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

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Overview

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Timeline

- Project Start – Jan. 2011
- Project End – Dec. 2014
- Overall % Complete: **85%**
  - FY 2014 % Complete: 40%

Barriers

- Energy density
- Cycle life
- Battery component compatibility

Budget

Total project funding: $826K

FY 2013: $157K

FY 2014: $214K ($80K funded)

Partners

- **Jason Zhang (PNNL)**
- **Gao Liu and Vince Battaglia (LBNL)**
- **Nissan R&D Center (USA)**

Relevance

Objectives

- Achieve high performance Si anode materials by developing novel structured Si-carbon nanocomposites and polymer binders.
- Improve Si-based anode electrode kinetics and cycling life.
- Decrease initial irreversible capacity loss and increase coulombic efficiency of Si-C anodes.
- Understand their structure-performance relationships in the new Si-based anode materials and new polymer binders.

Impact

The optimized silicon anode electrodes from this project will provide electrochemical performances which are essential to achieving higher energy densities in plug-in hybrid vehicles (PHEV) and electric vehicle (EV) applications.

Milestones - Approach

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Month / Year	Milestones or Go/No-Go Decision	Description	Status
Dec. 2013	Go/No-Go	Stop the metal composites coating approach and focus on carbon coating approach if the capacities are less than 1500 mAh/g	Completed
Dec. 2013	Milestone	Synthesize, characterize, and evaluate Si-based composite with novel coating (e.g. non-oxidic metal composites)	Completed
Mar. 2014	Milestone	Identify and demonstrate the optimized composition, structure, and surface modification of micro-sized Si-C and porous Si-C composites	Completed
Jun. 2014	Milestone	Synthesize acidic/semiconducting polymer binders using grafting approach	Ongoing
Sep. 2014	Go/No-Go	Determine if semiconducting polymer approach can generally be applied to Si anodes.	Ongoing
Sep. 2014	Milestone	Synthesize and electrochemically evaluate Si/Si alloy composites.	Ongoing
Sep. 2014	Milestone	Fully characterize acidic/semiconducting polymer binders	Ongoing
Sep. 2014	Milestone	Supply laminates of the optimized Si/Si alloy electrodes with electrode capacity of 800 mAh/g that cycle 100 cycles to BATT PIs	Ongoing

Technical Approach

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

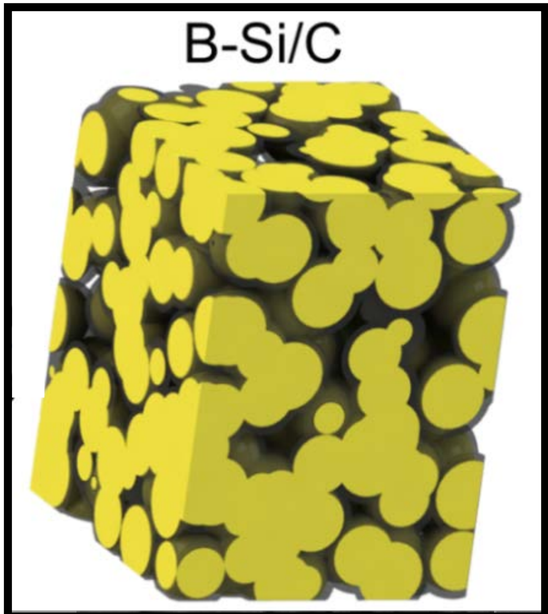
  - Boron-doping of previously accomplished silicon-carbon active materials
  - Alternative synthesis route to SiO_x for silicon-carbon composite
  - Titanium nitride surface coating of silicon nanoparticles

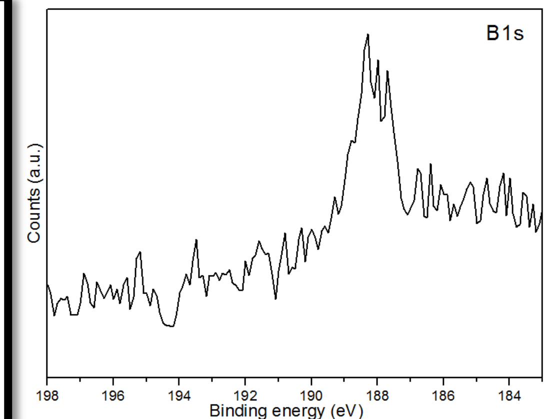
- ❑ **Design functional polymers with varying functional groups composition to test structure-property relationships. Understand the function of binders in Si anodes and uncover the key design features for new materials.**

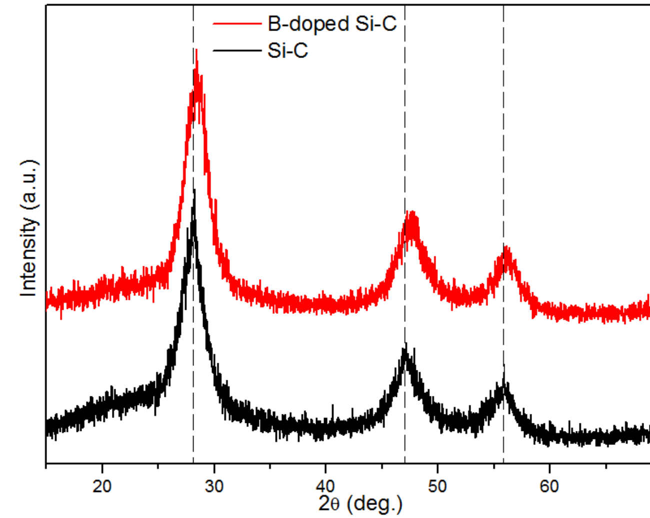
  - Develop a semiconducting polymer binder based on precarboxylation of main chain and postsulfonation of the binder structure
  - Develop functional aromatic binders with controlled electrolyte uptake via ionic groups

