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

Xingcheng Xiao

General Motors Global R&D Center

Yue Qi

Michigan State University

Brian Sheldon, Huajian Gao

Brown University

Yang-Tse Cheng

University of Kentucky

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Overview

Timeline

- Project start date: 5/17/2013
- Project end date:4/1/2017
- Percent completed: 80%

Barriers addressed

High energy materials with

- Short 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 FY15: $300,000
- Funding for FY16: $300,000

Partners

Interactions/ collaborations

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

Project lead: General Motors

Objective and Relevance

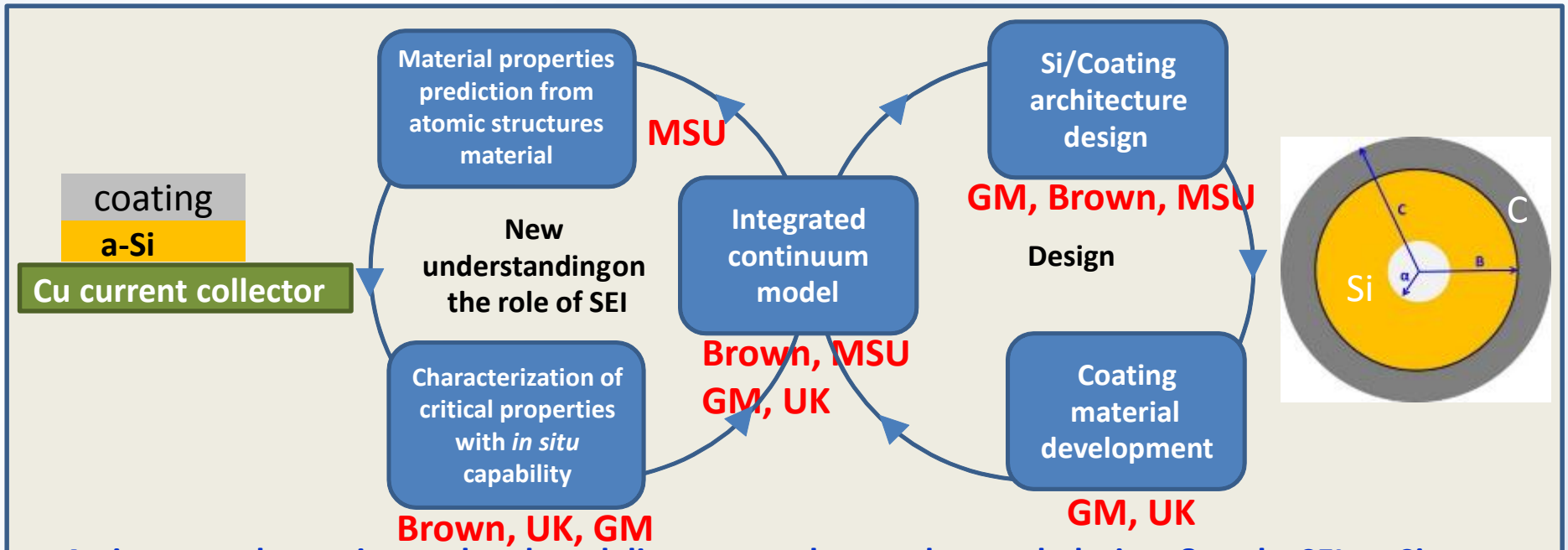
Objective: A validated model to understand, design, and fabricate stabilized Si anode with high capacity and high Coulombic efficiency.

Relevance

- Si-based electrodes were limited by coupled mechanical/chemical degradation.
- Controlling SEI formation and/or applying surface coating as artificial SEI combining with right Si architecture can mechanically stabilize active materials.
- **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.



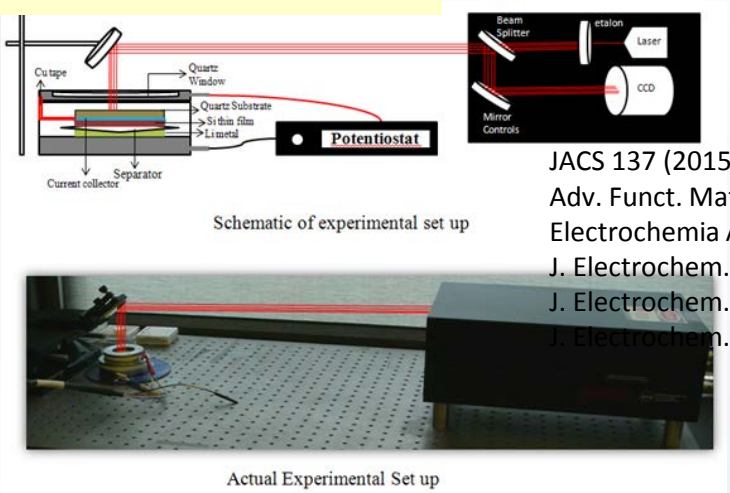
An integrated experimental and modeling approach to understand, design, & make SEI on Si

Project Milestones

Month/ Year	Milestone of Go/No-Go Decision	Status
June 2015	**Identify SEI failure mode by using combined in-situ electrochemical experiments and modeling techniques developed in 2014.**	**completed**
Sept. 2015	**Reveal detailed SEI failure mode by using MD simulations with ReaxFF for Li-Si-Al-O-C system to model the deformation of SEI on a Si as it undergoes large strain.**	**completed**
Dec. 2015	**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.**	**completed**
March 2016	**select oxide, fluoridated, or carbon artificial SEI chemistry based on comparisons of their mechanical stability and transport properties.**	**ongoing**

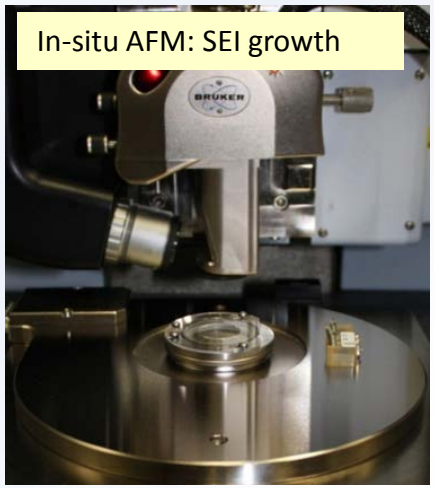
Accomplishment 1: Established *in-situ* diagnostic techniques to investigate mechanic degradation of SEI and Si electrode

Moss: stress evolution



JACS 137 (2015) 13732
Adv. Funct. Mater. 23(2013) 2397
Electrochemia Acta, 66(2012)28
J. Electrochem. Soc., 159 (2012) A38
J. Electrochem. Soc., 159 (2012) A1520
J. Electrochem. Soc., 161(2014) A58

In-situ AFM: SEI growth



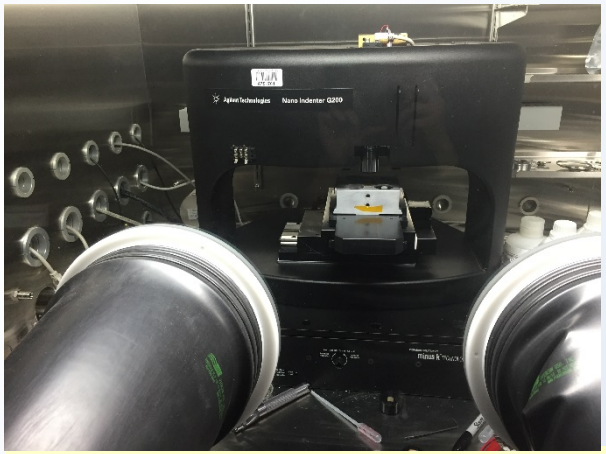
ACS Appl. Mater. interfaces 6(2014) 6672
Adv. Energy Mater. DOI: 10.1002/aenm.201502302

Optical Microscope: Si deformation

J. Power Sources, 206(2012)357
Nano Letters, 13(2013)4759

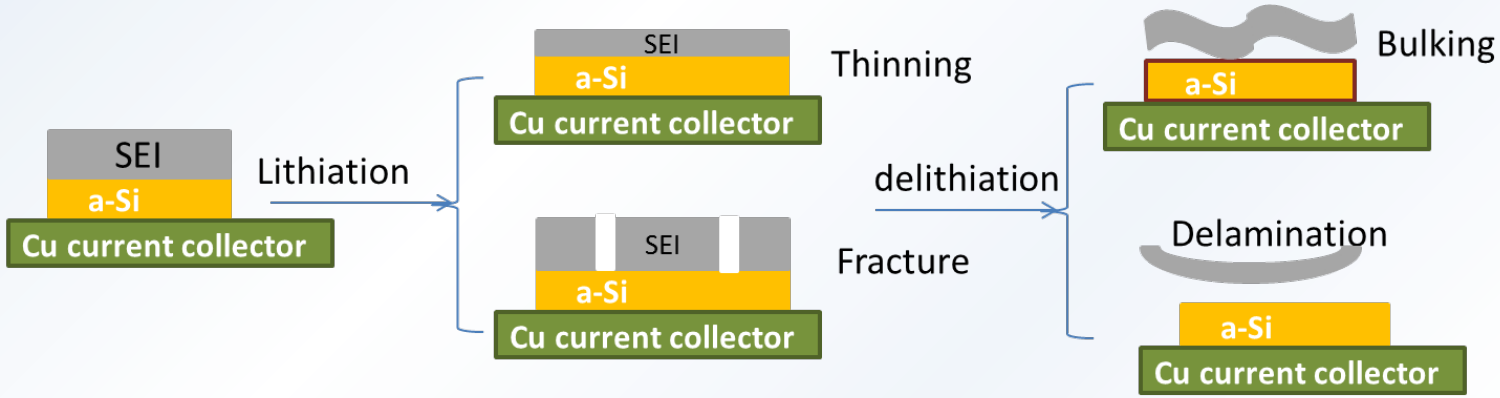
In-situ dilatometer: electrode expansion

