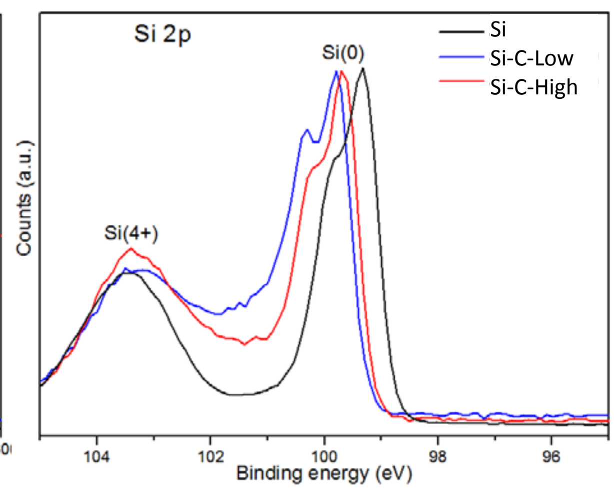
IV. Carbon-coating Effect

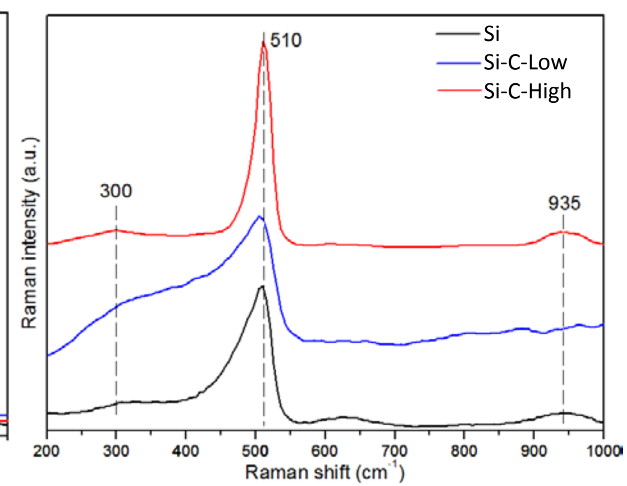
Si building block size 15 nm	D/G Ratio	1st Efficiency
Without C-coating	N/A	75%
Carbon coating	2.3	78%
Carbon coating at higher temperature	2.1	86%



C-coating: A) Reducing SiO_x content; B) Increasing electrical contact.







V. Porous Si-C Composites: (A) Self-assembled Porous Structure

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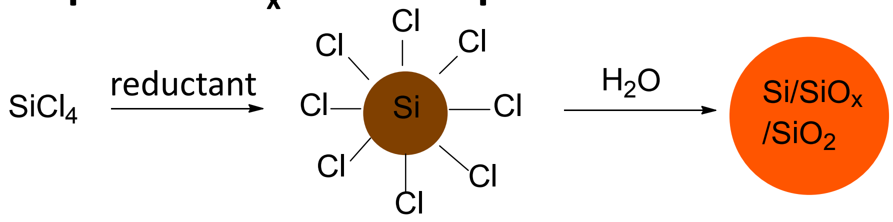
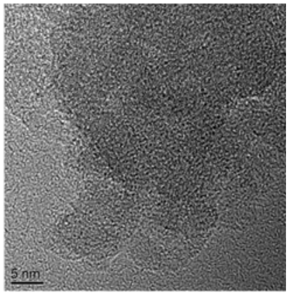
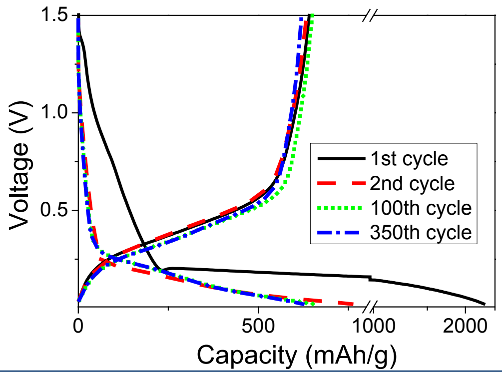
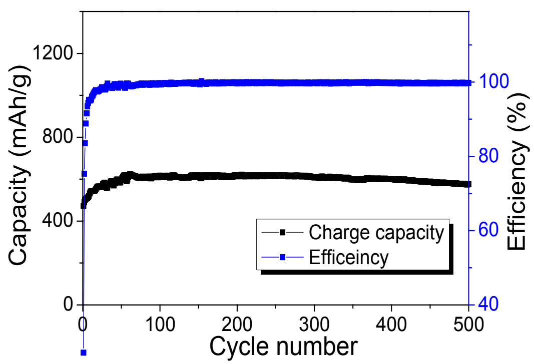
Amorphous SiO_x nanocomposite



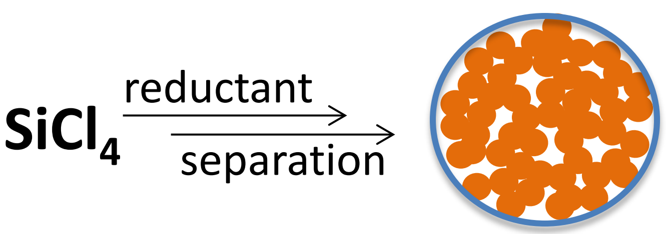






Excellent long cycling performances (retention >95% for 350 cycles)

