Development of Silicon-based High Capacity Anodes

Ji-Guang Zhang and Jun Liu

Pacific Northwest National Laboratory

2014 DOE Vehicle Technologies Program Review
June 16-20, 2014

This presentation does not contain any proprietary, confidential, or otherwise restricted information

Pacific Northwest
NATIONAL LABORATORY

Project ID #: ES144

Overview

Timeline

- ➢ Project start date: Oct. 2010
- ➢ Project end date: Sept. 2014
- ➢ Percent complete: 88%

Barriers addressed

- Low energy density
- High cost
- Limited cycle life

Budget

- Total project funding
  - DOE share 100%
- Funding received in FY13: $300k
- Funding for FY14: $400k

Partners

- Univ. of California, San Diego
- Florida State University
- Princeton University
- Vorbeck Materials Corporation
- LBNL
- Stanford University

Pacific Northwest
NATIONAL LABORATORY

Relevance/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.

- Investigate the failure mechanism of Si.
  - Understand the SEI layer evolution and develop new additive and binder to improve the interfacial stability of the Si-based anode.
  - Understand the volume expansion and stress effect to the capacity fading of Si-based anode.

Pacific Northwest
NATIONAL LABORATORY

Milestones

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

FY14

- Identify the fading mechanism in the thick Si electrode vs. thin electrode. (Dec. 2013) **−*Completed***
- Achieve Coulombic efficiency of the anode >90% during the first cycle, through application of SLPMs and sacrificial Li electrode to Si based anode. (March 2014) **−*Completed***
- Achieve high loading Si-based anode capacity retention of >1.2 mAh/cm^2 over 150 cycles using new binders/electrolyte additives. (June 2014) **−*Completed***
- Achieve improved cycling stability of thick electrodes (> 3 mAh/cm^2). (Sept. 2014) **−*on going***

Pacific Northwest
NATIONAL LABORATORY

Approach

Improve Mechanical Stability of Si-Based Anode:

- Use silicon composite with either pre-vacant space (macroporous Si) or preoccupied structure stabilizer (B_4C) to retain mechanical stability of Si anodes.
- Use simulation and in situ TEM to predict and verify the volume expansion and mechanical stability of Si composite.

Improve the Cyclability of High Loading Si-Based Anode:

- Use porous Si with optimized structural parameters.
- Optimize the composition of the rigid skeleton supported Si nanocomposite.
- Improve the fabrication technique of thick electrode.

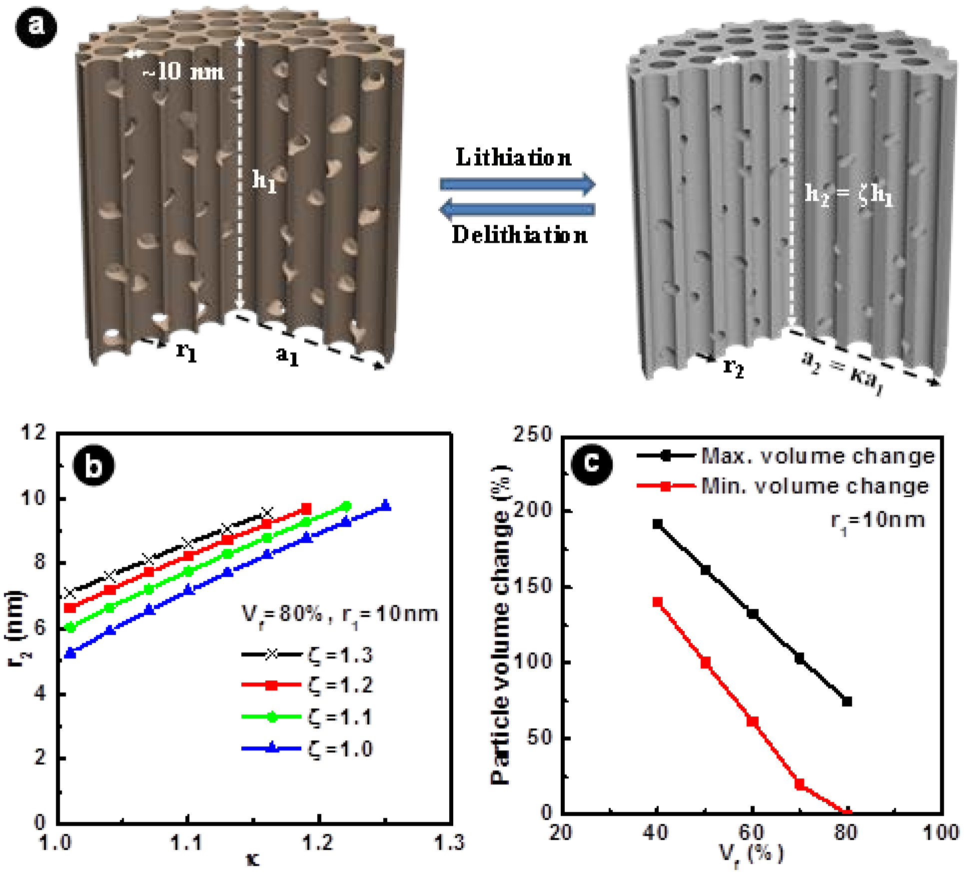
Use Analytical methods to Reveal SEI formation Mechanism:

- Analyze the compositions of SEI films as a function of electrolyte additives and cycled numbers.
- Model the additive structure to predict the formation products.

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments

Simulation Shows Small Volume Expansion of Porous Si Particles



$$V_1 = \pi a_1^2 h_1 (1 - V_f)$$

$$N\pi r_1^2 h_1 / (\pi a_1^2 h_1) = V_f$$

$$N = V_f a_1^2 / r_1^2$$

$$V_2 = a_2^2 \pi h_2 - N\pi r_2^2 h_2 = (a_2^2 - V_f a_1^2 r_2^2 / r_1^2)\pi h_2$$

$$V_2 = 4V_1$$

$$a_2^2 h_2 - V_f a_1^2 r_2^2 h_2 / r_1^2 = 4a_1^2 h_1 (1 - V_f)$$

$$if \quad a_2 = \kappa a_1 \ and \ h_2 = \xi h_1$$

$$\xi\kappa^2 - V_f \xi r_2^2 / r_1^2 = 4(1 - V_f)$$

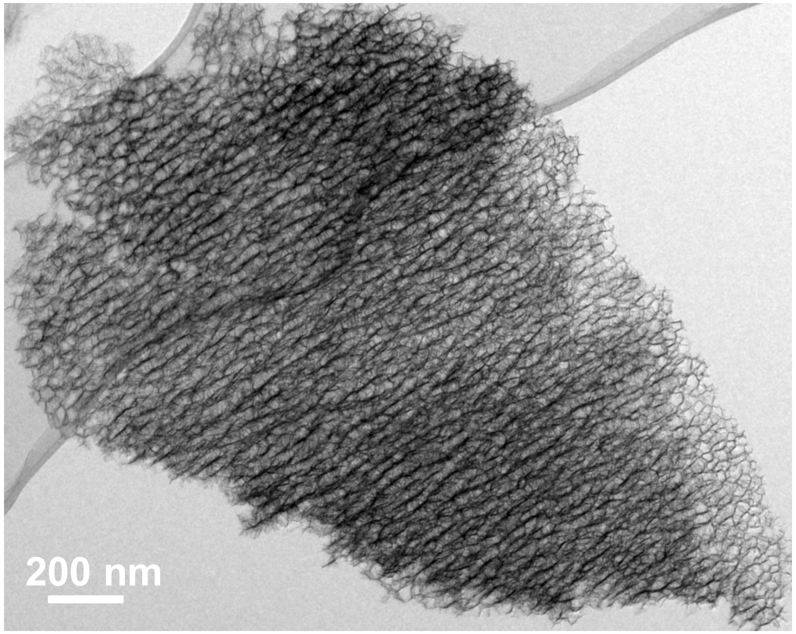
$$r_2^2 = (-4 + \xi\kappa^2 + 4V_f) r_1^2 / (V_f \xi)$$