Adv. Funct. Mater., 5 (2015)1426
SCIENTIFIC REPORTS 4 (2014) 3684 |

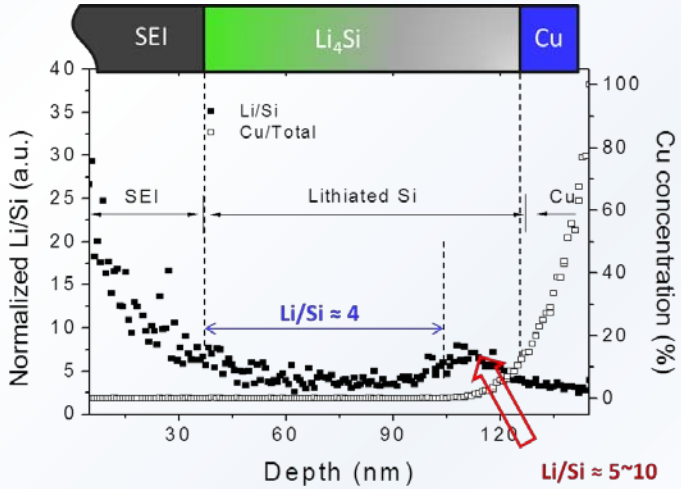


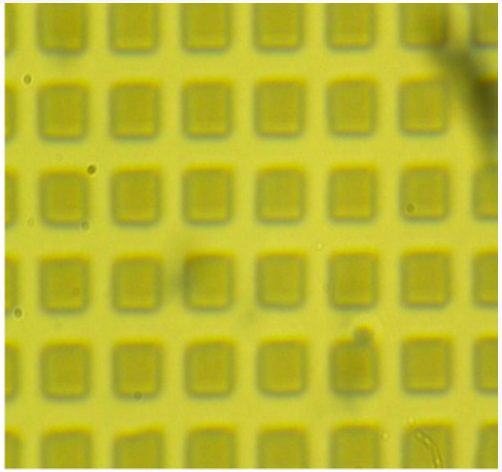
Nanoindentation: mechanical properties

Accomplishment 2: Established a model system combined with in situ AFM and simulations to investigate SEI failure mechanisms



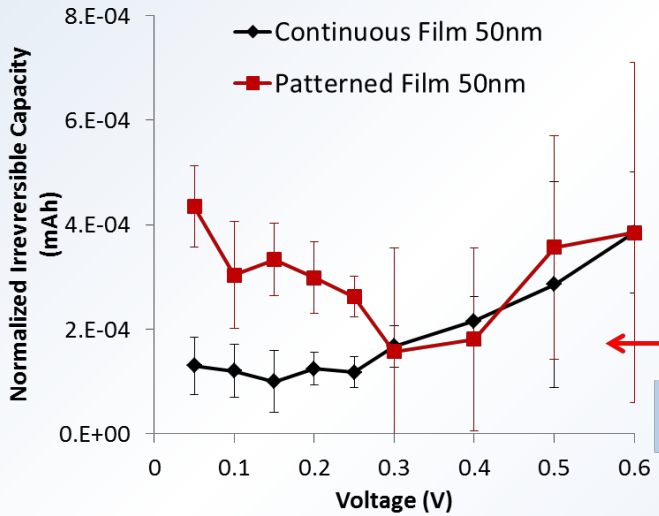
Advanced Energy Materials, DOI: 10.1002/aenm.201502302

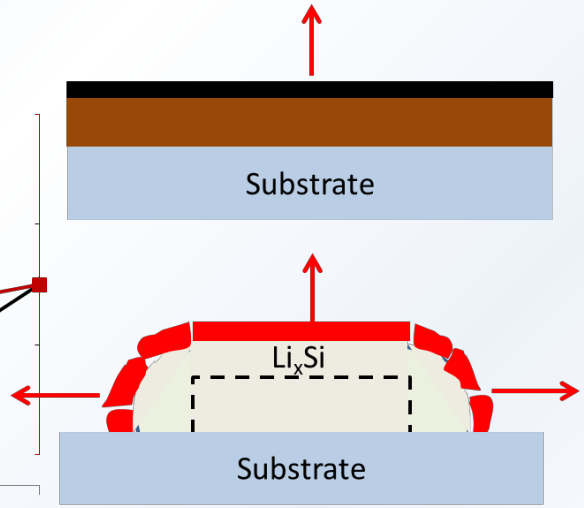


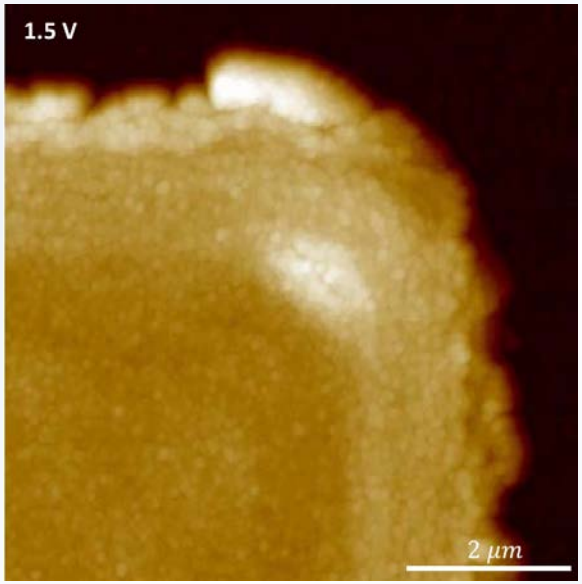


Li segregation at Si/Cu interface leads to the patterned Si slide, which creates an ideal system for investigating the mechanical stability of SEI on Si with large deformation.

Accomplishment 2.1: Identified SEI failure mechanism at initial stage via in-situ AFM

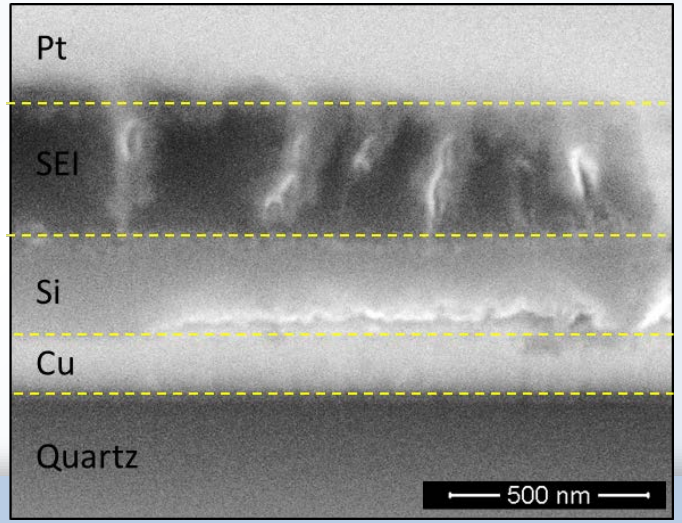






in-situ electrochemical AFM

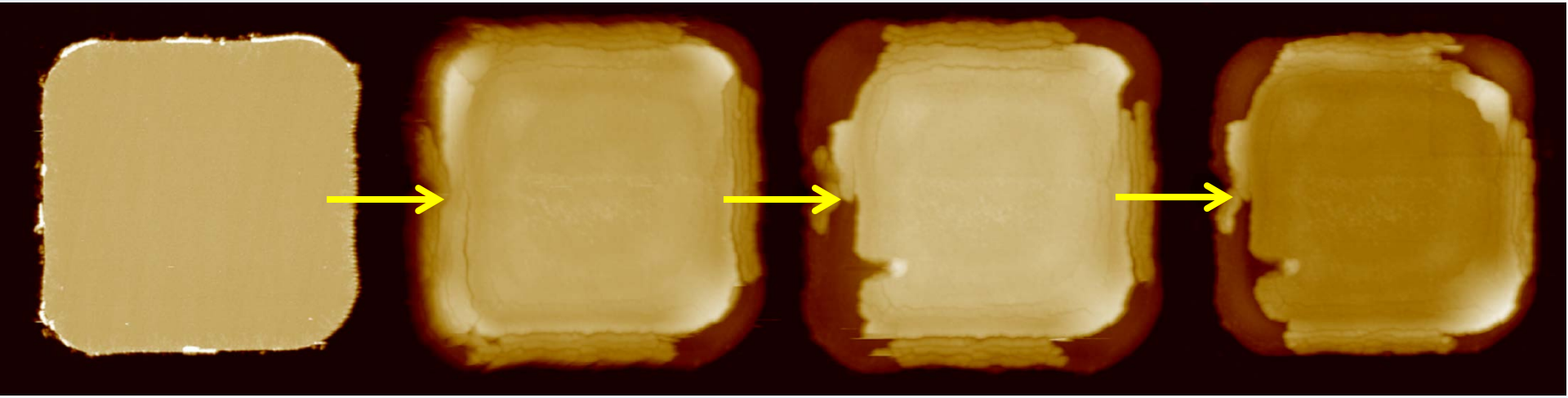
capacity losses from Si pattern and continuous film



Both electrochemical test and in-situ AFM indicate the SEI failure occurs during the lithiation stage