Self-assembled porous Si materials with tunable pore size



Novel Wet Chemical Synthesis Method: Large-scale, Mild condition, Structure tunable

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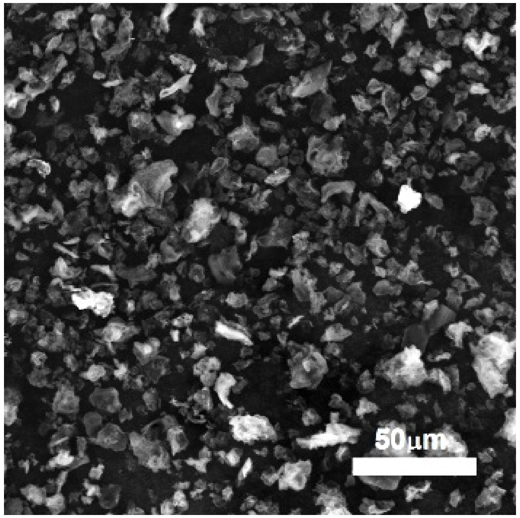
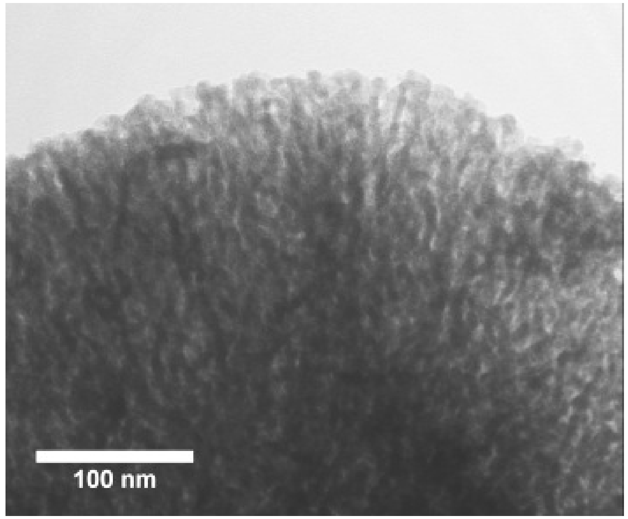
Self-assembled Porous Si-C Composites

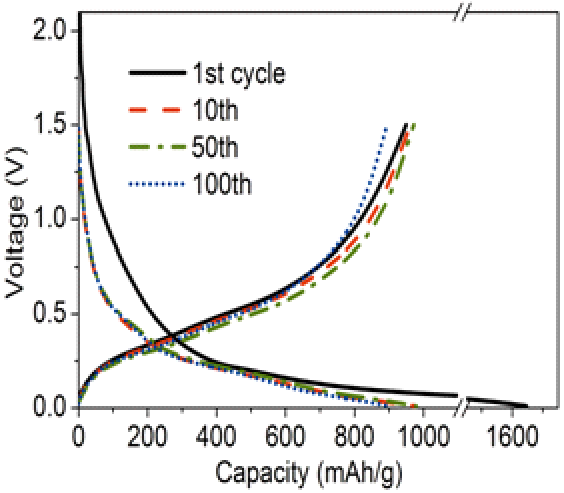


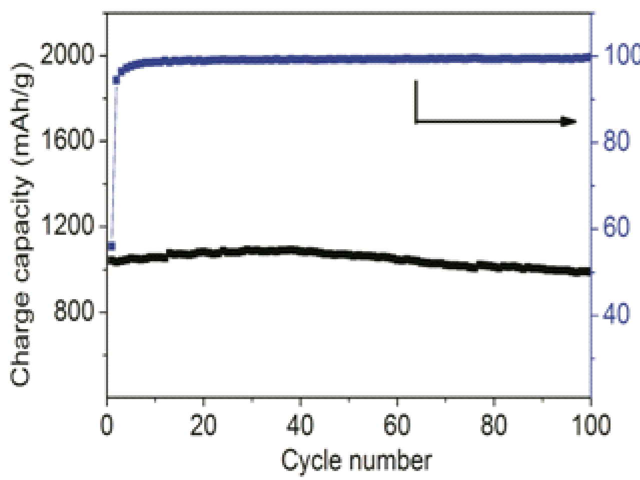


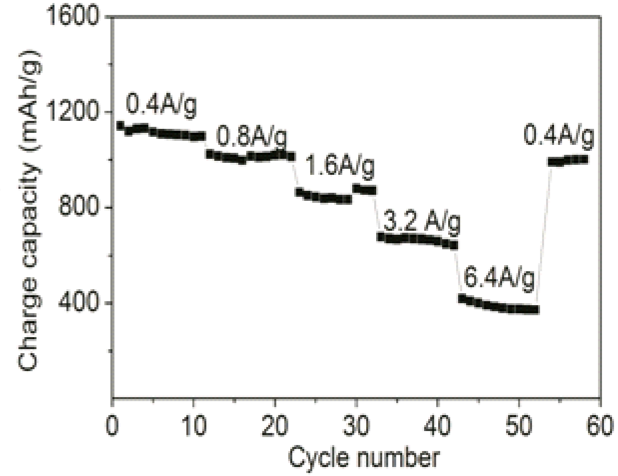
The self-assembled porous Si contains mesopores.

