Development of Silicon-based High Capacity Anodes

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Pacific Northwest National Laboratory (PNNL)

2013 DOE Vehicle Technologies Program Review

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Overview

Timeline

- Project start date: Oct. 2010
- Project end date: Sept. 2014
- Percent complete: 65%

Barriers

- Low energy density
- High cost
- Limited cycle life

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY12: $300k
- Funding for FY13: $300k

Partners

- Univ. of California, San Diego
- Princeton University
- Vorbeck Materials Corporation

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Objectives

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

- Develop new approaches to enable electrodes with high Si mass loading and low capacity fade.

- Understand the volume expansion and stress effect to the capacity fading of Si-based anode.

- Understand the SEI layer evolution and develop new additive and binder to improve the interfacial stability of the Si-based anode.

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Milestones

FY12

- Identify the main failure mechanisms of the Si-based anode (March 2012). **−*Completed.***

- Improve the performance of Si-based anode with a capacity retention of >700 mAh/g (based on full electrode) over 150 cycles. (Sep. 2012) **−*Completed.***

- Select binders and electrolyte additive to improve the Coulombic efficiency of Si-based anodes to more than 98%. (Sept. 2012) **−*Completed.***

FY13

- Optimize porous Si and the rigid skeleton-supported Si composite for high capacity and stable cycling (March 2013) **−*Completed***

- Improve the performance of Si-based anodes with a capacity retention of >700 mAh/g (based on full electrode) over 250 cycles using new binders/electrolyte additives (Sep. 2013) **−*Ongoing***

- Develop new approaches to improve the cyclability of thick electrodes (>3 mAh/cm^2). (Sept. 2013) **−*Ongoing***

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Approach

Improve Mechanical Stability of Si-Based Anode:

- Use silicon composite with either preoccupied structure stabilizer (B_4C) or pre-vacant space (macroporous Si) to retain mechanical stability of Si anodes. Their theoretical capacity is higher than 1500 mAh/g for the full electrode even after considering the extra weight of the space holder.
- Use simulation and in situ TEM to predict and verify the volume expansion and mechanical stability of Si composite.

Enhance Electrical Stability of Si-Based Anode:

- Use ball mill to coat mechanically stabilized Si with graphite.
- Use CVD to coat macroporous Si particles with carbon film.

Improve Long-Term Cyclability of Si-Based Anode:

- Develop and use new techniques (such as NMR) to investigate the effect of electrolyte additive and SEI evolution.
- Minimize electrode impedance of thick electrode by highly conductive additive and binder.

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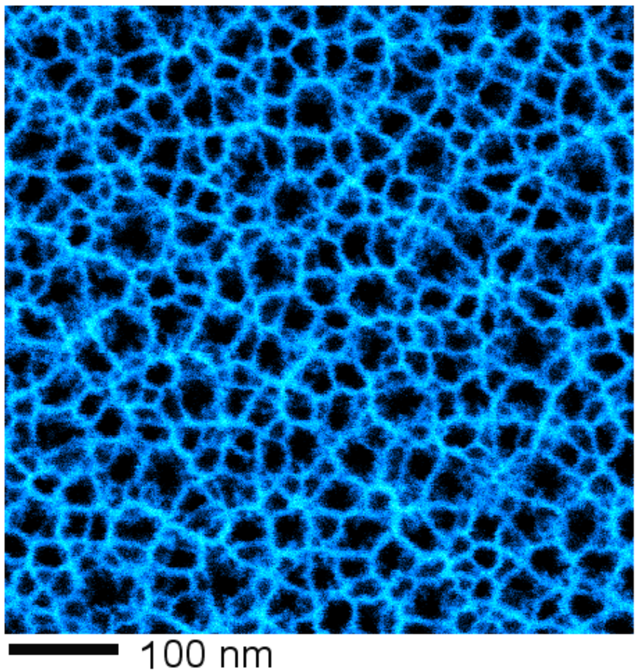
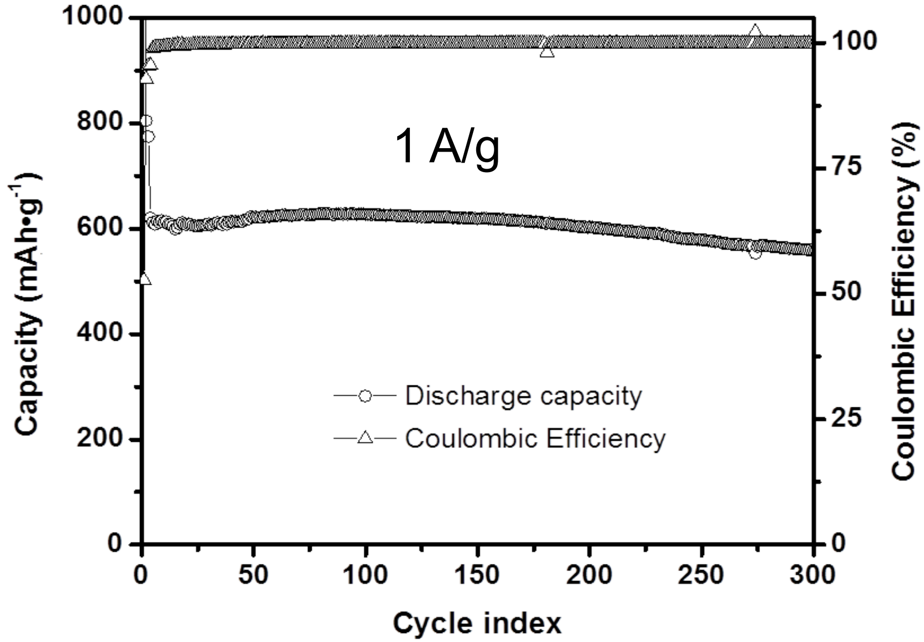
Technical Accomplishments

Macroporous Si as Stable Li-Ion Battery Anodes





- Capacity: ~600 mAh/g (based on the full electrode)
- Capacity retention: ~89% after 300 cycles