Cracking → Buckling → Delamination/Spallation

Identified SEI failure mechanism at initial stage via in-situ AFM

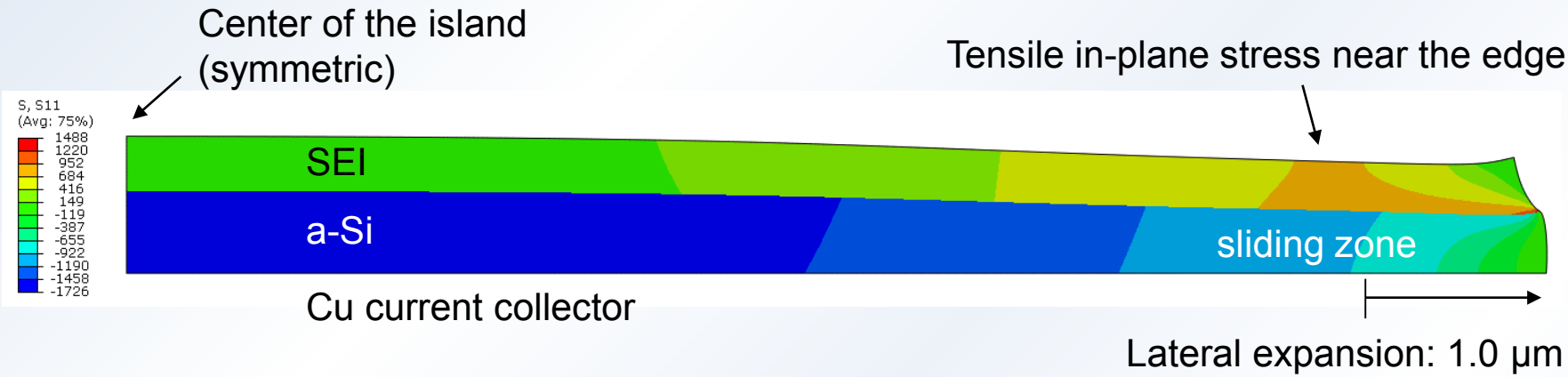


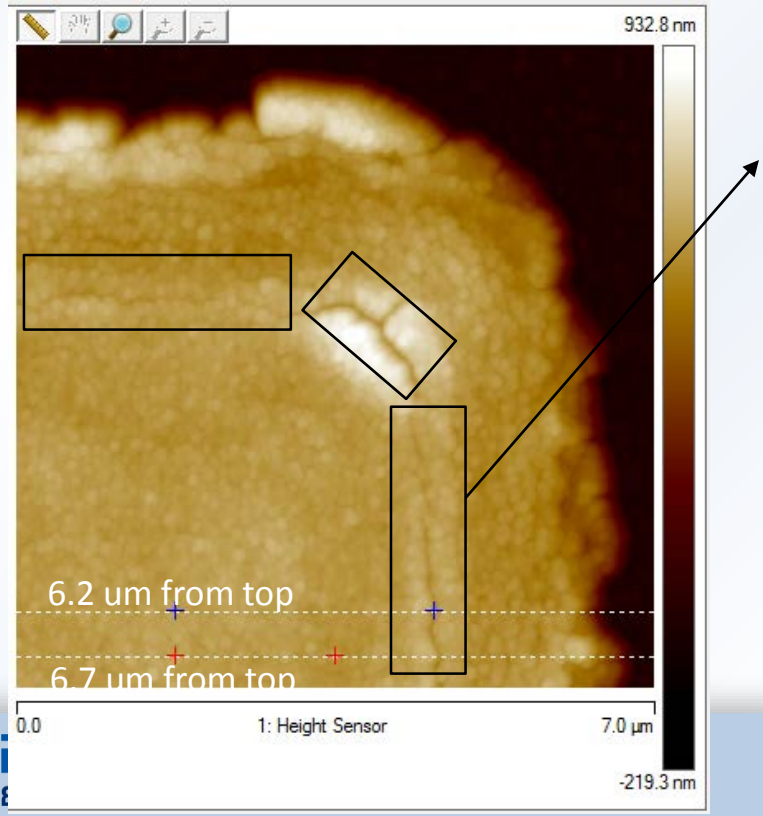
Cracking → Buckling → Delamination/Spallation

$10\ \mu m$

1. During 1st cycle lithiation, tensile stress in the SEI (due to expansion of Si) leads to through-thickness cracking;
2. These cracks dynamically evolve as cycling continues, and eventually reach to the interface of SEI and lithiated Si;
3. With further cycling, these cracks deviate towards SEI/LixSi interface and result into spallation of SEI.

Surface cracking of SEI near the edge of the island





Surface cracking has been observed in the region that SEI is under tension.

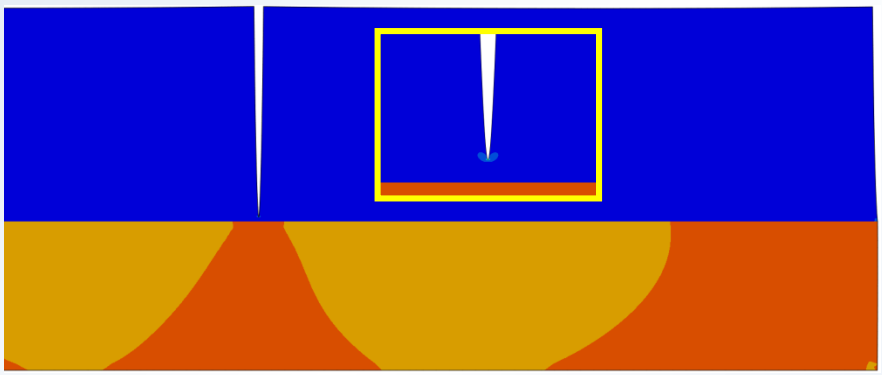
If surface crack penetrates the SEI layer, it cannot go across the SEI/Si interface and propagate in the a-Si island under compression.

We calculated the energy release rate of the SEI surface crack to investigate the energetically favorable path for crack propagation.

