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: 25%

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 FY13: $329,000
- Funding for FY14: $300,000

Partners

Interactions/ collaborations

- 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: to develop a **validated mechanics model** that imports material properties, measured or computed, to understand, design, and make coated Si anode structures with high coulombic efficiency and cycle stability.

Relevance

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

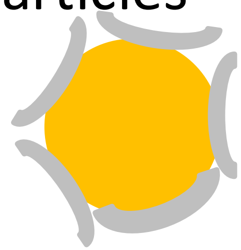
Initial Mechanics Analysis

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

- Fracture of Si particles

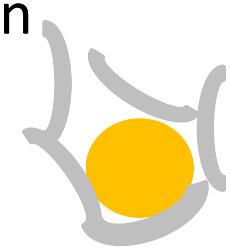
$$l_{frac} \propto \left(\frac{\Gamma(1-\nu)F^2 D^2}{E(1+\nu)\Omega^2 I^2} \right)^{1/3}$$

- SEI peel-off from Si particles during lithiation



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

- Buckling delamination during delithiation

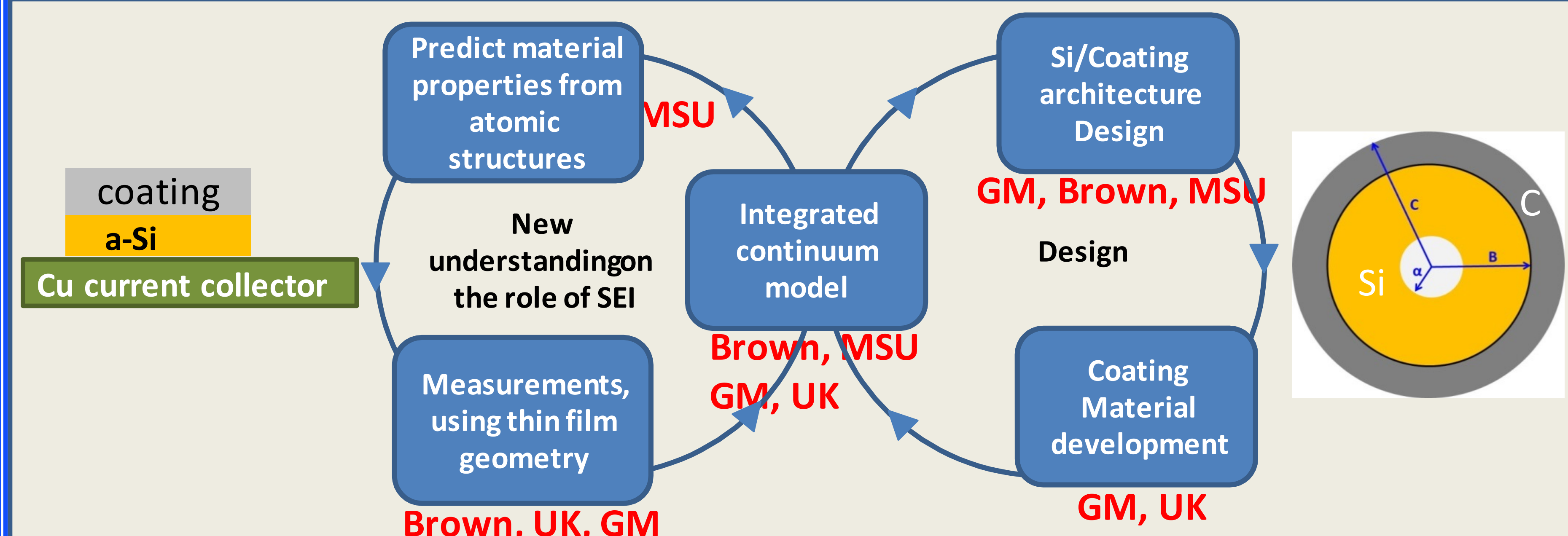


$$l_{buckle} = \frac{(\alpha_1 \Gamma_{\mathrm{int}} + \alpha_2 \Gamma)(1+\nu)(1-2\nu)}{2\pi E \varepsilon_0^{\ 2}}$$

Experimental validation and material properties are required in order to DESIGN SEI and Si nanostructures.

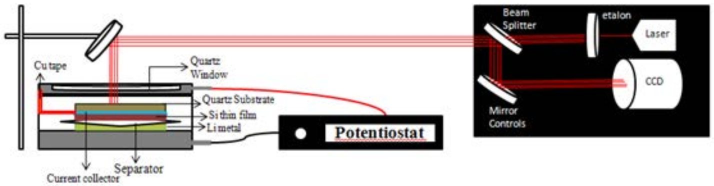
Approach/Strategy

- Develop a multi-scale model to establish a correlation between coulombic efficiency and mechanical degradation.
- Combine simulation with experiments for critical material properties.
- Develop *in-situ* electrochemical approaches to understand the critical mechanical and electrochemical behaviors of SEI and Si.
- Use the validated model to guide surface coating design and Si size/geometry/architecture.

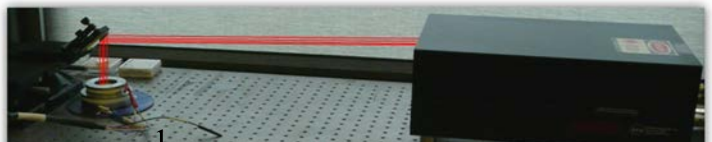


An integrated experimental and modeling approach to understand, design, & make SEI on Si

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



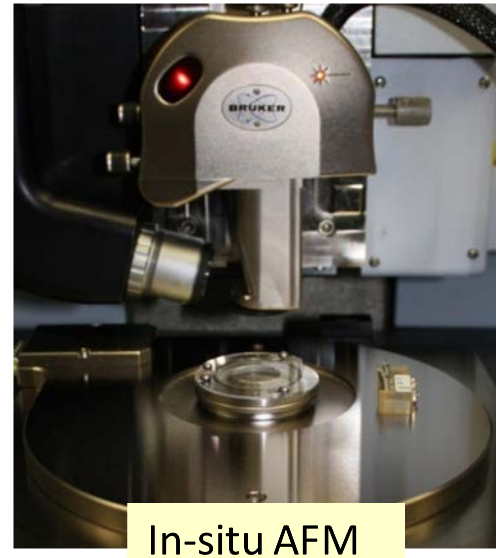
Schematic of experimental set up



$$<\sigma>h=\frac{1}{6}M_sH_s^2*L*C \quad \alpha*M$$

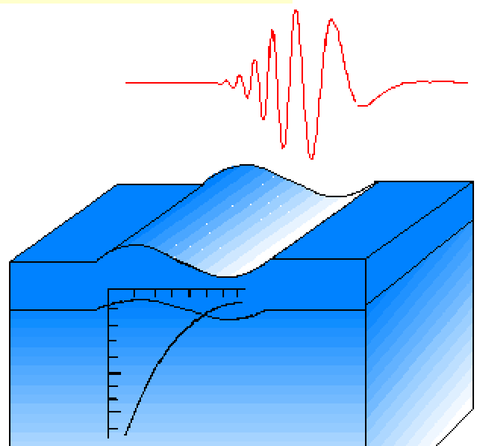
Actual Experimental Set up

Moss to investigate stress evolution



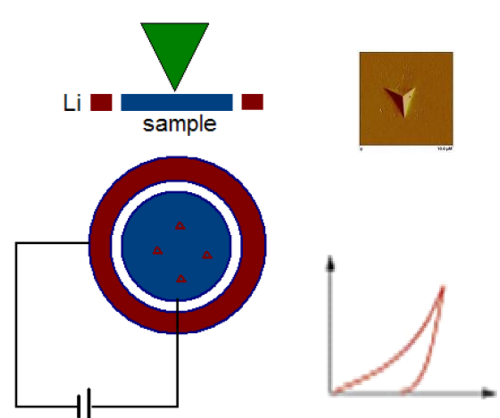
In-situ AFM

Optical Microscope



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

Laser Acoustic Wave system



Nanoindentation

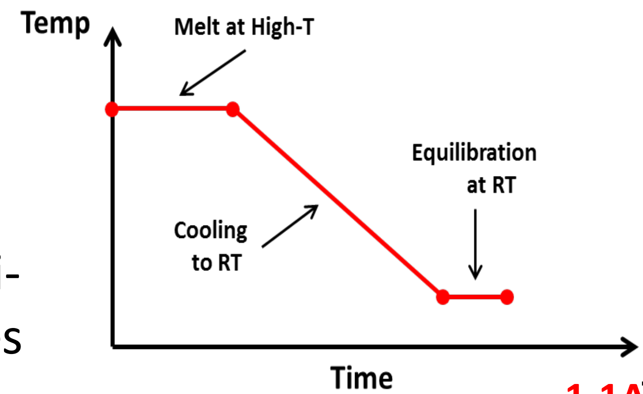
Project Milestone

Month/ Year	Milestone of Go/No-Go Decision	Status
Jun. 2013	Determine the elastic properties of artificial SEI on Si via both atomic modeling and laser acoustic wave measurements.	completed
Sept. 2013	Correlate the interfacial charge-transfer kinetics and coating thickness on Si film electrode .	completed
Dec. 2013	Compare SEI evolution on coated and uncoated Si surface. • Evaluate the chemical composition of the initial SEI on uncoated Si. • Design new method to evaluate the evolution of stress of the Si electrode during SEI formation and growth in *in situ* cells. • Formulate a theoretical framework to connect mechanical degradation and columbic efficiency.	Completed
Jan. 2014	Compare the basic elastic properties of ALD coatings (e.g., Al_2O_3) computed from MD simulations with ReaxFF and measured by AFM and laser acoustic wave for method validation.	completed
April 2014	Predict the interface strength of given coatings on Si substrate from QM calculations and compare with nanoindentation and scratch tests.	Simulation completed and experiment in progress