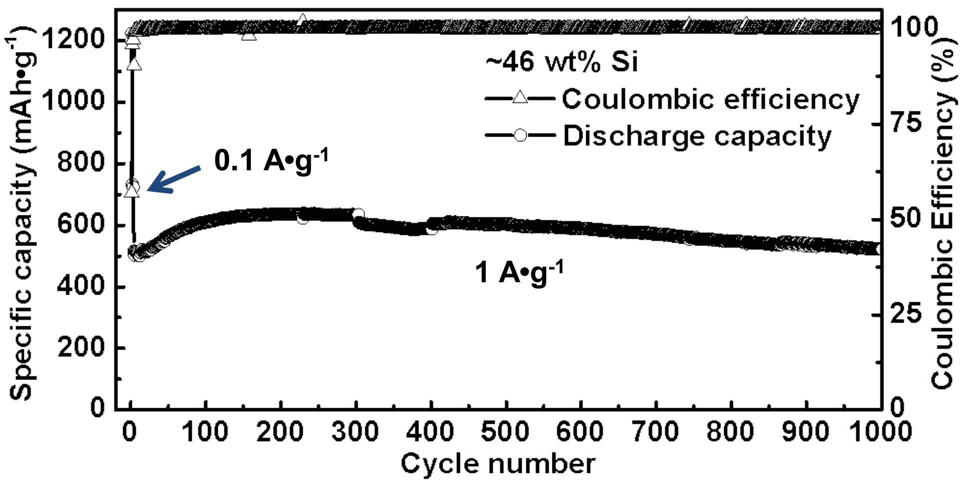
V_f : The volume fraction of voids or porosity
N : The total number of voids in the particle
h_1 : The height of particle before lithiation
h_2 : The height of the particle after lithiation
a_1 : The radius of the particle before lithiation
a_2 : The radius of the particle after lithiation
r_1 : Average radius of pores before lithiation
r_2 : Average radius of pores after lithiation
V_1 : The volume of solid before lithiation
V_2 : The volume of solid after lithiation

- The apparent expansion of a porous Si particle can be less than ~75% when the volume fraction of voids is ~80%.

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments
Porous Si as Stable Li-Ion Battery Anodes



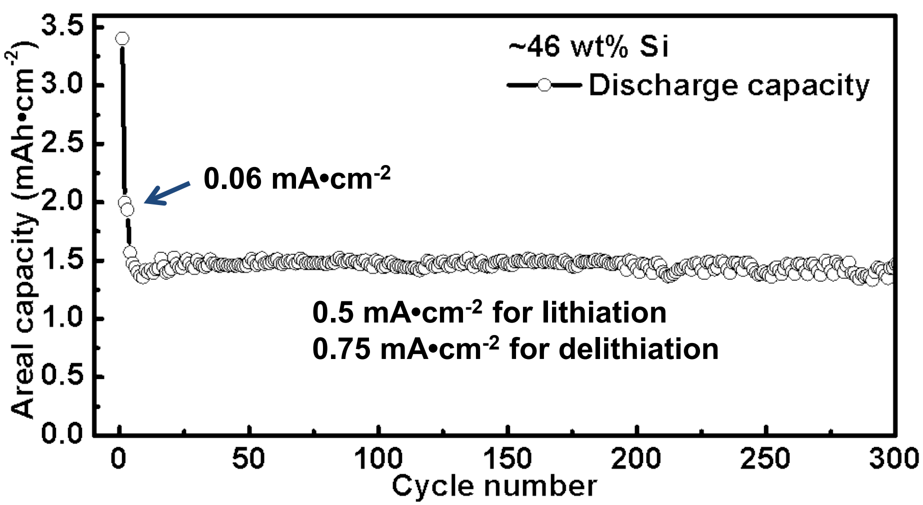


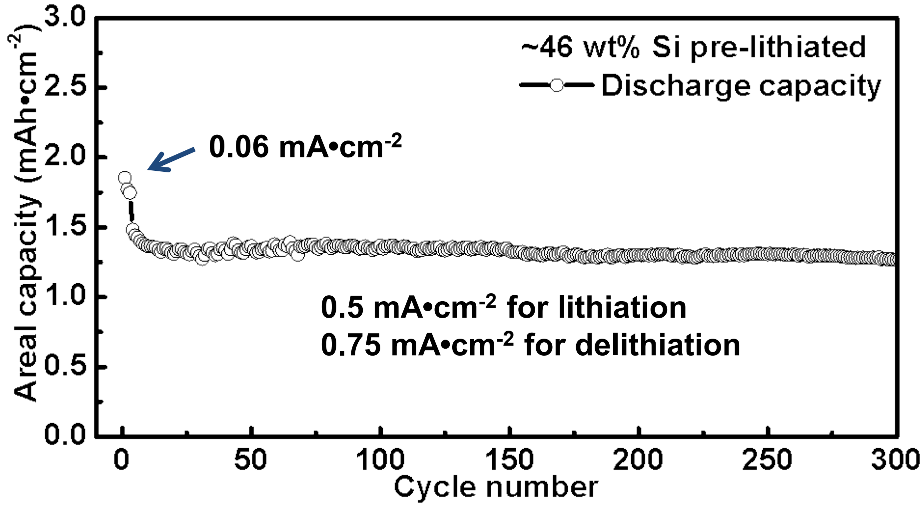
- Capacity: ~640 mAh/g (based on the full electrode)
- Capacity retention: ~81% after 1000 cycles