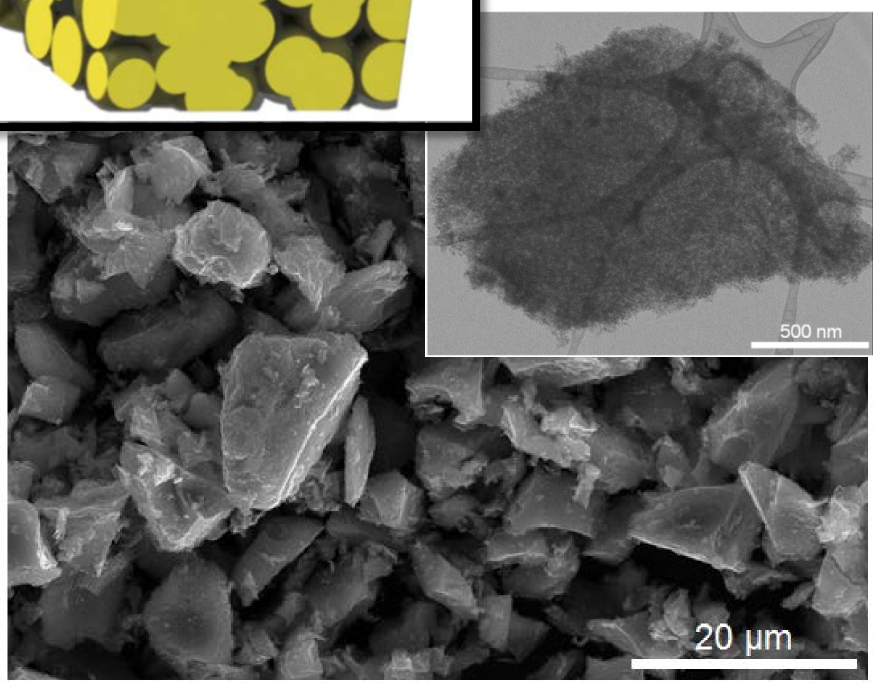
Technical Accomplishment

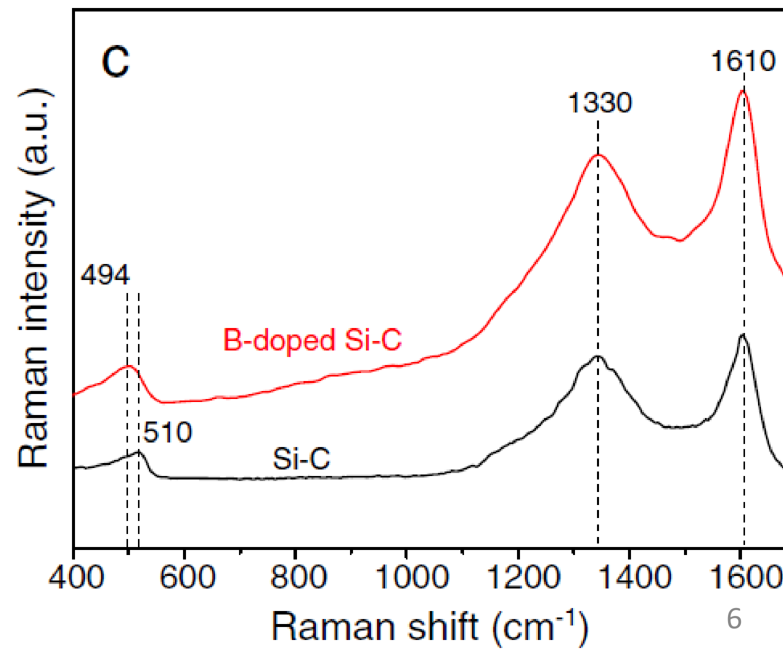
1. Boron-doped silicon-carbon composites





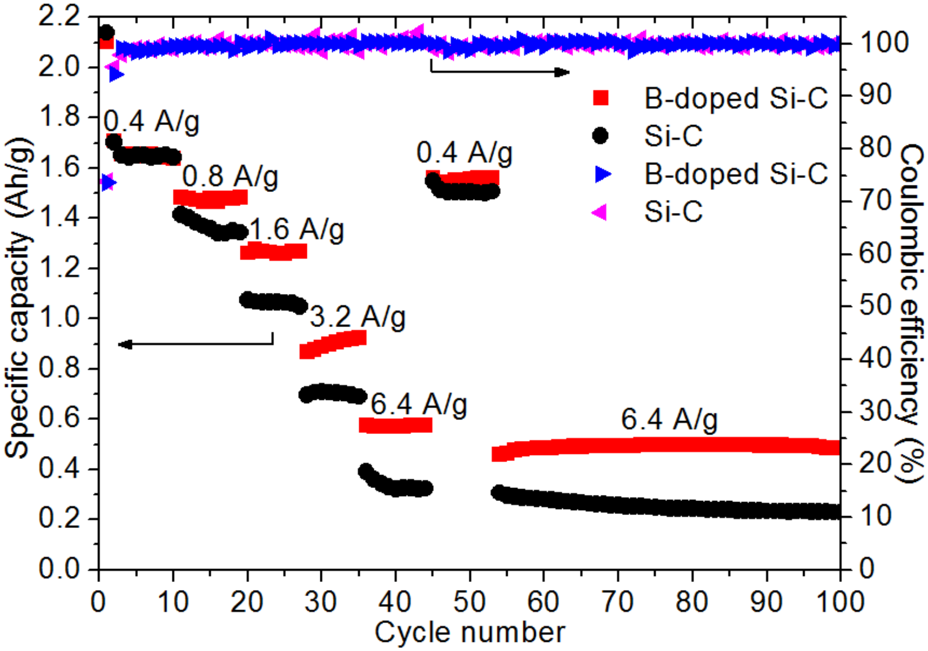




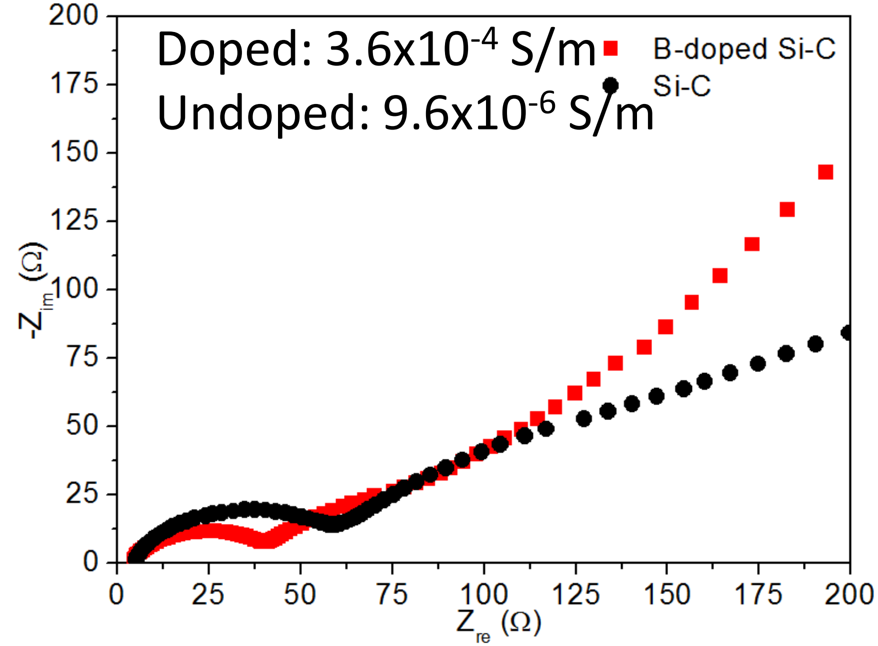


Technical Accomplishment

1. Boron-doped silicon-carbon composites-good rate performance



Rate performance of B-doped Si-C and Si-C



Impedance spectra of B-doped Si-C and Si-C

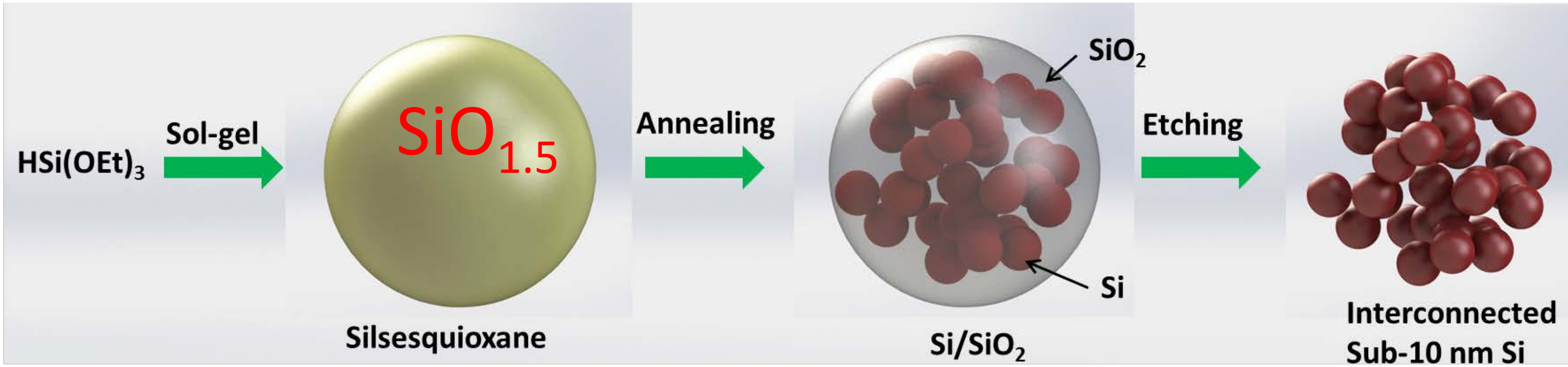
No external carbon additive (Super P, etc.)