Toward Accomplishment 1:
Atomic simulation of ALD-Al_2O_3 thin film

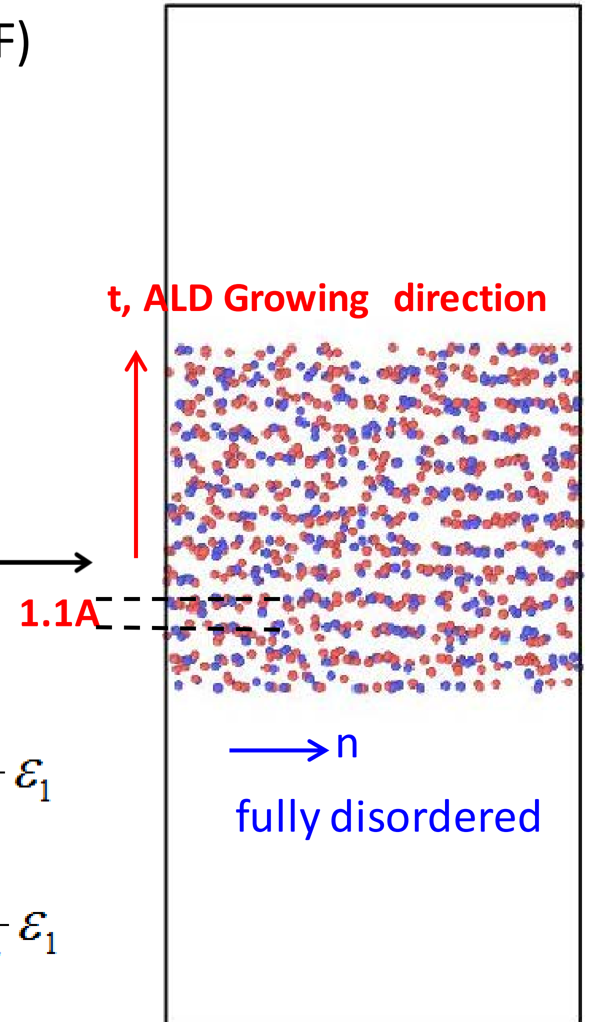
- Molecular Dynamics with Reactive force field (ReaxFF) tailored for Al-O system

- Melting-quenching method starting from defect containing α-Al_2O_3 was developed to generate semi-disordered atomic structures of ALD-Al2O3 thin films



- Uniaxial Tension; Calculate the Young's modulus and Poisson's ratio of the ALD film.

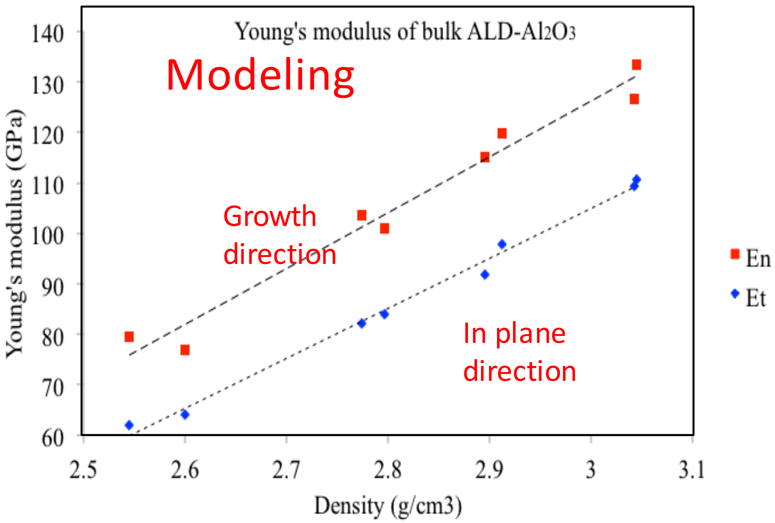
$$\begin{cases} \sigma_1 = \dfrac{E}{1-\nu^2}\varepsilon_1 \\ \sigma_2 = \dfrac{\nu E}{1-\nu^2}\varepsilon_1 \end{cases}$$

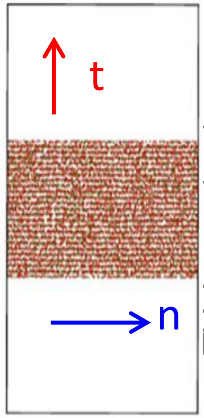


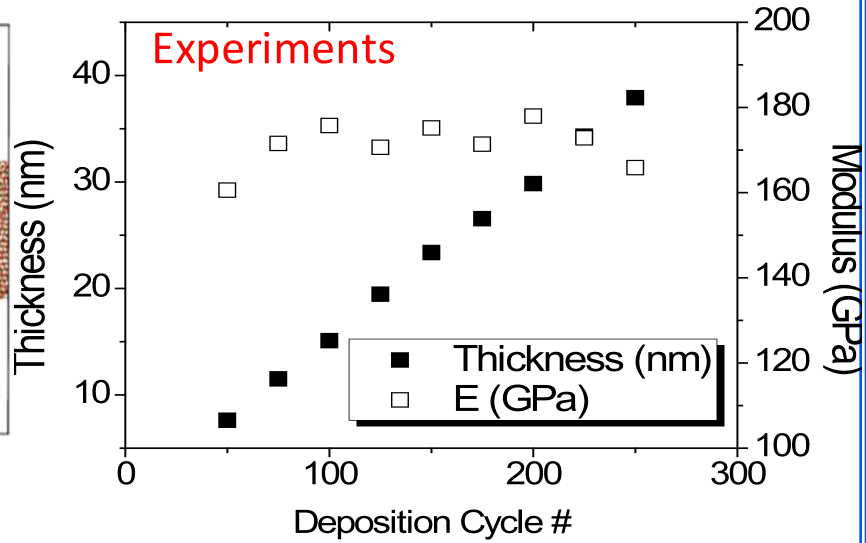
* **Ongoing effort: develop Li-O-Al-Si ReaxFF**

Accomplishment 1:

Compare the computed and measured ALD-Al_2O_3 Young's modulus







Method: molecular dynamics with ReaxFF.

Structure: Semi-disordered structure with O-O distance of 1.1 A along growth direction.

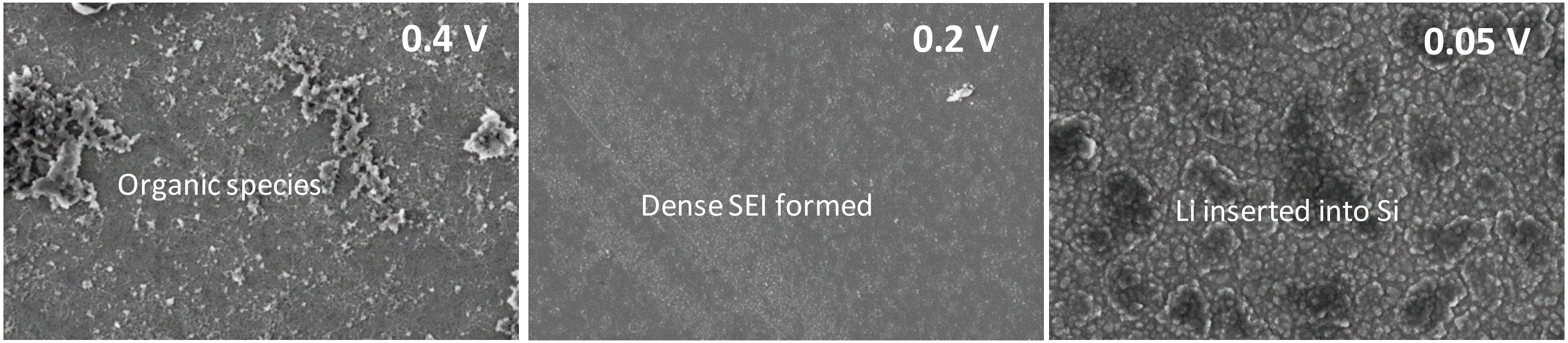
Results: Modulus increase linearly with the film density. At the experimental density ($3.26 g/cm^3$), the predicted E_n=130GPa.

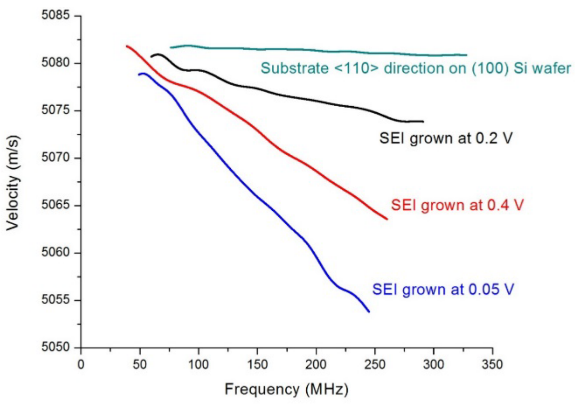
Methods: X-ray reflectometry and ellipsometry for growth rate and density; laser acoustic wave system for the modulus (growth direction).