Total electrode loading: ~0.5 mg/cm^2
Si loading: ~0.2 mg/cm^2

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
Porous Si Electrode of ~1.5 mAh/cm^2 With and without Pre-lithiation



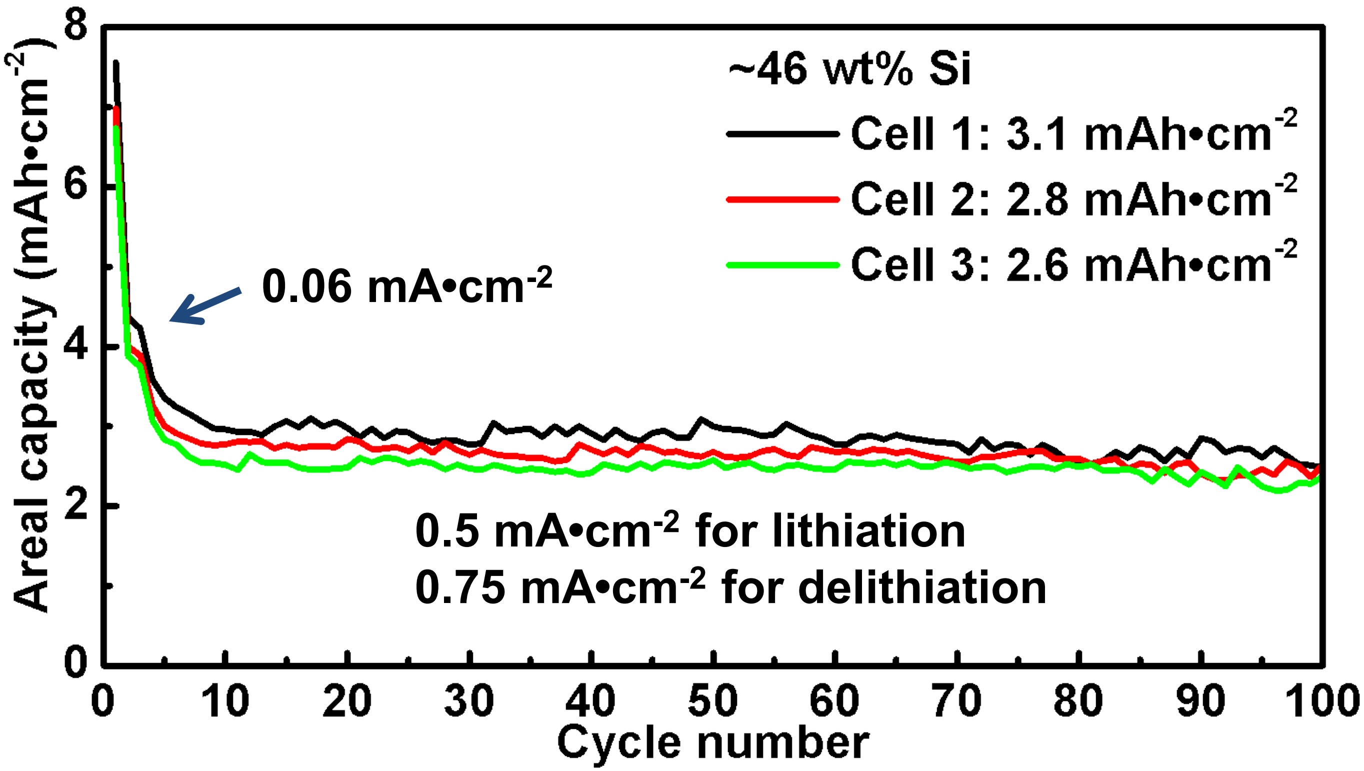


- Specific capacity: ~750 mAh/g (based on the full electrode)*
- Capacity retention: ~96% after 300 cycles
- First cycle irreversible loss is greatly reduced after prelithiation

Total electrode loading: ~2 mg/cm^2
Si loading: ~1 mg/cm^2
* See technical backup slides

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments
Porous Si Electrode of ~3 mAh/cm^2