Total electrode loading: ~1 mg/cm^2
Si loading: ~0.3 mg/cm^2

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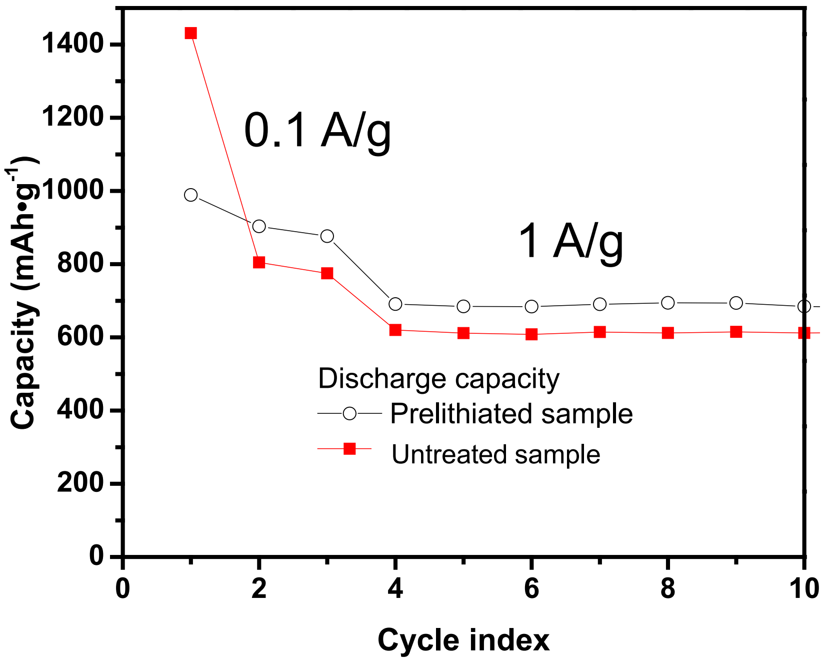
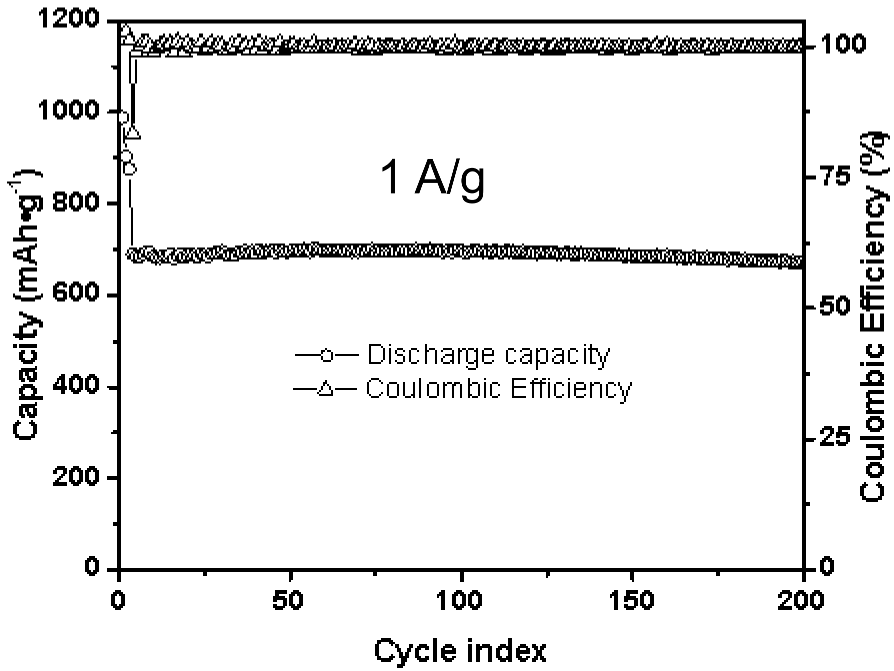
Technical Accomplishments

Prelithiation Treatment of Macroporous Si





- Capacity: ~700 mAh/g (based on the full electrode)
- Capacity retention: ~96% after 200 cycles
- First cycle irreversible loss is greatly reduced

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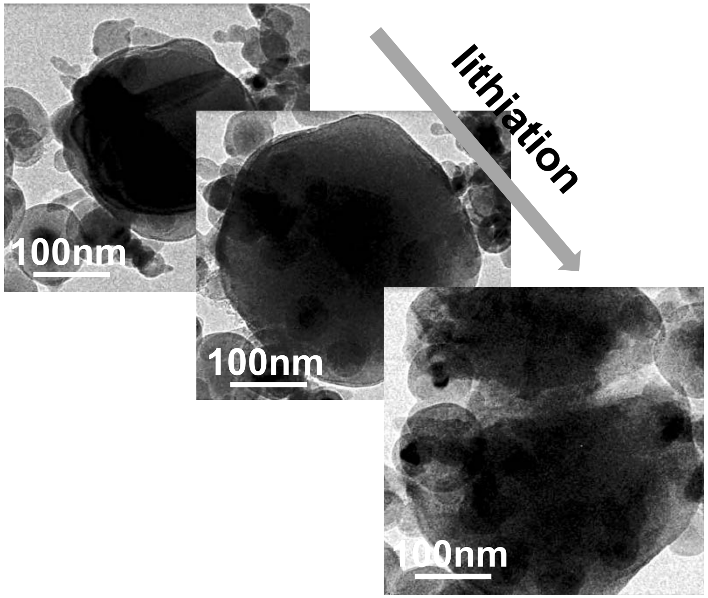
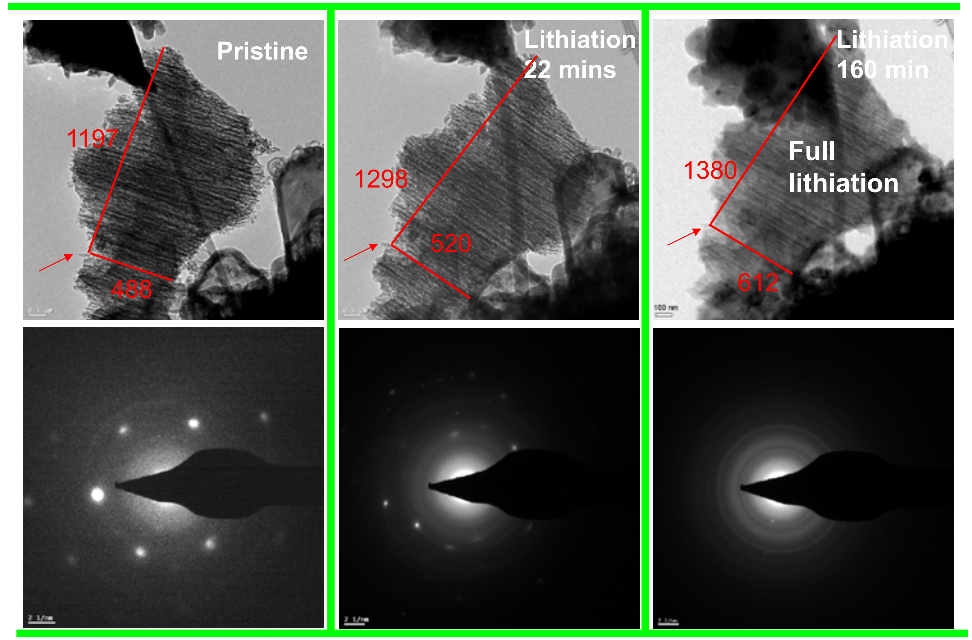
Technical Accomplishments:
<u>Macroporous Si Suppresses the Volume Change</u>



