A Combined Experimental and Modeling Approach for the Design of High Coulombic Efficiency Si Electrodes

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Project ID: ES221

Overview

Timeline

- Project start date: 5/17/2013
- Project end date:4/1/2017
- Percent complete: 60%

Barriers addressed

High energy materials with

- Low calendar and cycle life
- Low coulombic efficiency
- High cost

Budget

- Total project funding: $1,318,947
- DOE share: $1,318,947
- Contractor share: $0
- Funding received in FY14: $300,000
- Funding for FY15: $300,000

Partners

Interactions/ collaborations

- U. Waterloo: Zhongwei Chen, Si nanostructure
- LBNL: Gao Liu: polymer binder
- PNNL: Chongmin Wang: in-situ TEM
- NREL: Chunmei Ban: Advanced surface coating
- Sandia: Kevin Leung: e transport in ALD

Project lead: General Motors

Objective and Relevance

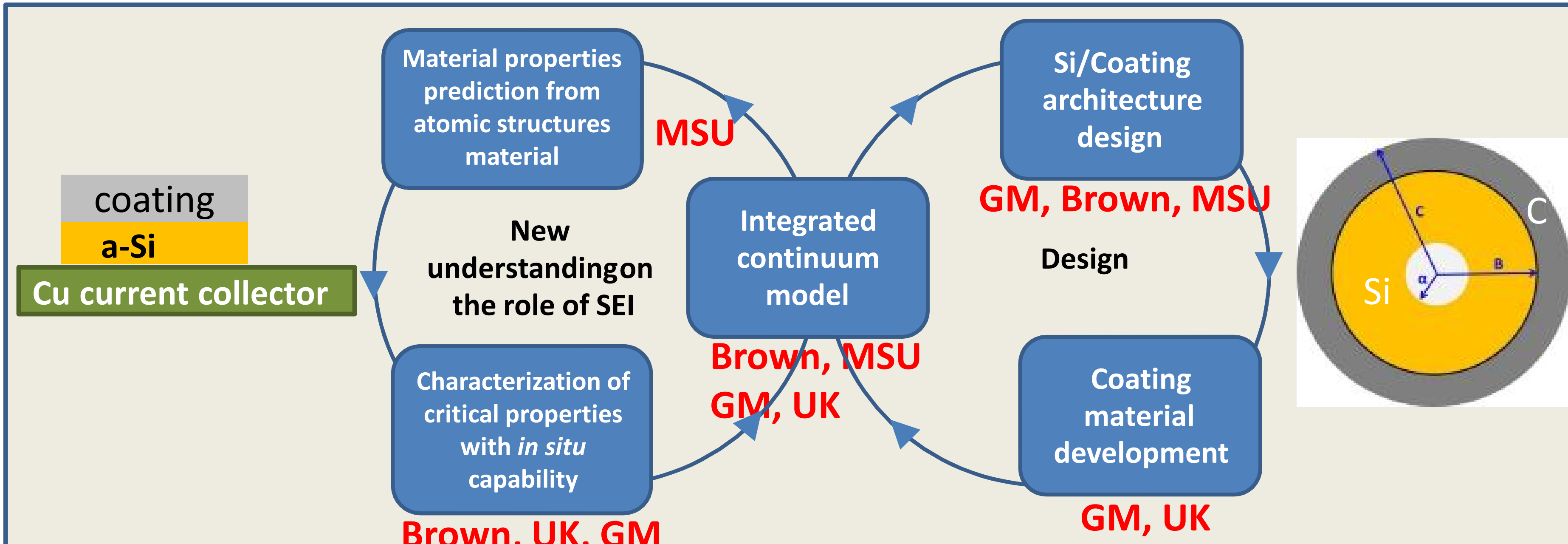
Objective: A validated model to understand, design, and fabricate stabilized nano-structured Si anode with high capacity and high coulombic efficiency.

Relevance

- Si-based electrodes were limited by coupled mechanical/chemical degradation. Instability of the Si SEI leads to low coulombic efficiency and short life.
- A surface coating as artificial SEI can be mechanically stable despite the volume change in Si, if the material properties are **optimized**.
- **A validated model with known material properties** shall guide the synthesis of surface coatings and the optimization of Si size/geometry/architecture to stabilize the SEI and Si, enabling a negative electrode with high capacity and coulombic efficiency, and long-term cycle stability.

Approach/Strategy

- Combine simulation with experiments to obtain critical material properties of SEI layer and lithiated Si.
- Develop a multi-scale model to establish correlation between coulombic efficiency and mechanical degradation of SEI on Si.
- Use the validated model to guide synergetic design of surface coating with Si size/geometry/architecture.



An integrated experimental and modeling approach to understand, design, & make SEI on Si

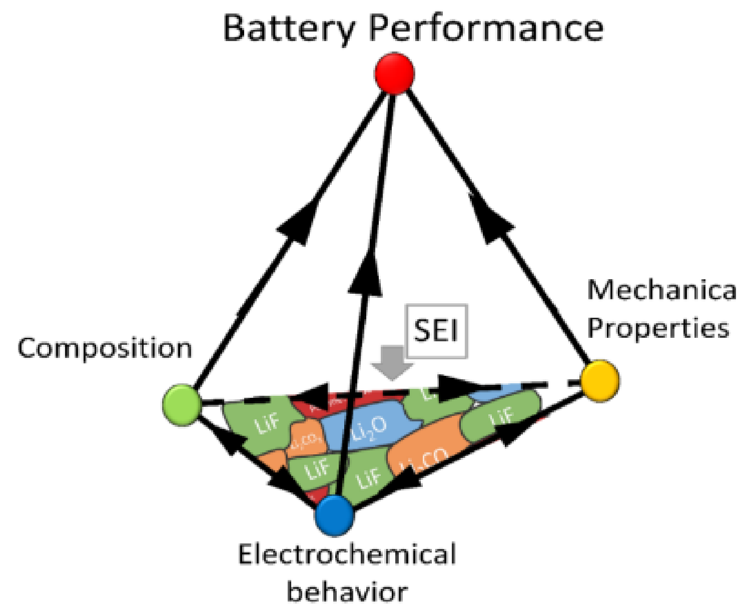
Project Milestones

Month/ Year	Milestone of Go/No-Go Decision	Status
Jun. 2014	**Compare the basic elastic properties of ALD coatings computed from MD simulations and experiments for method validation.**	**completed**
Sept. 2014	**Establish a combined experimental and atomic scale model to understand the mechanical properties of both natural and artificial SEI layers.**	**completed**
Dec. 2014	**Develop multi-component and multi-functional artificial SEI paired with a variety of Si nanostructure from both experiment and simulation. Identify the critical coating properties as the artificial SEI**	**completed**
Jan. 2015	**Develop a multiscale modeling approach to predict the mechanically stable size of Si-C core-shell and yolk-shell structure.**	**completed**
April 2015	**Develop a continuum frame work to model SEI deformation and stability on Si film and compare with in situ MOSS measurement.**	**ongoing**

I. Learn from Naturally Formed SEI

Key Questions to Address

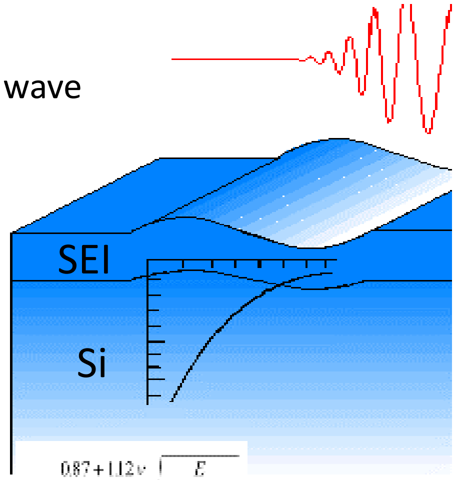
- How does SEI evolve during cycling?
- Which SEI compounds are desirable/ undesirable ?
- How can we modify or control the SEI layer?
- How does mechanical deformation influence SEI ?



1. Control lithiation voltage
2. Identify different SEI components
3. Measure properties for each component
4. Correlate with Cell performance

Accomplishment 1.1: Developed a simple approach to characterize the mechanical properties of naturally formed SEI

Laser acoustic wave (LAW) system

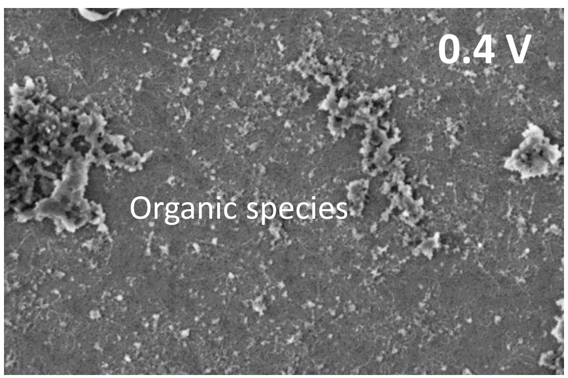


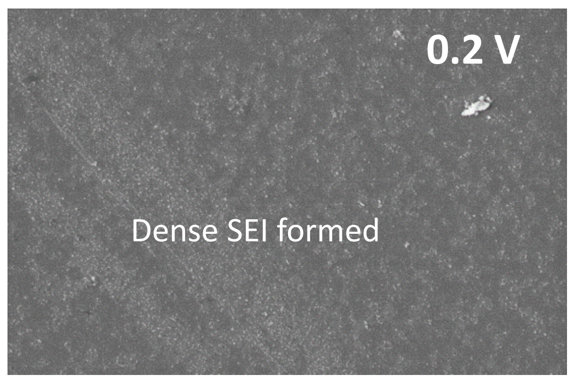
$$c = \frac{0.87+1.12\nu}{1+\nu}\sqrt{\frac{E}{2\rho(1+\nu)}}$$

Mechanical properties of ultrathin Al_2O_3 coating

Deposition temperature (°C)	Thickness (nm)	Testing method	Elastic modulus (GPa)	Reference
300	60	Nanoindentation*	220±40	K Tapily et.al
177	300	Nanoindentation	180±8.2	M. K Tripp et.al
177	100	Nanobeam deflection	168±8	M. K Tripp et.al
177	50	Nanobeam deflection	182±32	M. K Tripp et.al
120	**7.62**	**LAW**	**160.56±2.96**	**This work**
120	**11.5-38**	**LAW**	**170-180**	**This work**
100	300	Nanoindentation	150-155	C.F. Herrmann

*Continuous stiffness method combined with simulation results





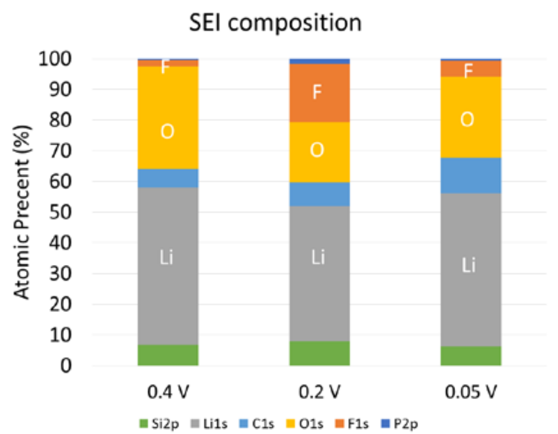
Potential held	0.4 V	0.2 V
Thickness (nm)	57.18	24.31
Young's modulus (GPa)	48.08	69.18
Substrate C11 modulus (GPa)	165.98	165.54
Least-square errors	0.214	0.228

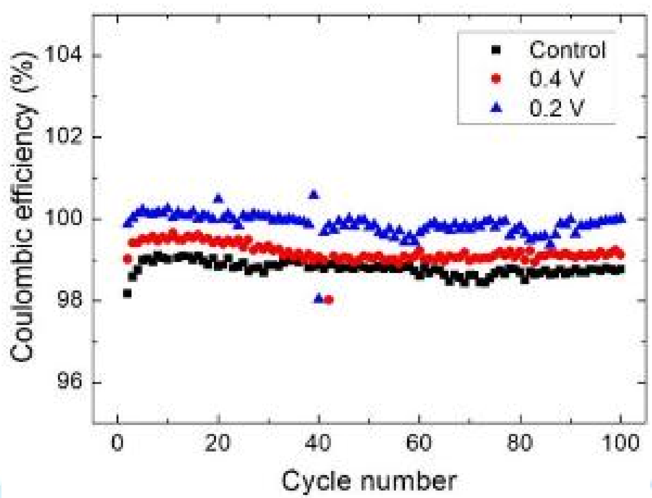
- ALD coated Al_2O_3 was used to verify the accuracy of LAW approach to ultrathin coating.
- Higher modulus of SEI formed at low potential due to the inorganic compounds.