Structure: growth rate =1.5 nm/cycle and density=$3.26 g/cm^3$.

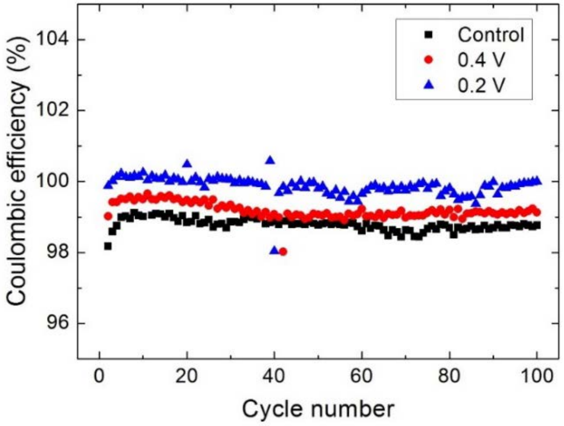
Results: E_n=170GPa

Extension from Accomplishment 1:
Critical voltage to control SEI structure and modulus on uncoated Si



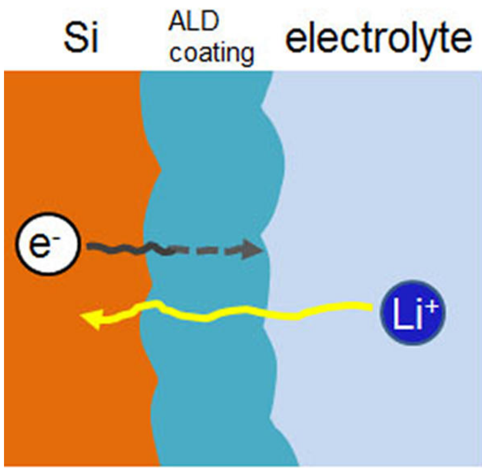


Potential held	0.4 V	0.2 V
Thickness (nm)	57.18	24.31
Young's modulus (GPa)	48.08±1.29	69.18±2.40
Substrate C11 modulus (GPa)	165.98±0.02	165.54±0.02
Least-square errors	0.214	0.228



- More organic compounds formed > 0.4 V; More inorganic compounds formed for 0.2 V < holding voltage < 0.4 V
- LAWS measurement shows higher modulus of SEI formed at low potential.

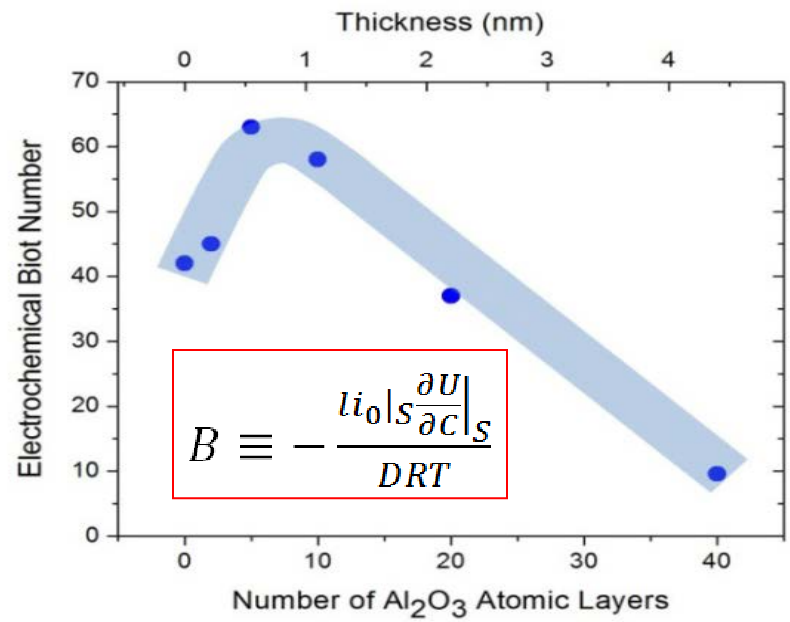
Accomplishment 2:
Optimized ALD-Al_2O_3 thickness exist by correlating the interfacial charge-transfer kinetics vs coating thickness



- Modified PITT quantifies overall interfacial resistance of ALD-Al_2O_3 coated Si electrodes.
- Artificial ALD SEI layers improve the cycle life and facilitate the charge transfer.

Table 1. Exchange Current Densities and Rate Constants of ALD Al_2O_3-Coated Si Measured from the Modified PITT

Al_2O_3 ALD atomic layers	exchange current density ($mA\ cm^{-2}$)	reaction rate constant ($cm\ s^{-1}$)
0	0.161	2.1×10^{-7}
2	0.172	2.2×10^{-7}
5	0.242	3.1×10^{-7}
10	0.223	2.9×10^{-7}
20	0.142	1.8×10^{-7}
40	0.037	4.8×10^{-8}

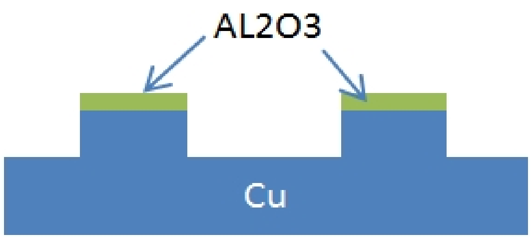


Accomplishment 3.1

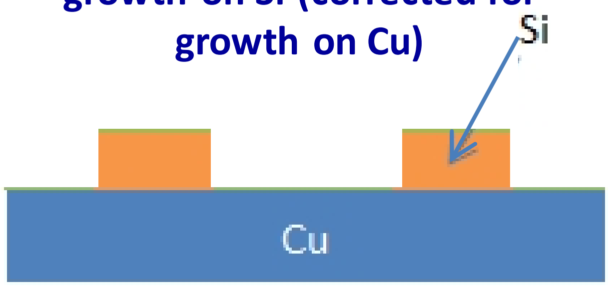
Design experimental methods to decouple volume change caused by SEI formation and lithiation of Si

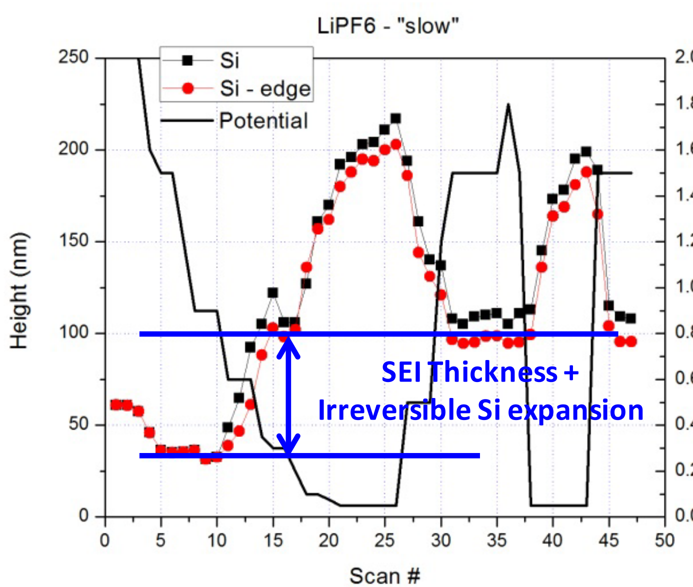
In Situ AFM and MOSS

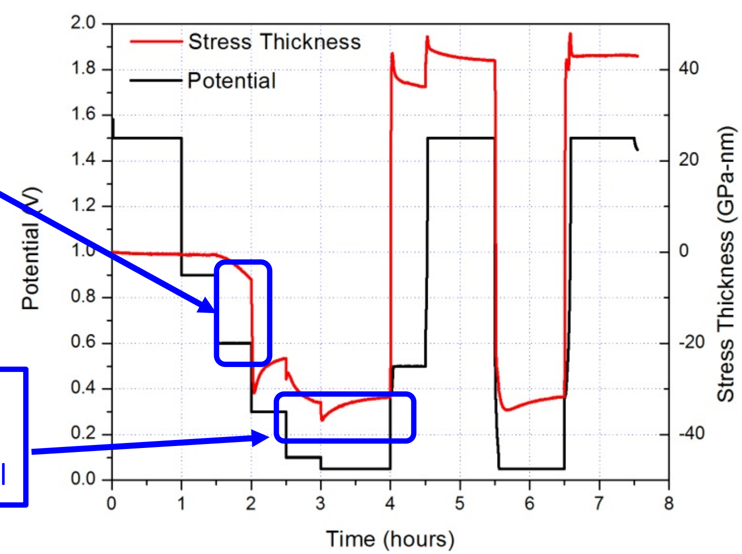
Configuration to measure SEI growth on Cu