In situ TEM images before and after lithiation:

• Nanoparticles with the size > 200 nm break after deep lithiation



In situ TEM images of macroporous Si before and after lithiation:

•Expansion along the channel direction = 25.4%

• Expansion perpendicular to the channel= 15%

Diffraction pattern: fully amorphized after lithiation

- ➢ Volume expansion~66% after lithiation which is much less than ~300% volume expansion in other Si.
- ➢ Long channel (20-50 μm) restricted SEI formation.

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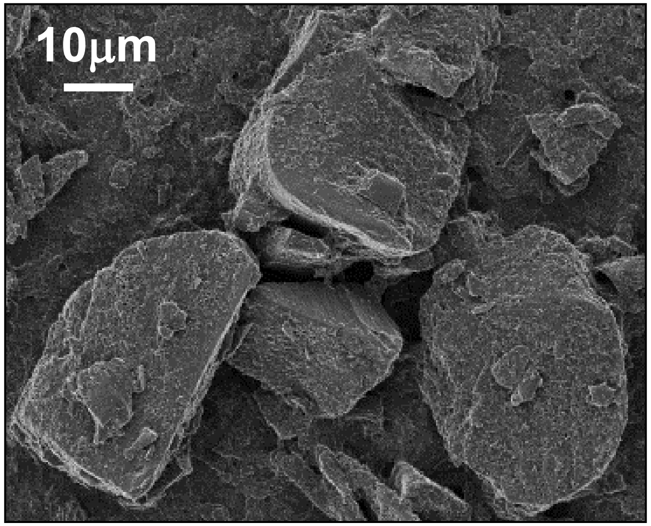
Technical Accomplishments

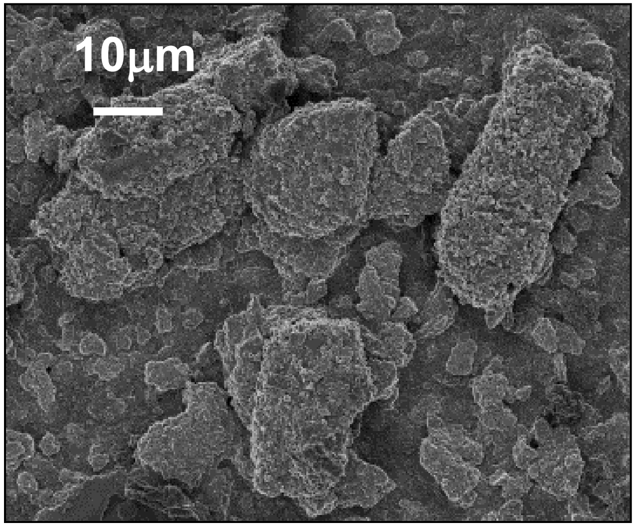
Macroporous Si Suppresses the Pulverization

Electrode morphology before cycling

Electrode morphology after cycling



lithiation

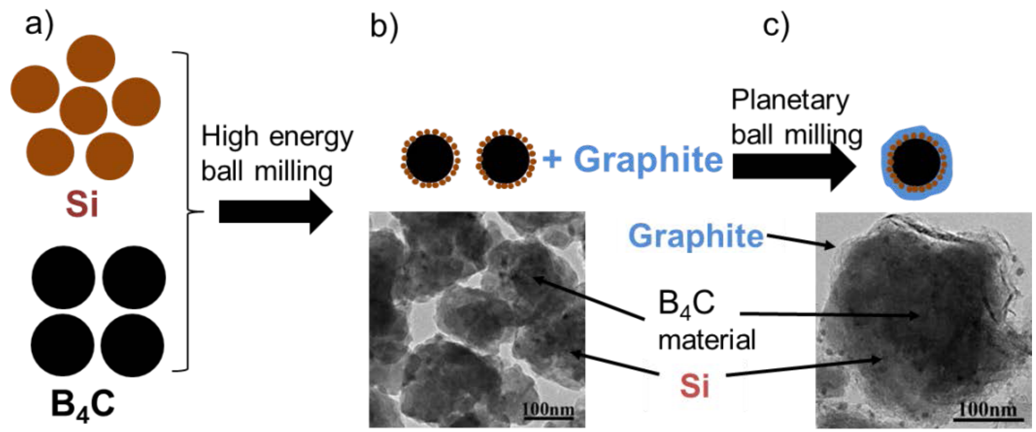


- SEM shows porous Si particles exhibit similar morphology before and after cycling.
- A layer of SEI formed on the particle surface after long-term cycling.

Technical Accomplishments

Optimize Conductive Rigid-Skeleton Supported Silicon

Preparation procedure of graphite coated silicon/B_4C composite (SBG)



Approaches:

- Simulate the mechanical stability of SBG structure before and after lithiation.
- Use TEM to measure the volume change before and after lithiation.
- Use new electrolyte additive to form a stable SEI layer and improve the cycle life.
- Improve the composition and the preparation process.