Appl. Phys. Lett., 2014, 105, 061901, Adv. Energy Mater. doi: 10.1002/aenm.201401398

Accomplishment 1.2: Coordinated mechanical properties, structure, and conductivity with cycle efficiency.

Chemical Composition of SEI formed at different formation voltage (XPS)





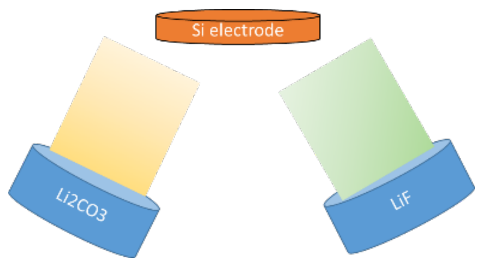
DFT modelling results

	LiF	Li_2CO_3
Diffusion carriers	Li^+ vacancy	Li^+ interstitial
Li^+ **σ**	Low	high
Band gap	8.77eV (GGA) 14~15 eV (exp)	5.04eV (GGA) 7.07eV (HSE06)
Work function	7.2eV	5.8eV
	Efficient e insulator (good for Si)	Good Li conductor

Phys. Rev. B (2015) submitted

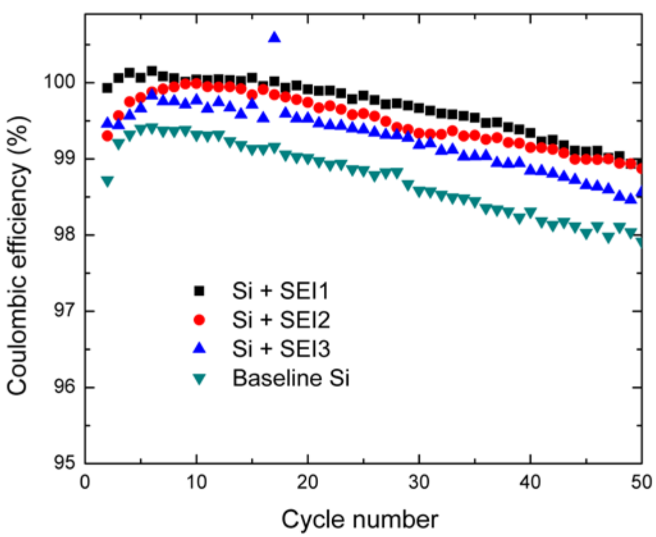
Adv. Energy Mater. (2014), doi: 10.1002/aenm.201401398

Accomplishment 1.3: Identified the desirable component in SEI enabling high cycle efficiency

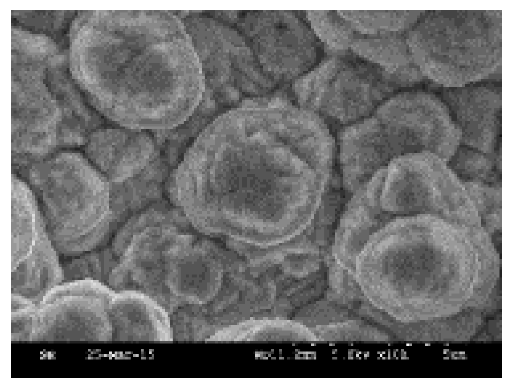


PVD process to mimic real SEI

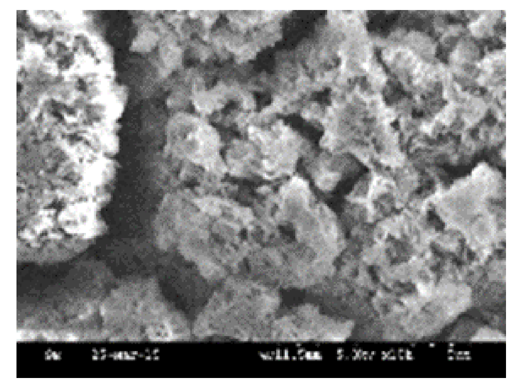
Artificial SEI	F concentration before cycling	F concentration after cycling
SEI1	30%	30%
SEI2	6%	5%
SEI3	<1%	<1%



SEI1-after cycle



SEI1-after cycle



- **Higher LiF concentration leads to denser and more stable SEI formed on Si surface, and higher cycle efficiency.**

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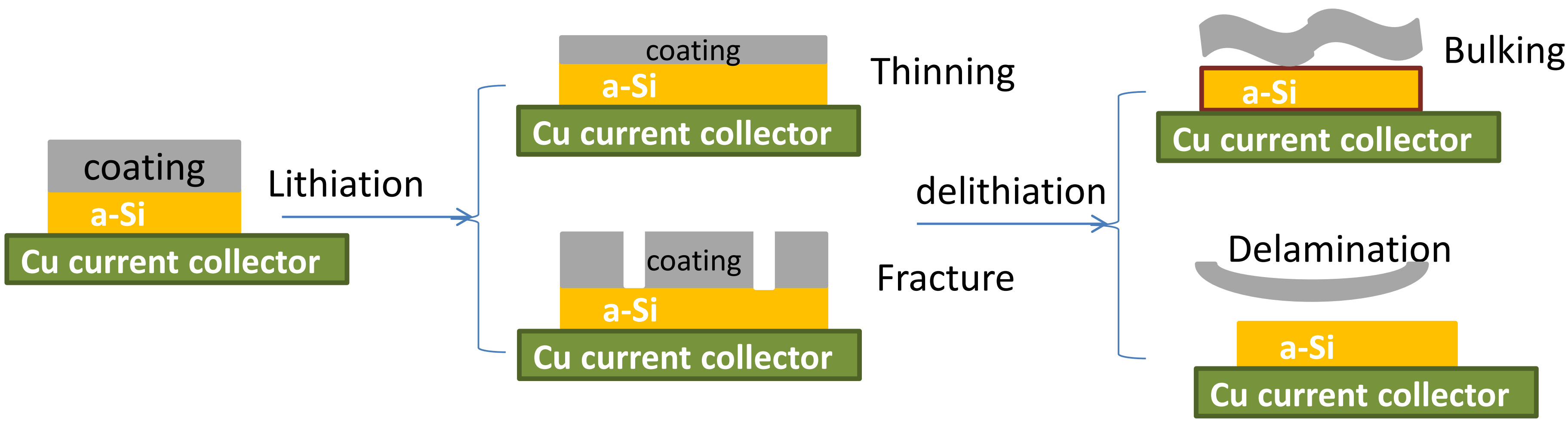
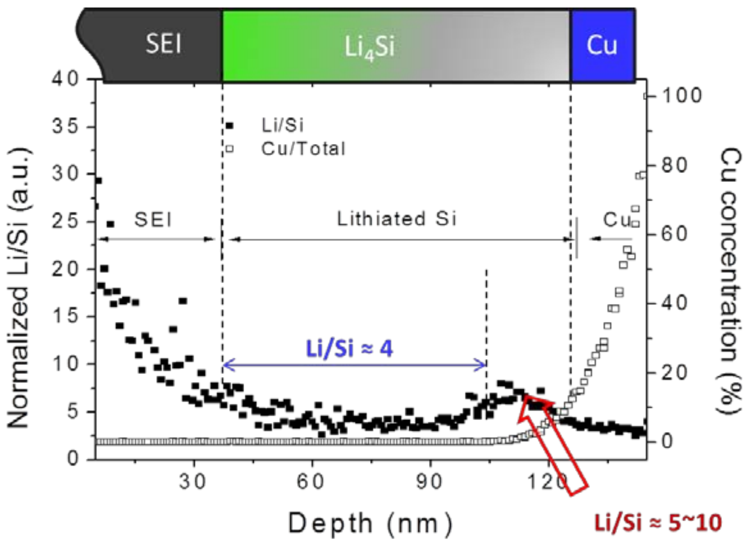
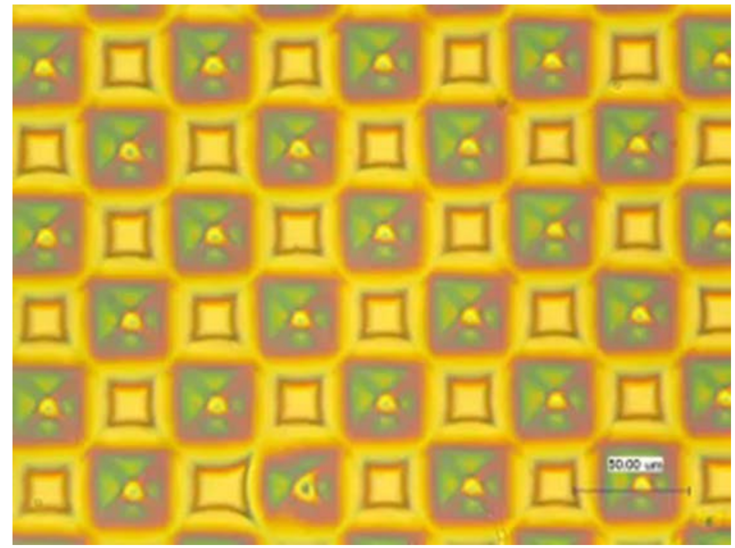
II. Systematic approach to identify SEI failure mechanisms (ongoing effort)



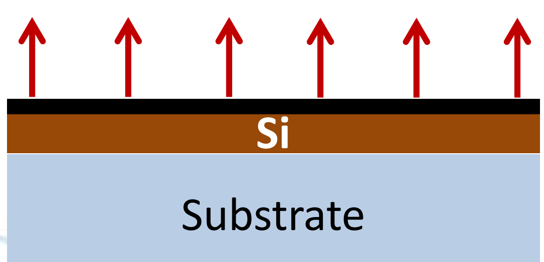
Using model system and simulations to investigate coating mechanical failure mechanisms

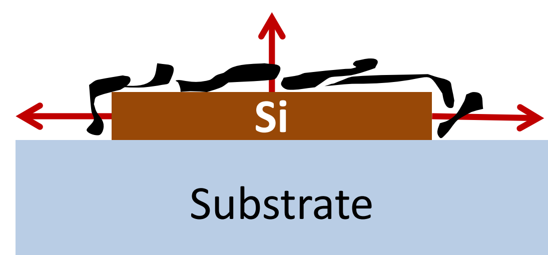
Accomplishment 2.1: Developed a new approach to systematically investigate SEI failure mechanisms with patterned Si films



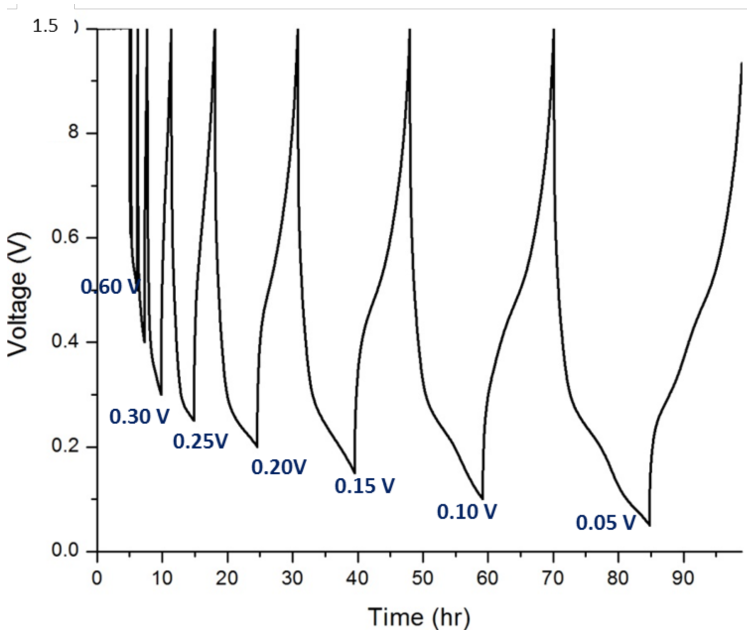


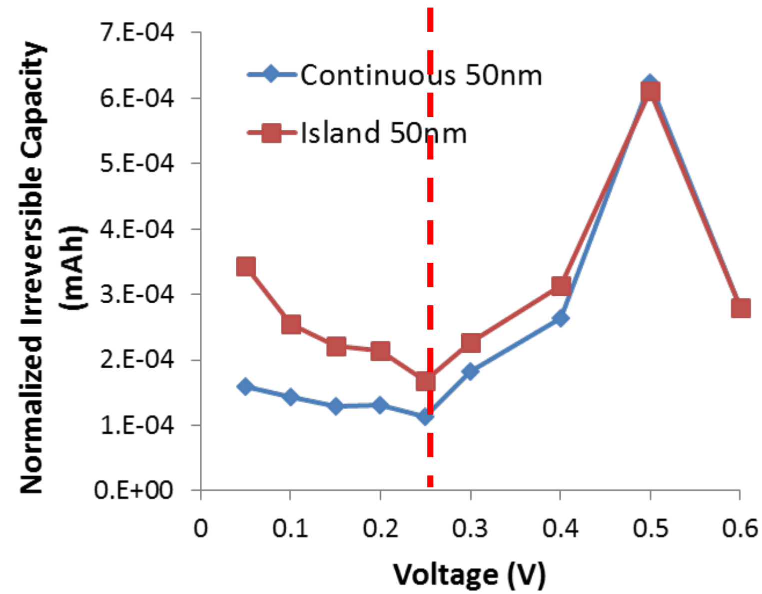
***Nano Letters**, 13 (10), 4759 (2013)*





Accomplishment 2.2: Identified SEI failure mechanism at initial stage





Absolute irreversible capacity shows a sharp rise around 0.25V for patterned sample indicating that SEI may become mechanically unstable (crack formation etc.) and hence more SEI formation

The patterned island system provides a sensitive and effective approach to investigate SEI mechanical response during cycling.