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





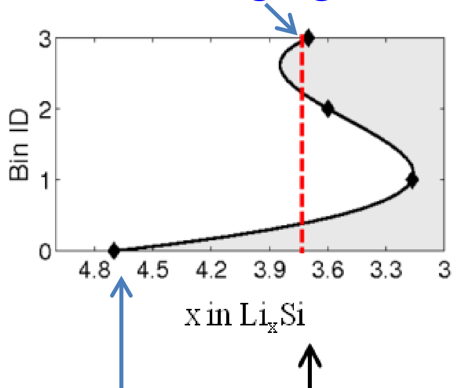


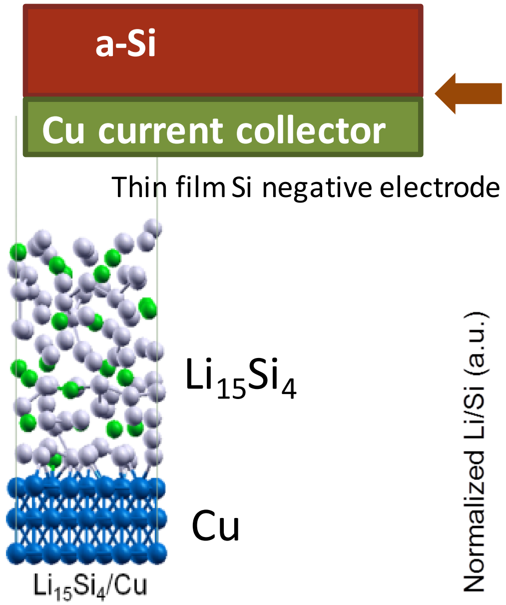
Accomplishment 3.2

Understanding interfacial sliding in patterned Si model system

Modeling

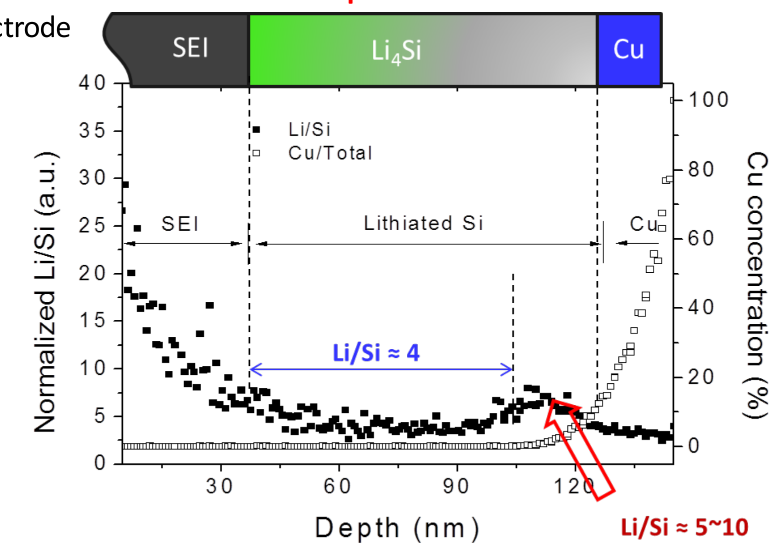
No surface segregation





Si/Cu interface

Experiments



Li segregation at LixSi/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.**

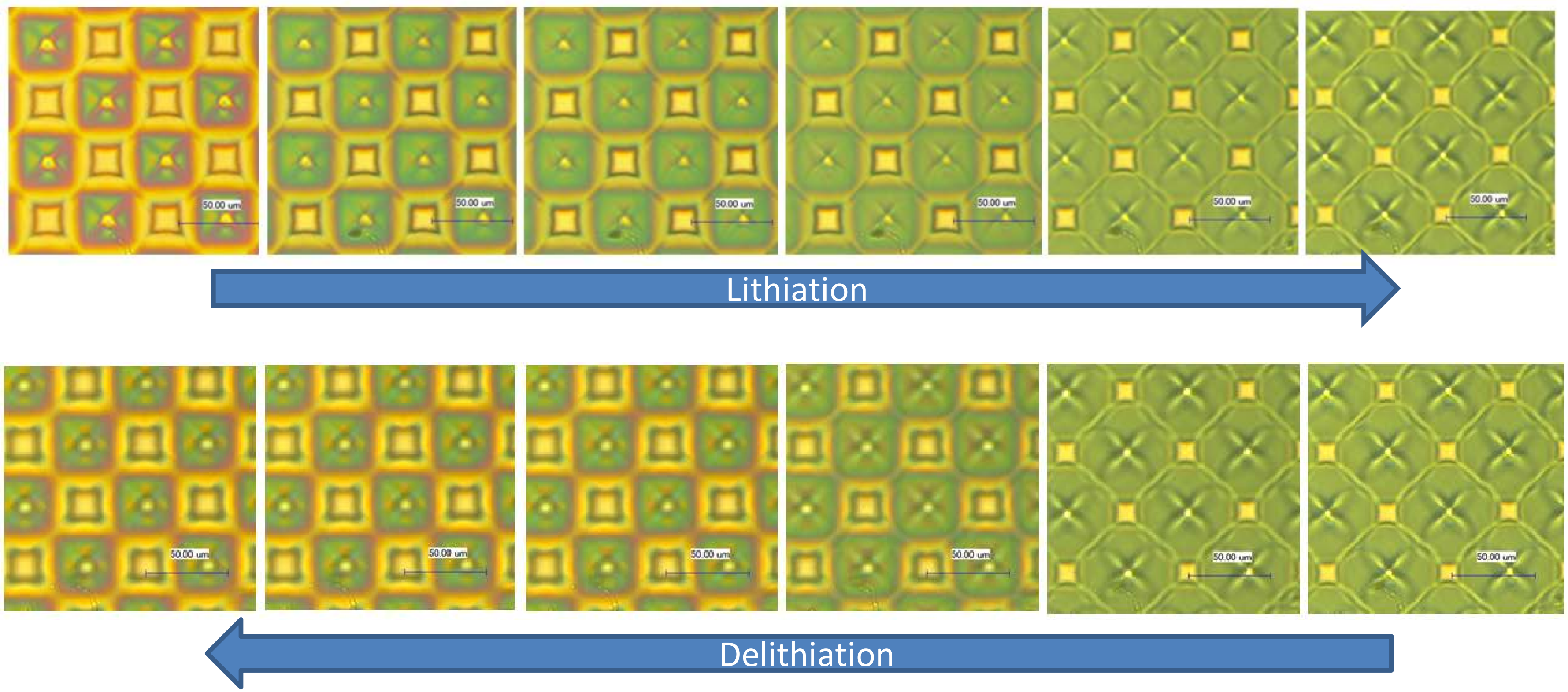
*M.E. Stournara et. al. "Lithium segregation induced structure and strength change at amorphous-Si/Cu interface", **Nano Letters**, 13 (10), 4759 (2013)*

Accomplishment 3.3

Design experimental methods to impose stress on SEI by taking advantage of Si island sliding on Cu current collector.

Optimized island dimension: 25um X 25um X 250nm:

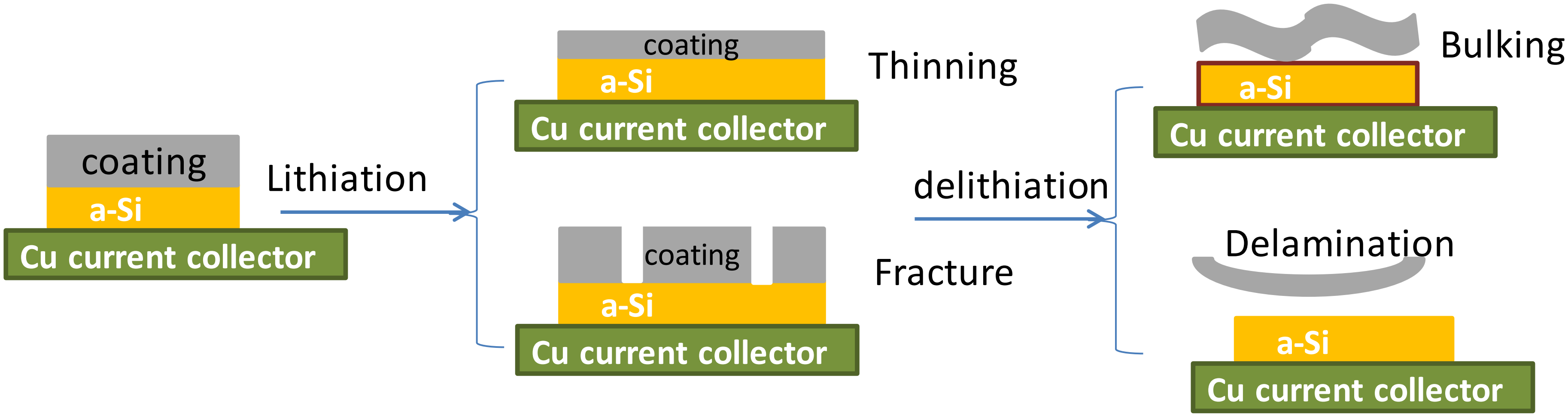
Ideal model system to quantitatively investigate the SEI mechanical behaviors.



Accomplishment 3.4

Connect coating/SEI failure mechanism with electrochemical performance

Hypothesize 2x2 failure mechanisms/models of coating during lithiation and delithiation.



The exposed surface or thinned SEI needs will be re-passivated at different rate. .