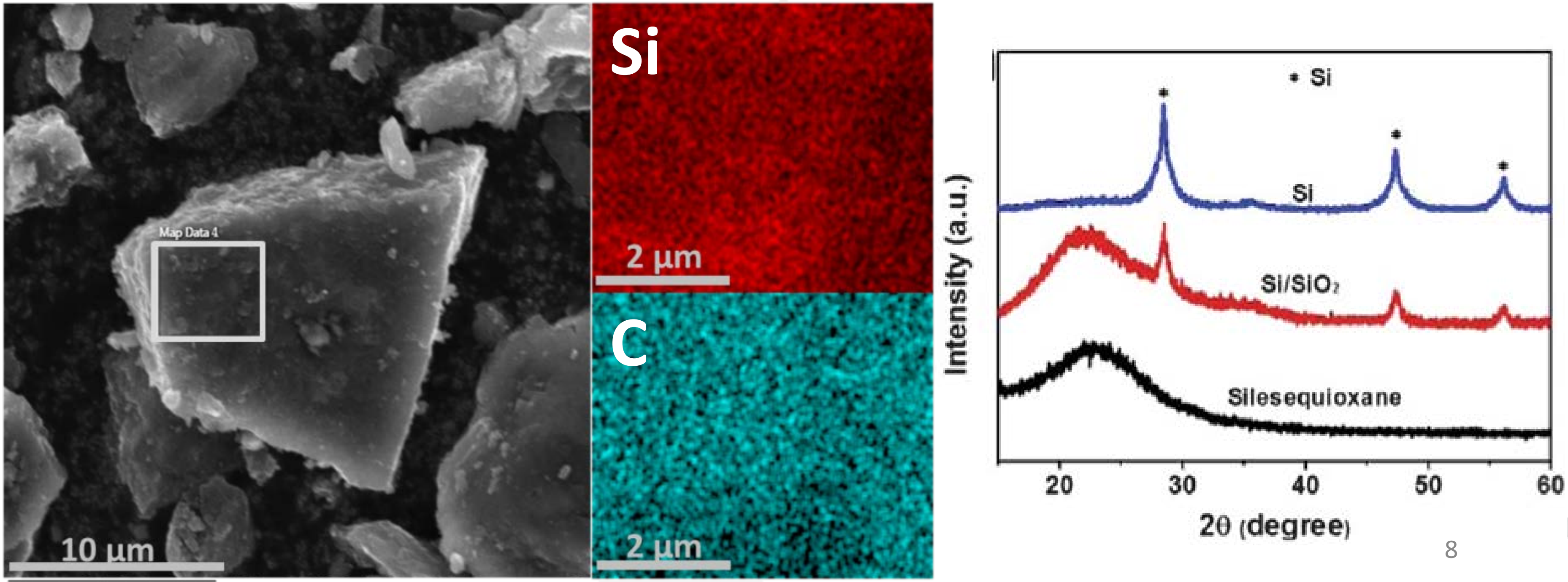
Key Factors:

- **B-doped Si-C: 575 mAh/g *vs.* Si-C: 323 mAh/g at 6.4 A/g**
- **Lower charge transfer resistance of B-doped Si-C**
- **Enhanced rate capability of Si-C composite**

Technical Accomplishment

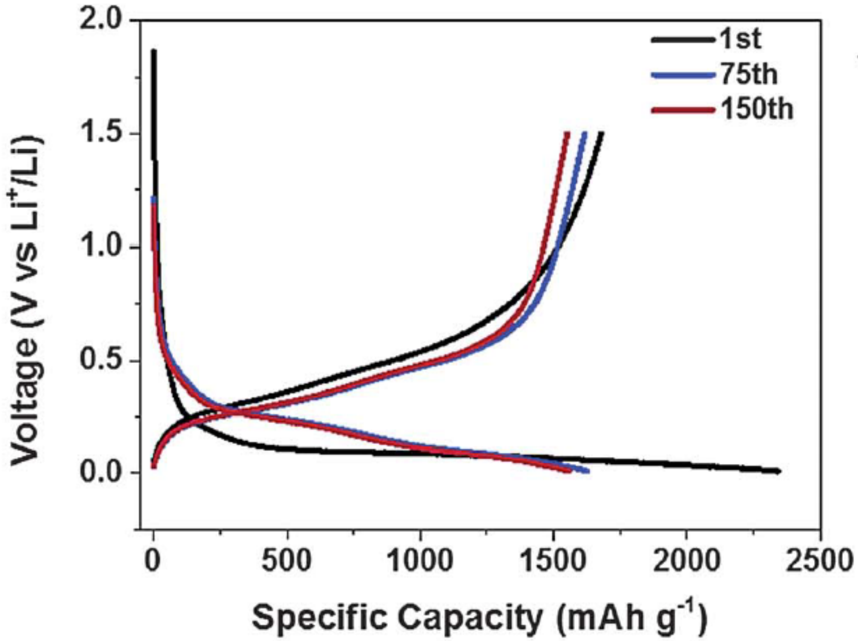
2. Micro-sized Si-C composite – alternative route to SiO_x

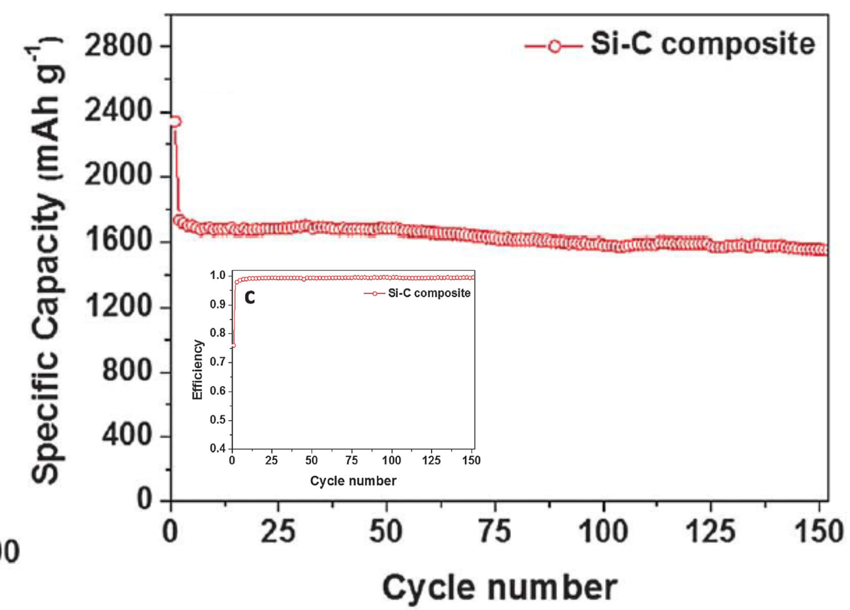




Technical Accomplishment

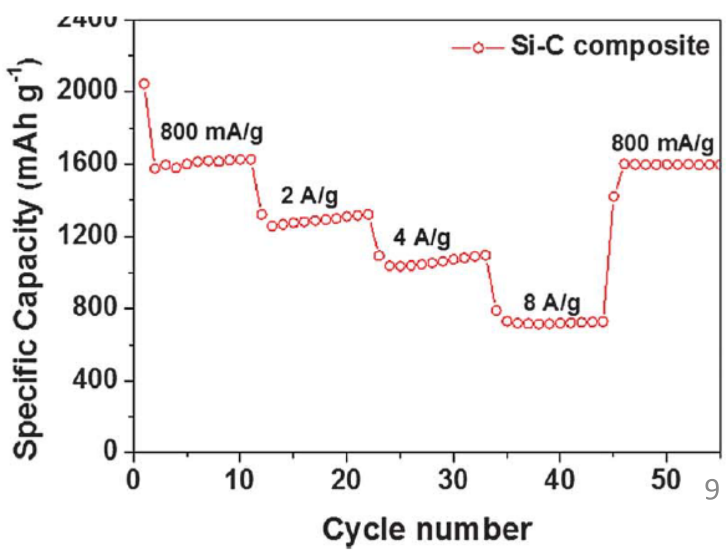
2. Micro-sized Si-C composite – excellent cycling stability