Pore size: 5-10 nm
Porous Si framework thickness : 10 nm
Particle size: ~20 µm

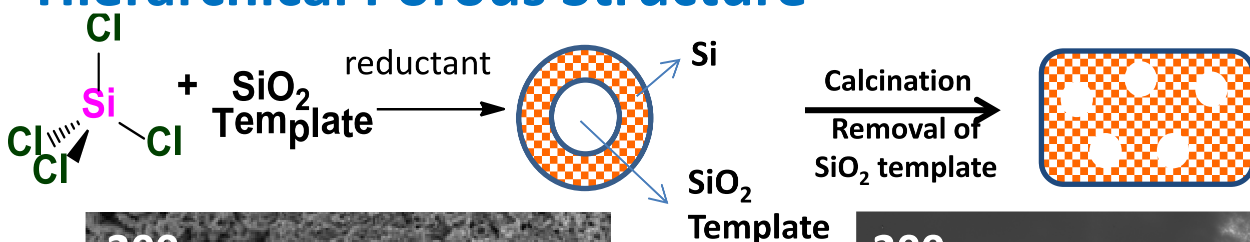
Electrochemical Performances

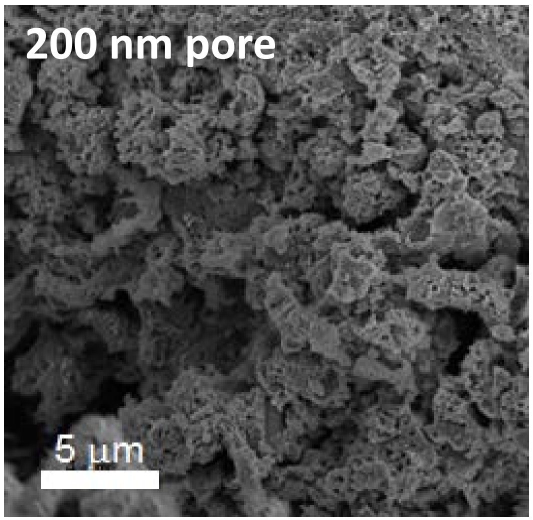


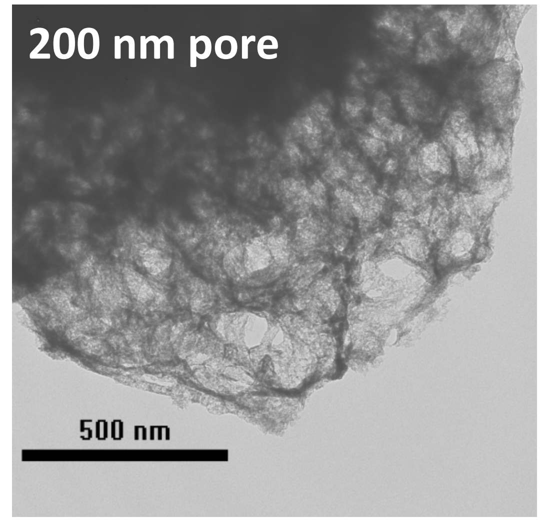


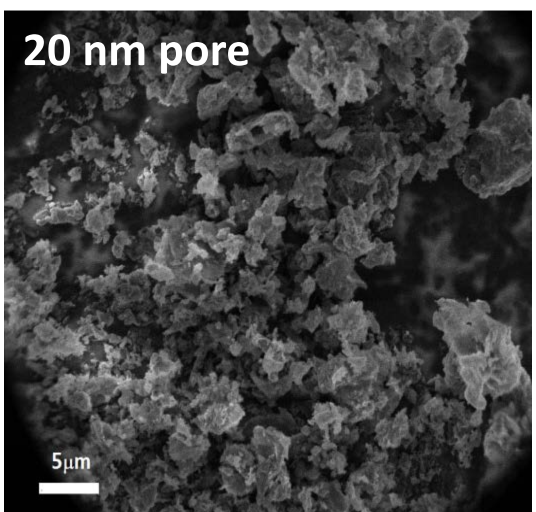


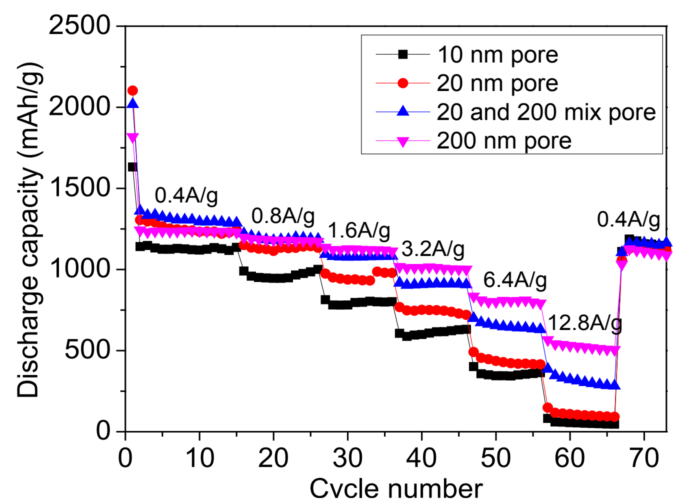
VI. Porous Si-C composites: (B) Templated Hierarchical Porous Structure