Propose: SEI growth limited by electrolyte transport (short times) and electron conduction (long times):

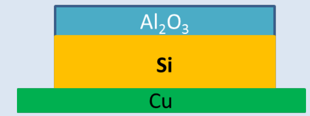
$$\frac{dh}{dt} \cong \frac{V_m\, c^S}{\left[\frac{1}{k} + \frac{h}{D}\right]} + \frac{V_m\, c^S_{el}}{\left[\frac{1}{k_{el}} + \frac{h}{D_{el}}\right]}$$

***Understanding coating failure mechanisms will be the focus for the next stage.**

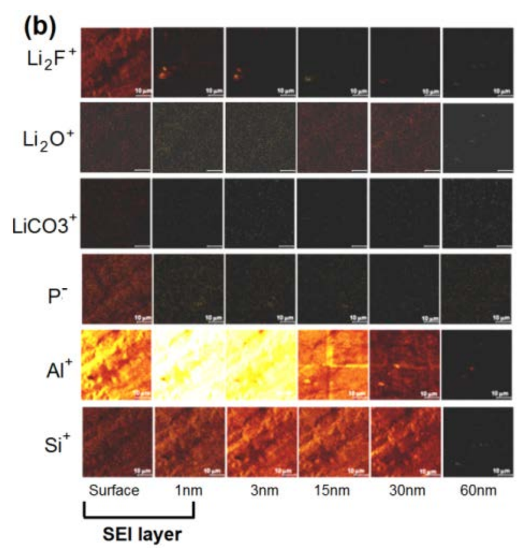
A. Tokranov, et. al, *ACS Applied Materials & Interfaces*, 2014

Accomplishment 4

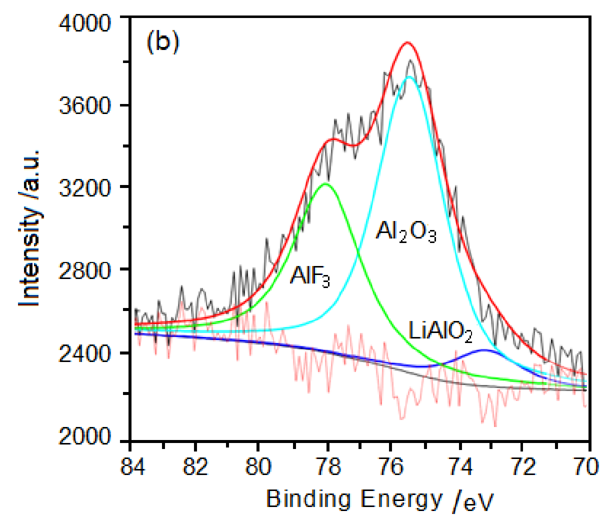
Demonstrate SEI composition and property changes after cycling

Observations	Bare Si electrode 	ALD coated electrode 
Lithiation Reaction (DFT)	$2Li + SiO_2 \rightarrow 0.5Li_4SiO_4 + 0.5Si$ $\langle V \rangle = 1.2V$	$1.5Li+Al_2O_3 \rightarrow 1.5LiAlO_2+0.5Al$ $\langle V \rangle=0.93V$
Young's Modules variation due to lithation*	$E(SiO_2) = 140$ GPa $E(Li_4SiO_4) = 143$ GPa	$E(a\text{-}Al_2O_3) =360$GPa $E(g\text{-}LiAlO_2)=150$GPa

- DFT: SiO_2 and Al_2O_3 lithiated above 0.8 V (EC decomposition).
- TOF-SIMS shows composition changes of the top surfaces
- Artificial SEI reduces natural SEI layer formation (30 nm to 2 nm), much less electrolyte decomposition.



Surface coating suppresses electrolyte decomposition



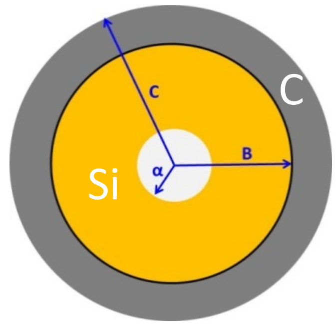
Al_2O_3 coating converted into artificial SEI layer

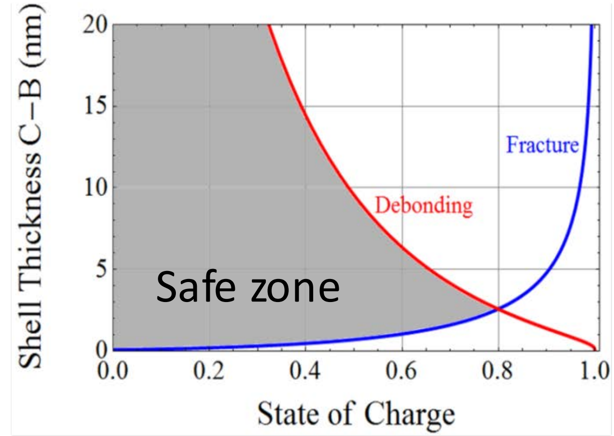
Accomplishment 5:
Mechanical properties at Li_xSi/Li_yC interfaces. Design of core-shell structures

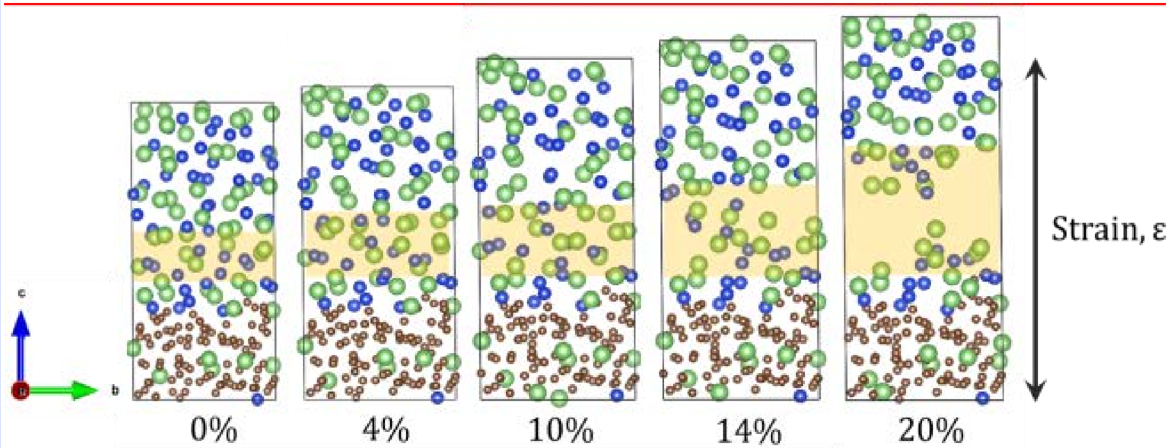
Modeling

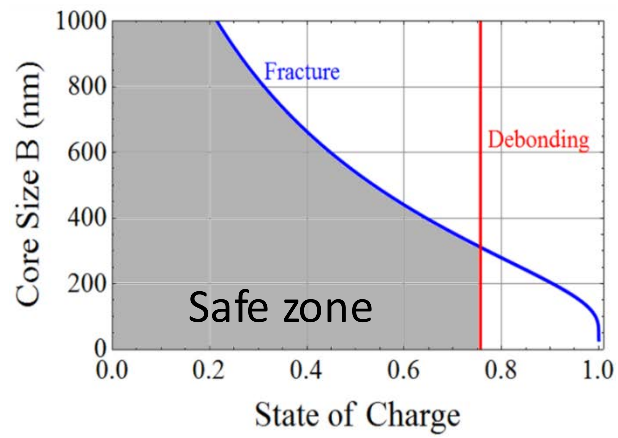
Method:

- 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.

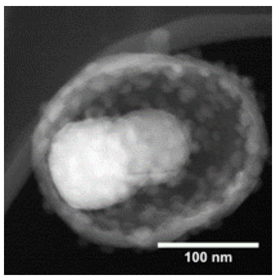
The safe zone: Core thickness < 200 nm, Shell thickness ~ 10 nm.

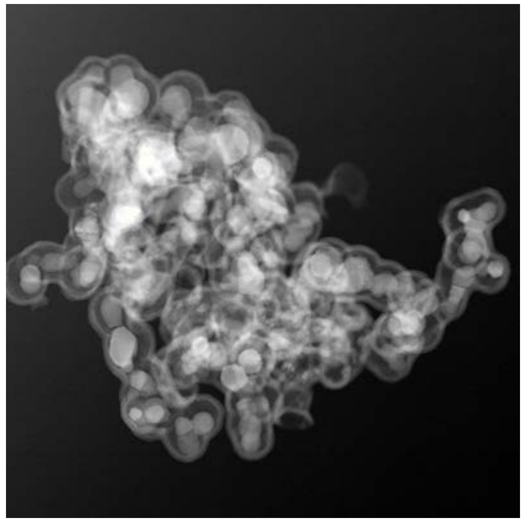
M. E. Stournara, *et. al*. From Ab Initio Calculations to Multiscale Design of Si/C Core–Shell Particles for Li-Ion Anodes , ***Nano Letters***, 14 (4), 2140–2149 (2014)

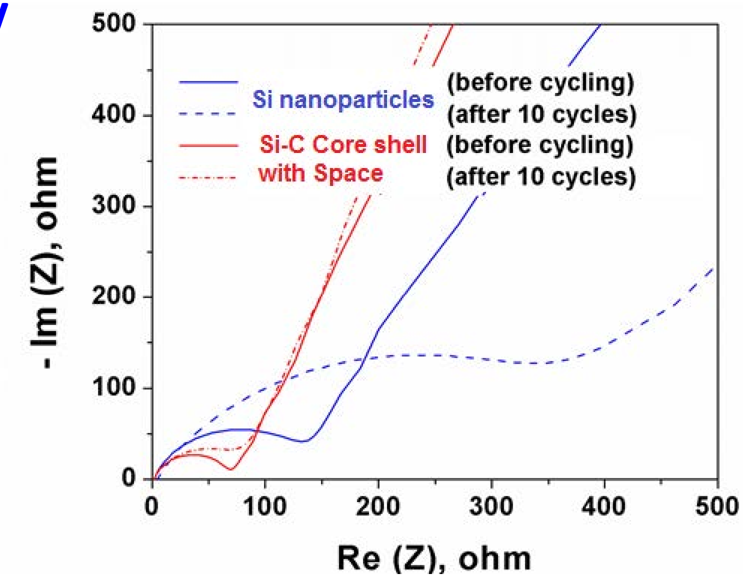
Experiments for Accomplishment 5:

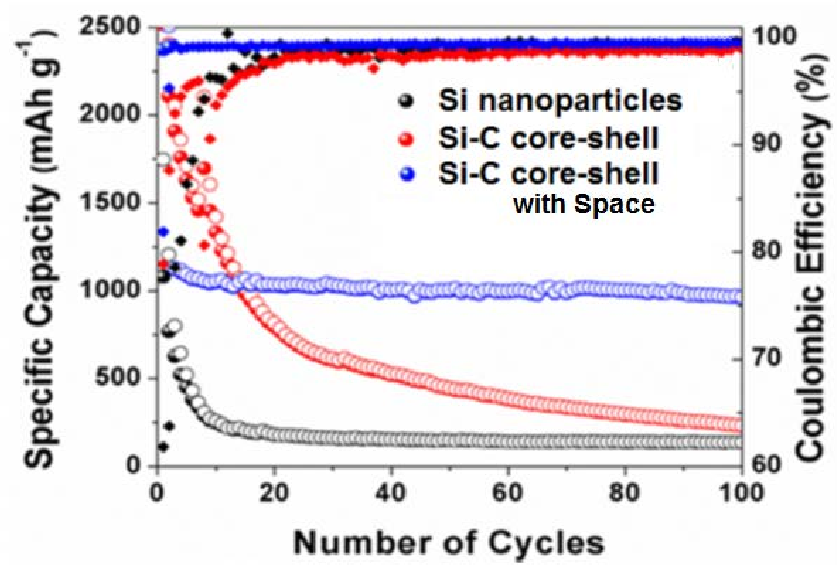
Si-C Core/shell structure with free space to stabilize SEI and increase coulombic efficiency

Lithiated Core/shell









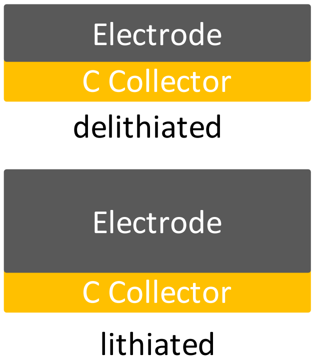
Benefits of yolk-shell structure:

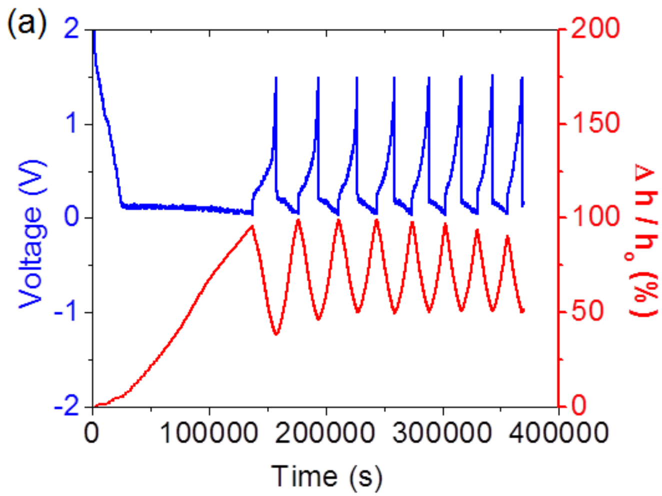
- Accommodate Si volume expansion
- Stabilize SEI layer
- Improve electrical conductivity
- Enhance Electrode integrity

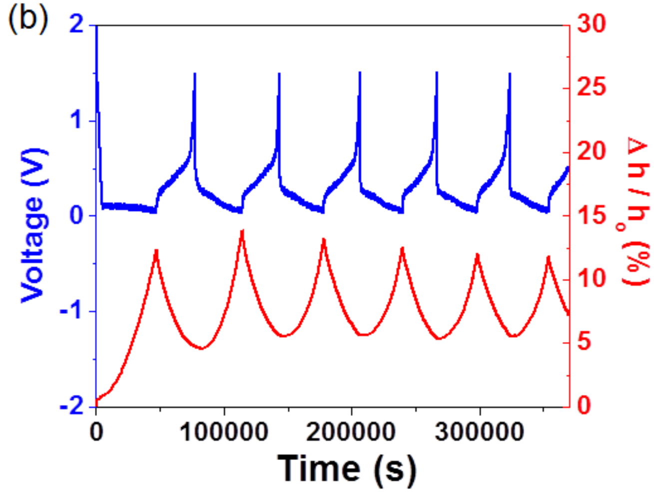
***Next: Optimize the geometry design based modeling insights**

Extension from Accomplishment 5

Minimized Breathing Effect at Electrode Level

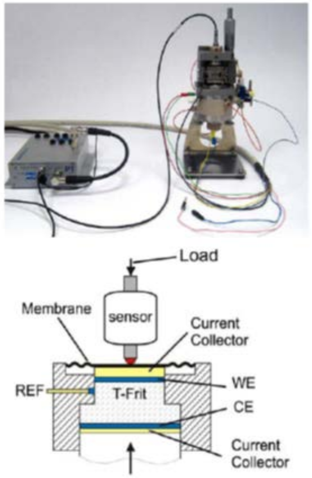






Electrode made with Yolk-shell Si/C

Electrode made with Si nanoparticles



In-situ EC Dilatometer

- Free space in core-shell structure accommodates volume expansion of Si particles ➔ less electrode deformation
- Core-shell structure with free space suppresses breathing of electrodes during the charge-discharge, minimizing damage to tabs in battery packs.

Collaborations and Coordination with Other Institutions

Apply advanced binders to improve electrode integrity, also characterize their mechanical properties utilizing the in-situ electrochemical approaches developed in this project.

Investigate the stability of artificial SEI on Si nanoparticles using *in-situ* TEM

Investigate the mechanical properties of advanced surface coating as artificial SEI utilizing in-situ electrochemical approaches and modeling

Large scale *ab inito* MD simulation of electron transport through ALD coatings to predict electrolyte reduction reactions rates

Interface modeling for Si-CNT bead-string nano-structures

Develop novel Si nanostructure, leveraged by Canada NSERC CRD funding and GM support

Publications

1. Anton Tokranov, Brian W. Sheldon, Chunzeng Li, Stephen Minne, and Xingcheng Xiao, In Situ AFM Study of Initial SEI Formation on Silicon Electrodes for Li Ion Batteries, *ACS Applied Materials & Interfaces*, DOI: 10.1021/ am500363t, 2014
2. Maria E. Stournara, Yue Qi, and Vivek B. Shenoy, From Ab Initio Calculations to Multiscale Design of Si/C Core–Shell Particles for Li-Ion Anodes, *Nano Letters*, 2014, 14 (4), 2140–2149
3. Xin Su, Qingliu Wu, Juchuan Li, Xingcheng Xiao, Amber Lott, Wenquan Lu, Brian W. Sheldon, Ji Wu, Silicon-based Nanomaterials for Lithium Ion Batteries - A Review, *Advanced Energy Materials*, 2014, 4, 1-23
4. Fathy M Hassan, Victor Chabot, Abdel Rahman Elsayed, Xingcheng Xiao, Zhongwei 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
5. Anton Tokranov, Xingcheng Xiao, Peng Lu, Brian 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
6. Hamed Haftbaradaran, Xingcheng Xiao and Huajian Gao, Critical film thickness for fracture in thin film electrodes on substrate, *Modeling and Simulation in Materials Science and Engineering*, 2013, 21, 074008
7. Maria E. Stournara, Xingcheng Xiao, Yue Qi, Priya Johari, Peng Lu, Vivek B. Shenoy, Brian Sheldon, Huajian Gao, Lithium segregation induced structure and strength change at amorphous-Si/Cu interface, *Nano Letters*, 2013, 13 (10), 4759-4768

Key Accomplishments

- A combination of experimental approaches and MD simulations has been developed to investigate the mechanical properties of ultrathin natural formed SEI and artificial. The preliminary test on ALD-Al_2O_3 coating shows agreement has been achieved.
- A patterned Si model system has been developed to investigate the mechanical failure of SEI. The *ab initio* MD simulations, supported by experimental measurement, explained that Si segregation at the interface decreased the interfacial resistance by one order of magnitude, responsible for interfacial sliding.
- A combined DFT and continuum model has been developed to predict the mechanically safe Si-C core-shell structures, which stabilize the SEI layer and accommodate the volume expansion of Si. As a result, the breathing effect of electrode has been significantly suppressed.

Future Plans

1. Select and optimize artificially-formed SEI, including:

- Apply the continuum model to search for material property design space for the most stable SEI;
- Vary SEI chemistry and perform property predictions at QM and MD level to investigate structure/chemistry to property relationship of SEI on Si;
- Correlate and determine the dominating material properties for stable SEI.

2. Design optimal architecture of artificially-formed SEI and Si, including:

- Predict the critical size and desirable material properties of SEI in a core-shell or yolk-shell structure;
- Investigate the surface reaction rate and charge transfer with modified PITT and EIS;
- Tailor the architecture to stabilize the SEI mechanically.