Numerical calculation of energy release rate of SEI surface crack

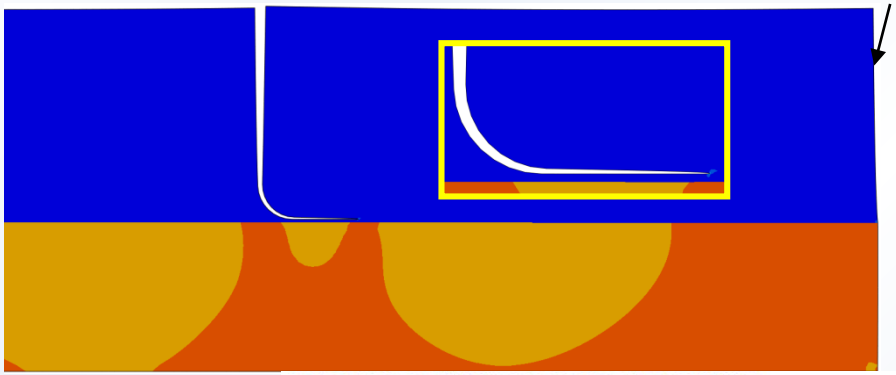
I. Vertical Path

Crack initiates at the position with maximum in-plane stress

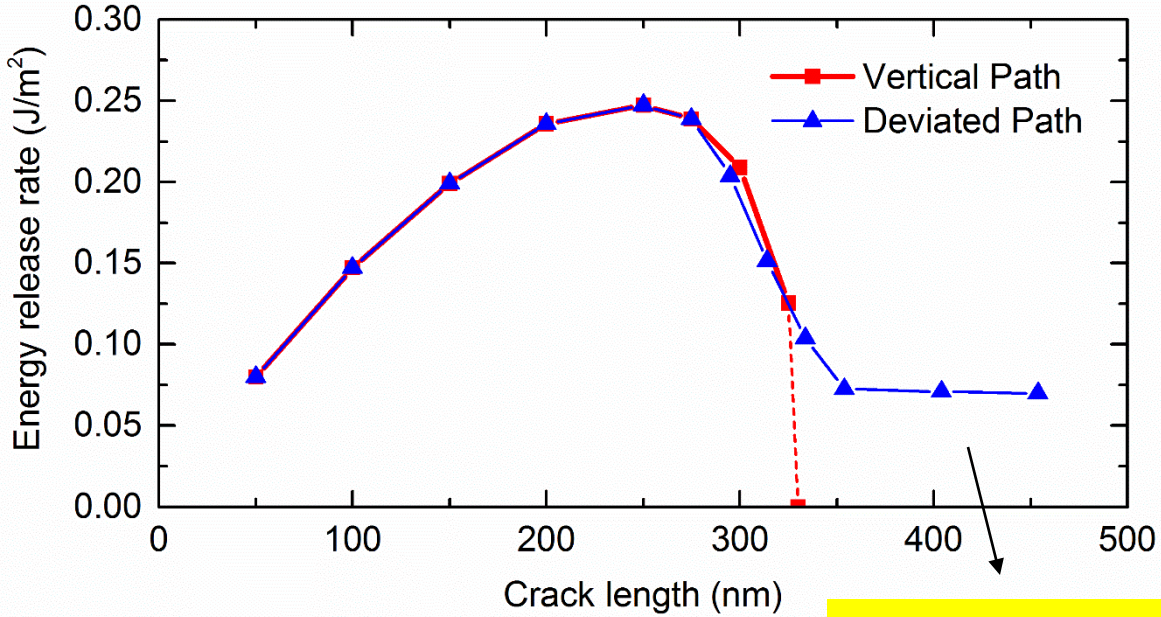


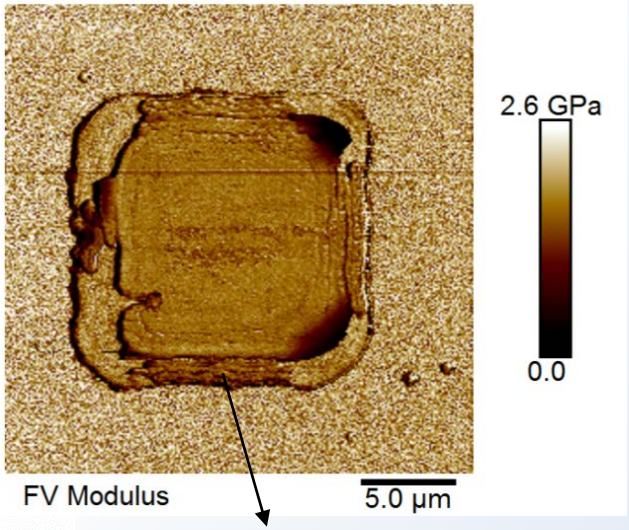
II. Deviated Path

Free Surface



Energy release rate of crack propagation vs. crack length

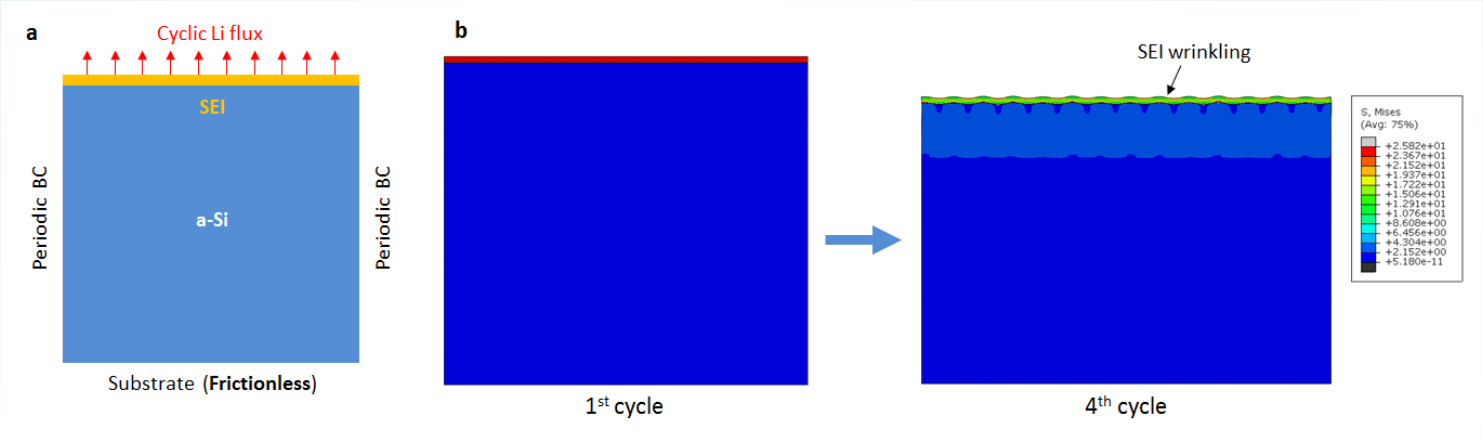




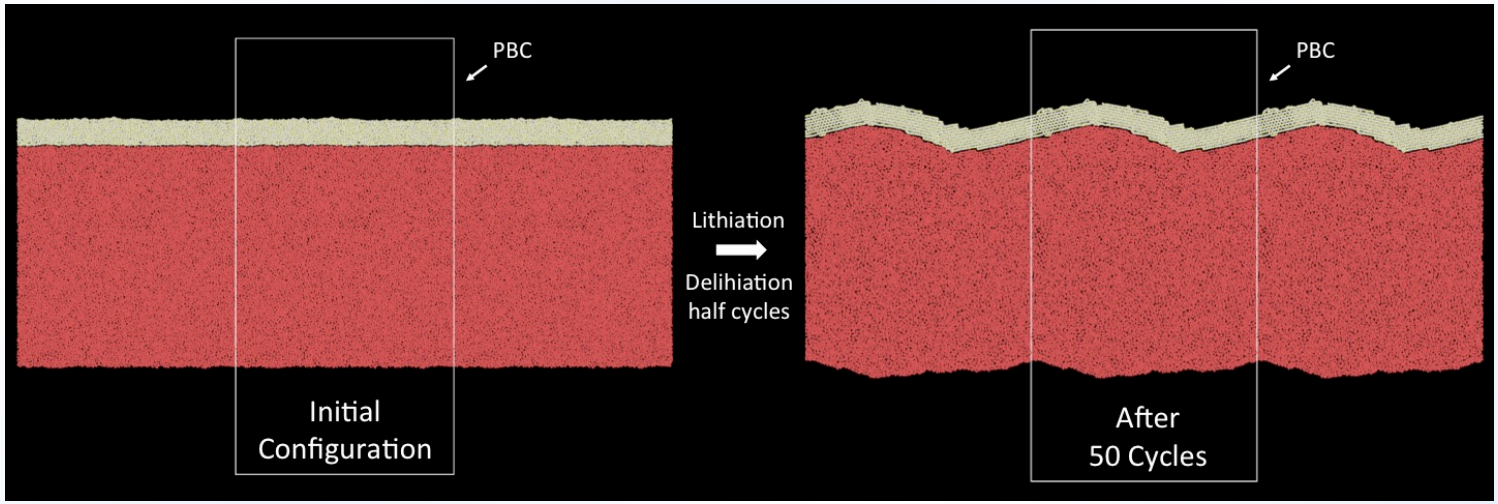
Peel-off of the SEI layer near the edge has been observed.

Crack deviation is energetically favorable.

Potential SEI failure mode induced by Si plastic ratcheting



(a) Schematic of the finite element model; (b) Snapshots of the finite element results upon 1st cycle and 4th cycle



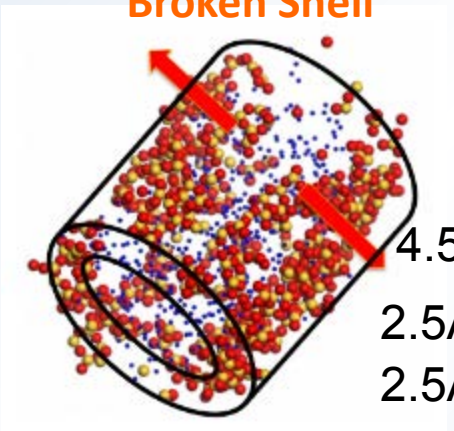
Snapshots of the molecular dynamics model before 1st cycle and after 50th cycle.

Upon cycling, a ratcheting mechanism of accumulative plastic deformation in the a-Si has been observed, leading to the gradual wrinkling and eventual SEI delamination.

Accomplishment 2.2: Identified SEI failure mechanism at initial stage via modeling

Reactive MD simulations show SEI coating failure mechanisms during lithiation.

Broken Shell

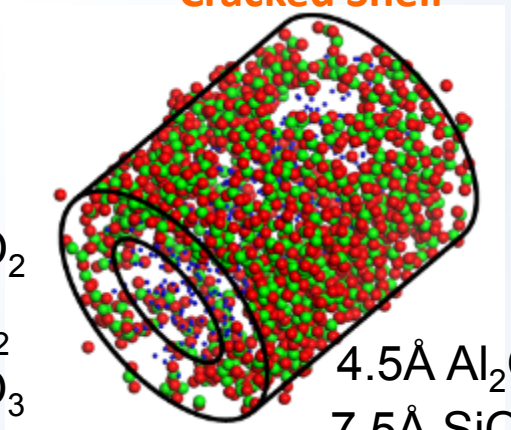


4.5Å SiO_2

2.5Å SiO_2

2.5Å Al_2O_3

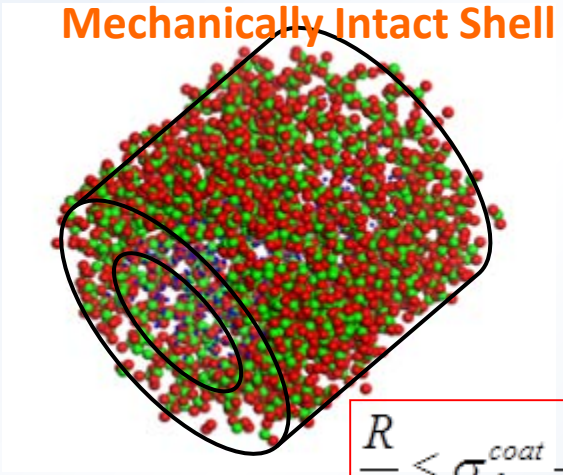
Cracked Shell



4.5Å Al_2O_3

7.5Å SiO_2

Mechanically Intact Shell



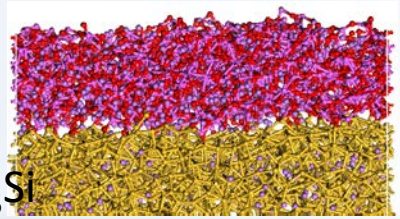
$$\frac{R}{h} \leq \sigma_f^{coat} \frac{\Omega}{\Delta G}$$

Design criteria

SEI coating delamination during fast delithiation rate.

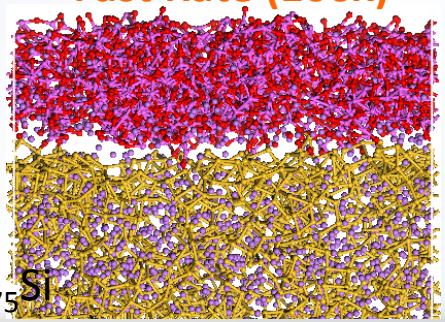
Continuously remove Li from the coating, followed by different MD relaxation time.

Slow Rate



$Li_{0.15}Si$

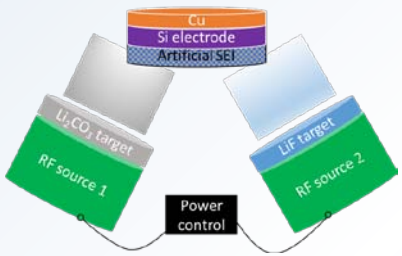
Fast Rate (100x)



$Li_{0.75}Si$

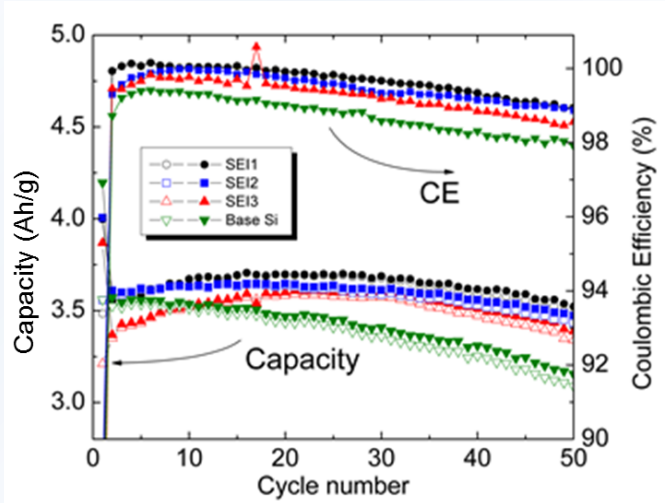
More Li was trapped in Si. Coating delamination is observed.