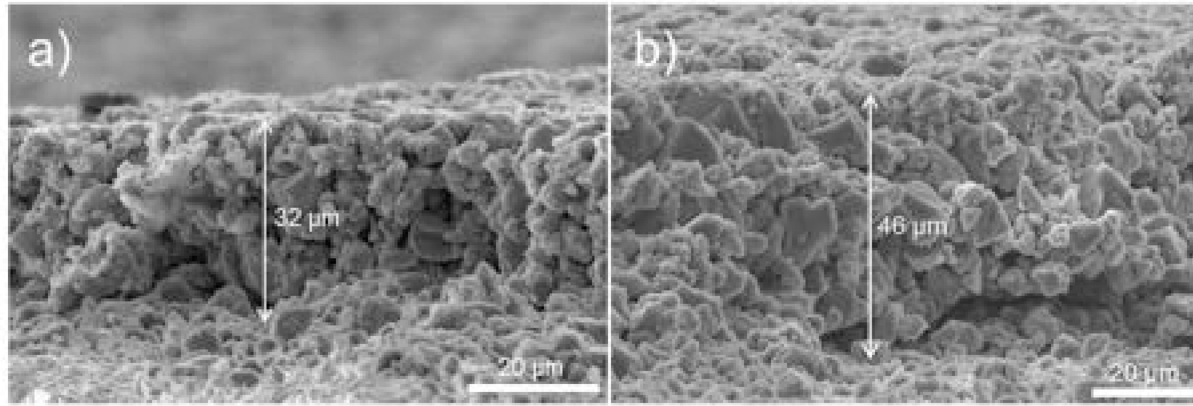


VII. Volume Change Tolerance of Porous Si-C Composites

Material	Specific capacity (mAh/g)	Tap density (g/cm³)
Graphite	372	1.3
Silicon nanoparticles (commercially available)	3572	~ 0.1
SiO_x nanocomposites	650	0.1
Porous Si-C composite	1450	0.7
Micro-sized Si-C composite	1961	0.8

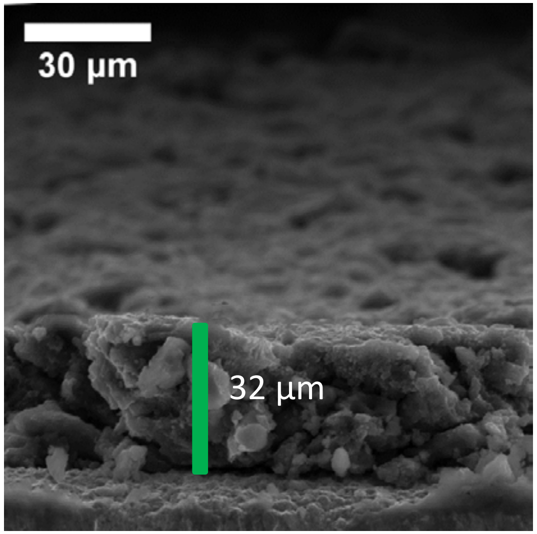
- **Porous structure helps compensate the volume change**