3. Engineer structures that can be made a high-volume, including:

- Engineer alternative Si structures that can be made at high-volume, for example: etched Si, porous Si, covered with the selected coating material;
- Couple single particle model with porous electrode model to improve the electrode integrity.

Acknowledgement

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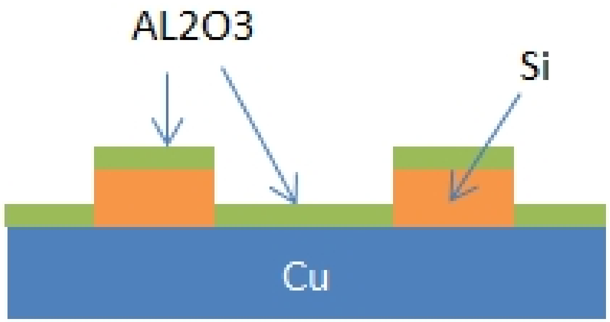
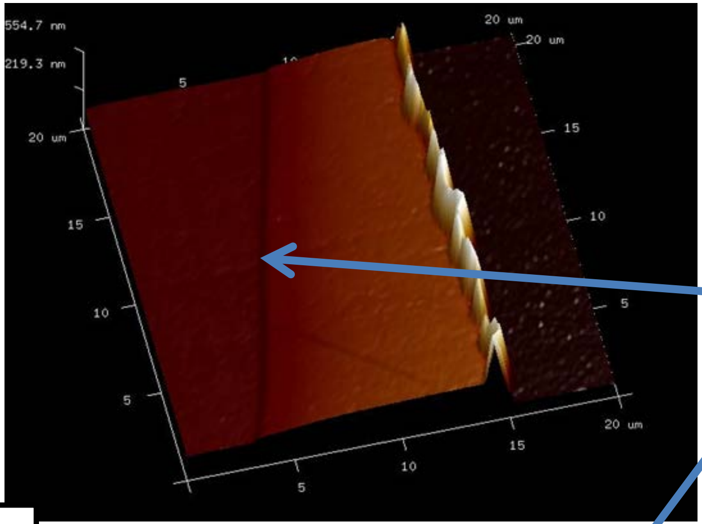
- We also acknowledge the graduate students and postdocs involved in this work:
  - Weidong Zhou, Anton Tokranov, Ravi Kumar, Ill Ryu, Kai Guo, Maria E. Stournara, Qinglin Zhang, Jie Pan, Sung-Yung Kim
- Peng Lu for TOF-SIMS

Back up Slides

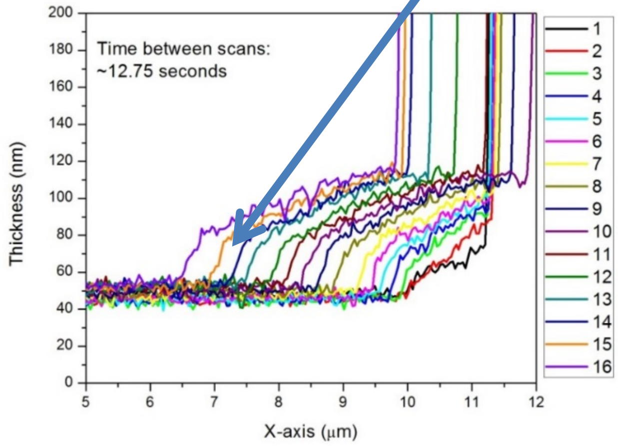
Irreversible Expansion of Silicon

In Situ Height Measurements Track Lithiation Front During the 1st Cycle





Lithiation Front

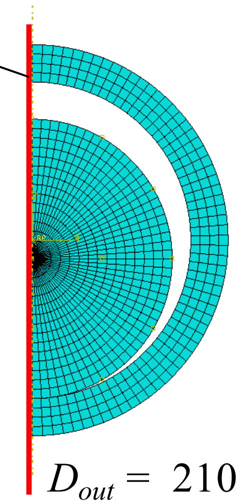


Results:

- Height of fully lithiated Si ~180nm → ~300% of the original volume.
- Fully delithiated height is ~70nm → *120% of the original volume*.
- A simple approach to investigate diffusion and interface motion kinetics

Deformation in the yolk-shell structure

- **Model Description**



- Lithiation with "phase boundary" motion is accounted for with a "regular solution" model (Ting Zhu, Nano Lett, 2011)
- Stress-dependent activation energy for Li diffusion

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

Activation energy

"Regular solution" model of Li diffusion (Zhu et al., Nano Lett, 2011)

- Potentiostatic charging ($\bar{c} = 1$ at the surface of core)

$D_{out} = 210[nm]$

$t_{shell} = 20[nm]$

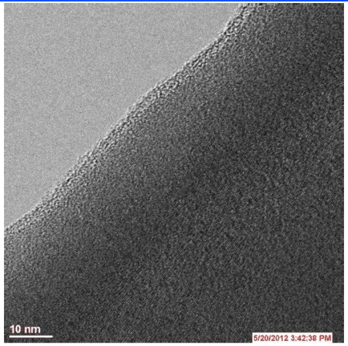
$D_{core} = 150[nm]$

- **Material properties**

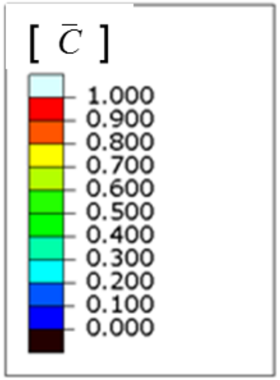
Material	Elastic		Plastic	D_0 $[m^2/sec]$	V_p $[m^2/mol]$	α_C^*	α_T^*
	E $[GPa]$	v	σ_Y $[GPa]$				
a- Si	35	0.22	1	10^{-16}	9×10^{-6}	0.5	0.5
C (Diamond)	1000	0.1	·	·	·		

(*: parameters assumed based on MD calculations for Ni-H system in Haftbaradaran et al, 2010)

Lithiation of a free-standing Si particle

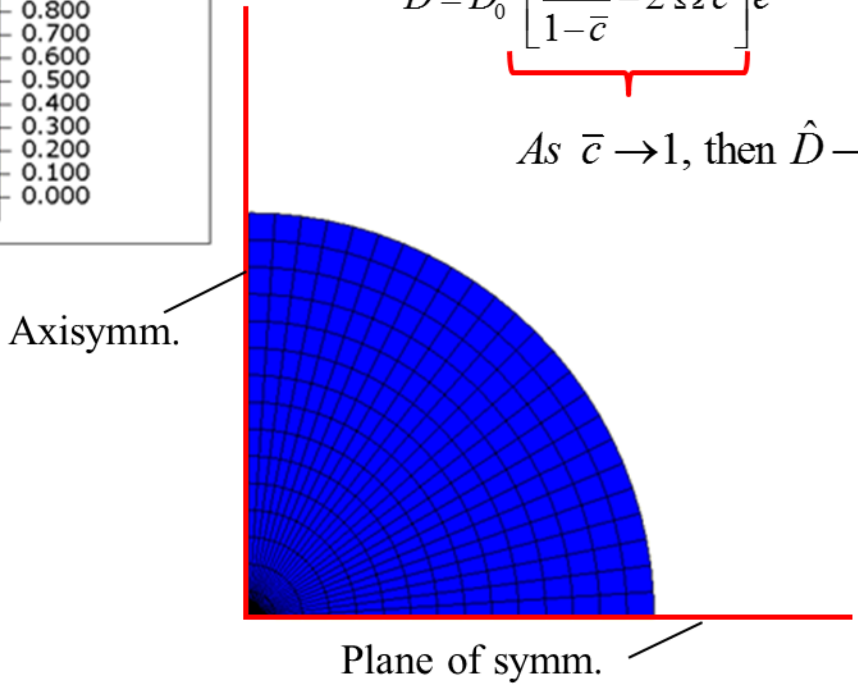


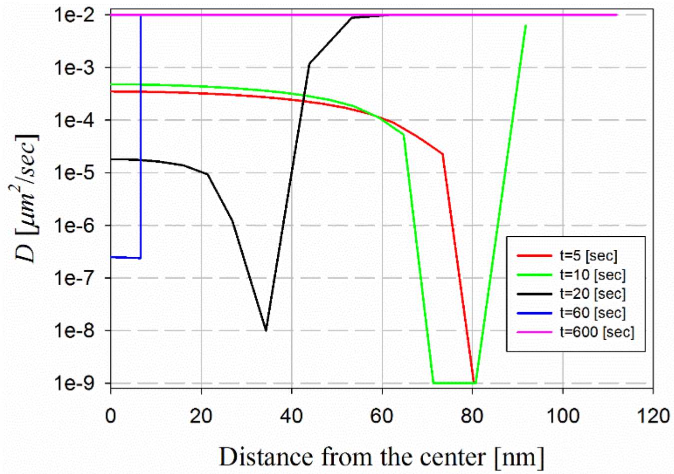
Step: Step-1 Frame: 0
Total Time: 0.000000