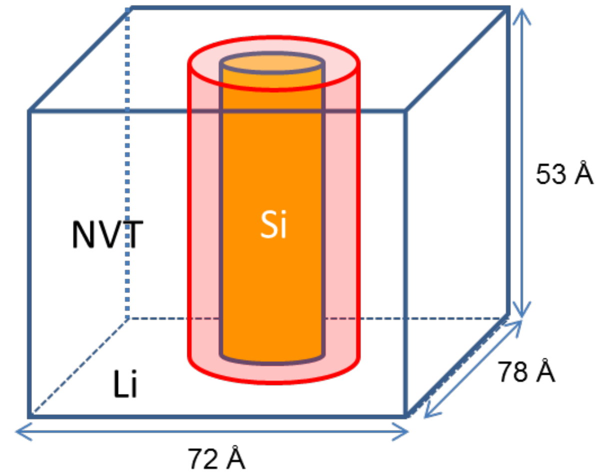
Accomplishment 2.3: Developed ReaxFF for molecular dynamics simulations to reveal mechanically stable coating thickness

DFT computed
Formation Energies
Diffusion Barriers
Equation of states

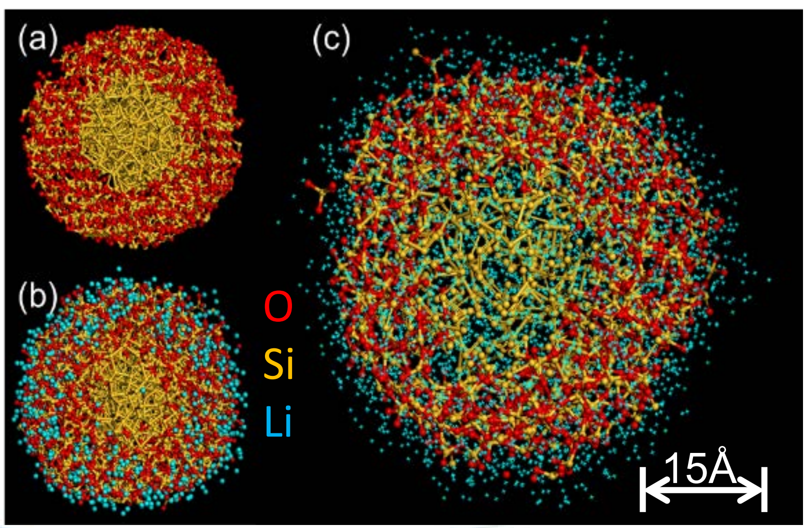
→

ReaxFF
Parameterized
for Li-O-Si-Al

→



Lithiation of SiO_2 and Al_2O_3 covered Si nanowires



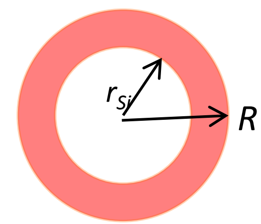
Compare different shell thickness
2.5 Å
4.5 Å
7.5 Å

Revealed the chemical and mechanical evolution within lithiation process.

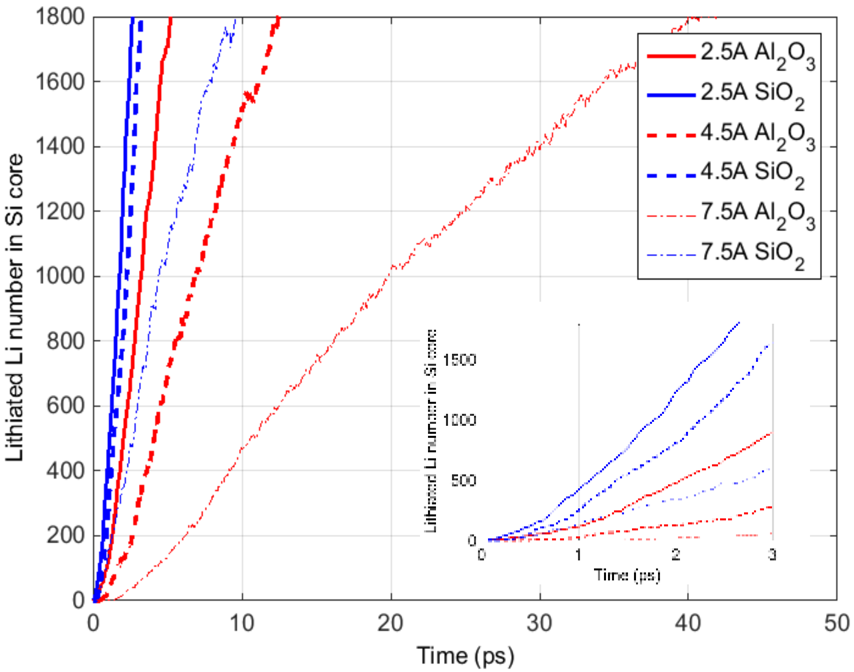
Accomplishment 2.4 : Identified the impact of the coating on the lithiation kinetics and mechanics of Si core

$$0 < r < r_{Si} \qquad \frac{\partial \Theta_{Si}}{\partial t} = D_{Si}\left(\frac{\partial^2 \Theta_{Si}}{\partial r^2} + \frac{1}{r}\frac{\partial \Theta_{Si}}{\partial r}\right)$$

$$r_{Si} < r < R \qquad \frac{\partial \Theta_{\beta}}{\partial t} = D_{\beta}\left(\frac{\partial^2 \Theta_{\beta}}{\partial r^2} + \frac{1}{r}\frac{\partial \Theta_{\beta}}{\partial r}\right)$$

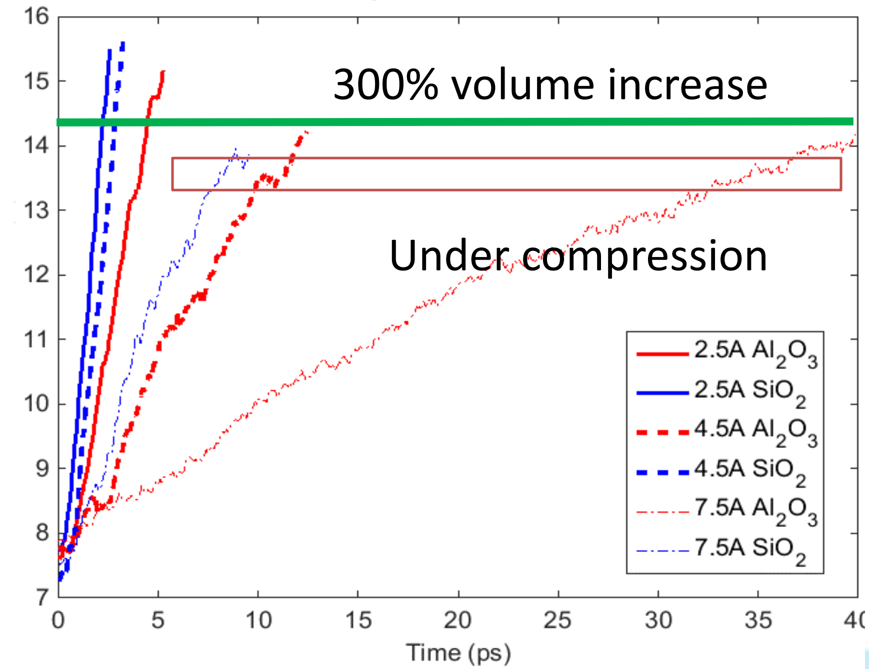


Li diffusion in Al_2O_3 is slower than in SiO_2



(a) Number of Li in the core

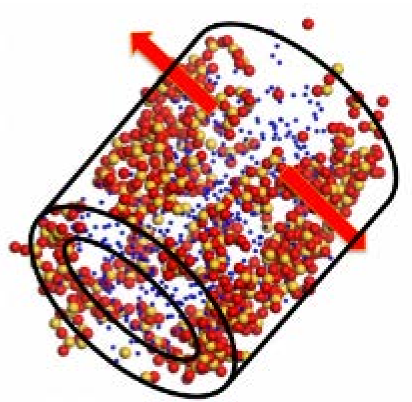
Thicker coating can better confine Si expansion during lithiation.



(b) Radius of the lithiated core

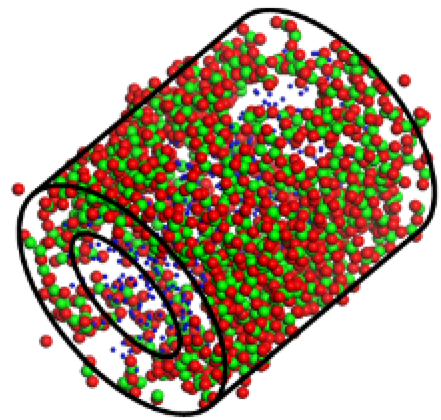
Accomplishment 2.5 : Identified the coating failure mechanisms during lithiation