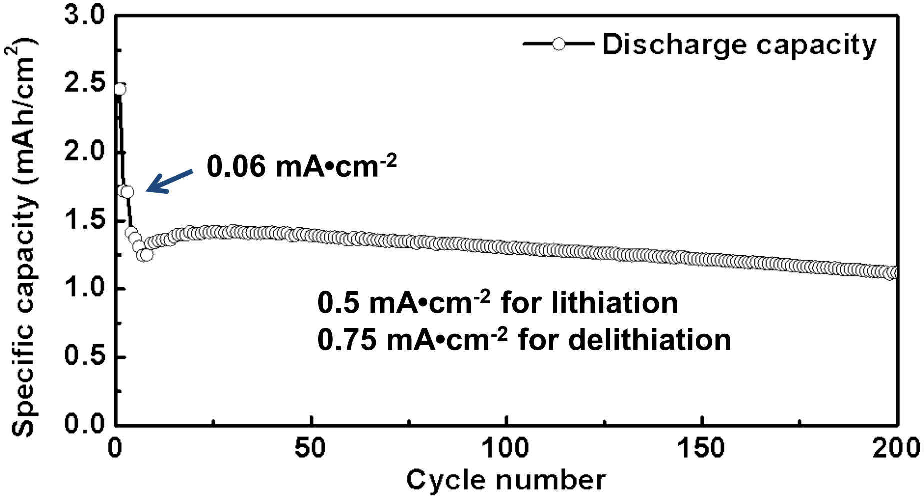


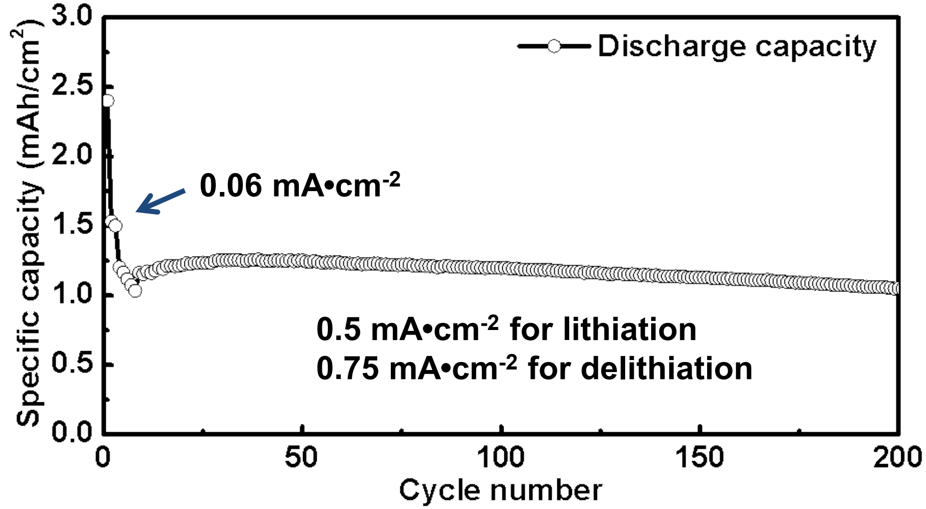
- Capacity retention: ~90% after 100 cycles

Total electrode loading: ~3.5 to 4 mg/cm^2
Si loading: ~1.7 mg/cm^2

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
Modified SBG Composite of ~1.3 mAh/cm²





- SBG-gen2 composite with total electrode loading of ~2 mg/cm² (Si loading: ~0.5 mg/cm²)
- Capacity: ~1.42 mAh/cm² (based on the full electrode), ~80% retention after 200 cycles.

- SBG-gen3 composite with total electrode loading of ~2 mg/cm² (Si loading: ~0.5 mg/cm²)
- Capacity: ~1.25 mAh/cm² (based on the full electrode), ~85% retention after 200 cycles.

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
SEI formation Mechanism and Its Evolution

Current understanding on SEI film formed by FEI:

- Fluoroethylene carbonate (FEC) is an effective electrolyte additive that can form a stable SEI layer and significantly improve the cycle-ability of silicon and other anode materials. However, the fundamental mechanism of this improvement is still not well understood.
- One possible reduction mechanism of FEC is that the FEC first converts into vinylene carbonate (VC) and then the resultant VC polymerizes. The main products from this mechanism are LiF and poly(vinylene carbonate).
- Another possible reduction mechanism is that the FEC is reduced through opening the five-member ring to form a $(CH_2CH\underline{F}OCO_2\underline{Li})_2$ dimer.
- According to these two mechanisms, the FEC reduction products formed in the SEI film should be LiF and poly(vinylene carbonate) $(CH_2CHFOCO_2Li)_2$. In both cases, the lithium-to-fluorine ratio of the reaction products is close to 1.