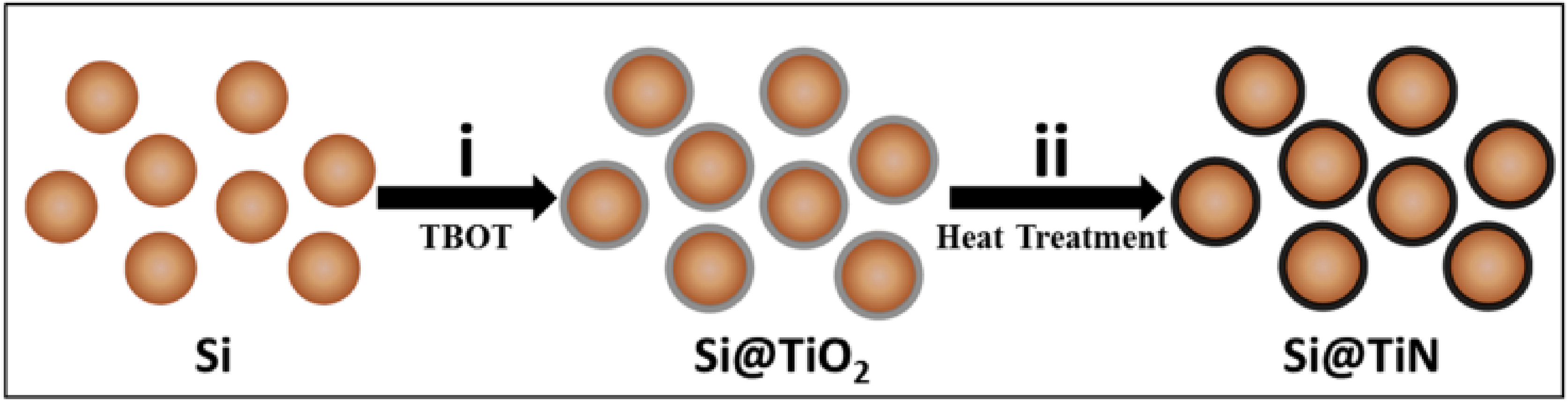
Key Factors:

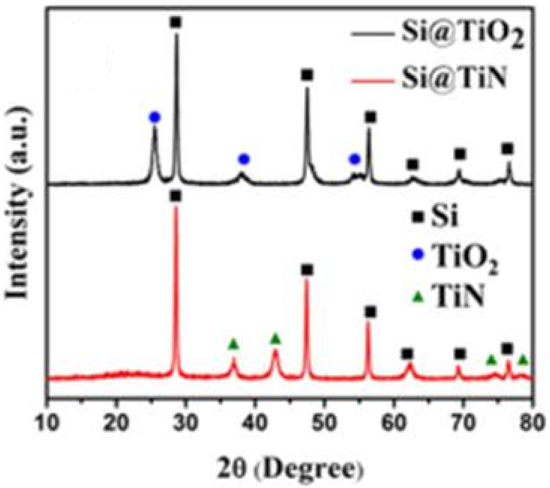
- **Micro-sized particle as a whole — enable high tap density**
- **Uniformly distributed carbon — improve conductivity**
- **Si building block of <10 nm — strengthen tolerance to volume change**