Broken Shell



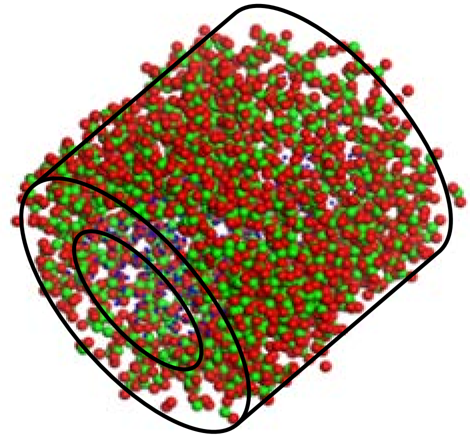
4.5Å SiO_2
2.5Å SiO_2
2.5Å Al_2O_3

Cracked Shell

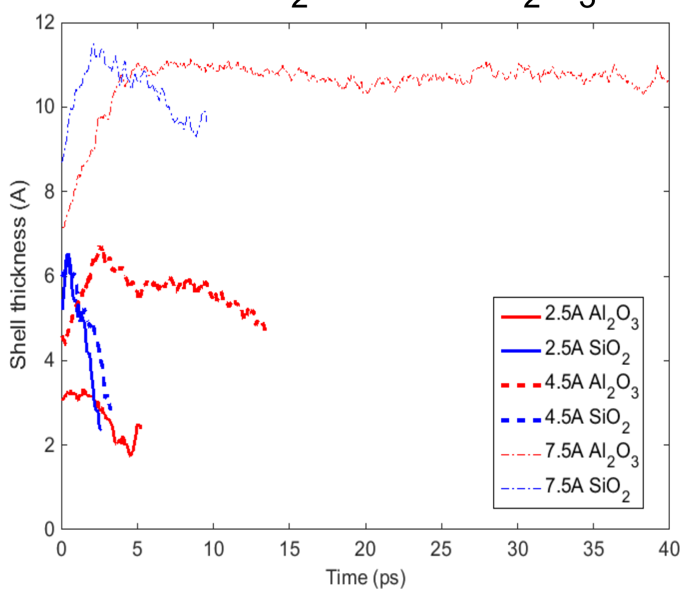


7.5Å SiO_2 4.5Å Al_2O_3

Mechanically Intact Shell



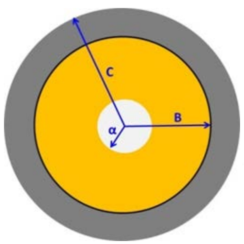
7.5Å Al_2O_3

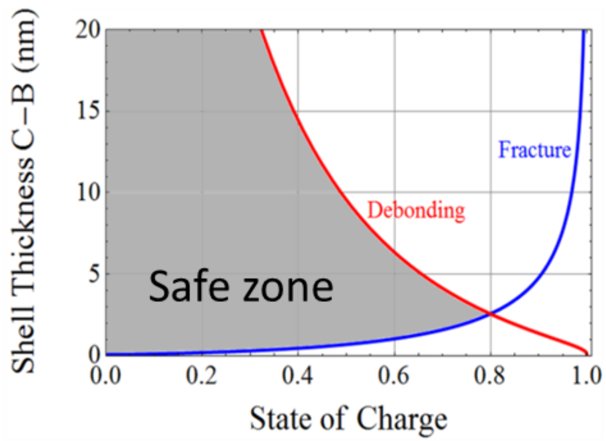


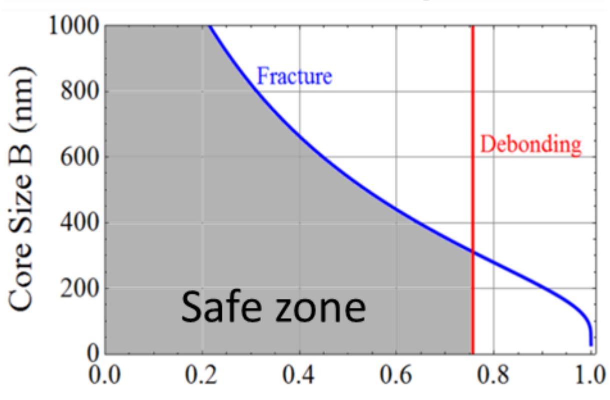
With proper thickness to size ratio, combining the right coating material, the mechanical stability can be achieved

III. Design Si structures toward practical porous electrode with high coulombic efficiency

Core-Shell

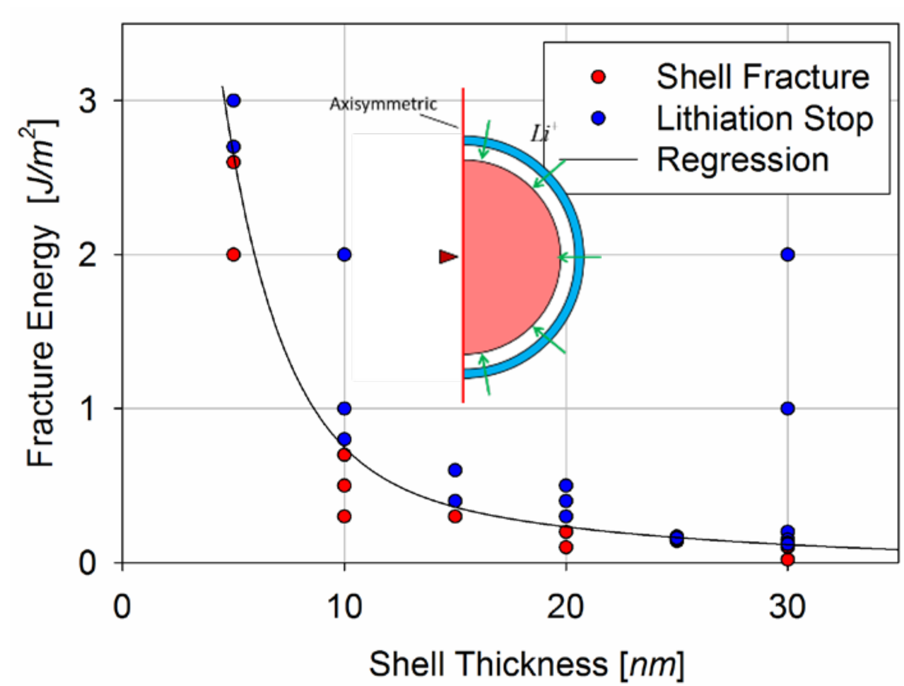






Si/C has strong interface and established a design map for core-shell structure

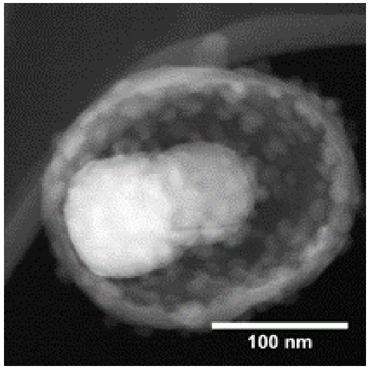
York-shell

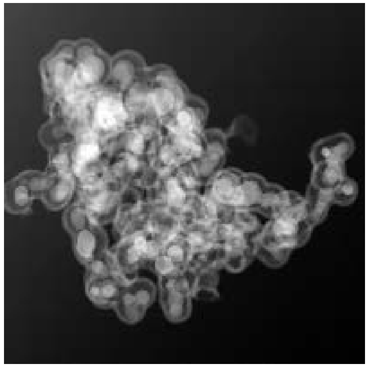


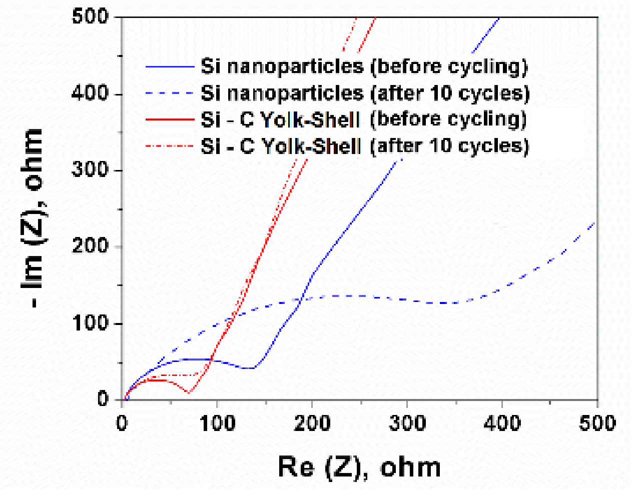
Continuum mechanical model identified the critical shell thickness of lithiation in Si-C yolk-shell structure

Nano Letters, 14 (4), 2140–2149 (2014)

Accomplishment 3.1. Synergetic design of surface coating with Si size/geometry/architecture toward practical electrode

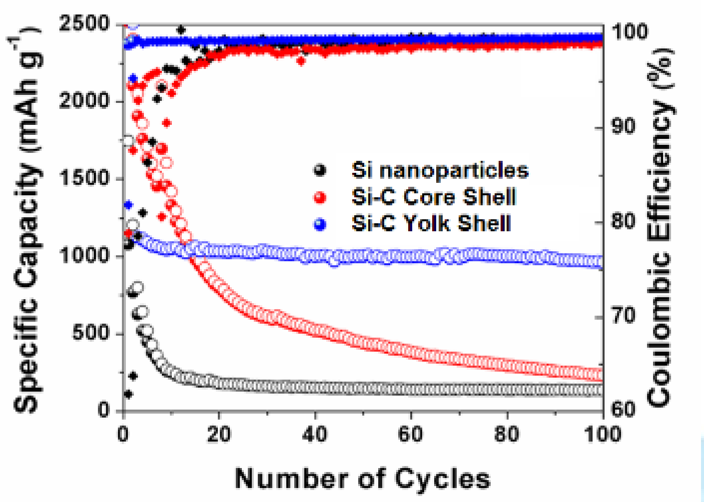






Benefits of yolk-shell structure:

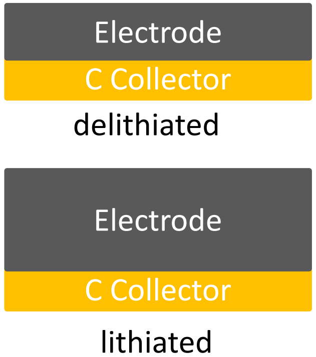
- Accommodate Si volume expansion
- Stabilize SEI layer
- Improve electrical conductivity
- Enhance Electrode integrity

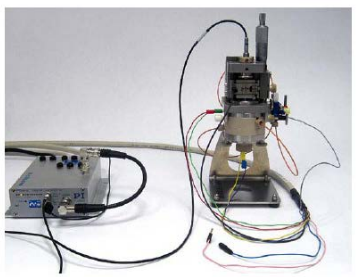


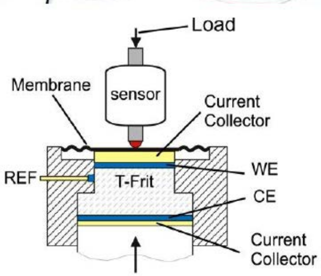
*Next: Optimize the geometry design based modeling insights

Adv. Fun. Mater. Vol. 5 (2015), 1426-1433

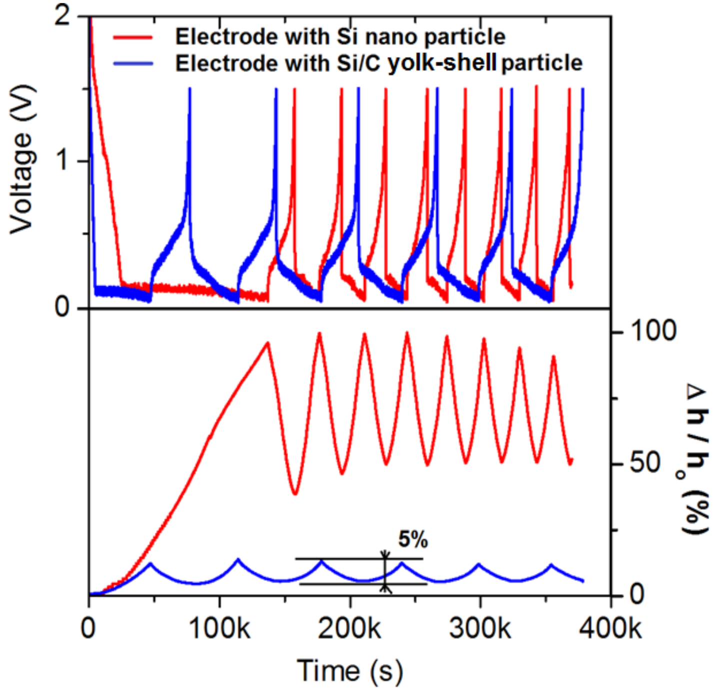
Minimized Volume Expansion at Electrode Level