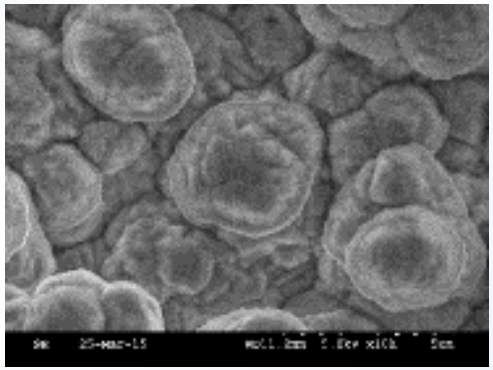
Accomplishment 3: Identified desirable components in SEI enabling high cycle efficiency



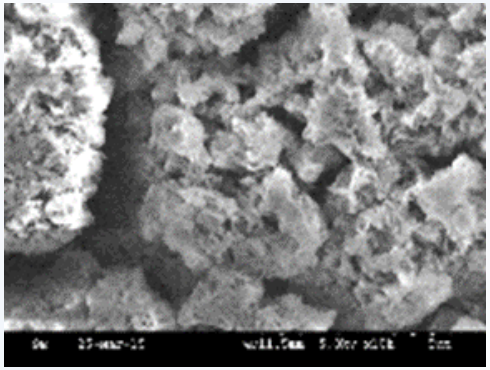
PVD process to mimic real SEI

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

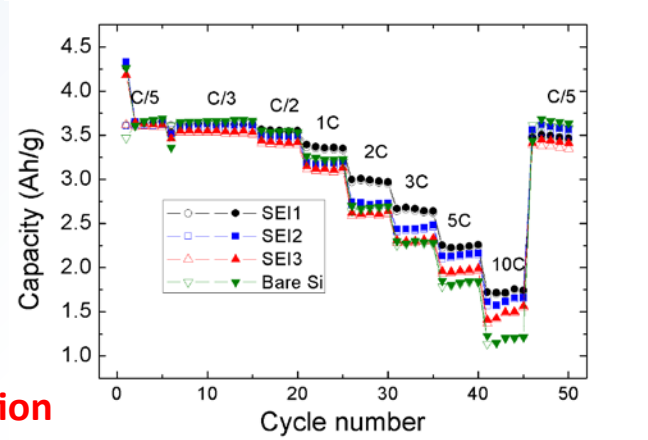




Higher LiF content



Lower LiF content
Rougher surface due to SEI formation

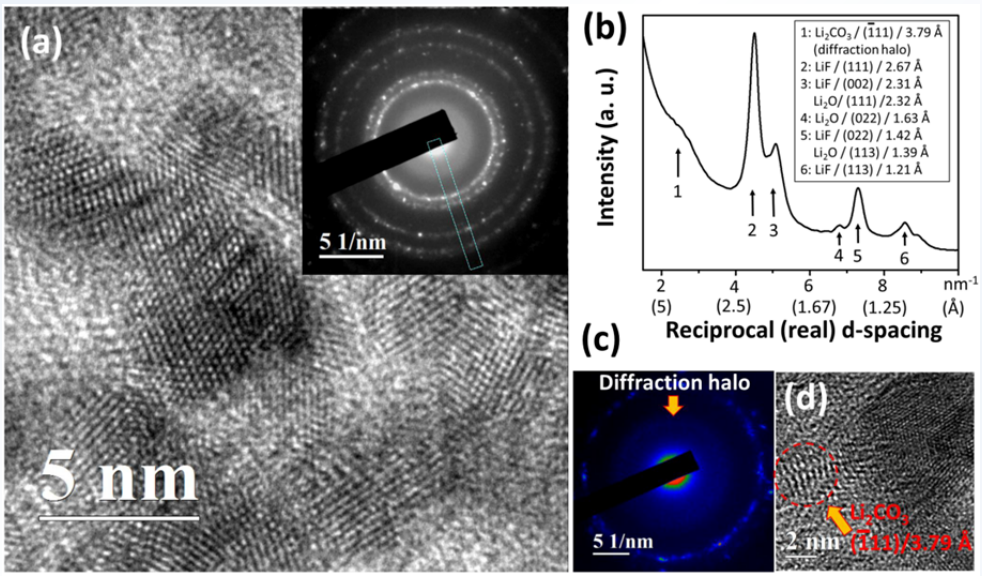


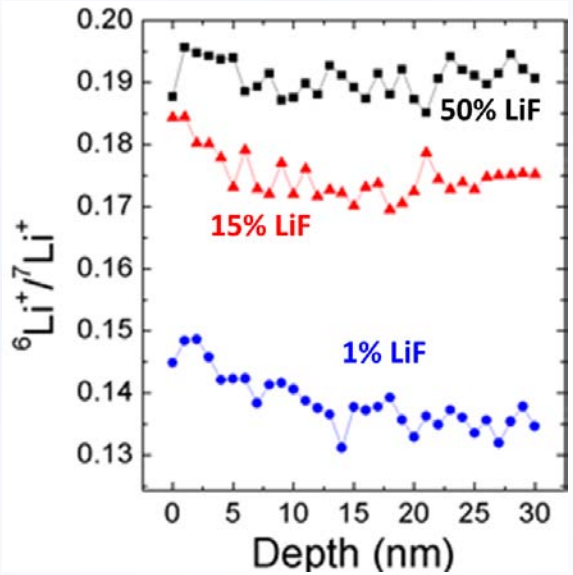
Surface morphologies of Si electrode after 50 cycles

Higher LiF content leads to robust SEI and better cycle efficiency

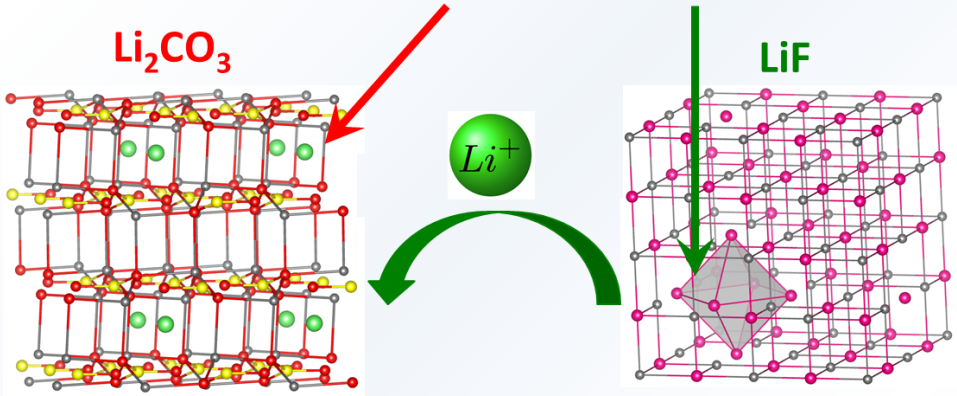
Nano Letters 2016, 16 (3), pp 2011–2016

Synergetic Effects of Inorganic Components in SEI





HR TEM

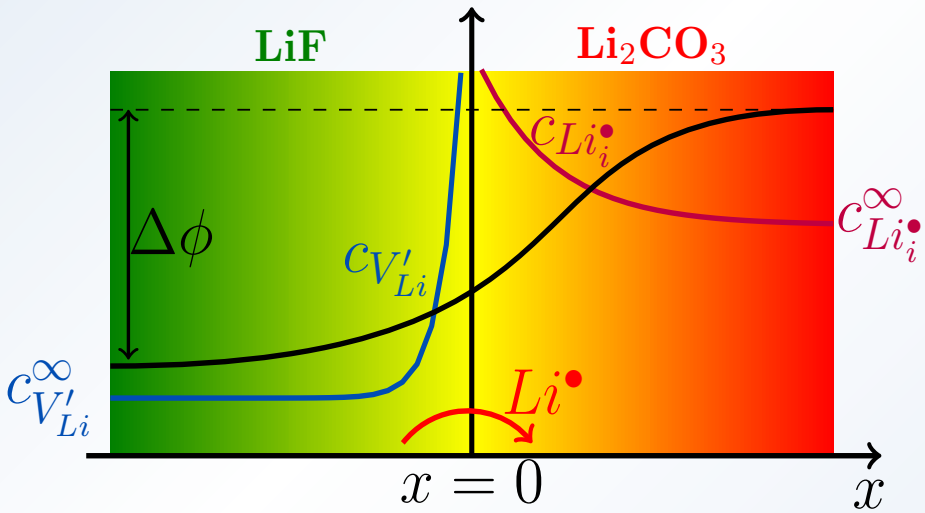


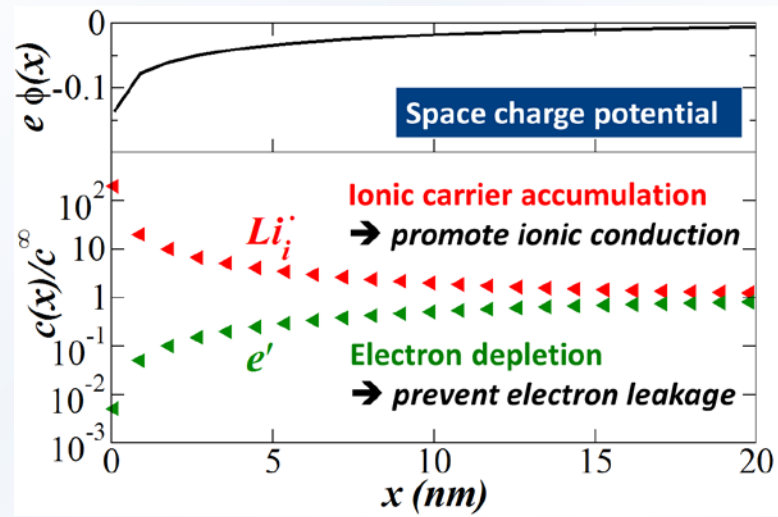
6Li isotope exchanges measured by ToF-SIMs

- The interfaces between Li_2CO_3 and LiF are defective.
- High fraction of the interfaces lead to more isotopes exchanges.

Nano Letters 2016, 16 (3), pp 2011–2016

Space charge layer near the interface facilitates Li ion transport





At equilibrium, the sum of electrochemical potential is uniform across the interface

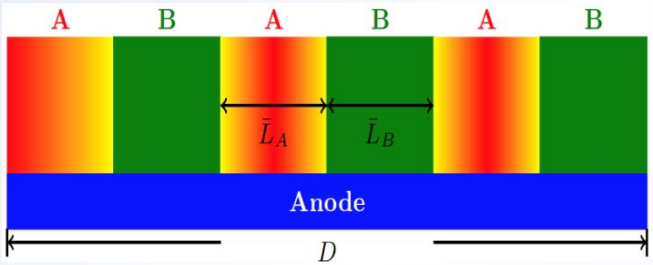
$$\sum \tilde{\mu}_i(x) = \sum \mu_i(x) + z_i e\phi(x) = 0$$

Space charge potential:

$$\Delta\phi = \phi^\infty_{Li_2CO_3} - \phi^\infty_{LiF} = 0.95V$$

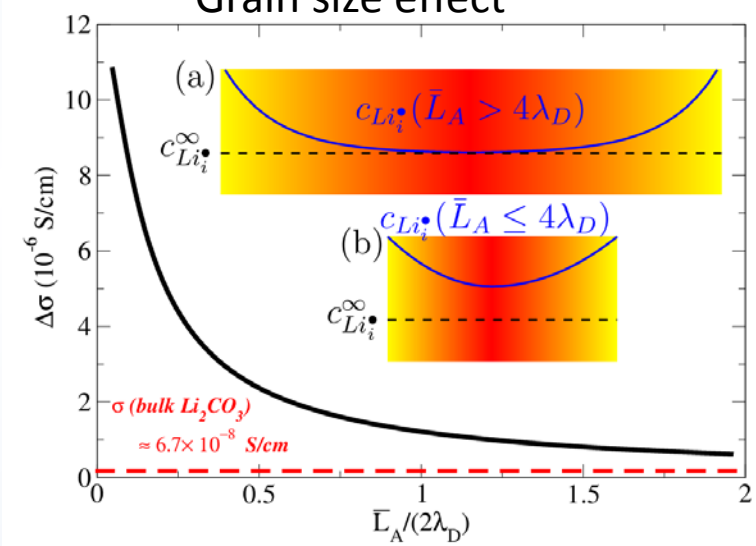
1. **Ionic carrier accumulation near the interface improves the rate performance of the electrode;**
2. **Electron depletion near the interface provides a better passivation to avoid additional electrolyte decomposition.**