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
FEC Reduction and SEI formation Mechanism

XPS analysis on Li/F ratio

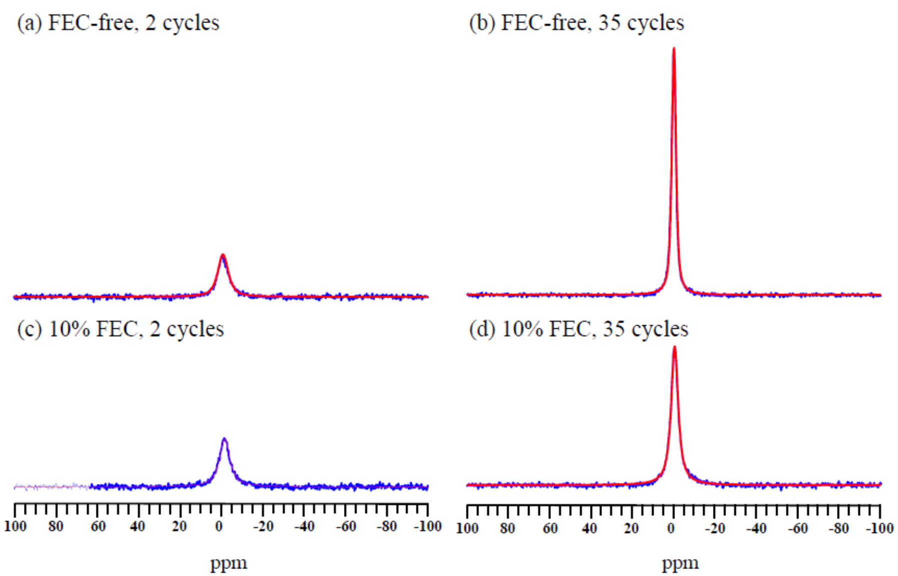
Elements samples	Li	C	O	F	Li/F ratio
Electrolyte (a), 2 cycles	27.7%	23.3%	24.1%	24.9%	1.11
Electrolyte (a), 35 cycles	22.7%	31.3%	37.6%	8.4%	2.70
Electrolyte (b), 2 cycles	22.9%	32.5%	32.1%	12.5%	1.83
Electrolyte (b), 100 cycles	21.0%	33.8%	31.9%	13.3%	1.58
Electrolyte (c), 2 cycles	21.1%	34.7%	32.2%	12.0%	1.76

(a) 1M $LiPF_6$ in EC/DMC (1:2 in vol), (b) 1M $LiPF_6$ in EC/DMC (1:2 in vol) with 10% FEC and (c) 1M $LiClO_4$ in pure FEC

- The ratio of Li/F in SEI layer formed in the FEC containing electrolyte is much larger than 1 and is not consistent with the value predicted by the conventional reduction mechanism.
- In the FEC-free electrolyte, composition of SEI film change significantly with increasing cycle number due to selective reduction of solvent.
- In the FEC-containing electrolyte, composition of SEI film does not change significantly with increasing cycle number, indicating the formation of stable protection layer.

Pacific Northwest NATIONAL LABORATORY

Technical Accomplishments
FEC Reduction and SEI formation Mechanism



The normalized peak area in FEC-free electrolyte is about 3.4 times that of the initial area

The normalized peak area in FEC containing electroltye is about 2.1 times that of the initial area

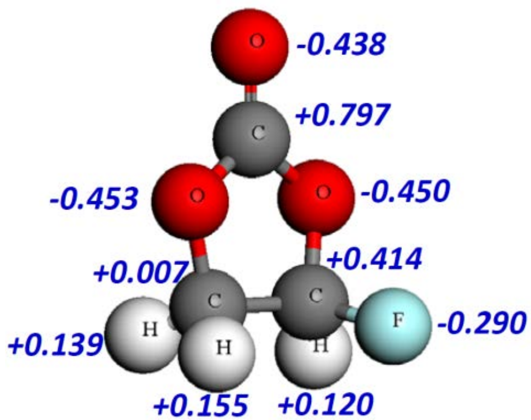
^{6}Li NMR spectra for SEI films formed in FEC-free electrolytes (a, b) and electrolytes with 10% FEC (c, d). Peaks in the figure represent Li source in SEI layer which are significantly different from the peaks of intercalated lithium in lithium-silicon alloys.

- FEC can effectively suppress the growth of SEI layer.