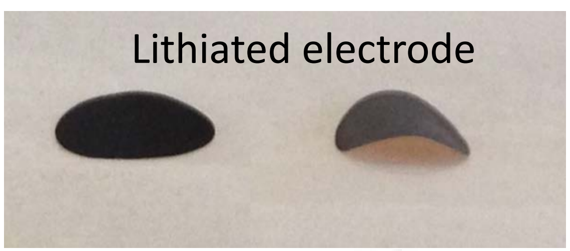






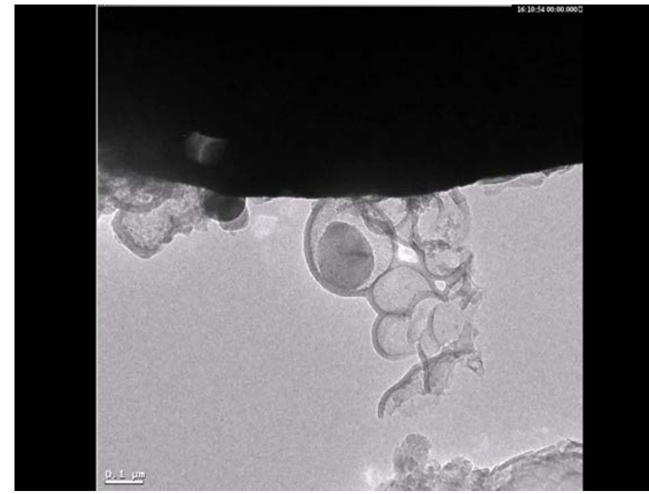
In-situ EC Dilatometer





Electrode made with Yolk-shell Si/C

Electrode made with Si nanoparticles



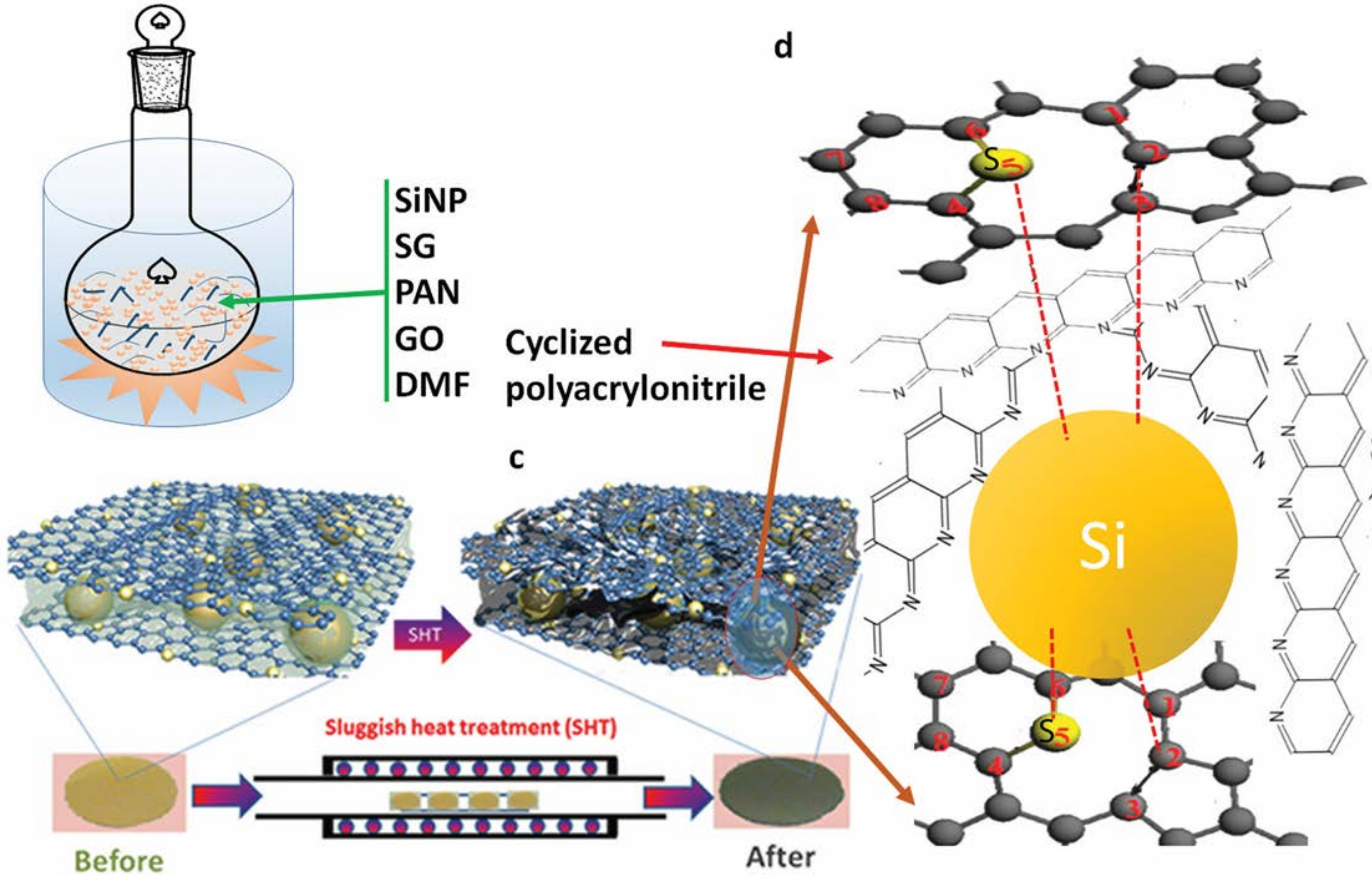
In-situ TEM

The core shell structure with free space suppresses the breathing effect of electrodes during the charge-discharge process, and should minimize the damage to taps in battery packs.

Adv. Funct. Mater. Vol. 5 (2015), 1426-1433

Accomplishment 3.2 : Established 3D network structure to stabilize both Si and SEI layers

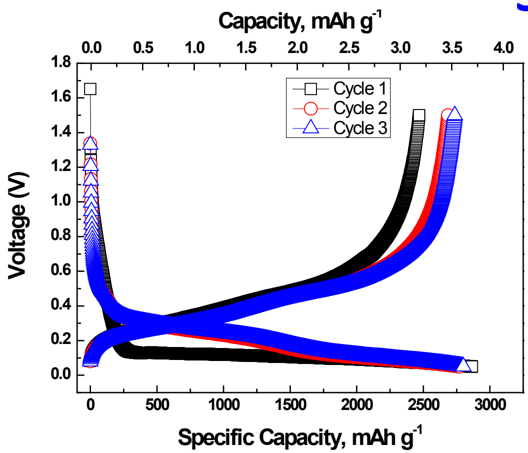
Collaboration with Prof. Zhongwei Chen, U. Waterloo

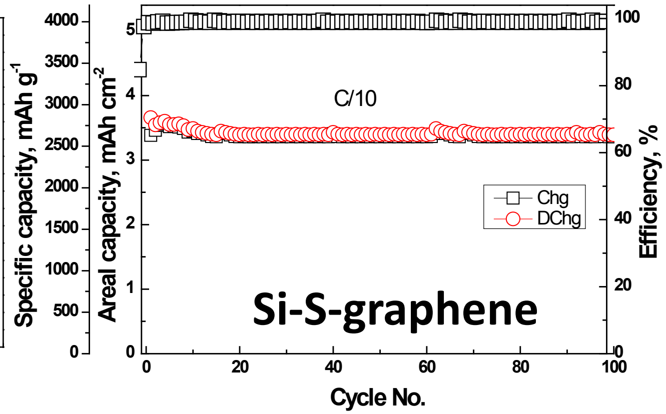


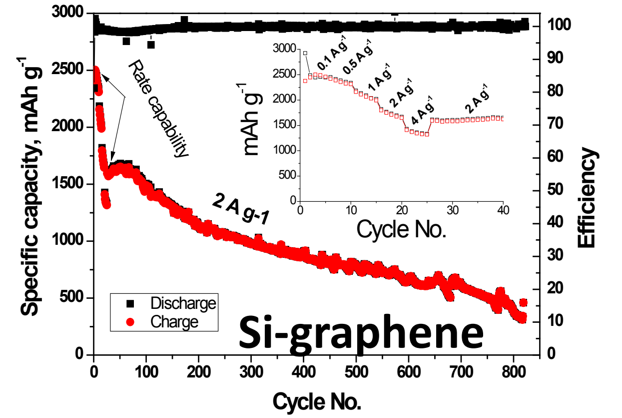
Mixing under ultrasonic irradiation → Coating → Sluggish heating to 450 ^{o}C → Hold 10 min. → Furnace cool

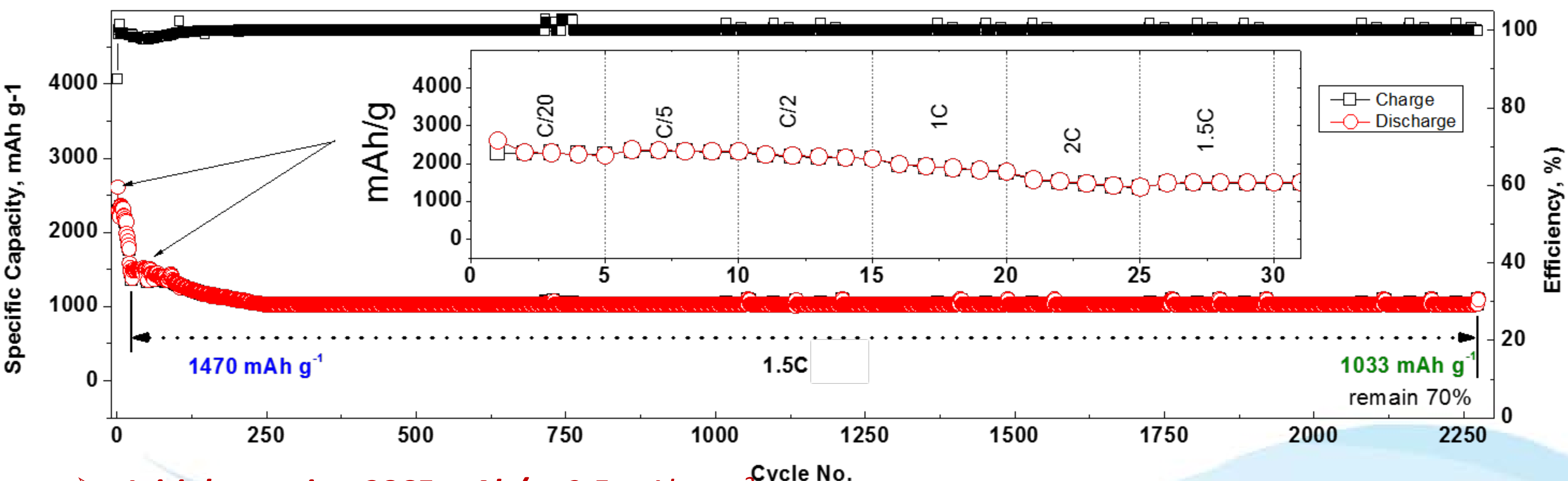
Nature Communications, submitted, 2015.

Accomplishment 3.2: Established 3D network structure to stabilize both Si and SEI layers









- ***Initial capacity: 2865 mAh/g;*** *3.5 mAh cm^{-2}*
- *Excellent rate capability @ 2 A g^{-1}, 1033 mAh g^{-1}, for 2200 cycles*

Nature Communications, submitted, 2015.

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Collaborations and Coordination with Other Institutions

Berkeley Lab	Apply advanced binders to improve electrode integrity, also characterize their mechanical properties utilizing the in-situ electrochemical approaches developed in this project;
Pacific Northwest National Laboratory	Investigate the stability of artificial SEI on Si nanoparticles using *in-situ* TEM;
NREL National Renewable Energy Laboratory	Investigate the mechanical properties of advanced surface coating as artificial SEI utilizing in-situ electrochemical approaches and modeling;
Sandia National Laboratories	Conduct large scale *ab initio* MD simulation of electron transport through ALD coatings to predict electrolyte reduction reactions rates;
Precision + Structure NEES	Conduct interface modeling for Si-CNT bead-string nano-structures;
University of Waterloo	Develop novel Si nanostructure, leveraged by Canada NSERC CRD funding and GM support.

Response to reviewers' comments last year

- The proposed future research as too physical, and added that some characterizations of the chemical nature of materials are recommended through collaborations.

  Response: We have put more efforts into characterizing the chemical composition and structure of the SEI layer and Si nanostructures (XPS, ToF-SIMS, HRTEM, EELS), and coordinating the chemistry, structure, and electrochemical performance. We have also expanded our collaboration with national labs and universities.

- The relevance would be improved with better attention to accuracy and uniformity of materials and coatings.

  Response: We focused more on naturally formed SEI, the mature ALD chemistry, and practically useful Si/C Yolk-shell, and Si/Graphene nanocomposites.

- It was hard to see how the funds supported the level of effort.

  Response: Although the funds are limited (one PI and 4 co-PIs, one company and 3 universities), we managed to support 2 postdocs and 3 graduated students, and extended the collaboration with other PIs under the BMR program. GM is also supporting one summer intern each year, hosting the visiting students, and covering materials expense at GM.

Summary

- Experimental approaches combined with MD simulations have been developed to investigate the mechanical properties of ultrathin natural formed SEI and artificial SEI layers, and validated by the tests on ALD-Al_2O_3 coating.
- By comparing the performance of various synthesized surface coatings of natural SEI components, we suggest that the desirable SEI should have high LiF concentration, uniform SEI morphology, high Young's modulus, and low impedance.
- A combined DFT and continuum model has been developed to predict the mechanically stable Si-C core-shell structures, which stabilize the SEI layer and accommodate the volume expansion of Si. As a result, the breathing effect of electrodes has been significantly suppressed.
- These results allowed us to make a "Go" decision that multi-component and multi-functional artificial SEI coatings paired with a variety of Si nanostructure can be mechanically and chemically stable.