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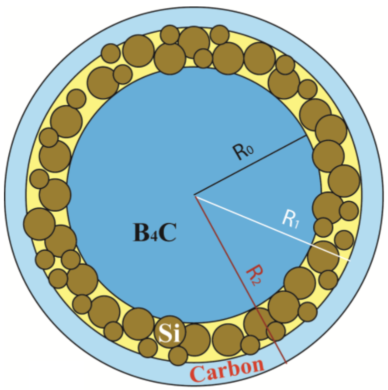
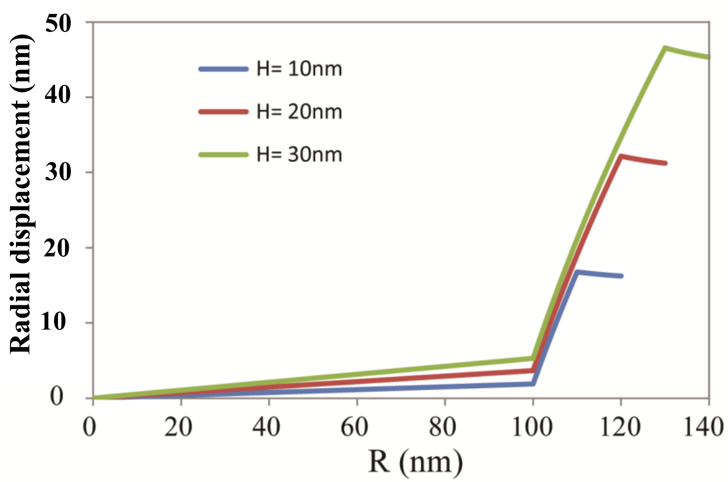
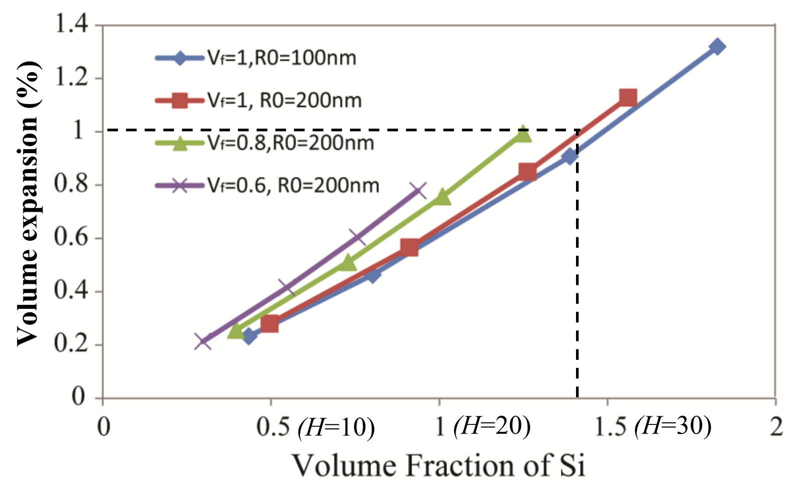
Technical Accomplishments

Simulation Shows Small Volume Expansion of SBG Particles



Materials	Poisson Ratio (ν	Young's Modulus (E)	Thickness	Si Volume fraction
B4C	0.18	472GPa	$R_0 = 100,200nm$	
Si	0.22	179GPa	$H = R_1 - R_0 = 10,20,30nm$	$V_f = 60,80,100\%$
C	0.12	821GPa	$R_2 - R_1 = 10nm$	





- The composite structure has very small volume expansion, and the volume expansion decreases with decrease in the core material diameter.

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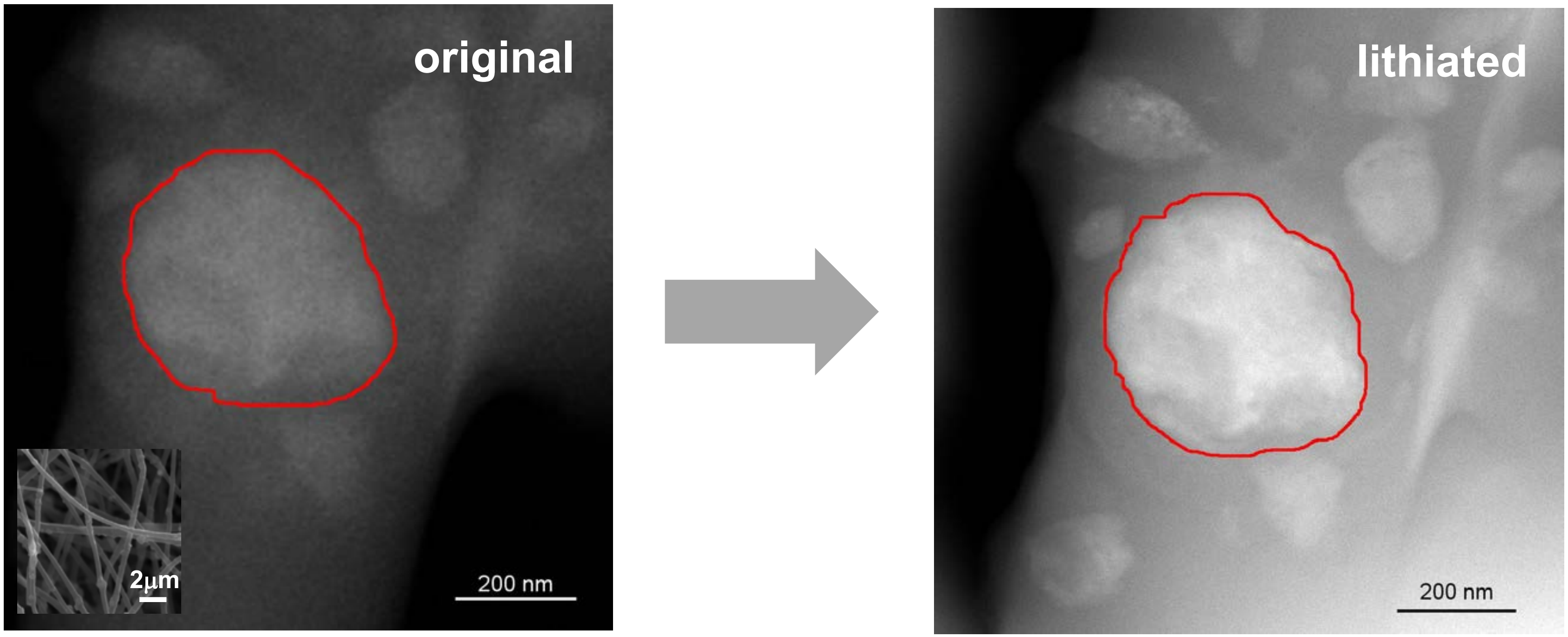
Technical Accomplishments

SBG Composite Demonstrated Small Volume Change during In Situ Lithiation



- SBG embedded in carbon fiber for in situ study.
- Only a small volume expansion is observed after lithiation.

