In Situ Diagnostics of Coupled Electrochemical-Mechanical Properties of Solid Electrolyte Interphases on Lithium Metal for Rechargeable Batteries

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Project ID # ES318

Overview

Timeline

- Project start date: 10/1/2016
- Project end date: 9/31/2019
- Percent completed: 10%

Barriers addressed

Li metal film electrodes with

- Low coulombic efficiency
- Dendrite growth
- Short calendar and cycle life

Budget

- Total project funding: $**1,815,845**
  - DOE share: $1,452,676
  - Contractor share: $363,169
- Funding received in FY2016: $0
- Funding for FY2017: $322,440

Partners

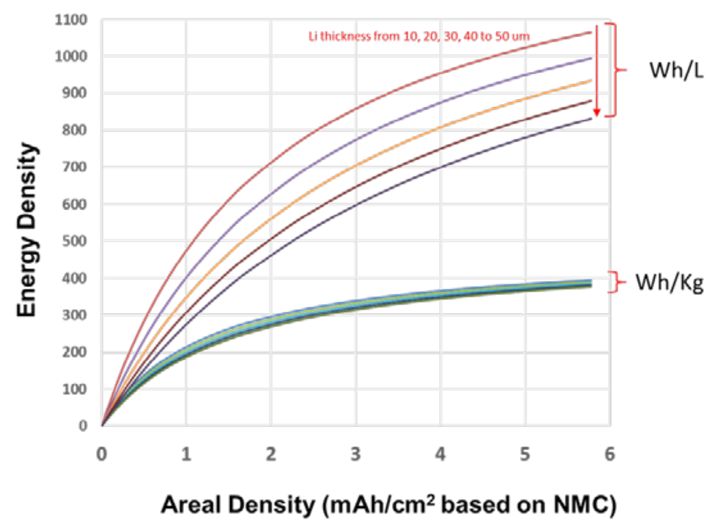
Interactions/ collaborations

- Brown University
- Michigan State University
- University of Kentucky

Project lead: General Motors

Relevance

- Mechanical incompatibility between the SEI layers and the soft Li metal leads to SEI breakage during Li plating/stripping processes. The mechanical characterization of an ultrathin SEI on a soft metal is a “grand challenge”.
- The evolution of the Li surface morphology is also closely tied to non-uniform current distribution that depends on Li diffusion through the SEI and the Li plating/stripping kinetics. Relationships between these processes and the interface mechanical integrity have not been studied in detail yet.
- The lack of a well-controlled system that can be used to conduct fundamental investigations on the coupled mechanical/chemical properties of the SEI layer with Li metal in an electrochemical environment.
- Most academia research work using large amount of access lithium, precisely control Li loading is critical to investigate the cycle efficiency.