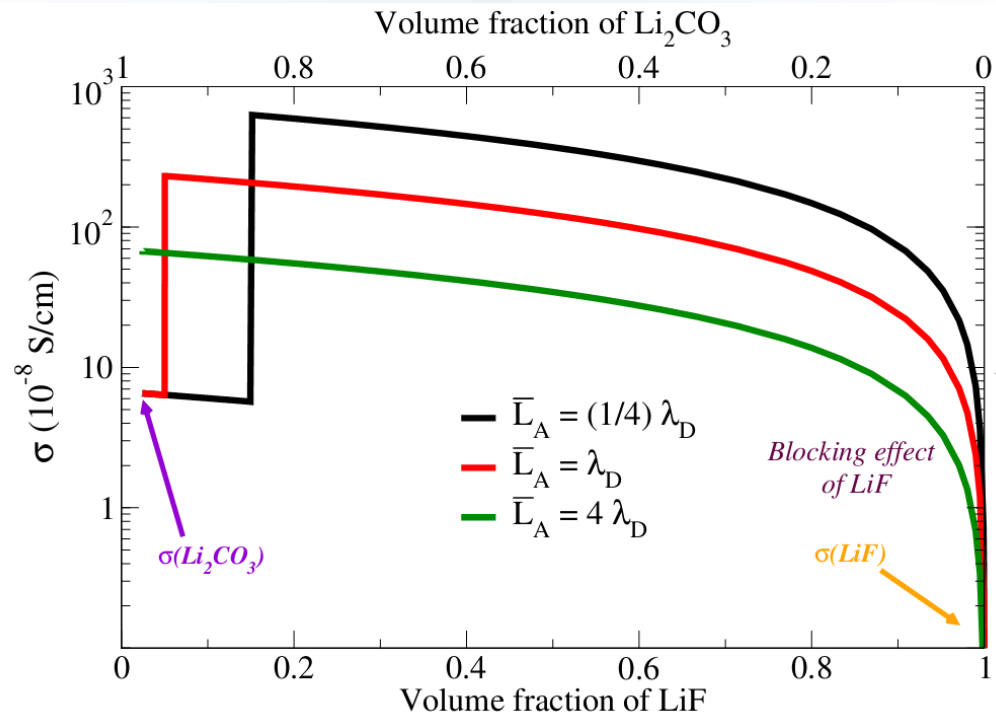
Tune grain size and ratio to achieve high ionic conductivity in multi-component solid electrolyte



2-D illustration of the topology of the designed SEI structure for optimized ionic conductivity. A: Li2CO3; B: LiF;

Grain size effect





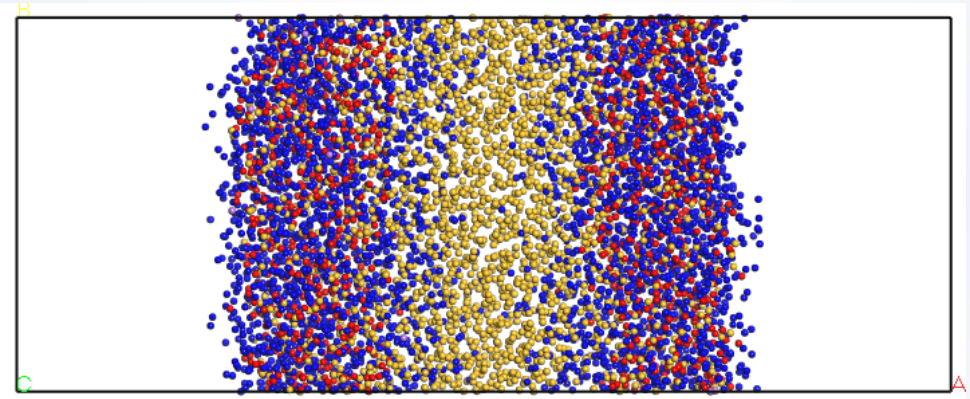
The increment of ionic conduction for different Li2CO3/LiF coating with different volumetric ratio and grain size

ACS Applied Materials & Interfaces, 8 (8), 5687-5693

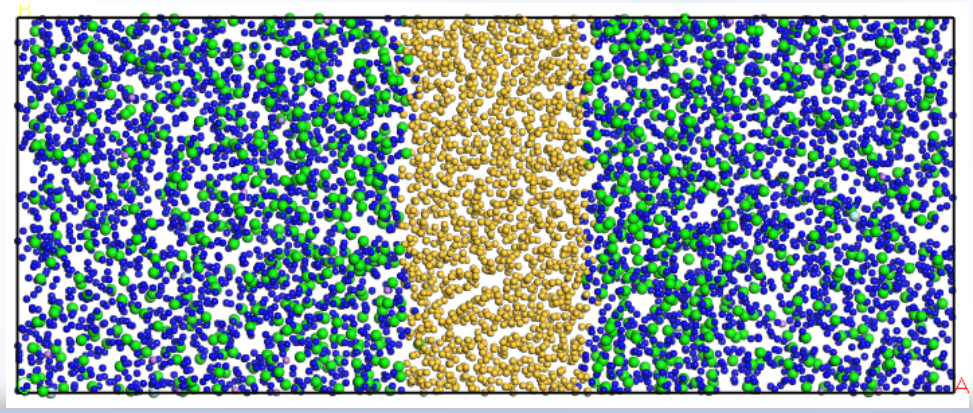
Explore multi-component SEI with high ionic conductivity

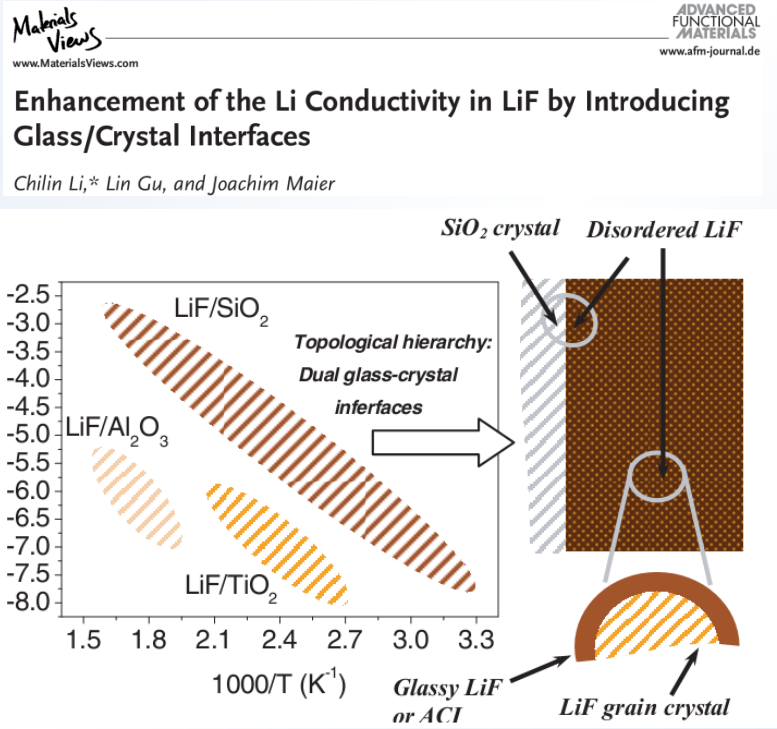
ReaxFF parameters were developed for Li-Si-O-Al and Li-Si-O-F systems, allowing us to explore mixed coating materials

Li diffused into and through SiO_2 layer on Si



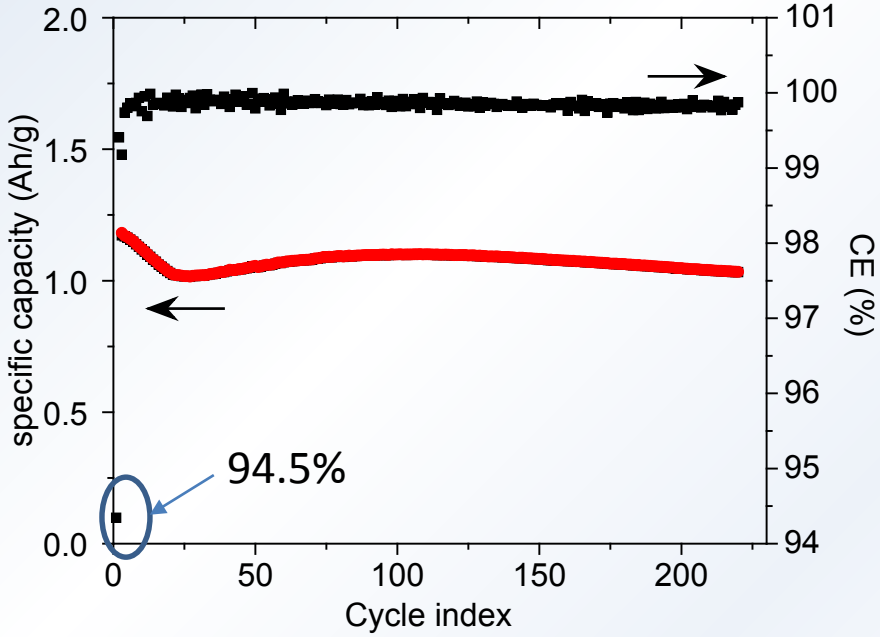
Li cannot diffuse through LiF layer to Si