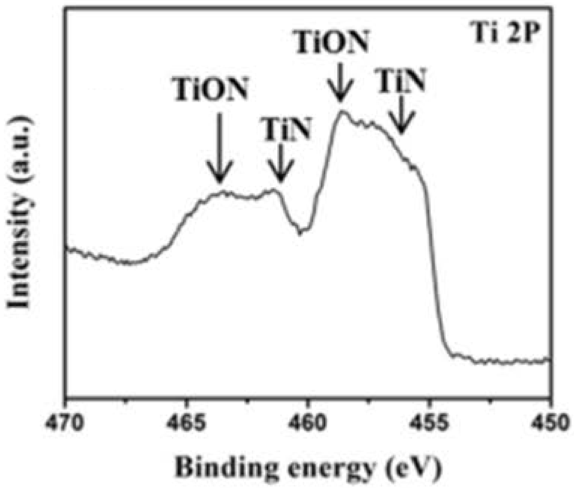
Technical Accomplishment

3. Synthesis of TiN-coated Si nanoparticles

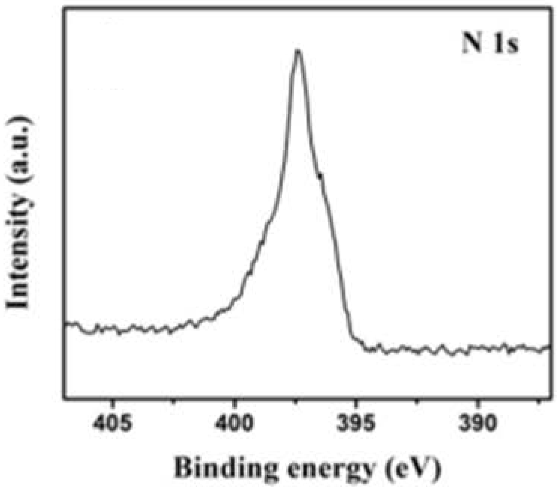




XRD patterns pf $Si@TiO_2$ and Si@TiN



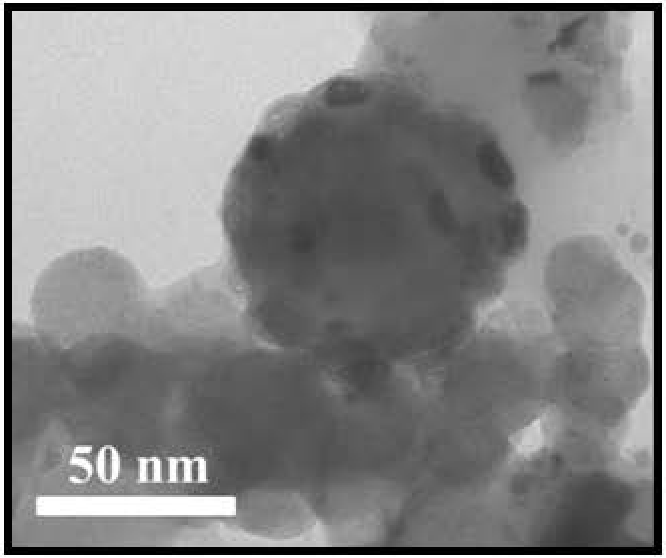
XPS spectra of Ti 2p in Si@TiN

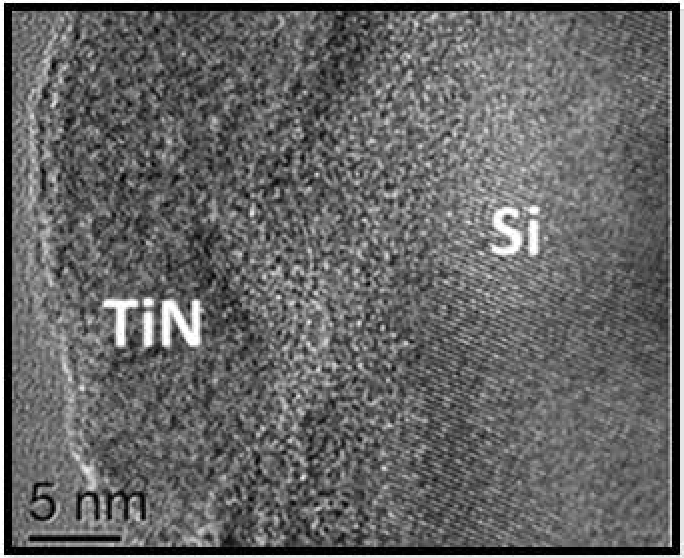


XPS spectra of N 1s in Si@TiN

Technical Accomplishment

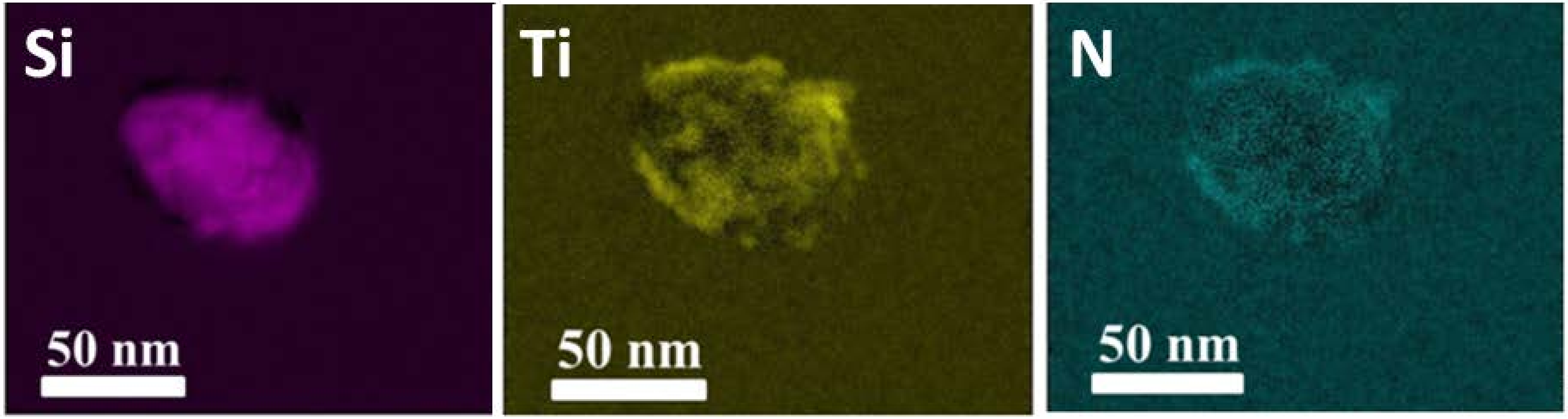
3. Characterization of TiN-coated Si nanoparticles





Key Factors:

- Ti and N elements are distributed in the selected region of the Si@TiN particle.
- Si nanoparticles in Si@TiN are coated with a TiN layer composed of crystalline TiN nanoparticles



Technical Accomplishment

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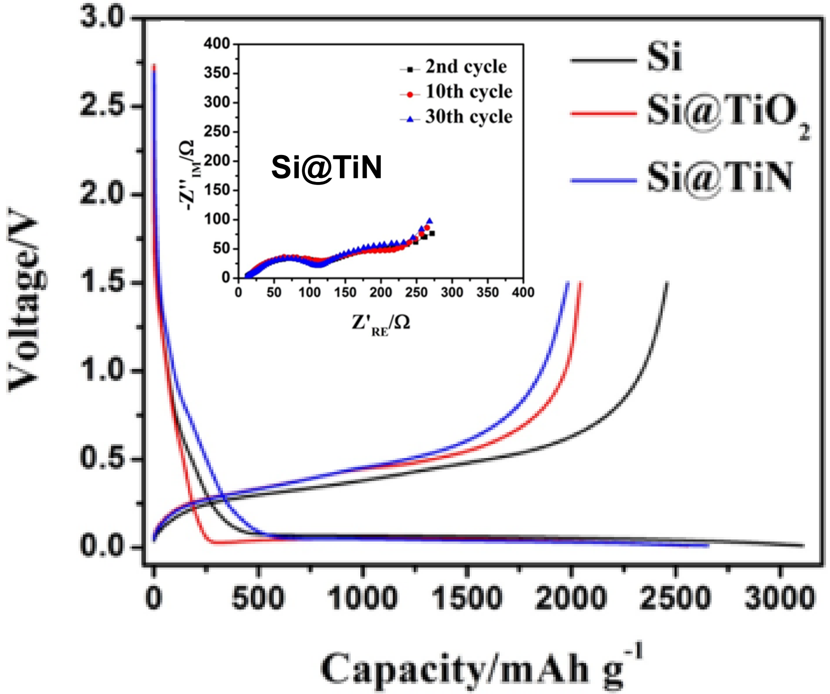
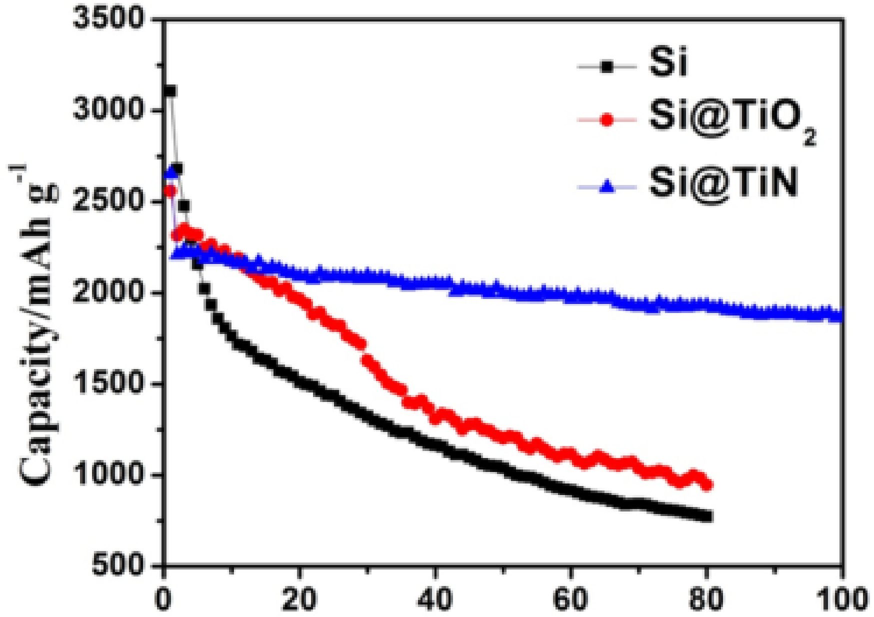
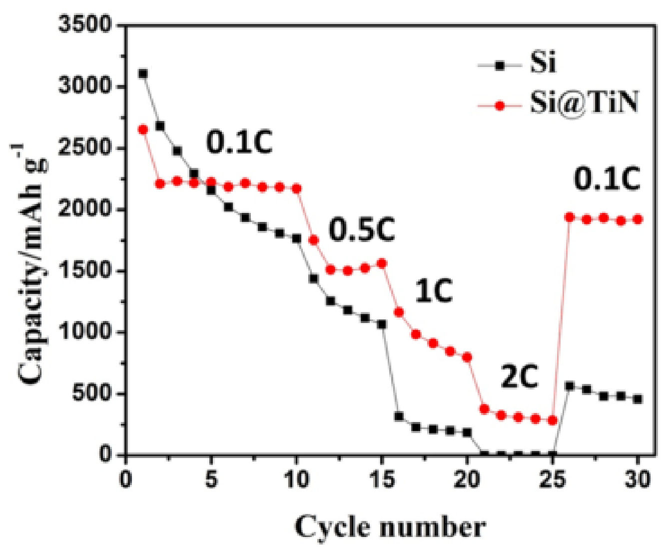
3. Performance of TiN-coated Si nanoparticles







Key Factors:

- Improved cycling stability compared to Si and Si@TiO_2
- High coulombic efficiency
- Stable rate performance