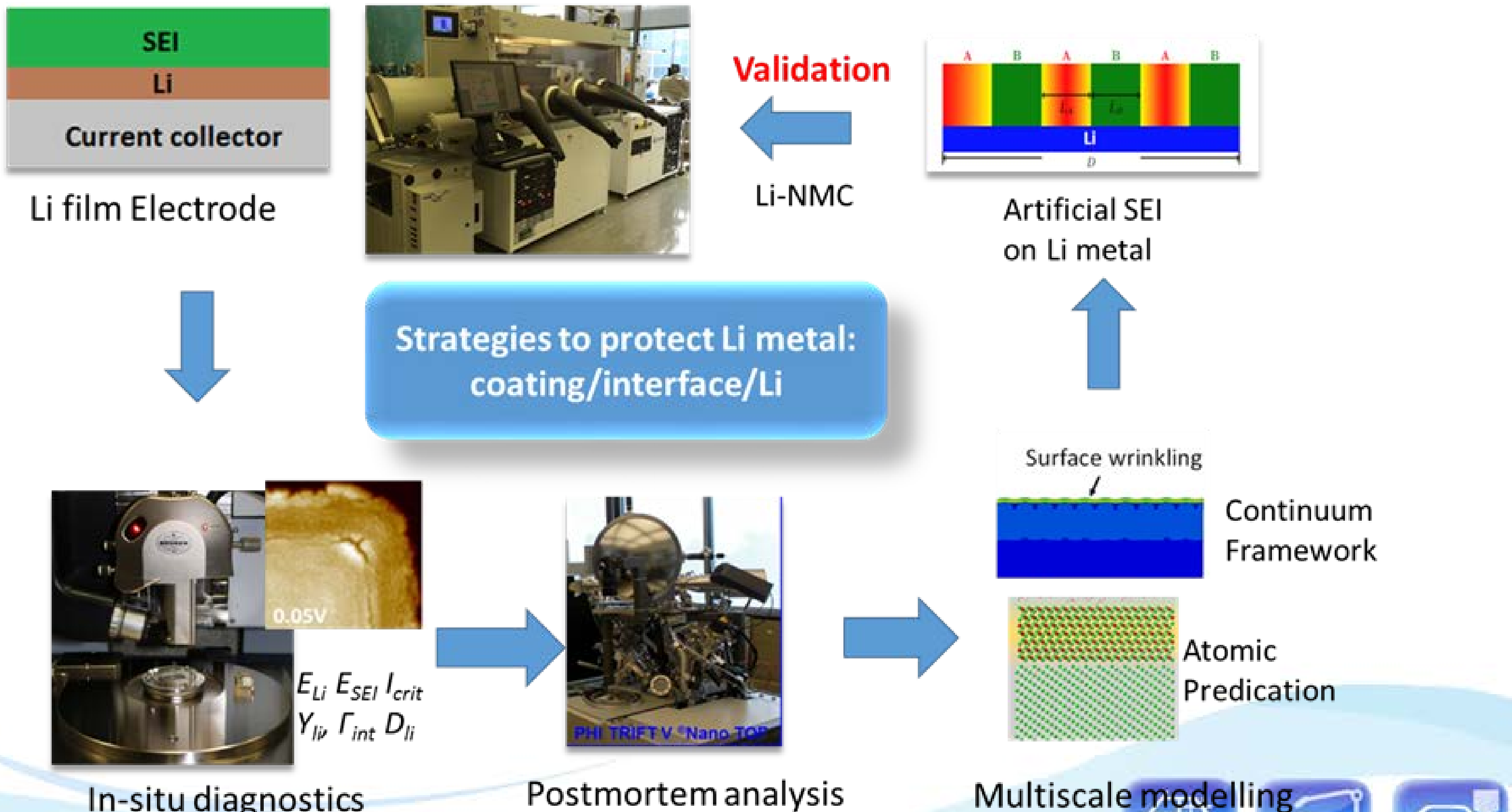


Project Milestones

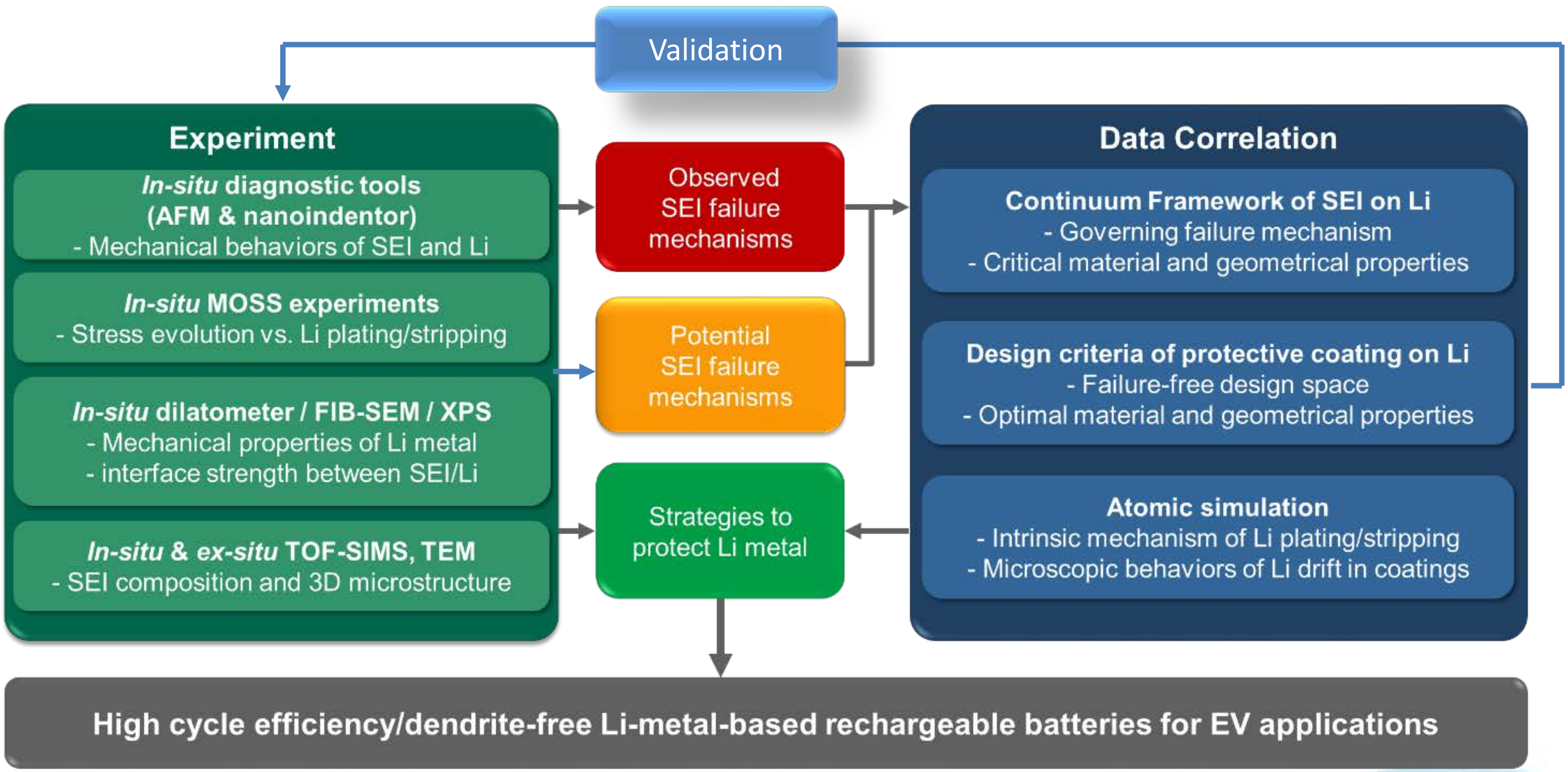
Month/ Year	Milestone of Go/No-Go Decision	Status
Dec. 2016	A well-controlled Li thin film electrode model system developed	**completed**
March. 2017	in-situ diagnostic tools developed to capture the mechanical and transport properties of SEI and Li metal	**completed**
June 2017	Link the knowledge obtained from in-situ experiments with the long-term electrochemical tests	**on track**
Dec 2017	**Make Go/No-Go decision based on the information obtained from in-situ and ex-situ experiments demonstrated to be complimentary and coherent.**	**on track**