Before cycling After the 1st cycling

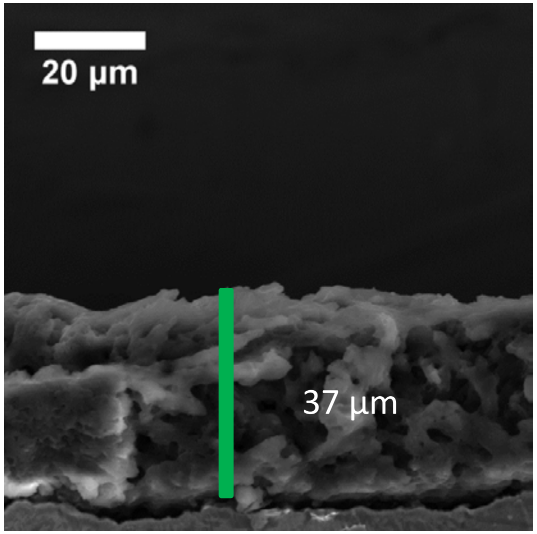


Comparison of lithiated electrode thickness change

Before cycling

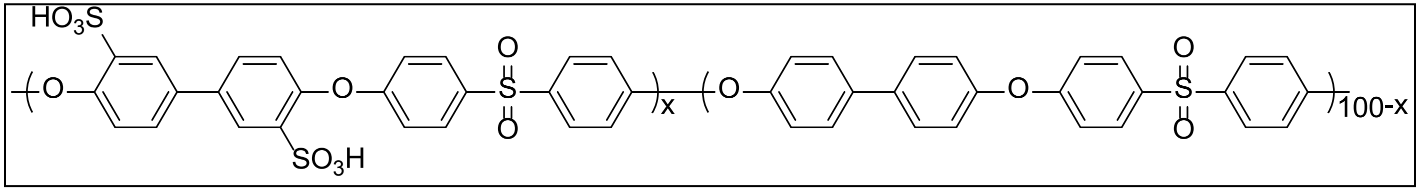


After 50 cycling

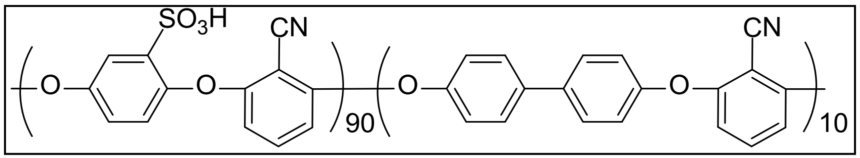


VIII. Functional Aromatic Binders

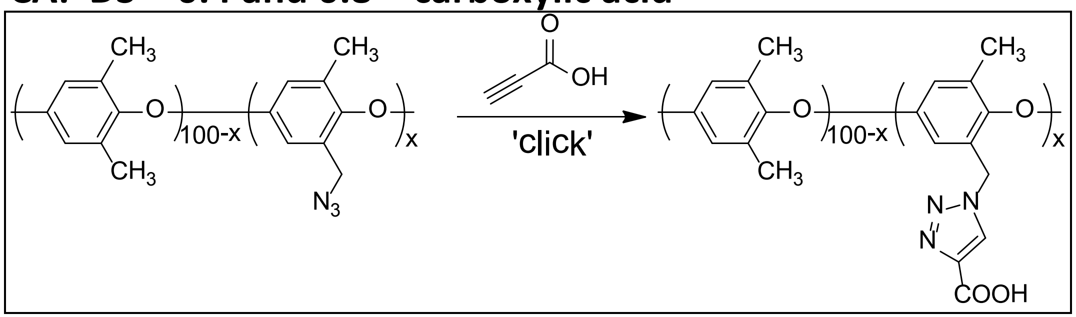
S-Radel: IEC=2.5 meq./g – sulfone and sulfonate-containing binder



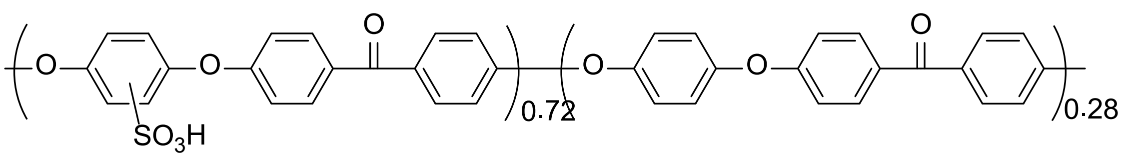
SPAEN: DS = 0.9; IEC=3.1 meq./g – sulfonate + nitrile