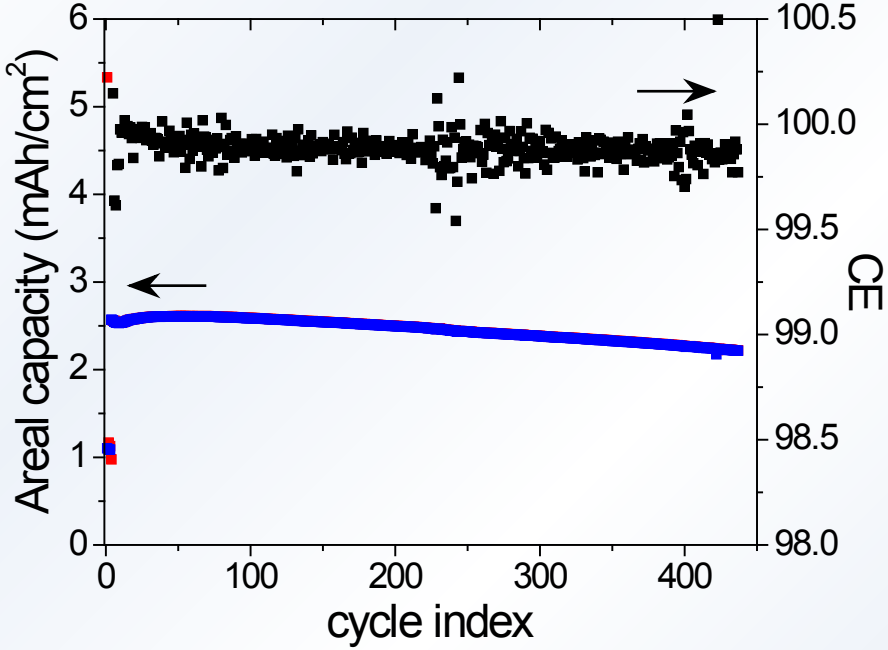


Adv. Funct. Mater. 2012, 22, 1145–1149

Accomplished 4: Achieved high current efficiency of Si based electrode with optimized SEI/Si electrode system



Half cell



Full cell, Si electrode paired with HENMC

With the optimized SEI formation and electrolyte additives (FEC), the high cycle efficiency can be achieved (>99.8% with first cycle CE>94%)

Summary

- Identified functions of individual component in nature SEI, LiF is critical for stabilizing the SEI layer and improving the cycling efficiency, due to the electrical insulating and mechanical protection.
- Demonstrated the synergetic effects of LiF and Li_2CO_3interfaces, which not only facilitate Li ion transport, but also further enhance the passivation function to suppress electrolyte decomposition.
- By using combined in-situ electrochemical experiments and modeling techniques, we were able to identify SEI failure modes, which is mainly due to the fracture during the lithiation process of Si active materials.
- With the optimized SEI formation protocols and electrolyte additives (FEC), the high cycle efficiency can be achieved (>99.8% with first cycle CE>94%)

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.

Responses to Previous Years Comments

- The reviewer stated that ALD coating definitely improves the stability of the Si anode and more experiments are needed rather than just performing computation.
  - The team has conducted a series of experiments and published a few papers (Adv Mater. 23(2011)3911, J. Phys. Chem. 116(2012)1472) . The purpose of the simulation is to fundamentally understand the mechanism on how ALD coating improves the mechanical stability of SEI and Si electrode. Based on this, the team will further develop ALD coating to improve the cycle efficiency as reviewer suggested.
- The reviewer stated that the technical progress that has been made so far is impressive. However, it is unclear if the milestone of comparing the modeling results of SEI deformation and stability with in situ multi beam optical stress sensor (MOSS) measurement has completed or not.
  - Following reviewer's comments, the work has been conducted and the results are being summarized.
- The reviewer explained that the 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. However, how the Si-C yolk stability is better than the Si-C core shell structure, needs to be explained.
  - The York-shell structure will provide a free space to accommodate Si volume expansion, and the majority of SEI will form on C shell which has much less volume expansion, comparing to the large volume expansion from core-shell structure. Therefore, the SEI formed on York-shell structure will be much stable, leading to better cycle efficiency.
- The reviewer noted that more experiments are recommended rather than computation work.
  - More experimental results have been included in the presentation, as the reviewer suggested.

Future Plans

- Design a practically useful Si electrode where degradation of the SEI layer is minimized during lithiation and delithation.
- Construct an artificial SEI design map for Si electrodes, based on critical mechanical and transport properties of desirable SEI for a given Si architecture.
- A validated design guidance on how to combine the SEI coating with a variety of Si nano/microstructures. Make Go/No-Go decision based on if the modelling guided electrode design can lead to high columbic efficiency >99.9%

Acknowledgement

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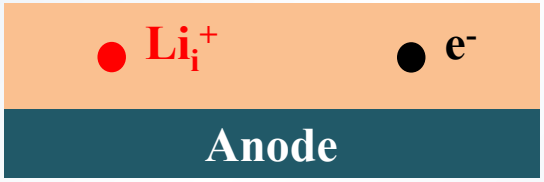
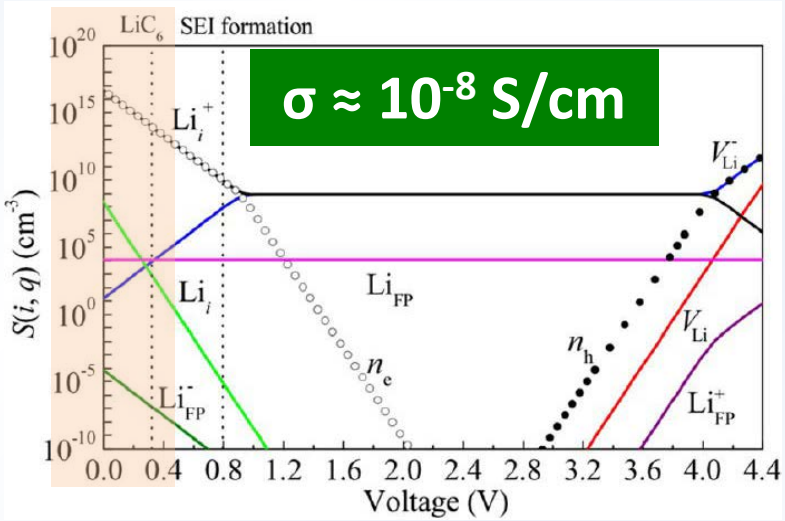
- We also acknowledge the graduate students and postdocs involved in this work:
  - Ravi Kumar, Qinglin Zhang, Jie Pan, Sung-Yung Kim, Kai Guo, Anton Tokranov, Ill Ryu, Jae-ha Woo
- Dr. Peng Lu for TOF-SIMS, Dr. Mei Cai and Dr. Mark W. Verbrugge for the support.

Backup Slides

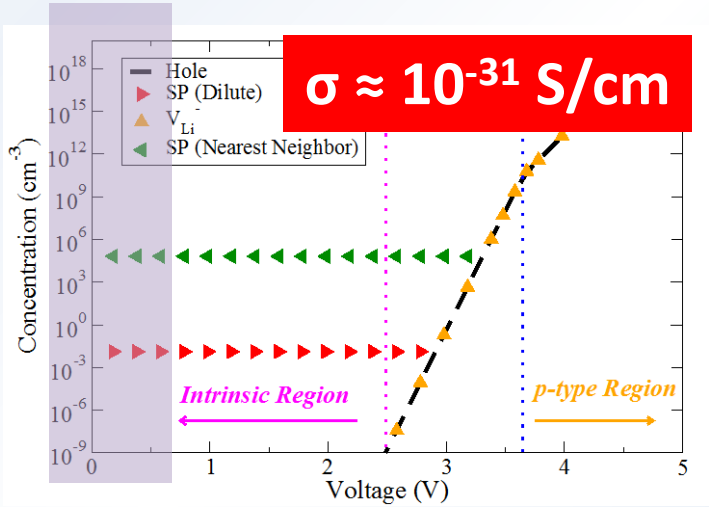
Voltage-dependent defect formation

Li_2CO_3 coated on anodes





LiF coated on anodes



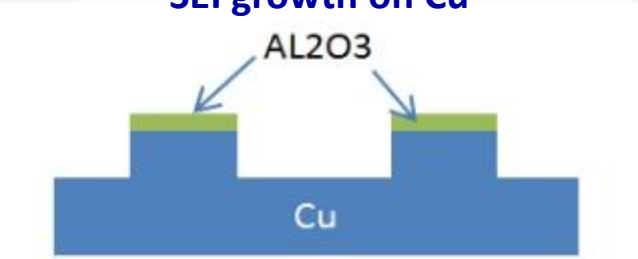
What will happen if LiF and Li_2CO_3 coexist in the SEI on anodes?

J. Pan, Y. T. Cheng and Y. Qi, Phys. Rev. B **91** (13), 134116 (2015).

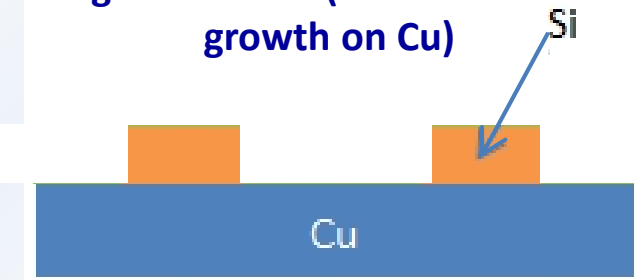
Established experimental methods to decouple volume change caused by SEI formation and lithiation of Si