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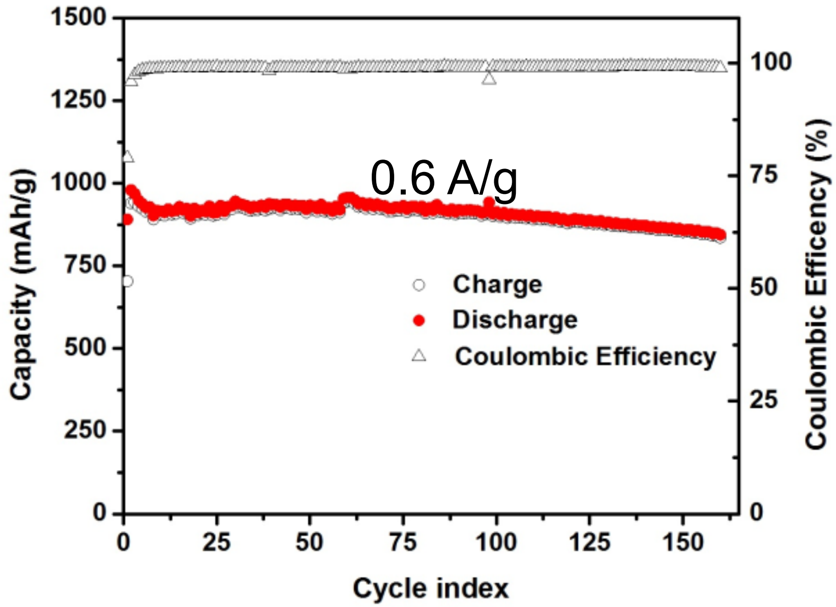
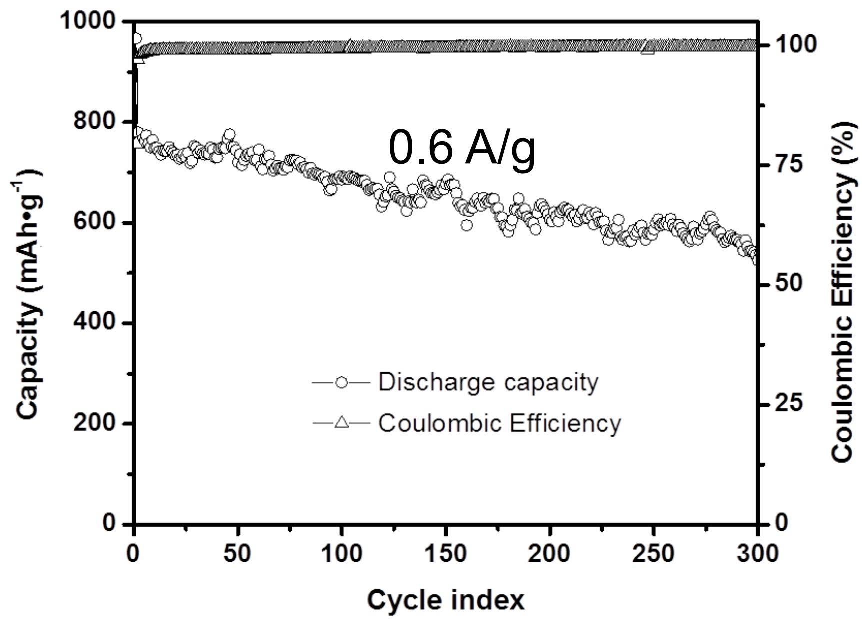
Technical Accomplishments

SBG Composite Demonstrated Improved Cyclability and Rate Performance-Additive Effects





- Capacity: ~900 mAh/g (based on the full electrode), ~90.7% retention after 150 cycles. (FEC additive)
- Capacity: ~800 mAh/g (based on the full electrode), ~72% capacity retention after 300 cycles. (VC additive)

Total electrode loading: ~1 mg/cm^2; Si loading: ~0.3 mg/cm^2

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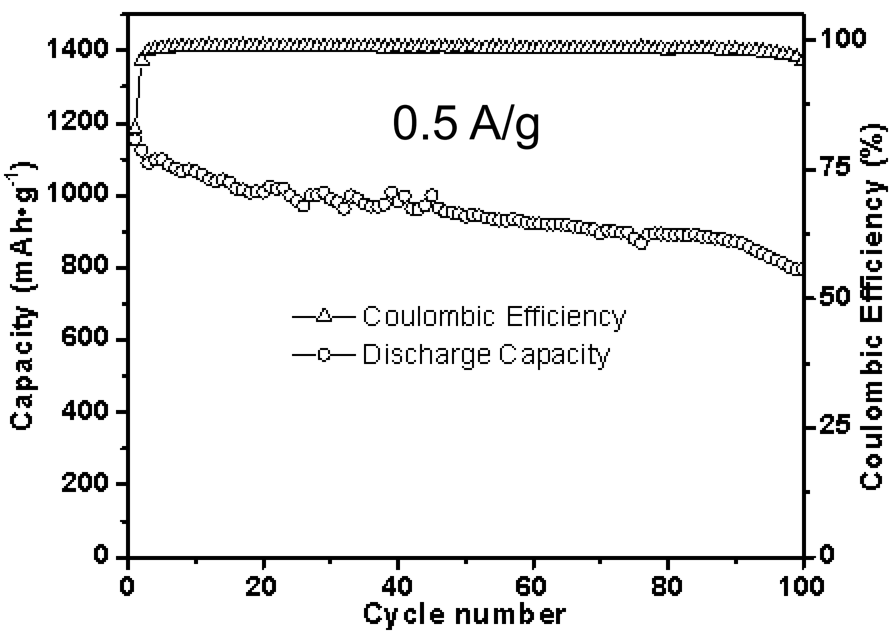
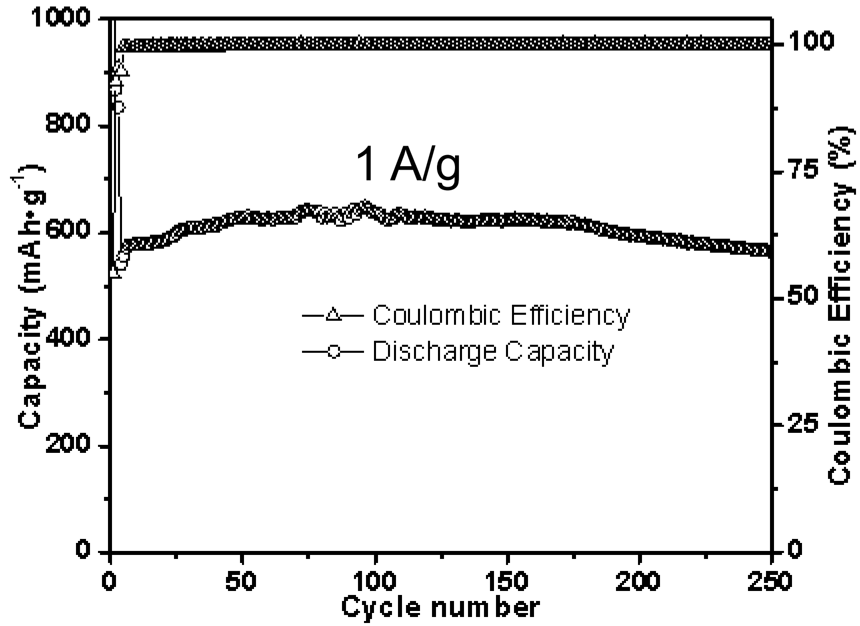
Technical Accomplishments
Increasing Si Mass Loading



- SBG composite with total electrode loading of ~1.75mg/cm^2 (Si loading: ~0.5 mg/cm^2)
- Capacity: ~1100 mAh/g (based on the full electrode), ~72% retention after 100 cycles.