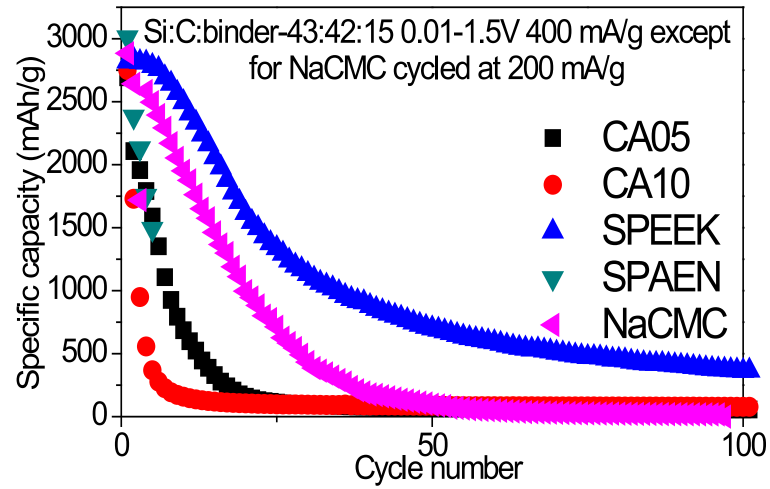


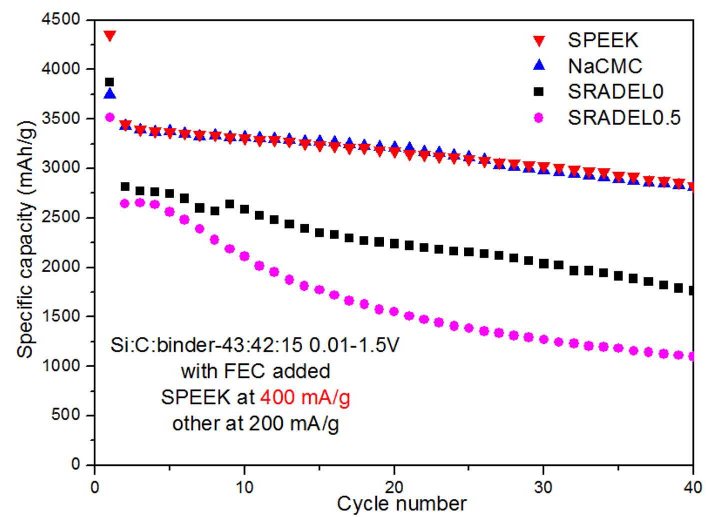
CA: DS = 0.4 and 0.8 – carboxylic acid



SPEEK: DS = 0.72; IEC=2.1 meq./g – sulfonate + ketone

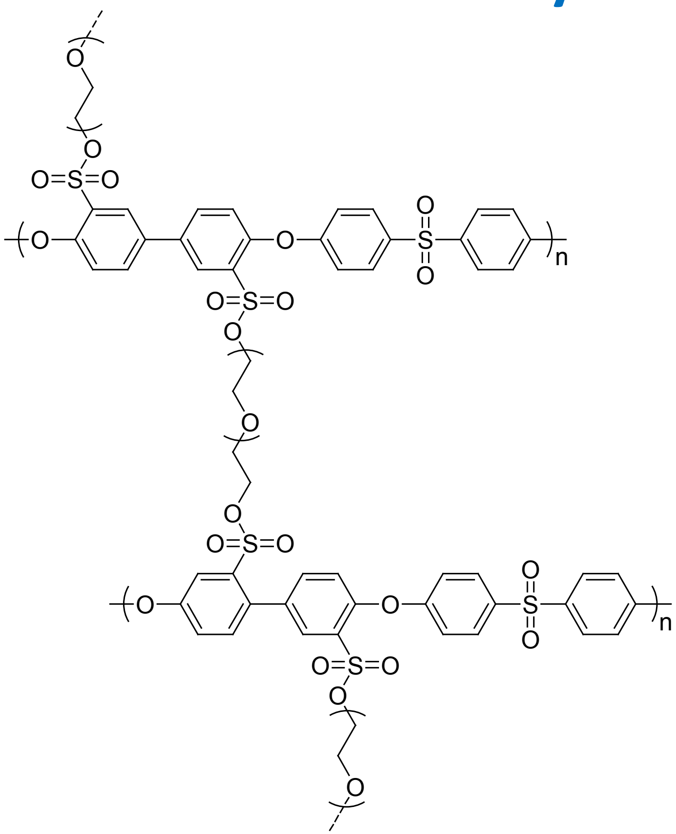




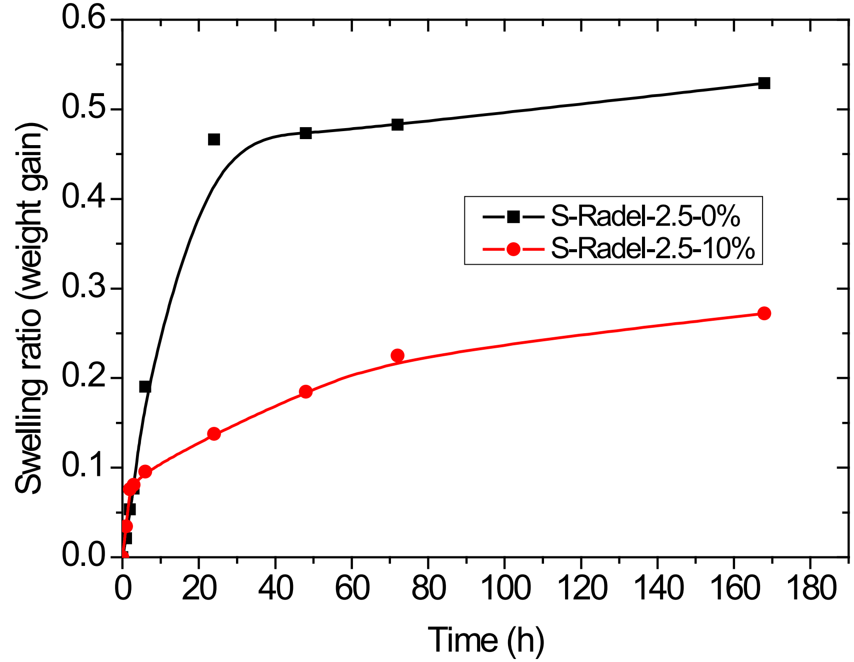


Presence of carbonyl groups in SPEEK seems to be key to good cycling performance.

IX. Crosslinking Polymers to Decrease Electrolyte Uptake



Swelling test in EC/DEC/DMC(1:1:1)



S-Radel based crosslinking polymer

S-Radel: IEC=2.5 meq./g – sulfone and sulfonate-containing binder

Lowers swelling to improve mechanical properties, but may decrease ion conductivity in the electrode.

Milestones

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- Synthesize and characterize three types of Si/SiO_x-carbon nanocomposites. (completed)
- Demonstrate new crosslinking chemistry involving sulfonates, carboxylates, and azide chemistries for low-swelling polymer binders. (ongoing)
- Identify at least one Si/SiO_x-carbon nanocomposite anode with a reversible specific capacity of at least 1000 mAh/g over 200 cycles. (completed)
- Identify and optimize at least one polymer binder and processing solvent that shows better cycling performance than the reported binders with commercial Si nanoparticles. (completed)
- Supply laminates of the optimized electrodes with electrode capacity of 800 mAh/g that cycle 100 cycles to BATT PIs. (Aug. 2013)

Future Work

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- Optimizing composition and nanostructures of Si/SiO_x-carbon composites (including Si/SiO_x ratio, Si/C ratio, nanoparticle size, porous structures) for improved electrochemical performance.

- Investigation on SEI of Si-based anode including formation, composition, structure and thermo-stability.

- Working to further understand new binder performance with micro-sized Si-C composite. Undertaking new spectroscopic measurements of binder/Si-C interactions in situ under electrolyte/potential conditions.