Approach/Strategy

- Develop a model system and identify the critical mechanical/chemical/transport properties of SEI/Li electrode responsible for the failure.
- Establish a multi-dimensional property map to correlate SEI/Li mechanical failure, morphology, and cycle efficiency, and provide a design guidance for developing the desirable artificial SEI layer to protect Li metal.



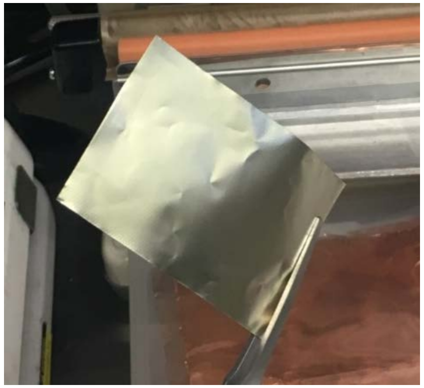
How to correlate experiments with simulations



Accomplishment 1: Established capability of making Li film electrode with controlled capacity.

PVD systems integrated with glovebox

- Sputtering system:
  - 2DC + 2RF sputtering guns
  - Solid electrolyte, metal, and oxide
- Evaporation system
  - 2 thermal +2 e-beam sources
  - Li film, metal films, polymer films

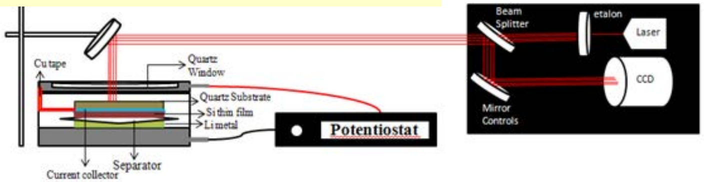


Li Metal film

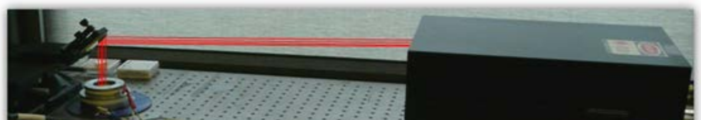
1. Li film electrode: high deposition rate (>20 µm/hr)
2. Flexibility to develop different types of ion-conductive coatings
3. precisely control the Li capacity (up to 10 mAh/cm^2) and texture, the microstructure and composition of artificial SEI, and the Li/SEI interface roughness and chemistry.

Accomplishment 2: Developed *In-situ electrochemical diagnostic techniques to investigate the mechanic behaviors of SEI and Li electrode*