- Macroporous Si electrode with total electrode loading of ~1.3 mg/cm^2 (Si loading: ~0.4 mg/cm^2)
- Capacity: ~600 mAh/g (based on the full electrode), ~87% retention after 250 cycles.

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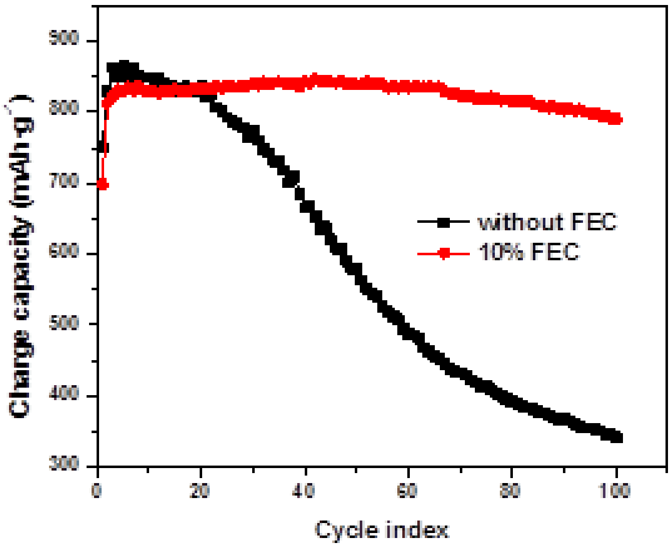
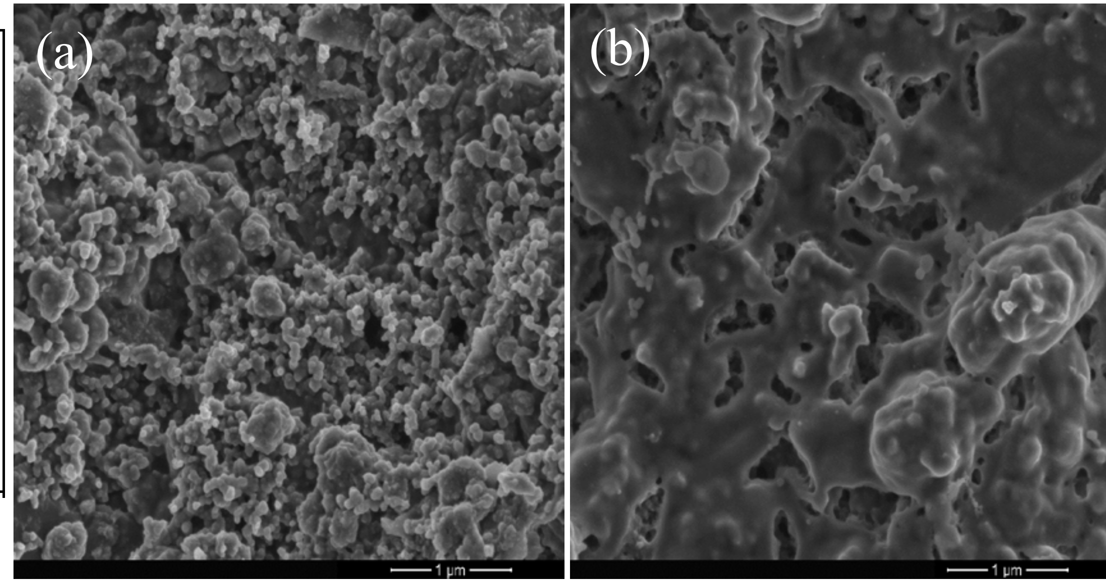
Technical Accomplishments
Investigate the Electrolyte Additive Effect





- Cycling stability of the Si anode was significantly improved with 10 wt% 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 more than ~50% was observed after 70 cycles with no FEC additive exhibited
- The SEI layer on the electrode without FEC is more than 3 times thicker than that with FEC and the electrode has larger volume expansion according to SEM and NMR study.

➢ NMR study reveals drastic change of the Li environment in the SEL layers.

Collaboration and Coordination with Other Institutions

Partners:

- University of California, San Diego: Collaboration on the macroporous Si work.
- Princeton University: Preparation and characterization of graphene.
- Vorbeck Materials Corporation: Provider of graphene sheet.

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Future Work

- Optimize porosity of porous Si and the architecture of rigid skeleton supported Si composites to further investigate the stress and volume effect to the capacity fading.
- Use *operando* TEM (with a liquid cell using practical electrolyte) and NMR to further investigate the SEI evolution and capacity fading mechanism during charge/discharge.
- Develop new electrolyte additives and binders to improve stability of the SEI layer and interfacial machinability of the Si-based anode.
- Develop new approaches and electrode structures to enable electrodes with high Si mass loading without compromising the long-term cycling stability.

Summary

- Low cost, scalable method has been developed for high-capacity Si anodes.
- Si electrode supported by a conductive, rigid skeleton has demonstrated highly stable cycling stability. <u>The full electrode has a capacity of ~800 mAh/g and a capacity retention of ~72% after 300 cycles.</u>
- Macroporous Si has demonstrated small volume change and excellent cycling stability with ~600 mAh/g (based on the full electrode) initial capacity and ~89% retention after 300 cycles.