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Summary

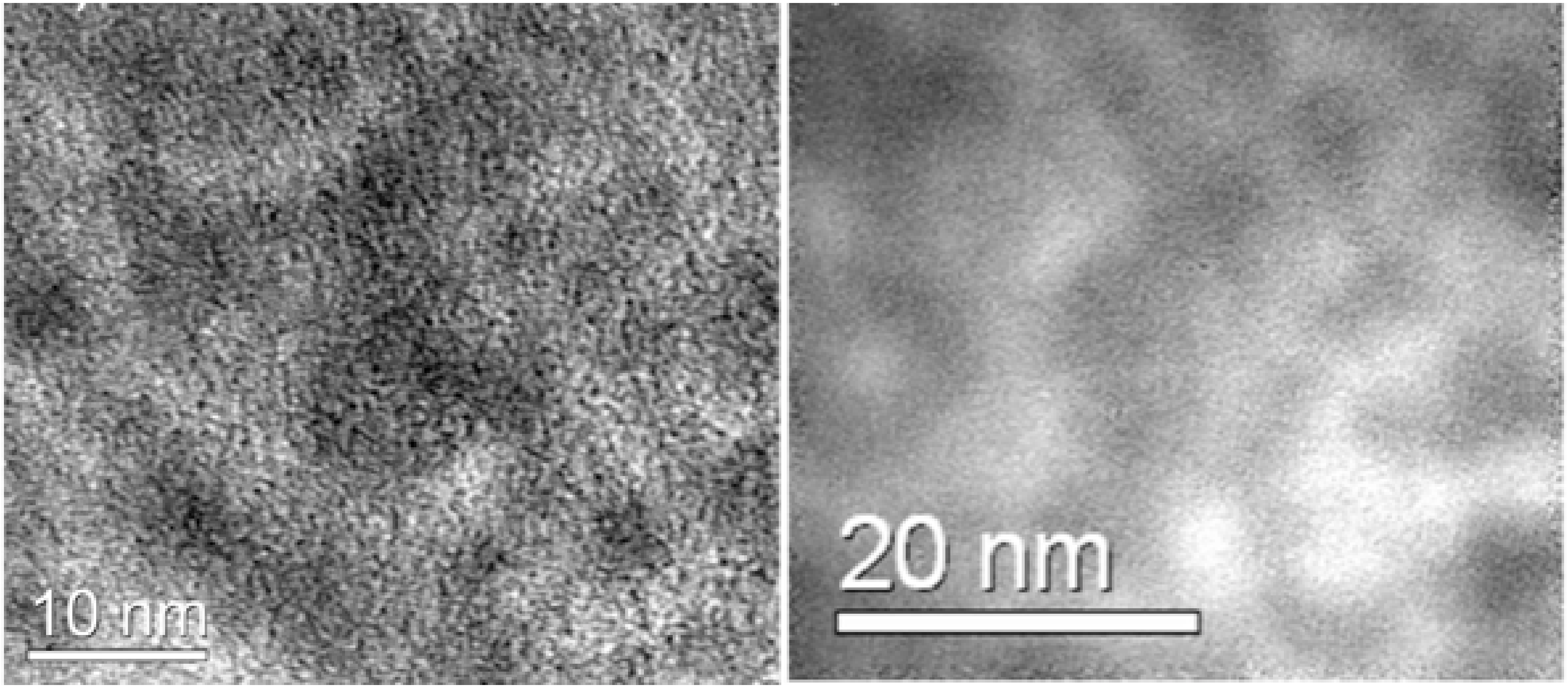
- Synthesize a novel SiO_x nanocomposite with excellent cycling ability.
- Development of micro-sized Si-C composite anode materials with high volumetric and gravimetric capacity, excellent cycling stability and improved coulombic efficiency.
- Development of micro-sized porous Si-C composite with tunable pore structures
- Investigated structure and surface modification and their effect on electrochemical performances of the materials
- Evaluate a series of functional binders and identify SPEEK binder for further design and improvement.