Moss :stress evolution



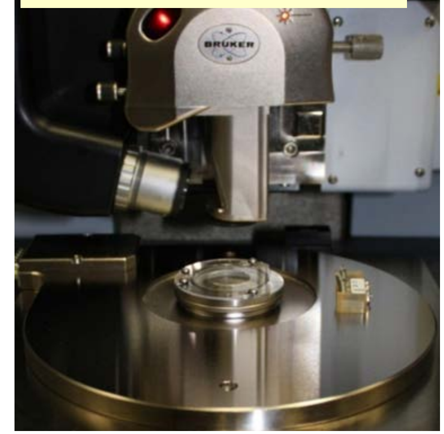
Schematic of experimental set up



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

Actual Experimental Set up

In-situ AFM: SEI growth

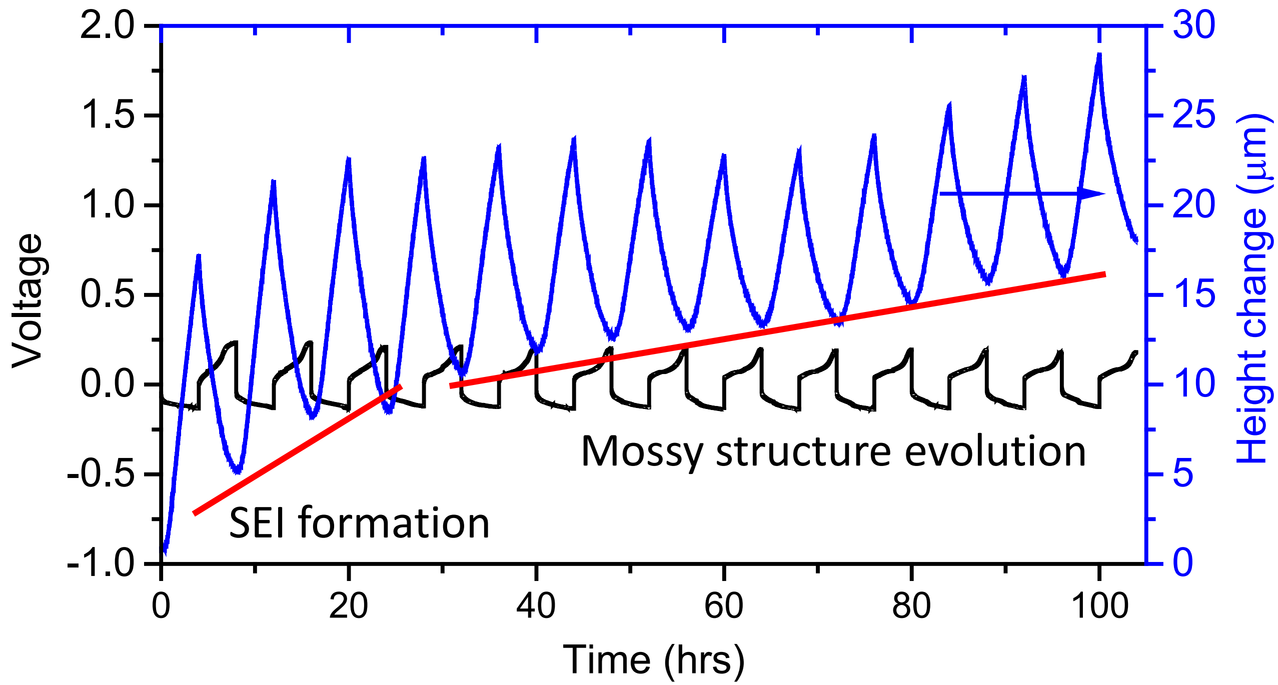


Optical Microscope: Li dendrite

In-situ dilatometer: electrode expansion

Nanoindentation: mechanical properties

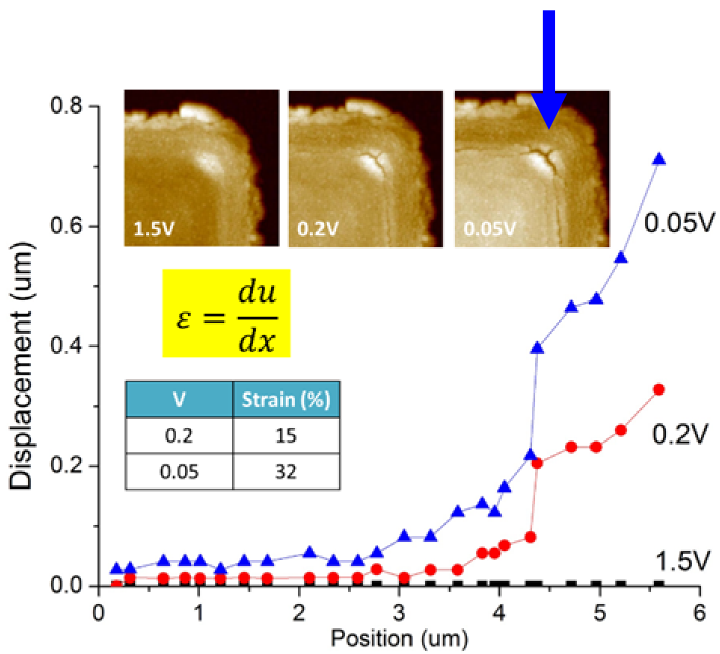
Monitor Li metal electrode deformation (*in-situ* dilatometer)



The irreversible thickness increase with cycle number indicates the formation of SEI layer and evolution of porous mossy structure in Li electrodes.