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Acknowledgments

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✓ Team Members:
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Technical Backup Slides

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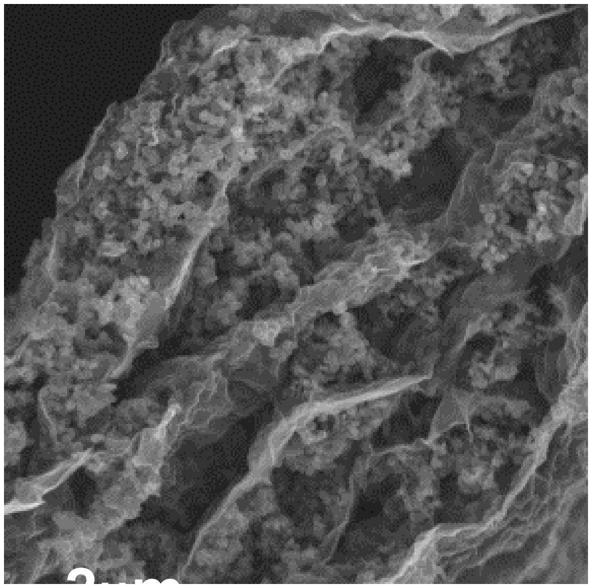
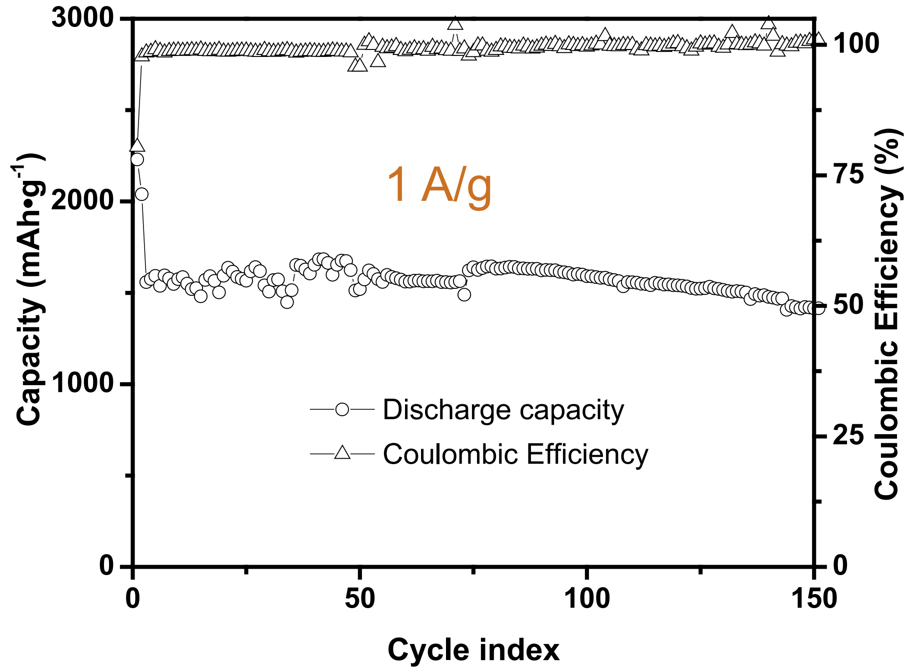
Technical Accomplishments

Sandwich-Structured Graphene-Sheet/Nano-Si Composite as Li-Ion Battery Anodes





Sandwich-structured graphene-sheet/nano-Si composite has demonstrated

- initial capacity of ~1500 mAh/g (based on the full electrode)
- capacity retention of ~89.7% after 150 cycles.

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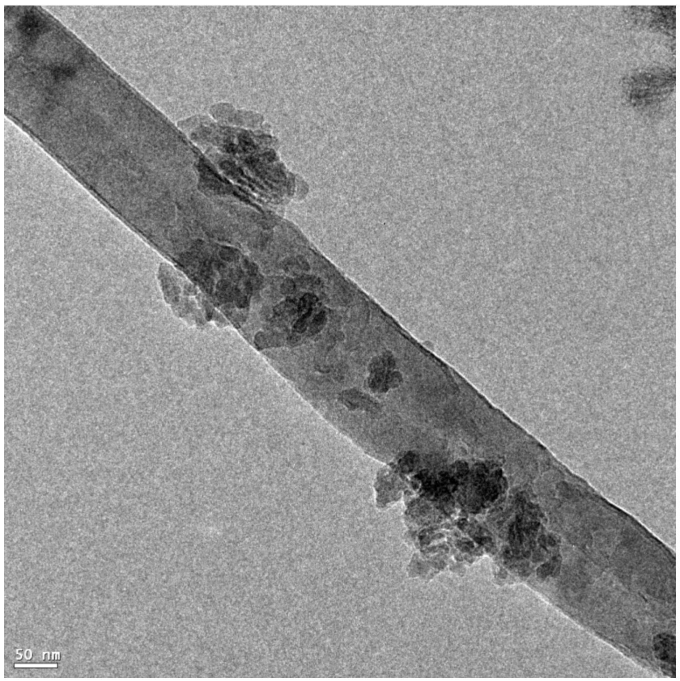
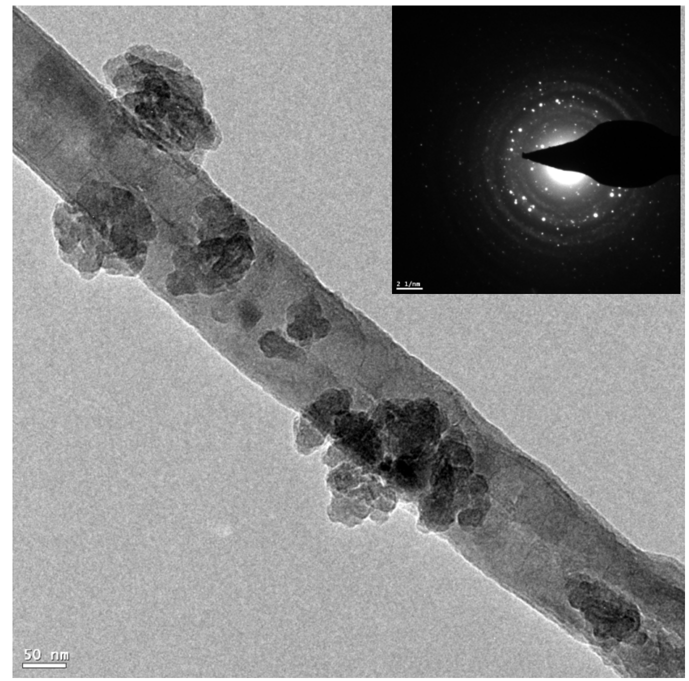
Technical Accomplishments