Technical Accomplishment

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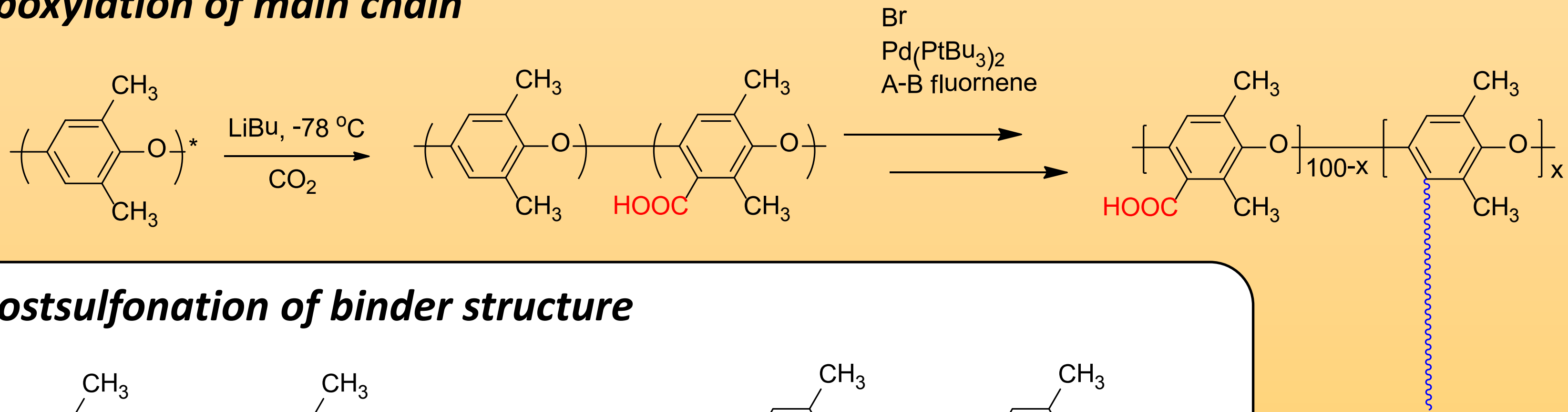
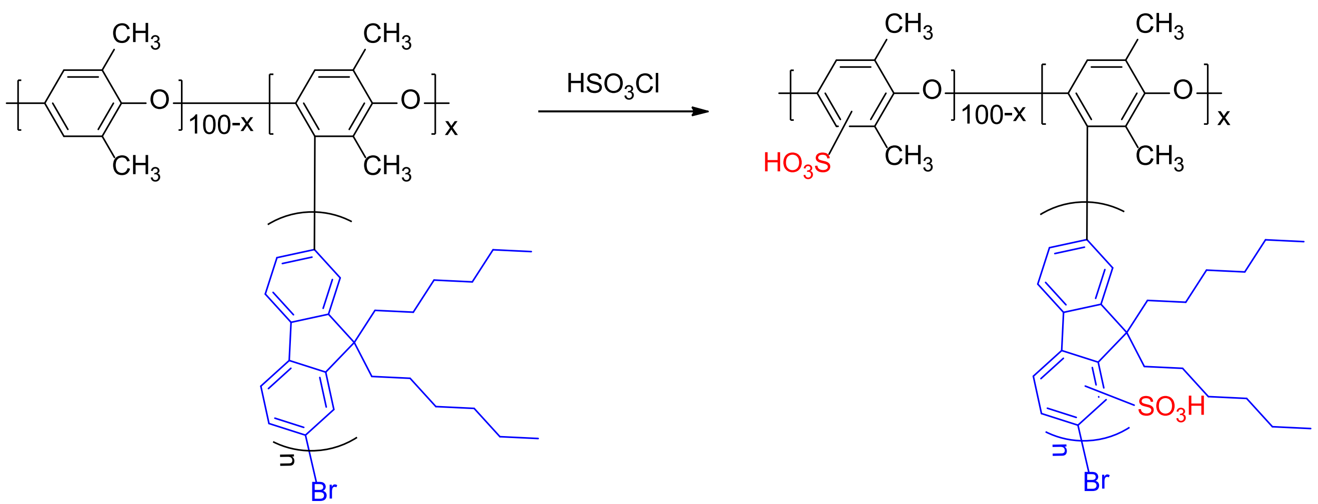
4. Multifunctional binders with mechanical, ionic, and semiconducting functionality

Synthesis Route

Precarboxylation of main chain



Postsulfonation of binder structure



Finalizing synthesis routes and new binder testing ongoing.

Technical Accomplishment

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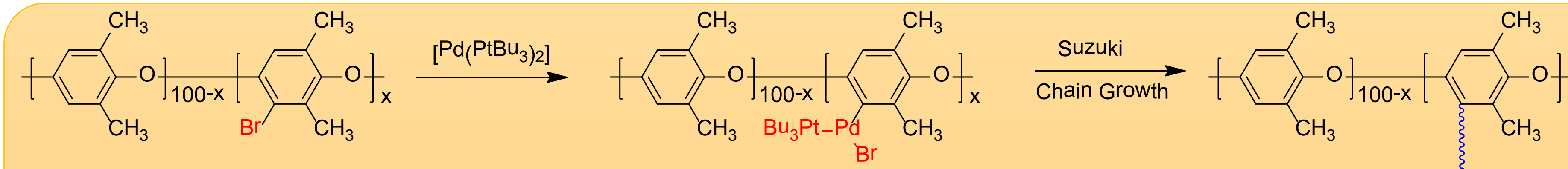
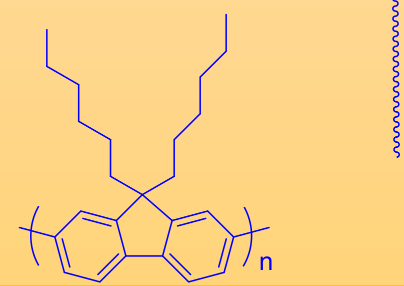
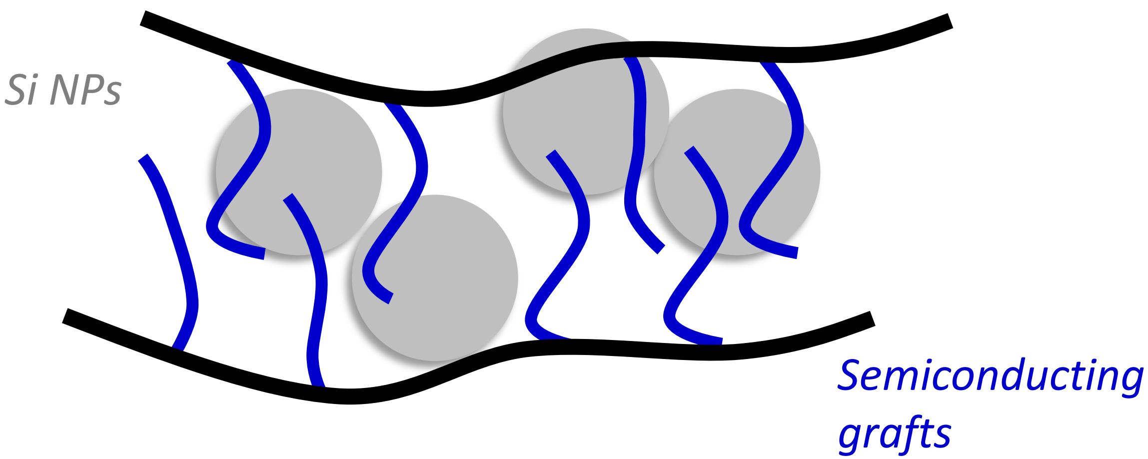
4. Multifunctional binders with mechanical, ionic, and semiconducting functionality



Semiconducting polymer chain grown from mechanically stable backbone support.



Mechanical stability and semiconducting functionality.