Monitor SEI and dendrite evolution (*in-situ* AFM)

Direct Observations of Strain Evolution and Cracking in Si SEI (previous BMR funded research)

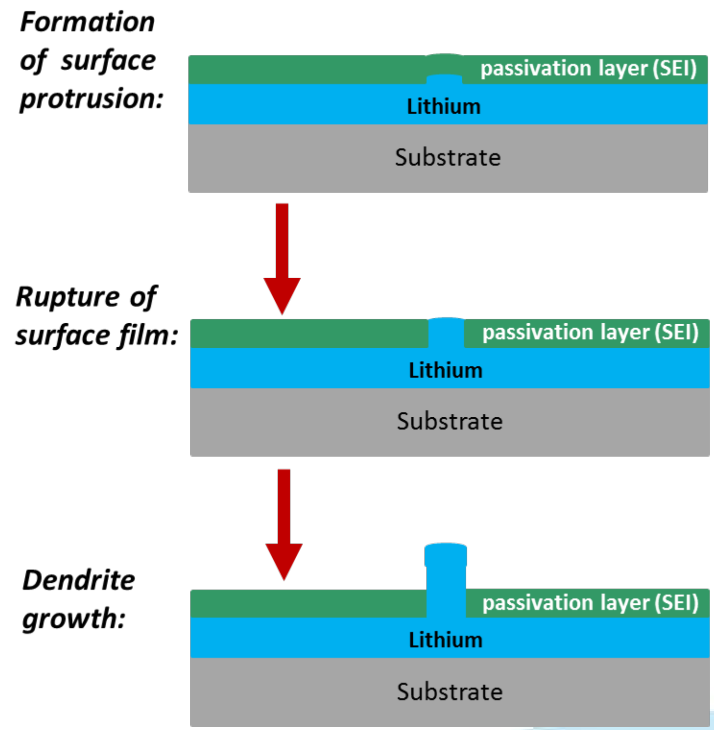


$$\varepsilon = \frac{du}{dx}$$

V	Strain (%)
0.2	15
0.05	32

The crack induced by lithiation of Si at low potential.

Proposed Investigations of Passivation Films on Li Metal



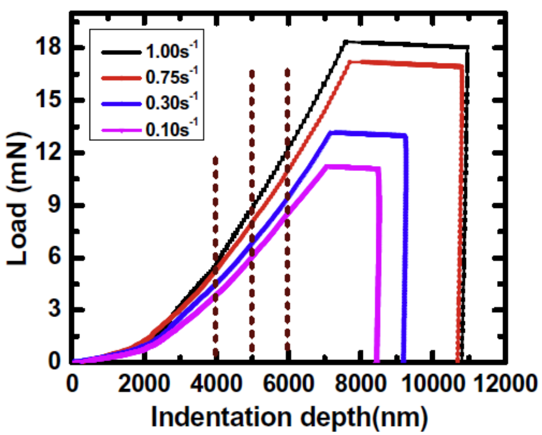
Local electron tunneling

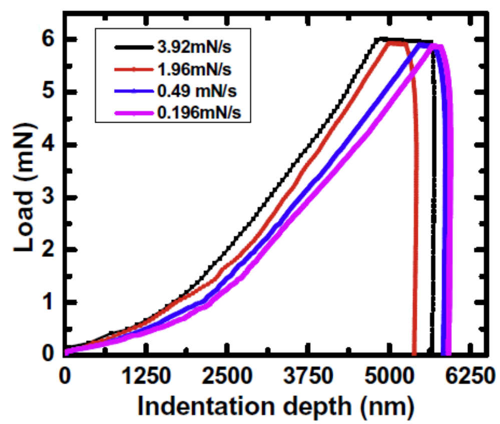
Peakforce mode to capture critical mechanical properties.

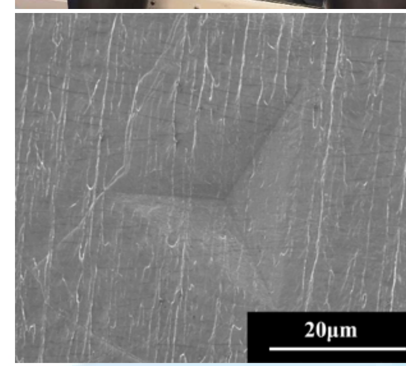
Mechanical behavior of lithium metal (in-situ nanoindentation)

Mechanical behavior		Reliability
➢ Constitutive law ➢ Creep	⟷	➢ Deformation of lithium caused by pressure in battery cells ➢ Damage to the separator caused by lithium dendrites ➢ Pressure and temperature necessary to suppress lithium dendrites