In Situ Investigation of the Lithiation of Macroporous Si

Lithiated state of small porous pieces



lithiation



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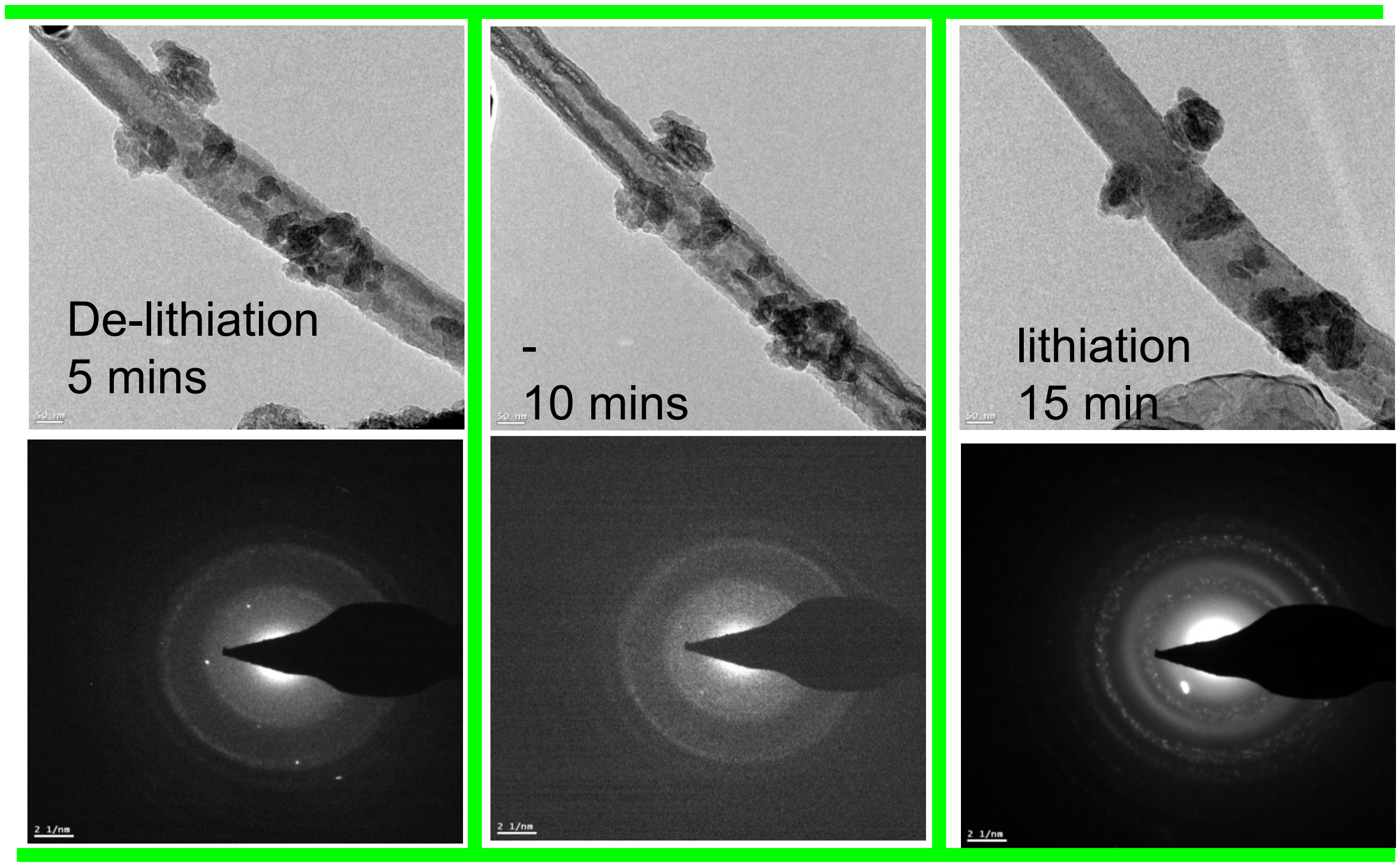
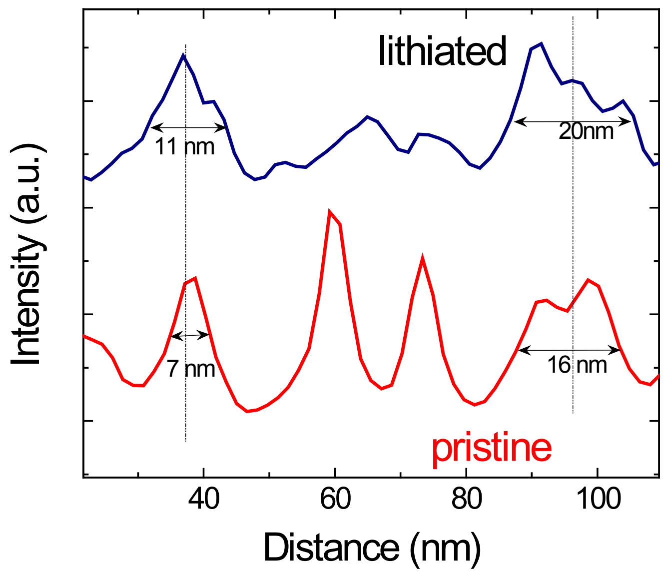
Technical Accomplishments

In Situ Investigation of the Lithiation of Macroporous Si

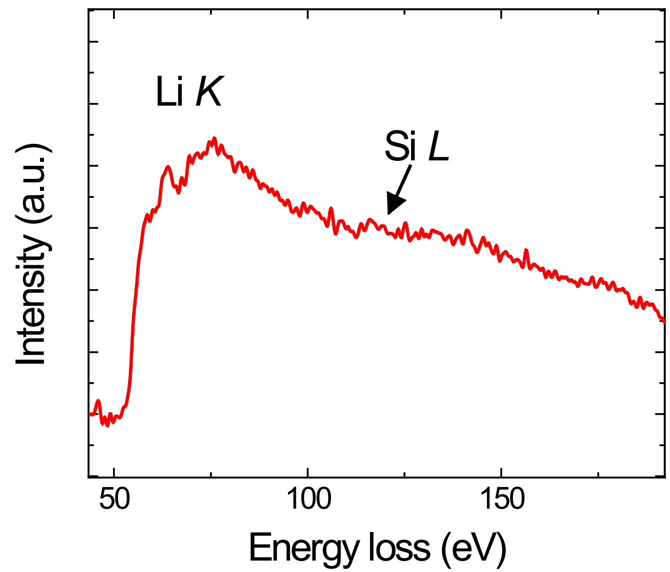


Technical Accomplishments

In Situ Investigation of the Lithiation of Macroporous Si



Intensity plot comparison of the porosity changes after lithiation, Si volume expansion and pore shrinkage.



Energy loss spectrum showing the lithiation of porous Si

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