Pacific Northwest
NATIONAL LABORATORY

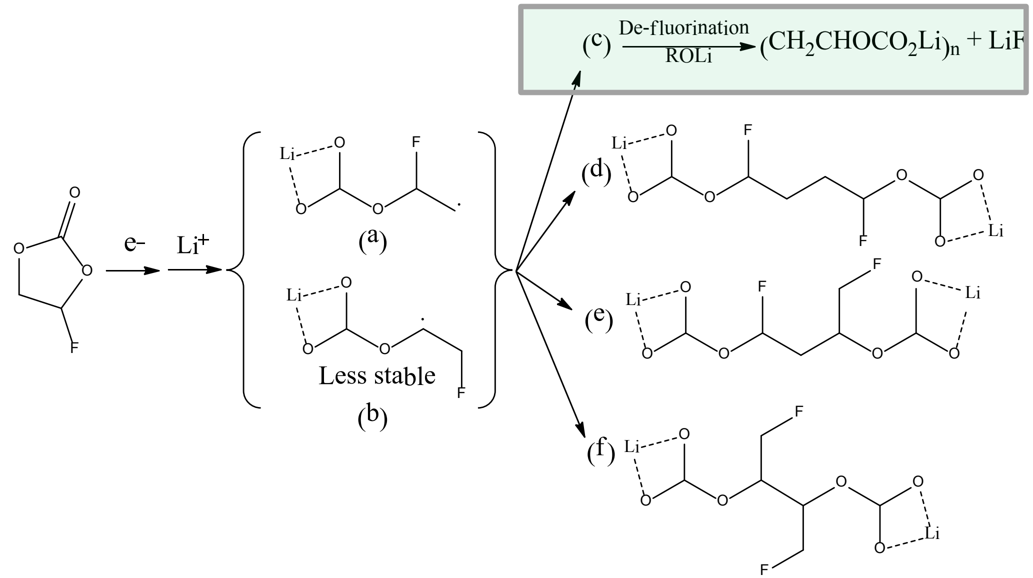
Technical Accomplishments
FEC Reduction and SEI formation Mechanism

Calculated Mulliken Charges of atoms in FEC



Fluoroethylene carbonate

Proposed possible reduction reaction of FEC



Li/F > 1

Li/F = 1

Li/F = 1

Li/F = 1

Based on the results obtained from XPS and other analysis, we propose a molecular-level mechanism for how FEC affects the formation of solid electrolyte interphase (SEI) film:

- FEC is reduced through the opening of the five-member ring leading to the formation of lithium poly(vinyl carbonate), LiF and some dimers
- The FEC-derived lithium poly(vinyl carbonate) has good mechanical strength and will enhance the stability of the SEI film.

The proposed reduction mechanism opens a new path to explore new electrolyte additives that can improve the cycling stability of silicon-based electrodes.

Pacific Northwest NATIONAL LABORATORY

Collaboration and Coordination with Other Institutions

Partners:

- University of California, San Diego: Collaboration on the macroporous Si work.
- Florida State University: pre-lithiation of Silicon anode.
- Princeton University: Preparation and characterization of graphene.
- LBNL: Investigate the properties of new binder
- Stanford University: Study the failure mechanism of Si

Pacific Northwest
NATIONAL LABORATORY

Future Work

- Develop low-cost, scalable approaches to porous Si with stable cycling.

- Develop new approaches and electrode structures to enable electrodes with high Si mass (thick electrode) loading with long-term cycling stability.

- Optimize the pre-lithiation process to reduce the first-cycle irreversible capacity loss.

- Develop new electrolyte additives based on the newly discovered SEI formation mechanism to improve the long term cycling stability of Si based anode.

Pacific Northwest
NATIONAL LABORATORY

Summary

- Low cost, scalable method has been developed for high-capacity and stable Si anodes.
- Porous Si has demonstrated highly stable cycling stability even at high mass loading. The full electrode with/without pre-lithiation has an areal capacity of ~1.5 mAh/cm^2 and capacity retention of~96% over 300 cycles.
- A novel molecular-level mechanism has been established to explain FEC reaction route and SEI formation mechanism.
- Porous Si electrodes with an areal capacity of ~3 mAh/cm^2 and capacity retention of~90% over 100 cycles have been demonstrated.
- Rigid skeleton supported Si electrode has been further optimized and demonstrated stable cycling stability at high mass loading. The full electrode has an areal capacity of ~1.3 mAh/cm^2 and capacity retention of >80% over 200 cycles.