- **Nanoindentation were performed over a range of loading rates (from 0.196 to 3.92mN/s), maximum loads, and holding periods (1s). Constant strain rate-controlled tests were conducted with constant $\dot{F}/F$ values ranging from 0.1 to 1.0 s^{-1}.**







- **Main results**
  - **a) Rate-dependent deformation is observed, demonstrating creep of lithium at RT**
  - **b) Creep behavior depends on the loading rate and the indentation strain rate**

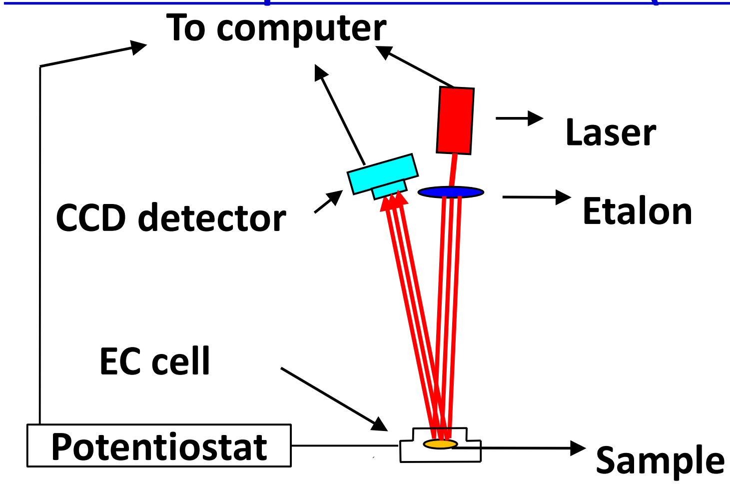
GM RESEARCH & DEVELOPMENT

Yikai Wang and Yang-Tse Cheng, Scripta Materialia, 2017, 130: 191-195.

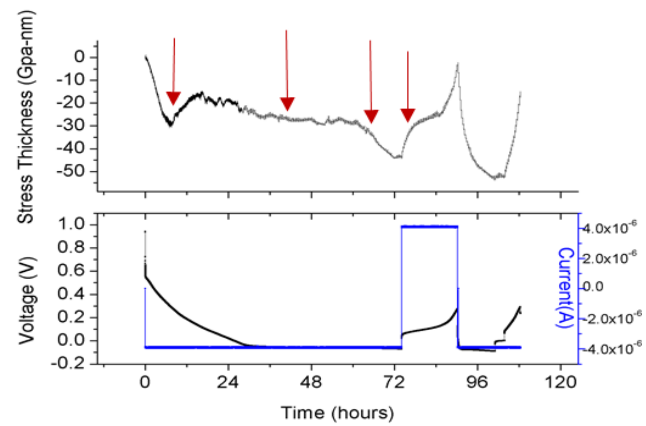
DESIGN BUILD SELL THE WORLD'S BEST VEHICLES

Stress evolution of Li plating/striping (*in-situ* Stress Sensor)

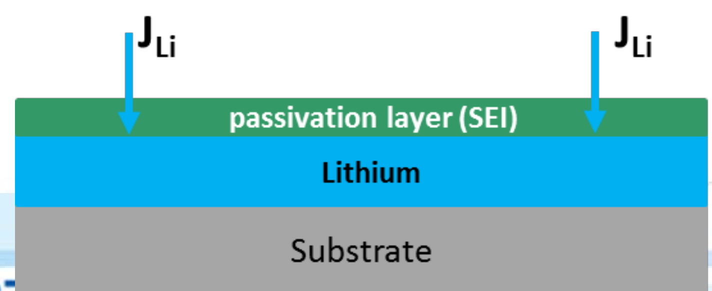
Multibeam optical stress sensor (MOSS)



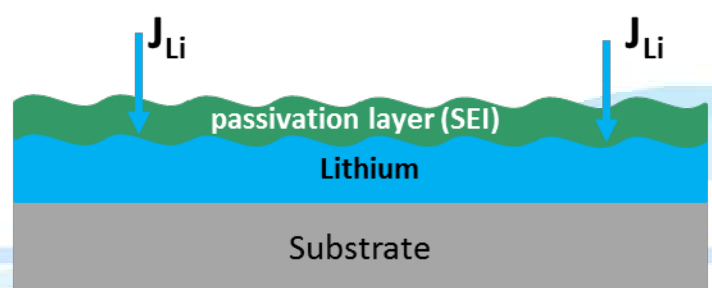
In situ stress data (top) collected during Li plating on a thin film Li electrode, in a solid PEO electrolyte