Future Plans

- Apply the continuum model to search for material property design space for the most stable SEI, and experimentally tailor the coating properties accordingly to validate the model.
- Correlate and determine the desirable material properties for stable SEI, by applying the continuum model and experimental nanomechanics. Establish the material property design methodology for stabilizing SEI on Si.
- Vary SEI chemistry and perform property predictions at QM and MD levels to investigate structure-chemistry-property relationship of SEI on Si.
- Make Go/No-Go decision on whether to adjust the critical parameters of SEI layer and core-shell structure to maximize the synergetic effect of coating and architecture.

Publications

1. X. Xiao*, W. Zhou, I. Ryu, M. Gu, C. Wang, G. Liu, H. Gao, Regulated Breathing Effect of Silicon Negative Electrode for Dramatically Enhanced Performance of Li-ion Battery, Advanced Functional Materials, 2015, 2015, Vol.25, 1426–1433.
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7. F. M Hassan, V. Chabot, A. R. Elsayed, X. Xiao, Z. Chen, Engineered Si electrode nano-architecture: A scalable treatment for the production of next-generation Li-ion batteries, *Nano Letters*, 2014, 14 (1), 277–283
8. A. Tokranov, X. Xiao, P. Lu, B. W. Sheldon, The origin of stress in the solid electrolyte interphase on carbon electrodes for Li ion batteries, *Journal of Electrochemistry Society*, 2014,161 (1), A58-A65
9. S. Kim, Y. Qi , "Property Evolution of Al2O3 Coated and Uncoated Si Electrodes: A First Principles Investigation", Journals of the Electrochemical Society, 161 (11) F3137-F3143 (2014)
10. Q. Zhang, X. Xiao, Y. Cheng, and M. W. Verbrugge "A non-destructive method to measure the mechanical properties of ultrathin film prepared by atomic layer deposition", Applied Physics Letters, 105, 061901 (2014)
11. Q. Zhang, X. Xiao, W. Zhou, Y. Cheng, M. W. Verbrugge, "Towards High Cycle Efficiency of Silicon-Based Negative Electrodes by Designing Solid Electrolyte Interphase", Advanced Energy Materials, 10.1002/aenm.201401398 (2014)
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13. F, M Hassan, A. Elsayed, V. Chabot, R. Batmaz, X. Xiao, and Z. Chen, "Subeutectic Growth of Single-Crystal Silicon Nanowires Grown on and Wrapped with Graphene Nanosheets High-Performance Anode Material for Lithium-Ion Battery", ACS Appl. Mater. Interfaces, 6 (16), pp 13757–13764 (2014)
14. A. Tokranov, B.W. Sheldon, C.Li, S. Minne, and X. Xiao, "In Situ AFM Study of Initial SEI Formation on Silicon Electrodes for Li Ion Batteries", ACS Applied Materials & Interfaces 6, 6672-6686 (2014).
15. V. Chabot, K.Feng, H. W. Park, F. M Hassan, A. R. Elsayed, A. Yu, X. Xiao*, Z. Chen, Graphene wrapped silicon nanocomposites for enhanced electrochemical performance in lithium ion batteries, Electrochimica Acta 130, 127-134 (2014)
16. F. M Hassan, V. Chabot, A. Elsayed, X. Xiao, Z Chen, Engineered Si electrode nano-architecture: A scalable treatment for the production of next-generation Li-ion batteries, Nano Letters, 2014, 14 (1), 277–283
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Invited talks

1. Yue Qi, “Defect facilitated electron leakage through the solid electrolyte interphase in Li-ion batteries” Invited talk at 248th ACS, Division of COMP, SESSION: Modeling and Simulations of Electrochemical Interfaces and Materials for Energy Storage, August 2014.
2. Yue Qi, “Integrating State of Charge (SOC) Dependent Material Properties into Li-ion Battery Failure Modeling”, Invited talk at 248th ACS : Division of ENFL: Applications of Theoretical Chemistry for Energy and Fuel Production. August 2014.
3. Yue Qi, “ Predicting the transport and mechanical properties of the solid electrolyte interphase (SEI) in Li-ion batteries.” Chemical and Biomolecular Eng. Department, University of Tennessee, Knoxville, TN. November 25, 2014
4. Yue Qi, “ Predicting the transport properties of the solid electrolyte interphase (SEI) in Li-ion batteries”. MRS 2014 Fall Meeting, Boston, MA. Dec, 02, 2014.
5. Yue Qi, “Predicting interface properties in Li-ion batteries”, 1st International Symposium on Energy Challenges and Mechanics, Aberdeen, Scotland, UK, July 8-10, 2014
6. Xingcheng Xiao, “Understanding Degradation Mechanism of Silicon Based High Energy Density Electrode Materials for Lithium Ion Batteries” 64thCanadian Chemical Engineering Conference, Niagara Falls, ON, October 21, 2014 (Keynote Lecture)
7. Xingcheng Xiao, “Toward high cycle efficiency of high energy density lithium ion batteries”, Invited talk at 249th ACS : Division of ENFL: Applications of Theoretical Chemistry for Energy and Fuel Production. March 2015.
8. Huajian Gao, "Modeling mechanical degradation in thin film electrodes for high energy density lithium batteries," Invited Talk, Prager Medal Symposium in Honor of Professor Robert M. McMeeking, The 51st Annual Technical Conference of the Society of Engineering Sciences, October 1-3, 2014, Purdue University.
9. Huajian Gao, "Modeling mechanical degradation in thin film electrodes for high energy density lithium batteries", Keynote Lecture, 1st International Symposium on Energy Challenges & Mechanics, July 8, 2014.
10. Huajian Gao, "Mechanical degradation in sliding thin film electrodes", Invited Talk, Symposium P: Lithium Ion Batteries, MRS Spring Meeting, April 22, 2014.
11. Yang-Tse Cheng, “Surface Engineering for Improving the Performance and Durability of Lithium Ion Batteries,” 41st International Conferences on Metallurgical Coatings and Thin Films, San Diego, California, April 29, 2014.
12. Yang-Tse Cheng, “Understanding coupled mechanical-chemical degradation mechanisms for improving the performance and durability of lithium ion batteries,” Seminar, Materials Science and Engineering, Northwestern University, Evanston, Illinois, June 3, 2014.
13. Yang-Tse Cheng, Rutooj Deshpande, Juchuan Li, Yunchao Li, Qinglin Zhang, Jie Pan, Jiagang Xu, Mark W. Verbrugge, Xingcheng Xiao, Yue Qi, and Steve Harris, “Understanding diffusion-induced stress and fracture for improving the performance and durability of lithium ion batteries,” 2014 Battery Congress, Troy, Michigan, June 11, 2014.
14. Brian W. Sheldon, “Electrochemically Induced Stresses in Energy Storage Materials”, 225th Electrochemical Society Meeting, Orlando, Florida, May 13, 2014.
15. Brian W. Sheldon, “Electrochemically Induced Stresses in Ceramics for Energy Applications”, XII International Conference on Nanostructured Materials, Moscow, Russia, July 14, 2014.
16. Brian W. Sheldon, “Electrochemically Induced Stresses in Energy Storage Materials”, Electrochemical Strain Microscopy Workshop, Oak Ridge National Lab, September 15, 2014
17. Brian W. Sheldon, “Electrochemically Induced Stresses in Energy Storage Materials”, Electrochemical Strain Microscopy Workshop, Oak Ridge National Lab, September 15, 2014.
18. Brian W. Sheldon, “Electrochemically Induced Stresses in Energy Storage Materials”, Society of Engineering Science Annual Meeting, Purdue University, October, 1 – 3, 2014.

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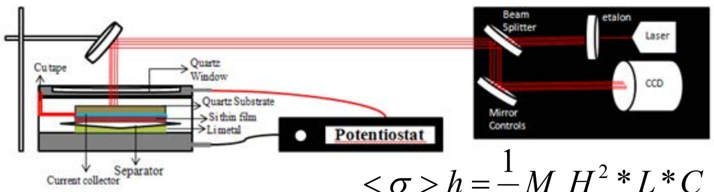
- Peng Lu for TOF-SIMS

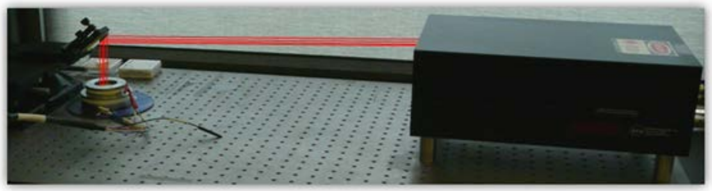
Backup Slides

In-situ experimental approaches to investigate SEI and Si mechanical behavior and validate the models



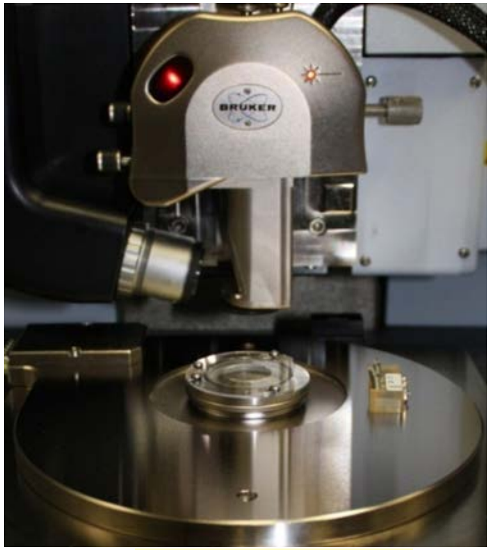
$$\langle \sigma \rangle h = \frac{1}{6} M_s H_s^2 * L * C \quad \alpha * M$$

Schematic of experimental set up



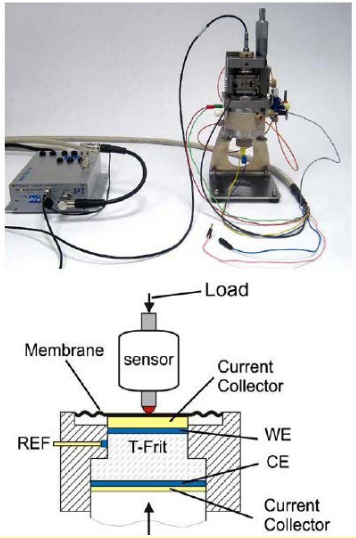
Actual Experimental Set up

Moss to investigate stress evolution

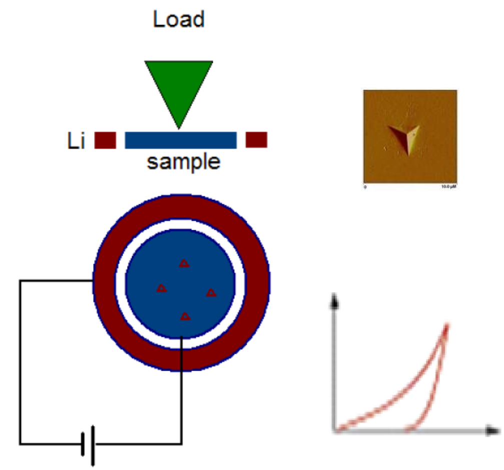


In-situ AFM

Optical Microscope



In-situ electrochemical dilatometer



Nanoindentation

Initial Mechanics Analysis

The size limit to mitigate each failure mechanism resulting in SEI instability is derived from solid mechanics.

- **Fracture of Si particles**

$$l_{frac} \propto \left(\frac{\Gamma(1-\nu)F^2 D^2}{E(1+\nu)\Omega^2 I^2} \right)^{1/3}$$

- **SEI peel-off from Si particles during lithiation**

$$l_{delam} / \sqrt{h} \propto \sqrt{E\Gamma_{\text{int}} / \tau_{\text{int}}^2}$$

- **Buckling delamination during delithiation**

$$l_{buckle} = \frac{(\alpha_1\Gamma_{\text{int}} + \alpha_2\Gamma)(1+\nu)(1-2\nu)}{2\pi E \varepsilon_0^{\,2}}$$

Ω: partial molar volume of Li in Si, D: Li diffusivity,
E: Young's modulus, υ: Poisson ratio,
Γ : fracture energy of lithiated Si, Γ_{int}: interfacial delamination toughness,
τ_{int}: interfacial sliding strength, H: SEI film thickness,
I: surface current density, F: Faraday's constant.