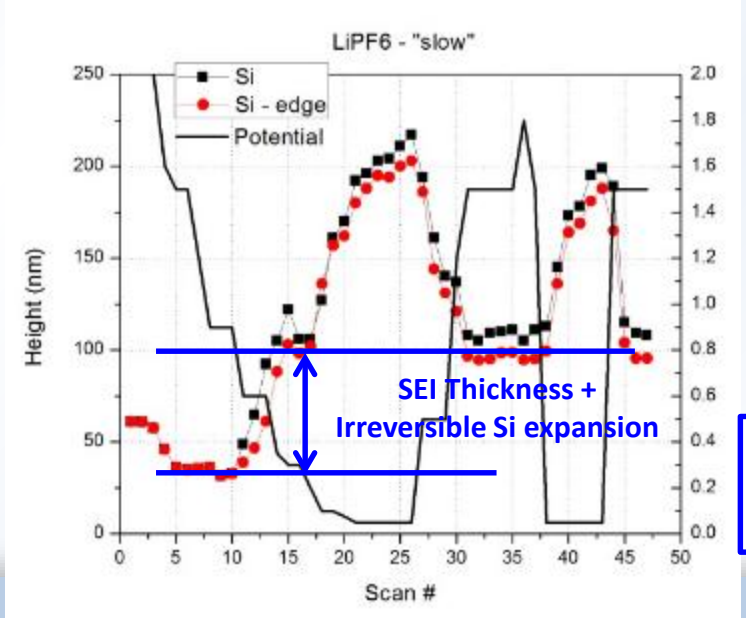
In Situ AFM and in-situ stress sensor

Configuration to measure SEI growth on Cu



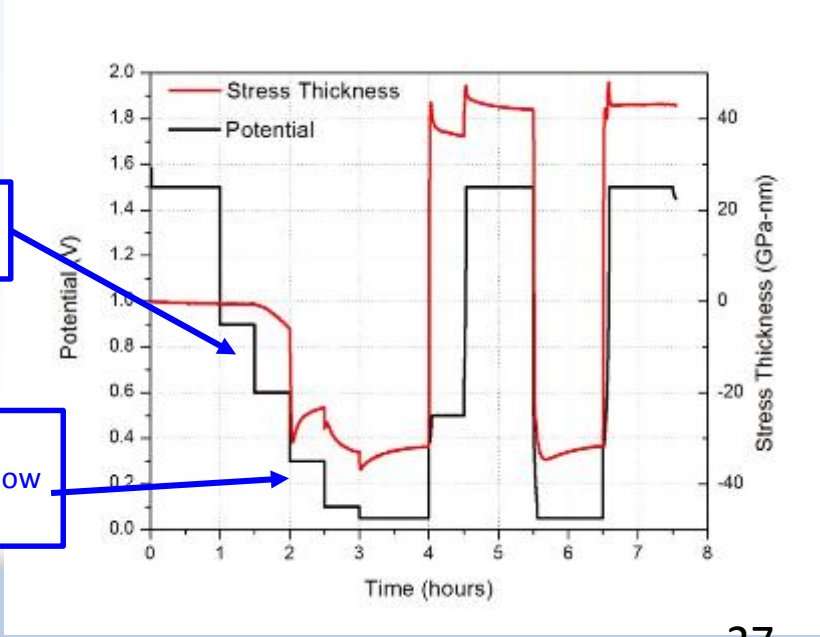
Configuration to measure SEI growth on Si (corrected for growth on Cu)



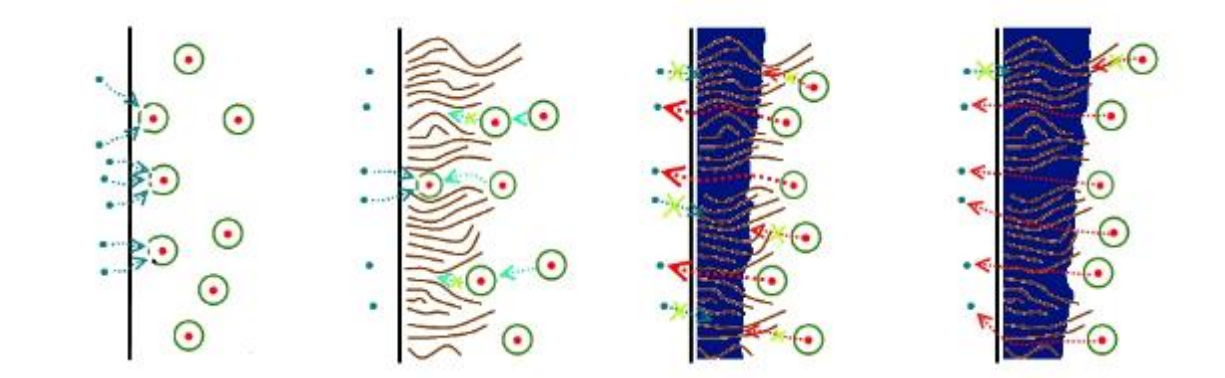


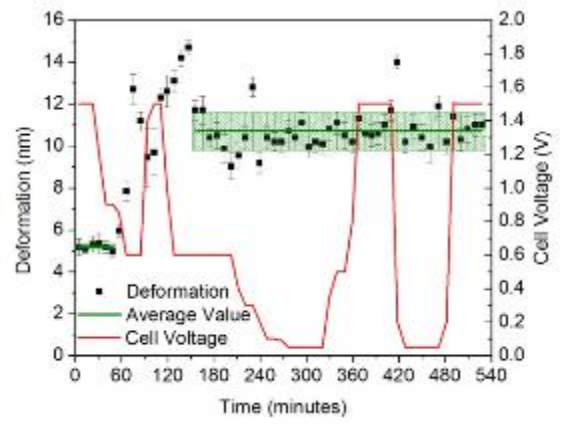
SEI formation begins at 0.6V

Stress relaxes through plastic flow to a certain level

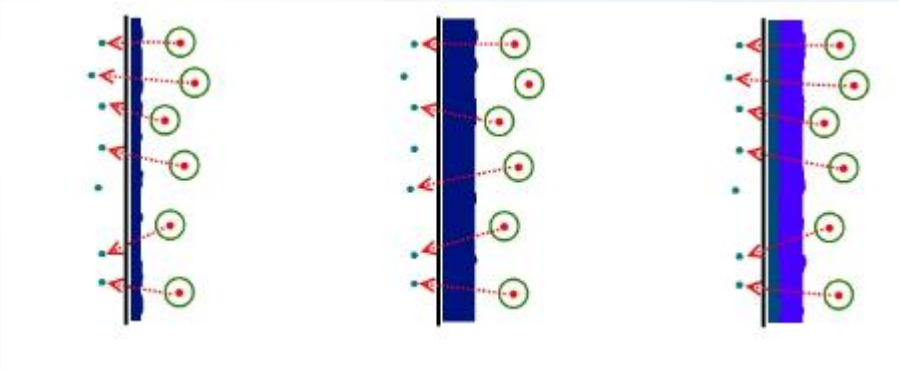


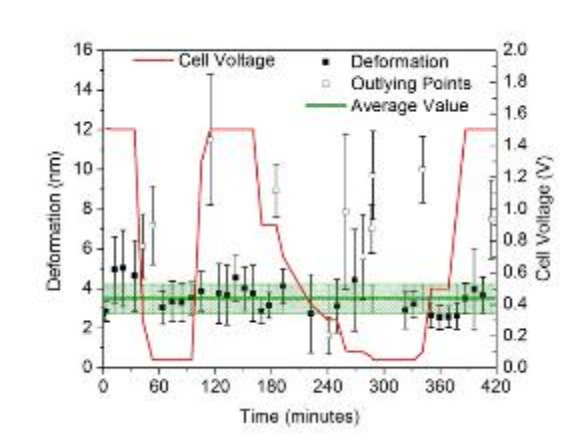
An Expanded Model of Initial SEI Formation





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.

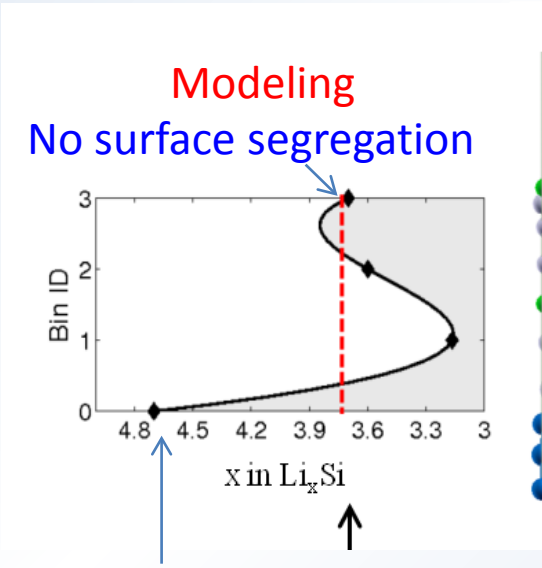


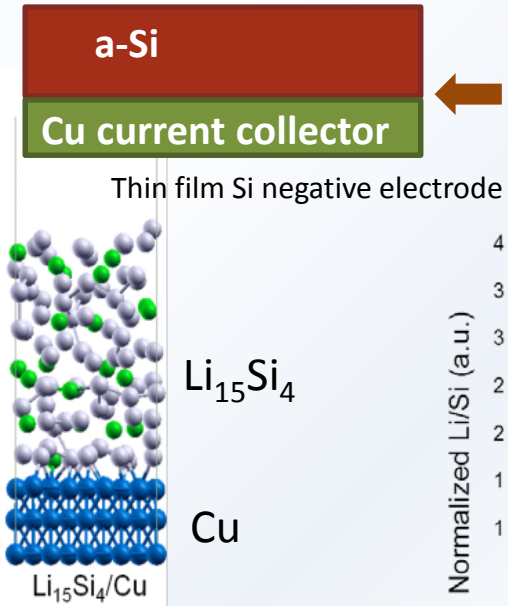


SEI growth with a fast first cycle: organic SEI does not have time to form instead creating inorganic passivation which prevents further organic SEI from forming. This SEI keeps increasing in thickness, over several cycles.

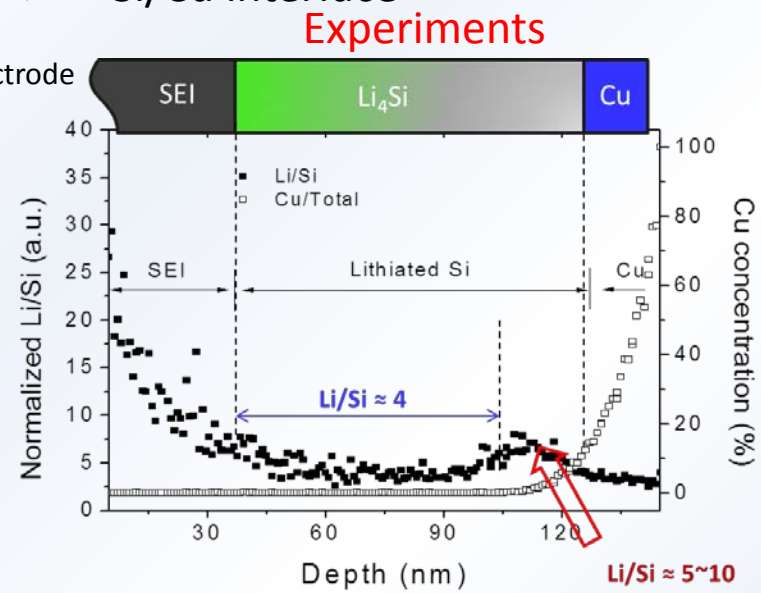
ACS Appl Mater & Interfaces (2014).

Understanding interfacial sliding in patterned Si model system





Si/Cu interface



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)*