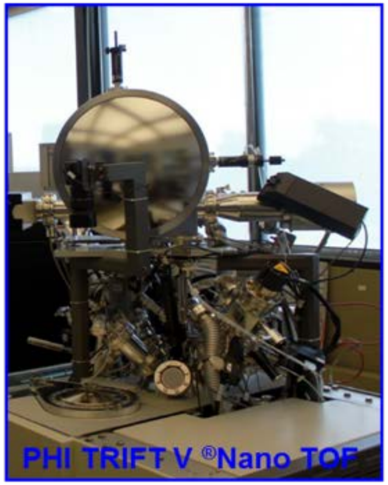
Uniform Film Growth:
Expect minimal stress in passivation layer



Non-Uniform Film Growth:
Stress evolution contributes to degradation of passivation layers

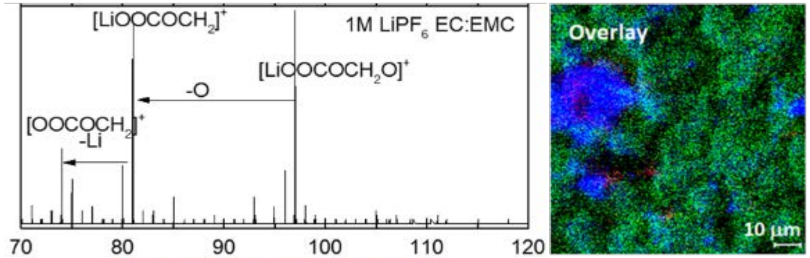


Accomplishment 3: Reveal SEI Chemistry and Micro Structure Evolution (ToF-SIMS)

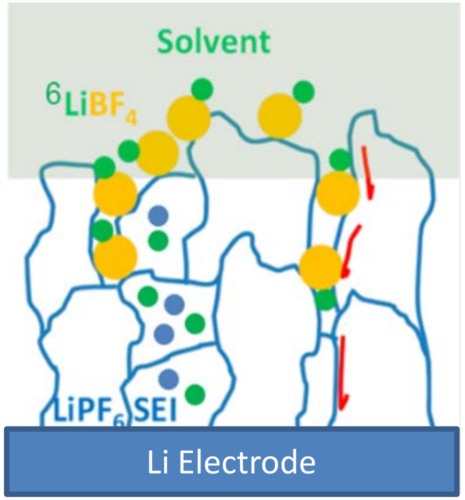


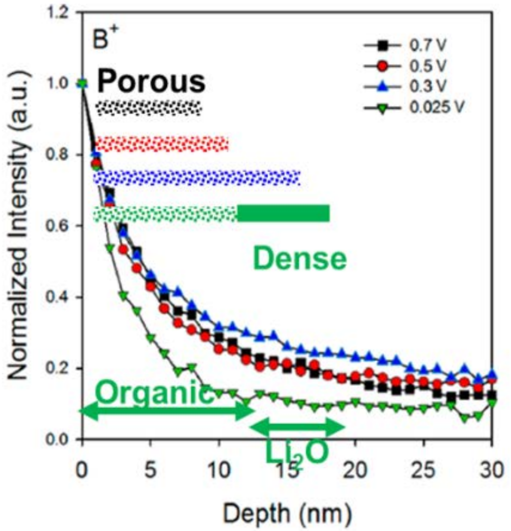
FIB TOF-SIMS:
Au^+, C_{60}^+, Ga^+ (FIB)
Sealed sample transfer

Transfer vessel



Reveal SEI Composition



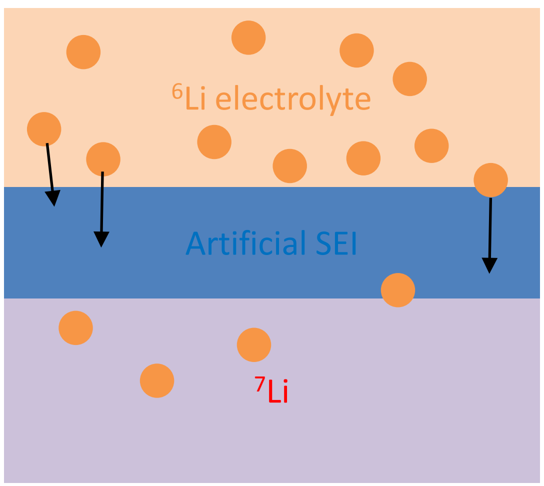


Ideal on Li thin film and coating
Eliminate Air or Moisture Interference
Reveal micro-structure with tracers

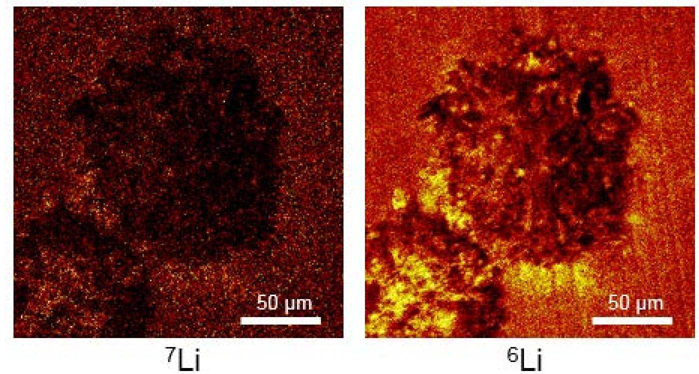
The chemistry and microstructure of SEI was monitored. The results were correlated with the SEI mechanical properties to predict desired SEI properties to reduce SEI degradation, with special focus on the SEI/Li interface.