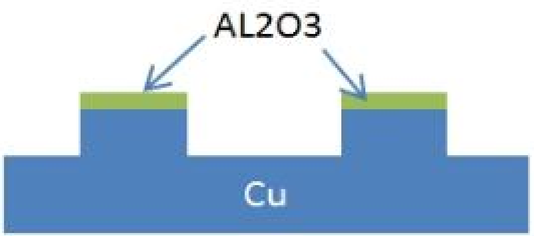
Missing: failure mechanisms and material properties are required in order to DESIGN SEI and Si nanostructures.

Require: Experimental validation

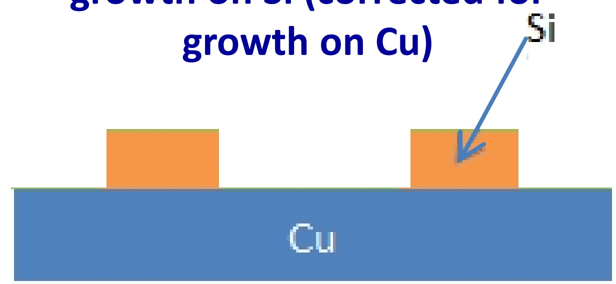
Established experimental methods to decouple volume change caused by SEI formation and lithiation of Si

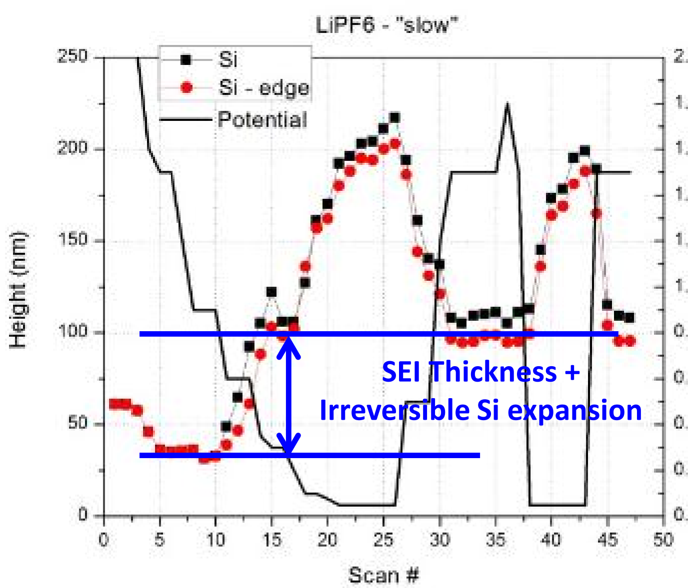
In Situ AFM and in-situ stress sensor

Configuration to measure SEI growth on Cu



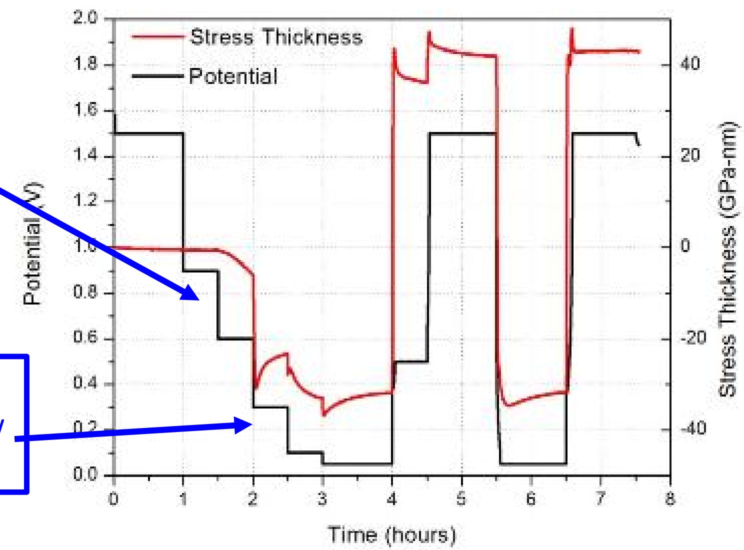
Configuration to measure SEI growth on Si (corrected for growth on Cu)



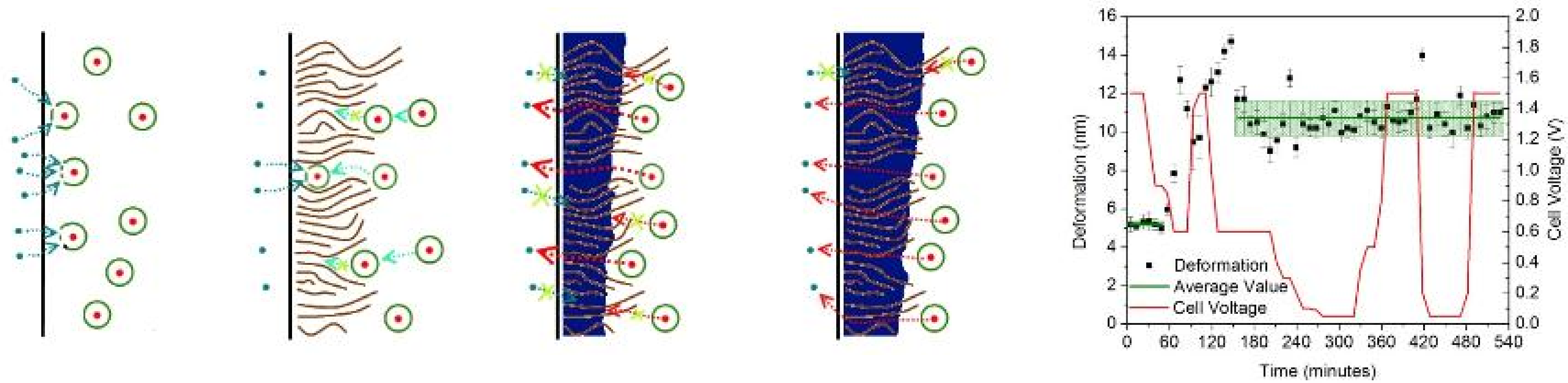


SEI formation begins at 0.6V

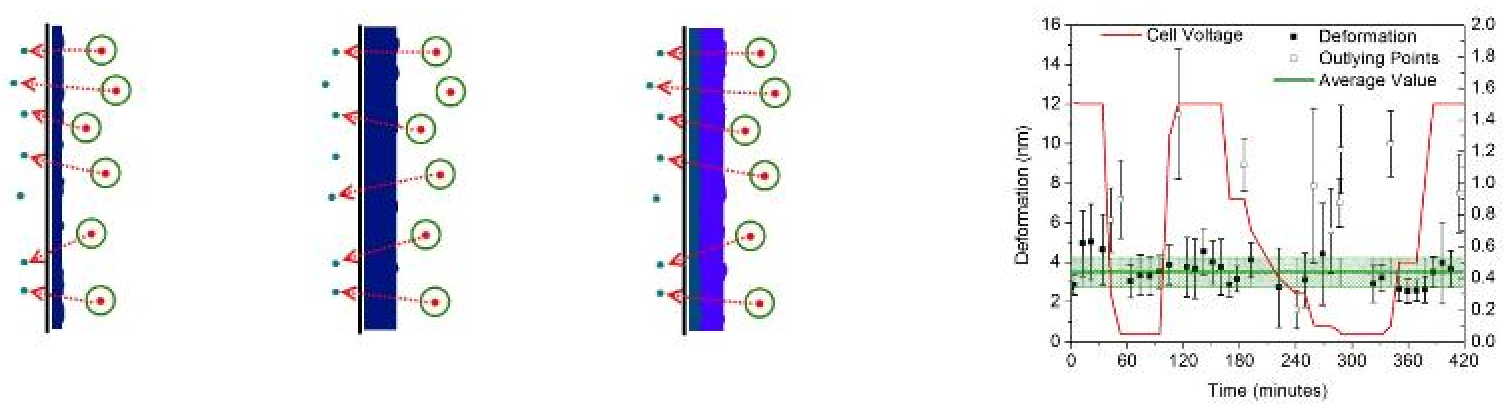
Stress relaxes through plastic flow to a certain level



An Expanded Model of Initial SEI Formation



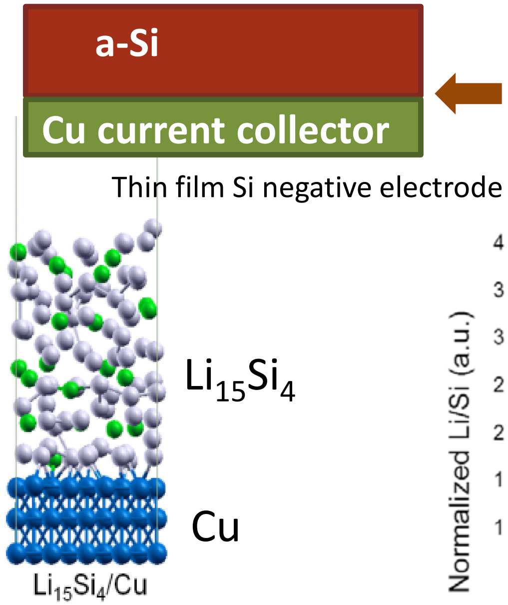
SEI growth with a slow first cycle: Initially organic SEI formed and grown, then inorganic SEI filled in the organic SEI at lower potential which allows Li ion diffusion, eventually most of the SEI is composed of inorganic materials.

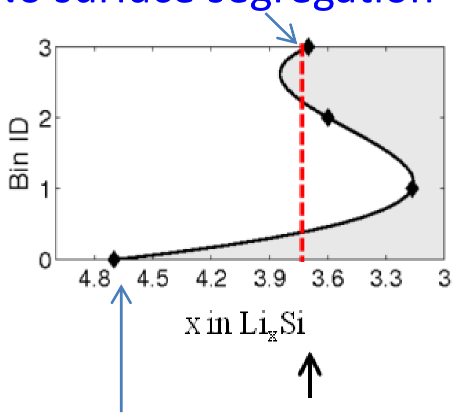


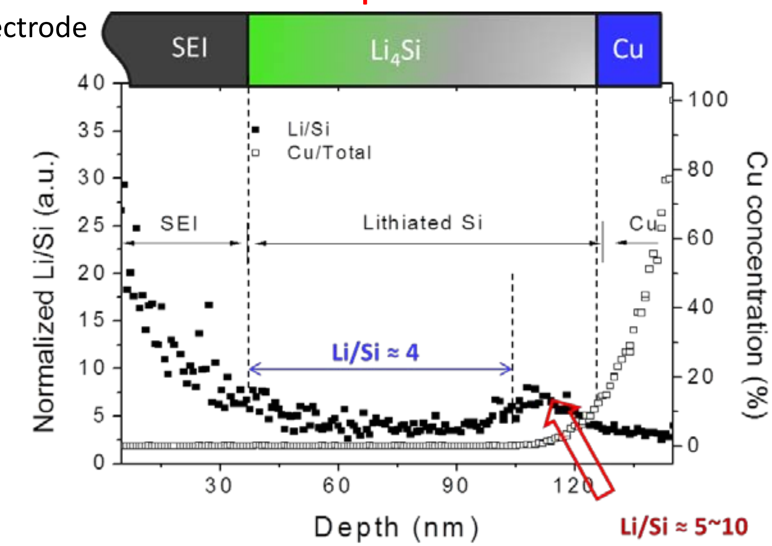
SEI growth with a fast first cycle: organic SEI does not have time to form instead creating inorganic passivation which prevents further organic SEI from forming. This SEI keeps increasing in thickness, over several cycles.

ACS Appl Mater & Interfaces (2014).

Understanding interfacial sliding in patterned Si model system







Method: *Ab initio* MD simulations
Results: Li segregation due to charge transfer from Li to Cu..