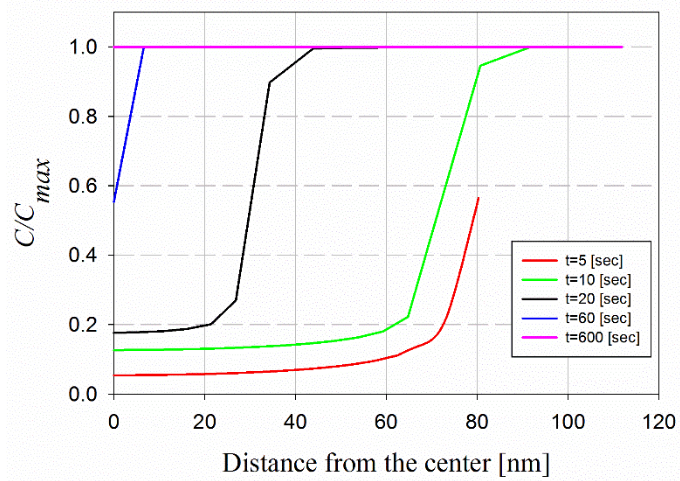


$$\hat{D} = D_0 \underbrace{\left[\frac{1}{1-\bar{c}} - 2\,\Omega\,\bar{c}\right]} e^{\alpha V_p \sigma_b / RT}$$

As $\bar{c} \rightarrow 1$, then $\hat{D} \rightarrow \hat{D}_{max}$







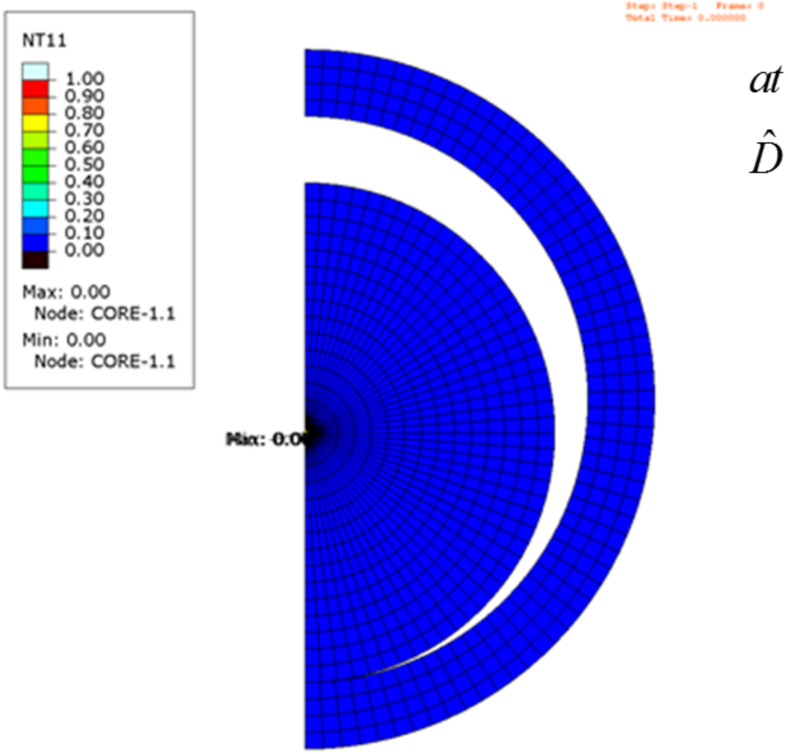
FEM simulation reproduces phase boundary motion in a free-standing Si particle!

Lithiation in Si core / C shell

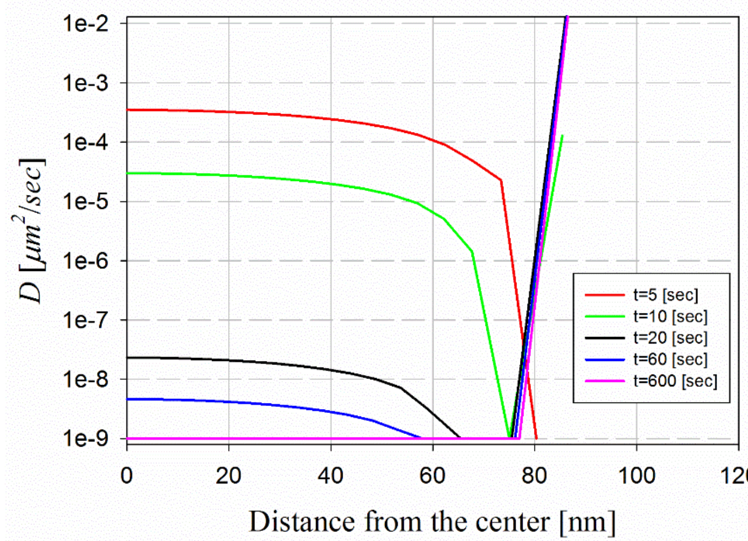
$$\hat{D} = D_0 \left[\frac{1}{1-\bar{c}} - 2\,\Omega\,\bar{c}\right] e^{\alpha V_p \sigma_b / RT}$$

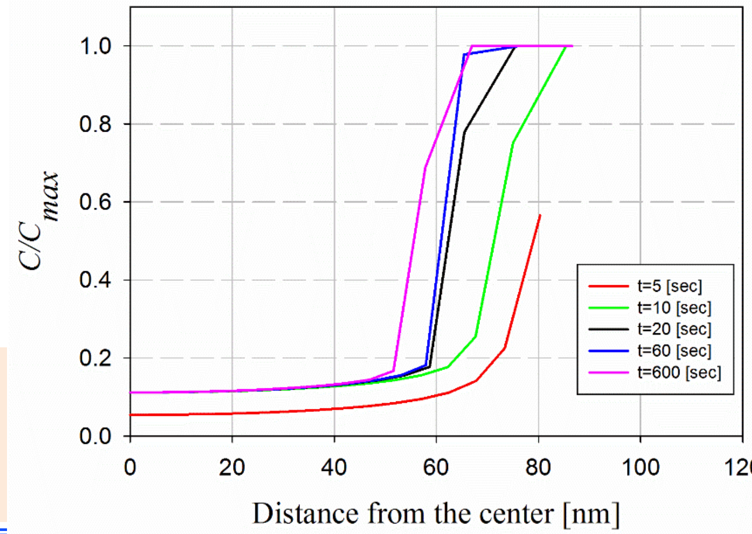
$$at\ \sigma_b = -3GPa$$

$$\hat{D} \approx 0.0002 D_0$$



- $t_{charging} = 1000[\mathrm{sec}]$, $t_{discharging} = 1000[\mathrm{sec}]$





FEM simulation shows that lithiation in the Si yolk can be stopped by the shell, as the diffusivity is suppressed by the compressive stress.

Model of Initial SEI Formation on Silicon

AFM Results:

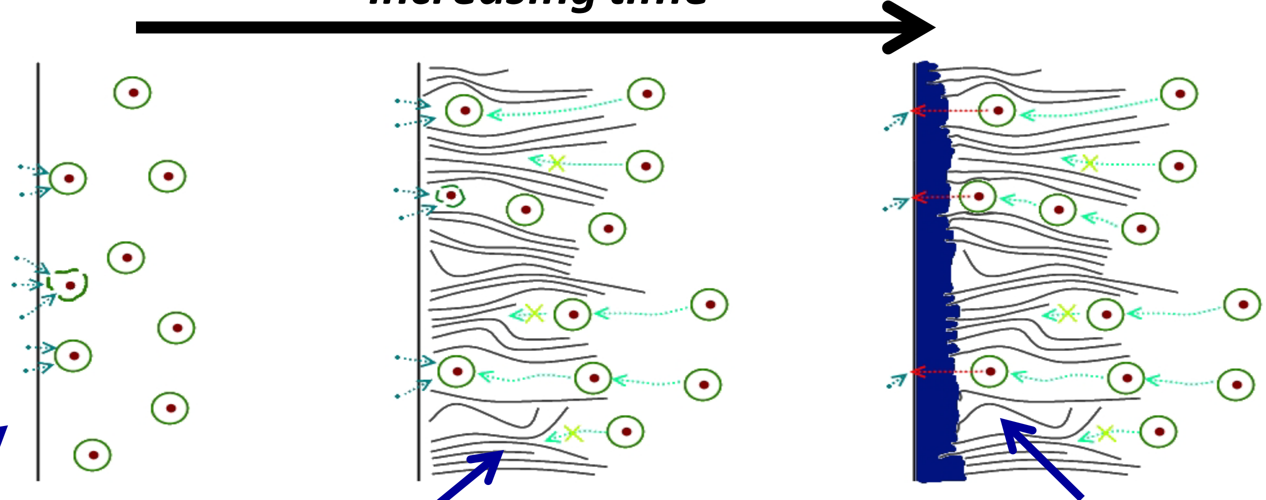
- On Cu, SEI thickness stabilizes quickly at higher potentials: ~20 nm
- On Si, SEI thickness stabilizes at lower potentials – thickness varies with conditions during first cycle: ~20-50 nm

SEI growth limited by electrolyte transport (short times) and electron conduction (long times):

$$\frac{dh}{dt} \cong \frac{V_m\, c^s}{\left[\frac{1}{k} + \frac{h}{D}\right]} + \frac{V_m\, c^s_{el}}{\left[\frac{1}{k_{el}} + \frac{h}{D_{el}}\right]}$$

A. Tokranov, et. al, *ACS Applied Materials & Interfaces*, 2014

Increasing time



initial electrolyte decomposition

continuing decomposition increases the SEI thickness and decreases porosity

a dense SEI forms .. allows Li-ion diffusion but limits electrolyte and electron transport