Key Factors:

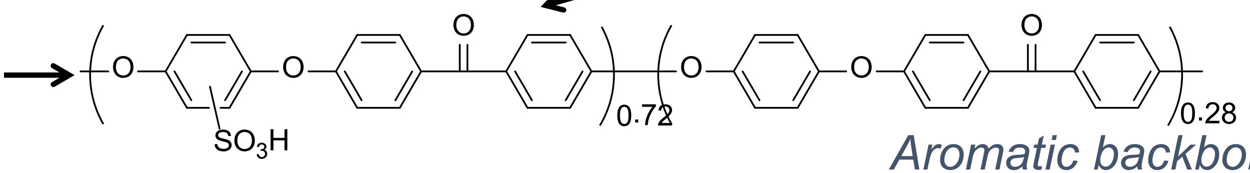
- Polymer binders specifically for enhancing properties of Si-based high capacity anodes have been developed
- The polymer binder has exceptional stability during particle volume expansion

Technical Accomplishment

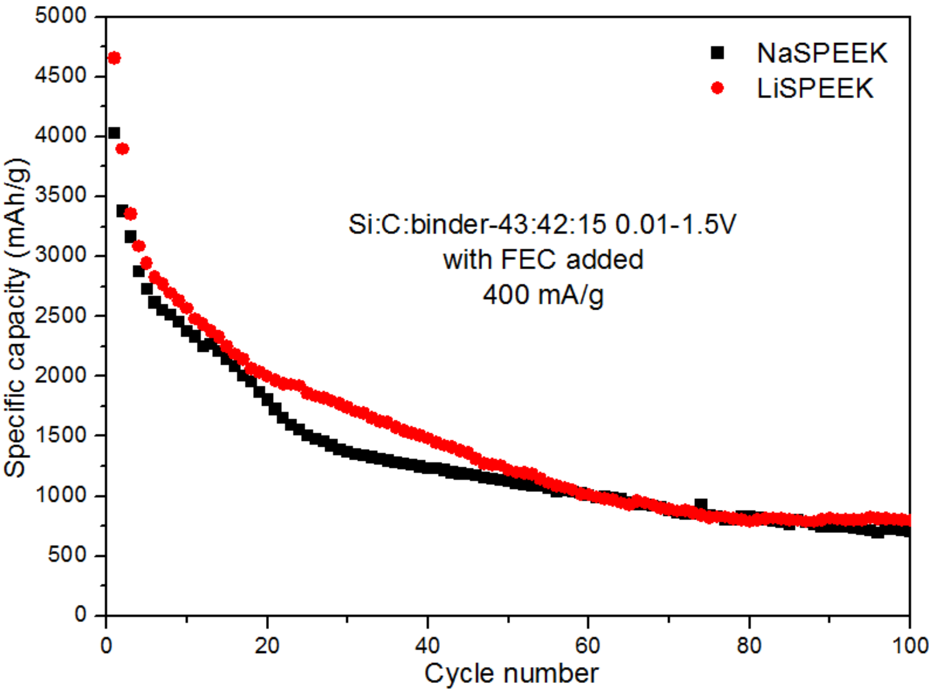
5. Functional Aromatic Binders

Carbonyl groups known to give good performance in other binders

Ionic group to control electrolyte uptake



Aromatic backbone for good mechanical properties



Key Factors:

- Presence of carbonyl groups in SPEEK seems to be key to good cycling performance – comparison to sulfone-containing polymers with nearly the same uptake.
- Crosslinking had limited effect on cycling fade.
- Acidic SPEEK binder performed better than Li- or Na- exchanged samples.

Previous Accomplishments

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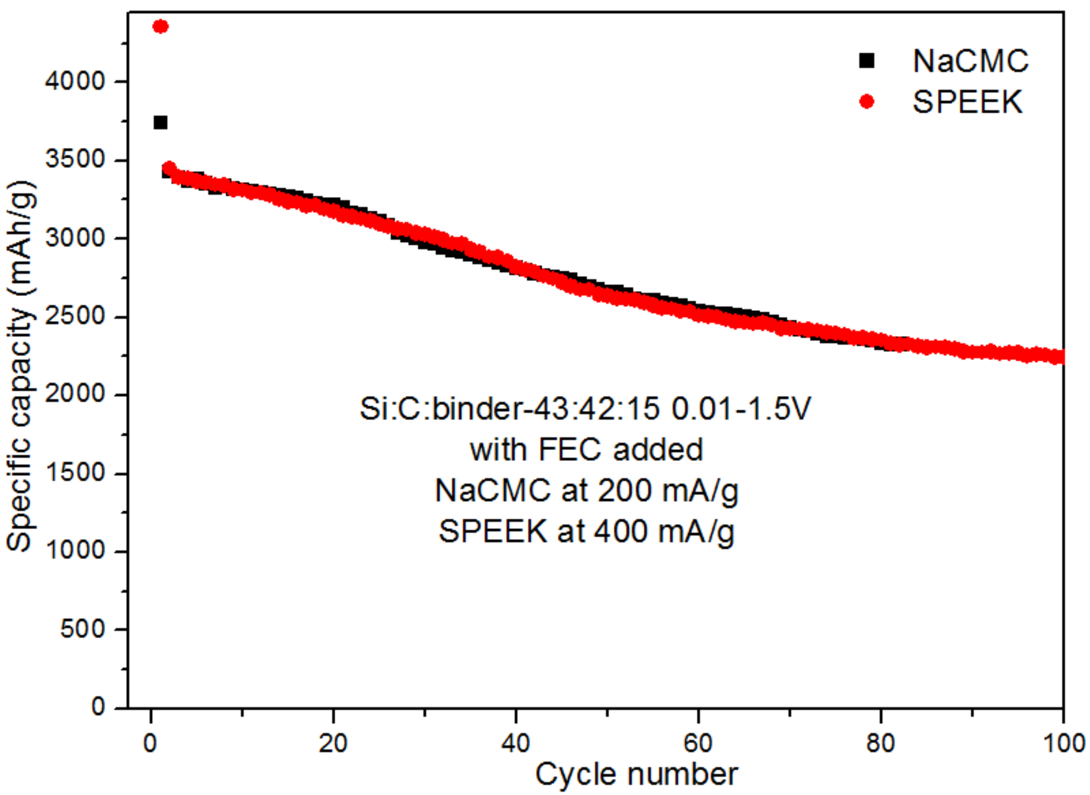
Ionic binder that matches capacity fade of NaCMC at higher rate