Method: TOF-SIMS depth profile
Results: High Li/Si ratio at the Si/Cu interface

- **Adhesion strength is reduced from 1.85 to 1.53 J/m^2 after full lithiation.**
- **Interface sliding resistance is reduced from 0.28 to 0.03 GPa upon full lithiation**
- **Stress buildup is released by interfacial sliding.**

Nano Letters, *13 (10), 4759 (2013)*

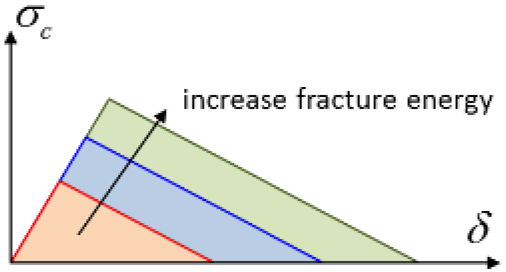
Established design guidance for stabilizing the shell

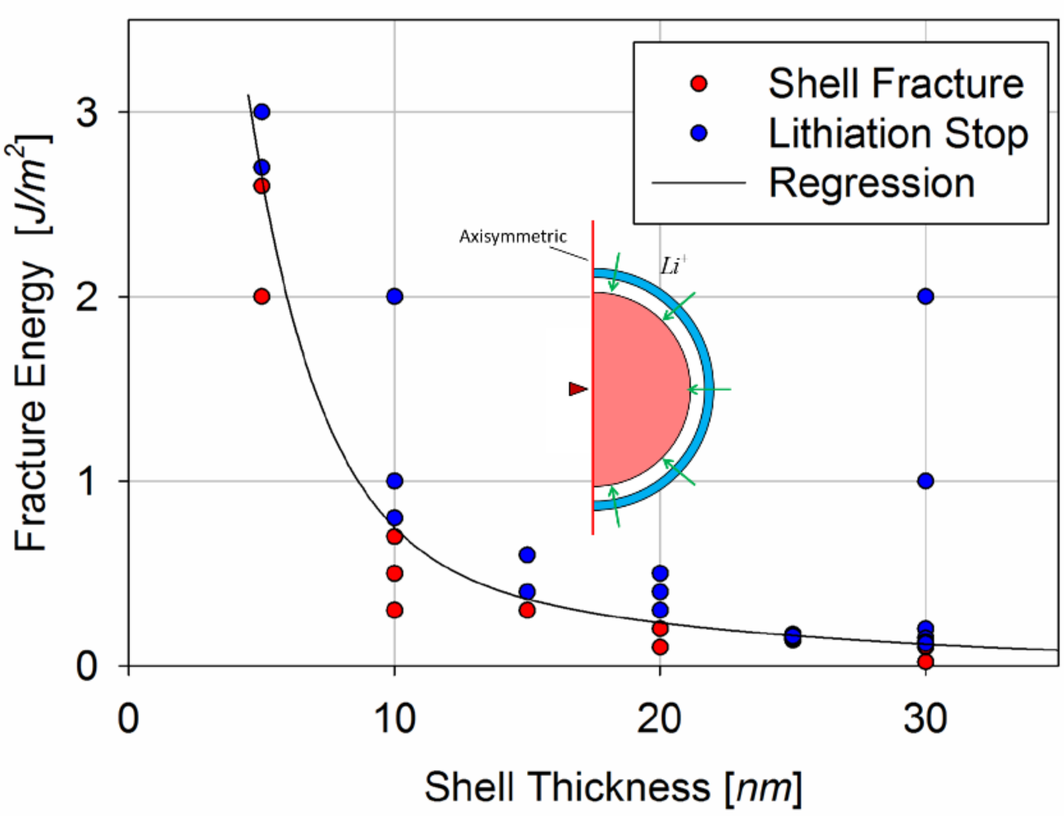
- Model Description

- Diffusion :

$$\hat{D} = D_0 \left[\frac{1}{1-\bar{c}} - 2\,\Omega\,\bar{c} \right] e^{\alpha V_p \sigma_b / RT}$$

- *Rout* = 220~250[*nm*], *rcore*= 75[*nm*]
- *tshell*= 5~30 [*nm*],
- Finite deformation formulation
- Galvanostatic boundary :
- W/ or W/O adhesive contact
- Bilinear cohesive model



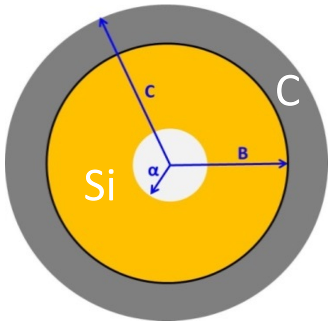


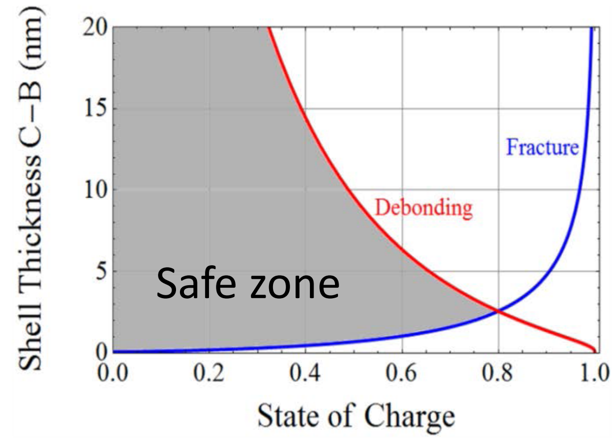
Critical shell thickness from the finite element simulations of lithiation in a Si-C yolk-shell structure

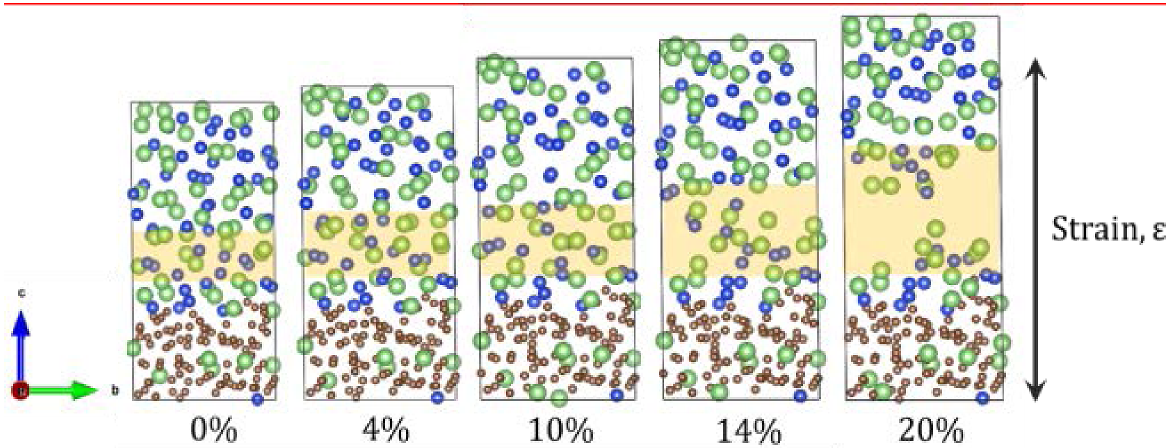
Proved Si/C has strong interface and established a design map for core-shell structure

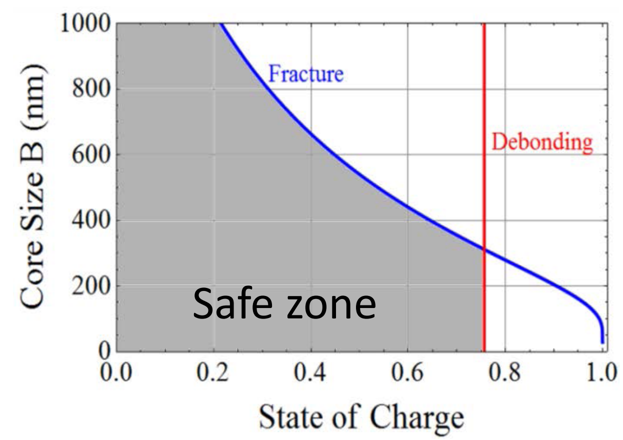
Method:

- DFT predicts debonding and Li_xSi fracture energies as a function of SOC
- Continuum model for optimizing geometry









Results:

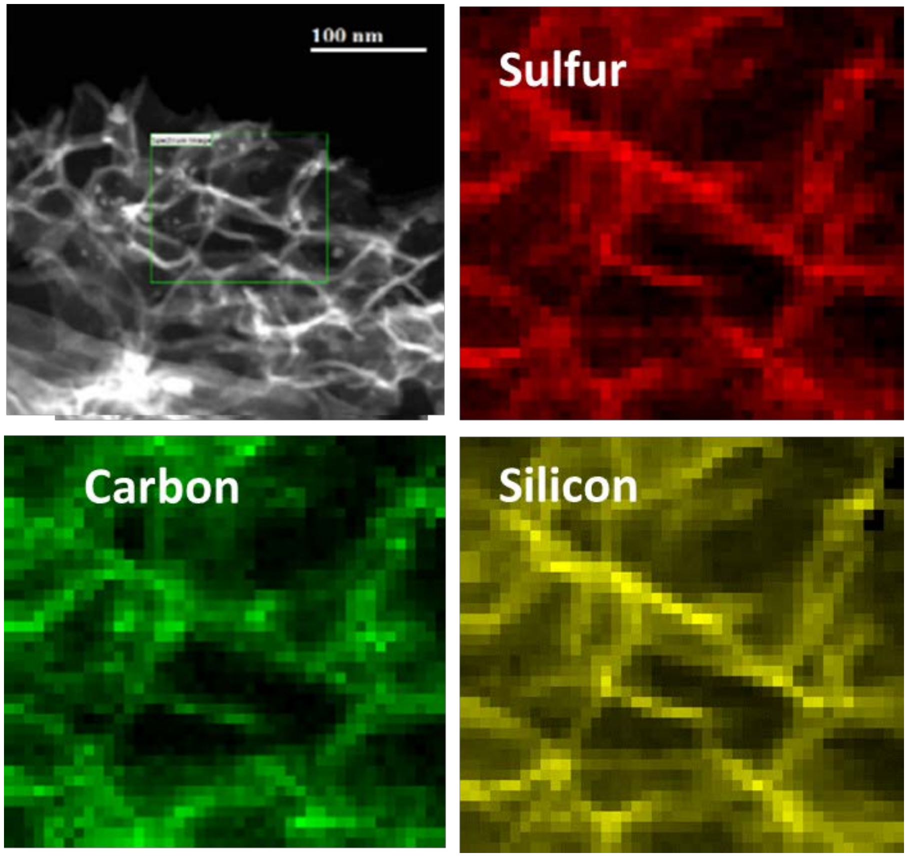
No Li segregation at Si/C interface, fracture occurs inside LixSi instead of Si/C interface.

The safe zone: Core thickness < 200 nm, Shell thickness ~ 10 nm.

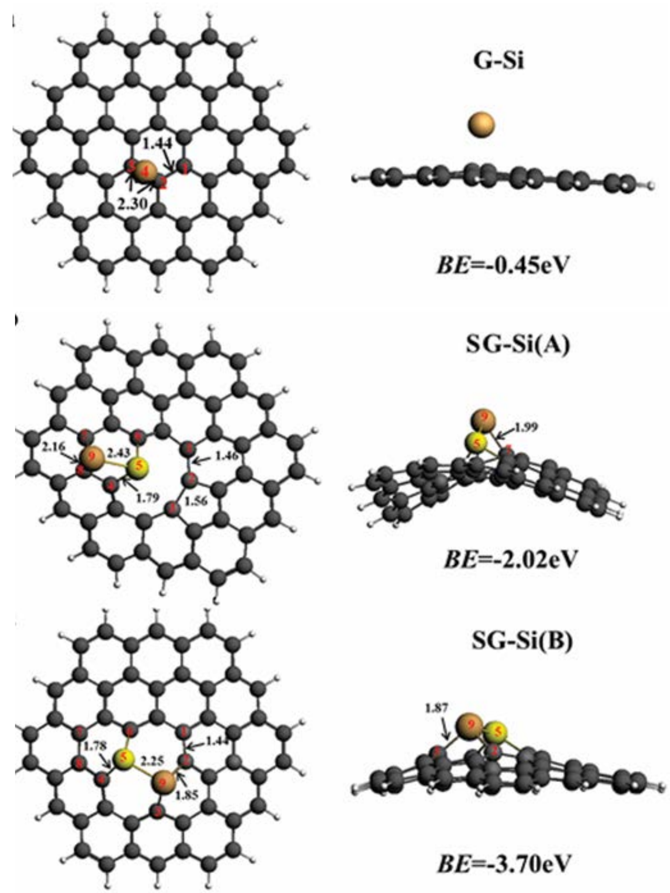
Nano Letters, 14 (4), 2140–2149 (2014)

3D network structure to stabilize both Si and SEI layers

Structure after Cycling



Crystalline silicon <u>by cycling</u> turn to amorphous nanowire-like structure caged in synergistic 3D of SG and caged by cyclized Polyacrylonitrile



DFT calculation showed that Silicon binds to S-graphene 8 times stronger than its binding to graphene

Nature Communications, submitted, 2015.