Acknowledgments

✓ Support from the DOE/OVT/BATT program is greatly appreciated

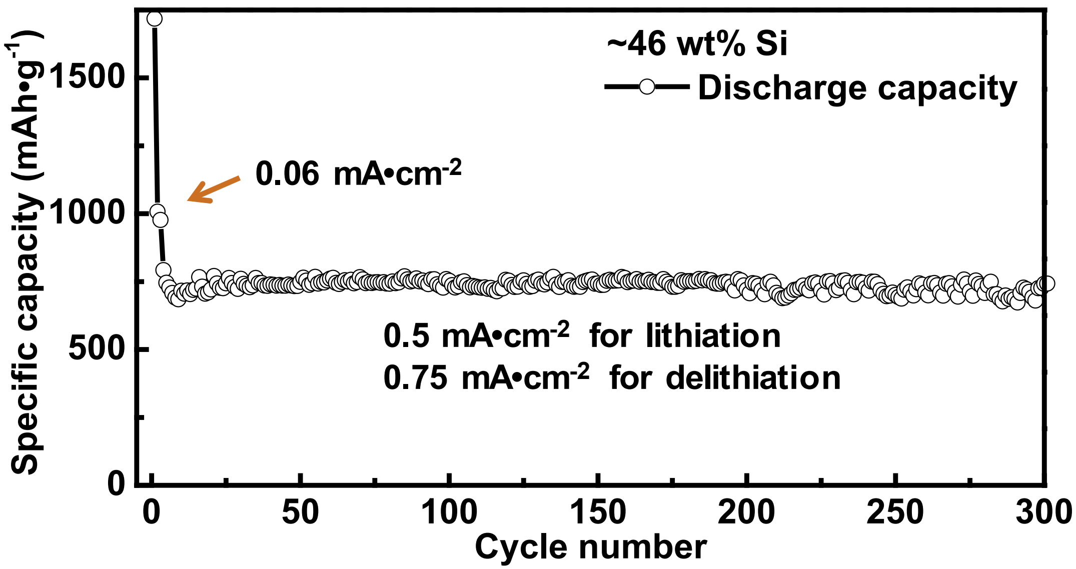
✓ Team Members:
Xiaolin Li, Xilin Chen, Chongmin Wang, Meng Gu, Pengfei Yan, Jianzhi Hu, Shenyang Hu, Wu Xu, Jie Xiao, Zimin Nie, and Gordon L. Graff

Pacific Northwest NATIONAL LABORATORY

Technical Backup Slides

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
Porous Si Electrode of ~1.5 mAh/cm^2



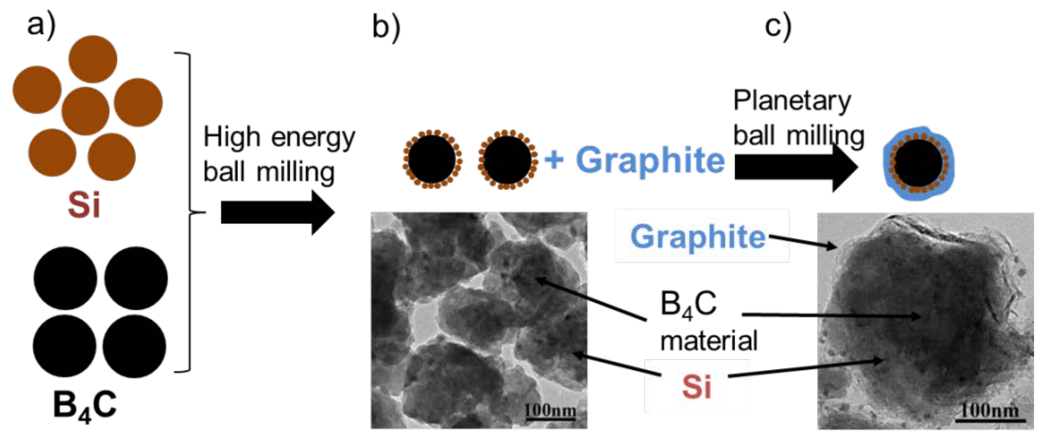
- Specific capacity: ~750 mAh/g (based on the full electrode)
- Capacity retention: ~96% after 300 cycles

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

Pacific Northwest
NATIONAL LABORATORY

Technical Accomplishments
Optimize Conductive Rigid-Skeleton Supported Silicon

Typical preparation procedure of the Si/B_4C/graphite composite (SBG)



Approaches:

•Improve the composition and the preparation process.

•Use new additive to improve the cycle stability of high loading electrode.

Pacific Northwest NATIONAL LABORATORY