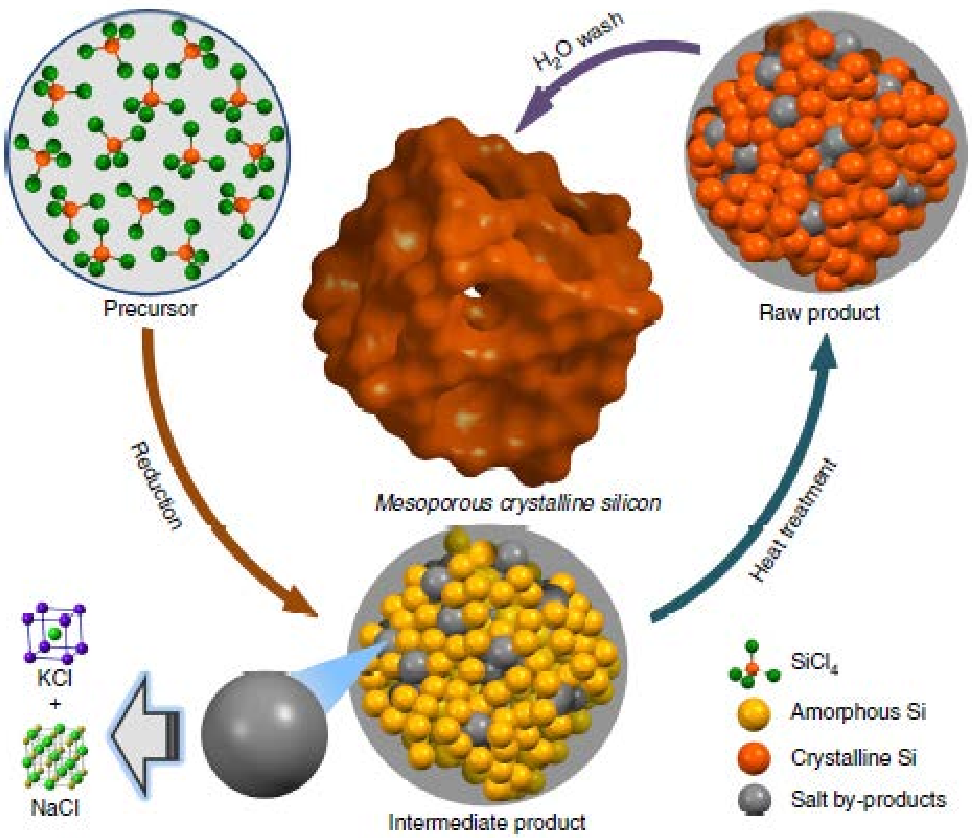


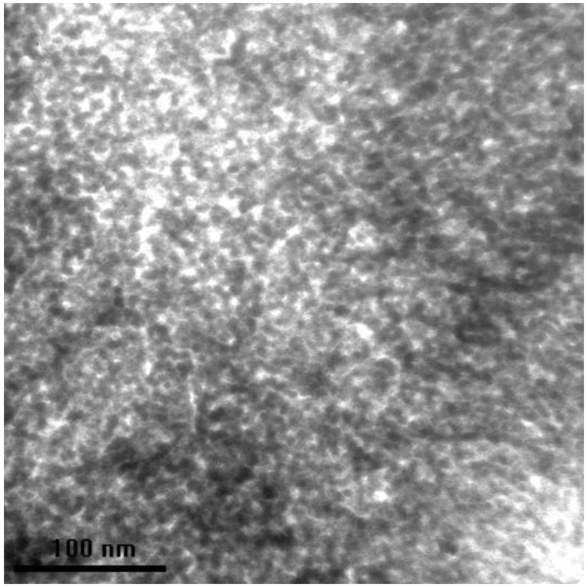
Key Factors:

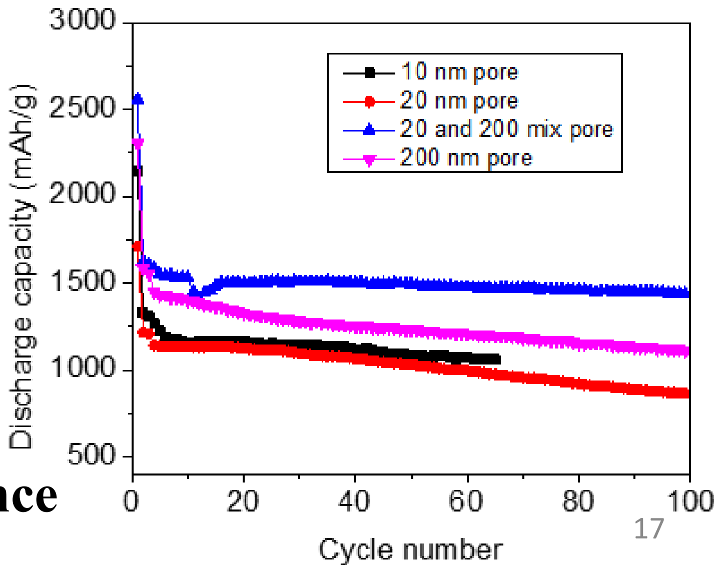
- $-SO_3H$ acidic group critical to binder performance.
- Use of commercial Si nanoparticles with acceptable capacity fade.
- Higher rage performance with SPEEK binder compared to NaCMC binder.
- SPEEK shows best properties so far as reported in last AMR presentation.
- Looking into SEI layer function with each binder.

Previous Accomplishments

Bottom-up synthesis of mesoporous crystalline silicon with controlled pore structures







Key Factors:

- **Exceptional cycling ability (retention >85% after 100 cycles) with volume change tolerance**
- **Promising high rate performance**

Responses to Previous Year Reviewers' Comments

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1. **Although the investigation on the relationship between binder conductivity and swelling was very relevant, have any other properties been considered?**

   We are working on measurements of binder degradation during potential cycling in in-situ and ex-situ experiments. These measurements are ongoing and will be reported in the last year of the project. In answer to another question: We have performed preliminary assessments of adhesion on nanoparticles, but it is a difficult experiment to quantify. We need to assess the relevance of nanoparticle vs flat Si wafer surfaces.

2. **Have the researchers taken advantage of any of the novel characterization techniques available at PNNL, such as *in situ* TEM?**

   We plan to collaborate with PNNL during the upcoming months to further characterize our materials with techniques such as *in situ* TEM.

Collaboration and Coordination with Other Institutes

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- **Lawrence Berkeley National Lab (LBNL)**
  - Personnel: Gao Liu and Vince Battaglia
  - Test and evaluate commercial Si materials.
- **Nissan Research and Development Center, USA**
  - Sample test and electrode material performance validation
- **Pacific Northwest National Laboratory**
  - Personnel: Jason Zhang
  - Coating method discussion and sample exchange

Future Work

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- Optimize surface modifications of Si and Si/SiO_x-carbon composites (including carbon , metal oxides, non-oxidic metal composite coating), in order to further improve the long cycling stability

- Develop the elemental doping of Si-based composites, which can help improve the conductivity of the material by adjusting the semiconductive properties of Si-based materials;

- Characterize the composites to obtain optimized electrochemical properties and energy densities

- Measure surface interactions of functional polymers and Si composites.

- Synthesize new functional binders with acidic and semiconducting functionalities.

Technical Summary

Goal: Novel synthesis routes to a family of micro-sized Si-C composites

Approach:
- SiO_x (SiO and $SiO_{1.5}$)
- Bottom-up synthesis approach using $SiCl_4$

Result:
- Micro-sized Si-C composite + boron-doping
- Micro-sized porous Si-C composite

Goal: New approach to stabilizing the SEI layer of silicon-based active material

Approach:
- Solution-based coating

Result:
- Si@TiN New coating and enabled improved cycling stability of Si nanoparticles

Goal: Synthesize acidic/semiconducting polymer binders

Approach:
- Design mechanically stiff polymers with varying functional group compositions to test structure-property relationships

Result:
- NaSPEEK

Publications and Presentations

Journal Publications

Dai, F., Zai, J., Yi, R., Gordin, M.L., Sohn, H., Chen, S., Wang, D. Bottom-up synthesis of high surface area mesoporous crystalline silicon and evaluation of its hydrogen evolution performance. *Nature Communications*, **2014**, 5,3605 .

Song, J. X., Chen S. R., Zhou, M. J., Xu, T., Gordin, M. L., Lv, D. P., Long T. J., Melnyk M., Wang, D. H. Micro-sized silicon-carbon composite composed of carbon-coated sub-10 nm Si primary particles as high-performance anode materials for lithium-ion batteries, *Journal of Material Chemistry A*, **2014**, *2*, 1257.

Yi, R., Zai, J. T., Dai F., Gordin, M. L., Wang, D. H. Improved rate capability of Si-C composite anodes by boron doping for lithium-ion batteries, *Electrochemistry Communications*, **2013**, *36*, 29.

Publications and Presentations

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Presentations

Wang, D. H. (presenter), Integrating Si Nanoparticles to Structured Micro-sized Composites for Electrochemical Energy Storage. In Materials Challenges In Alternative & Renewable Energy, American Ceramic Society, Clear Water, Florida, February 2014.

Yi, R.*(presenter), Dai, F.*, Gordin, M. L.*, Chen, S. R.*, Wang, D. H., Micro-Sized Si-C Composite with Interconnected Nanoscale Building Blocks as High-Performance Anodes for Lithium-Ion Batteries. Electrochemical Society (ECS) Fall Meeting, San Francisco, October 2013. (*Author supervised by Donghai Wang.)

Song, J.*(presenter), Chen, S. R.*, Xu, T.*, Wang, D. H., Micro-Sized Silicon-Carbon Composite Composed of Carbon-Coated Sub-10 Nm Si Primary Particles As High-Performance Anode Materials for Lithium-Ion Batteries. Electrochemical Society (ECS) Spring Meeting, Orlando, May 2014. (*Author supervised by Donghai Wang.)