Acknowledgment

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

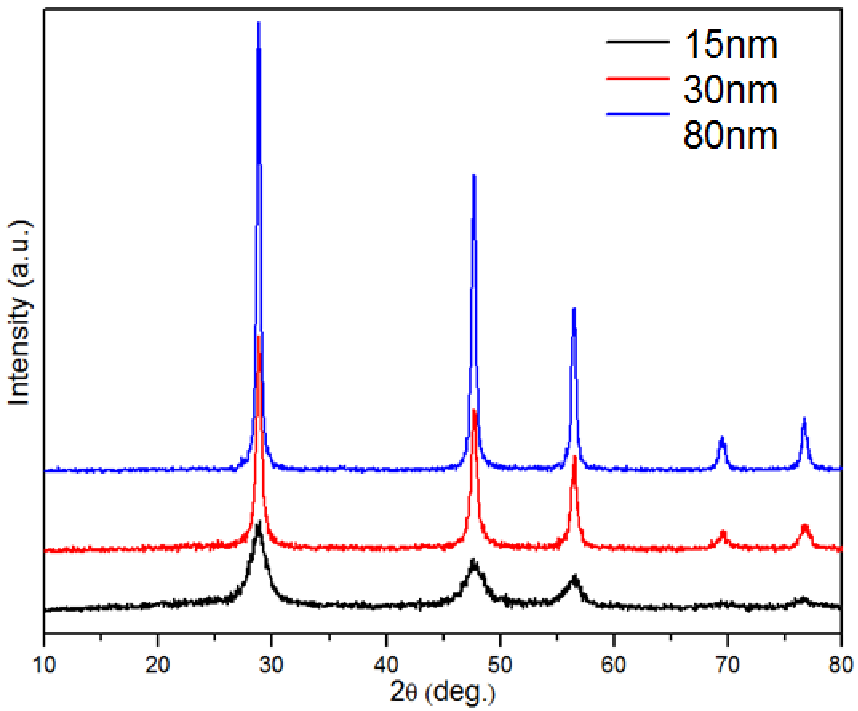
Technical Back-Up Slides

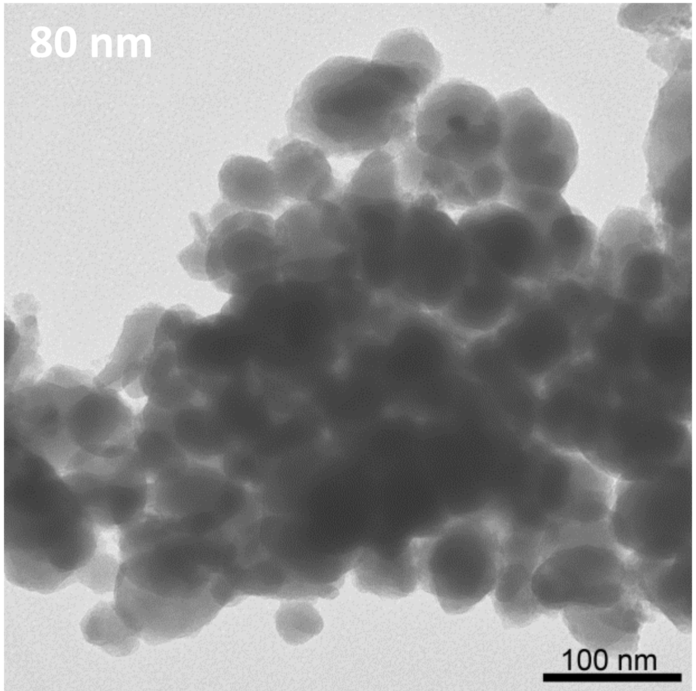
Technical back up



HRTEM (left) and corresponding EF-TEM mapping of carbon (right) in a cross-section of micro-sized Si-C composite

Technical back up

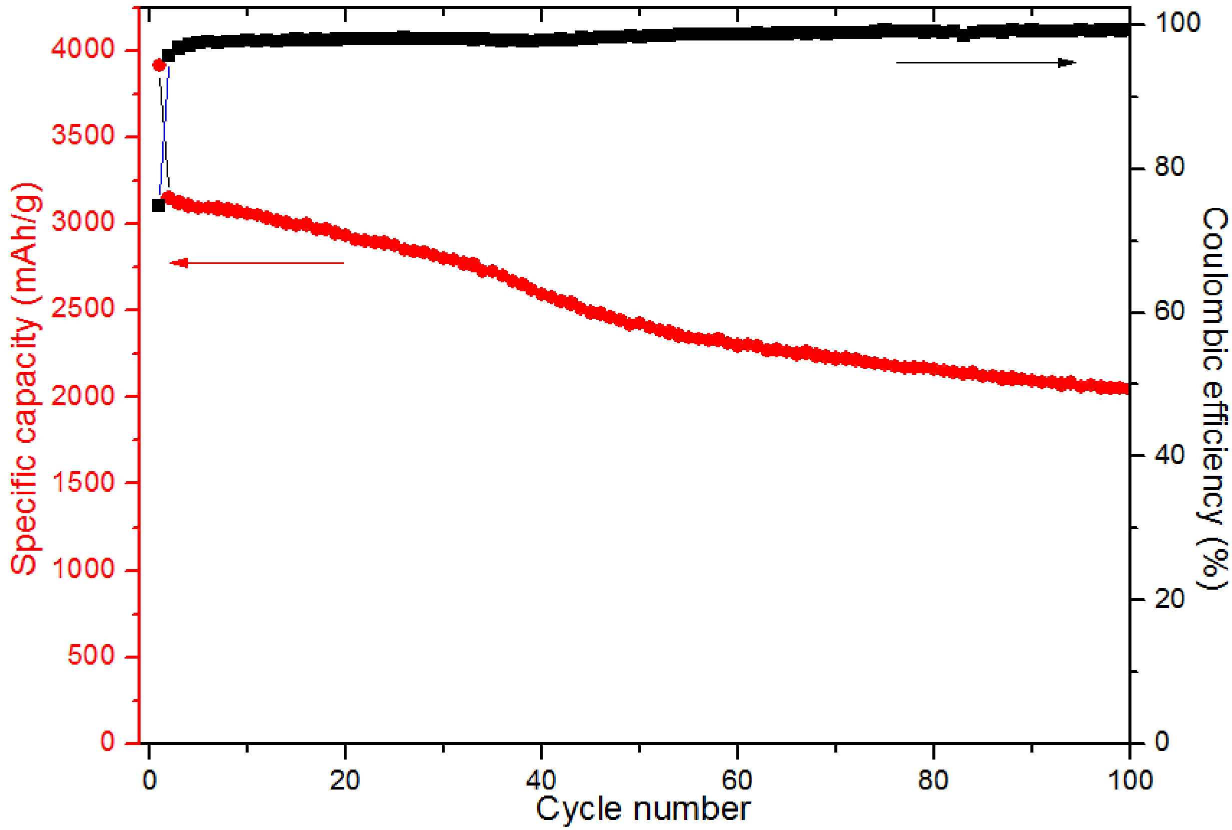




XRD of micro-sized Si-C composites with different sized Si nanoparticle building blocks

80nm nanoparticles in micro-sized Si-C composites does not break after 100 cycles.

Technical back up



A capacity retention of 65% (2044/3149, based on the discharge capacity of the second cycle) is obtained after 100 cycles using SPEEK binder for commercial Si nanoparticles.