TOF-SIMS: evaluated artificial SEI transport properties

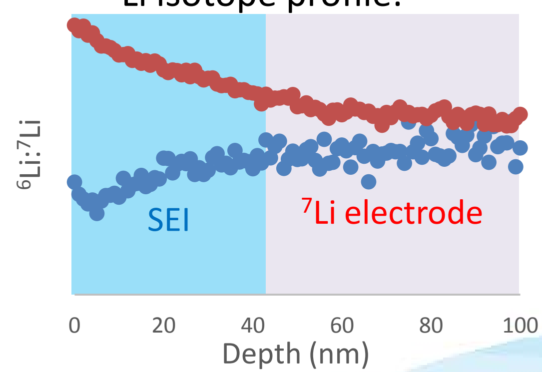
- **Reveal SEI Chemistry and understand how Li transports through SEI layer;**
- **Micro Structure Evolution**



Li isotope map:



Li isotope profile:



^{6}Li isotope labeled electrolyte was used to measure Li transport in artificial SEIs under well-controlled conditions. The results provided the guidance to how to tailor SEI to achieve desired transport properties

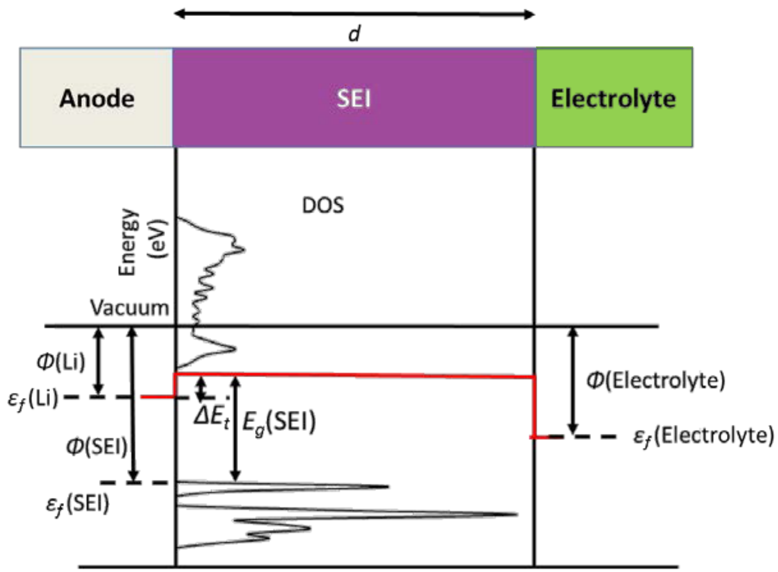
Accomplishment 4: revealed key properties of main SEI components

DFT prediction	Components in Naturally formed SEI due to electrolyte decomposition					Protection coatings	
Key Properties	Li	Li_2CO_3	LiF	Li_2CO_3 + LiF	Li_2O	$LiAlO_2$	LiPON
Young Modulus (Gpa)	4.9	67	65		163	380 → 146	
Decohesion Energy (J/m2)	0.92	0.36 (001)	0.72 (001)		1.15 (110)		
Adhesion with Li(100) (J/m2)		0.17	0.09		0.48		
Electron tunneling barrier (eV)		7.07	10.8		3.07		8.1
Li ion transport carrier & conductivity at 0V (Scm^{-1})		Li interstitial 10^{-7}	Li vacancy 10^{-31}	Space charging effect increases the ionic conductivity & reduces electron conductivity			

- **Perform** Density Functional Theory (DFT) – based modeling to predict key material properties, such as modulus, interface work of adhesion, electron tunneling property, SEI thickness and capacity loss due to SEI formation, Li ion conductivity for key coating components.
- **Construct** interface model to investigate the multi-component effect in artificial coating design.

Estimated electron tunneling thickness (2~3 nm)

For each component in SEI layer (Li_2CO_3, LiF, Li_3PO_4), perform DFT calculations. Align the work functions (Φ) with respect to vacuum.



Electron tunneling Probability

$$T = \frac{16\varepsilon_f . \Delta E_t}{(\varepsilon_{f+}\Delta E_t)^2} e^{-\frac{4\pi d}{h}\sqrt{2m \cdot \Delta E_t}}$$

Assume a critical thickness, d^* is required to prevent electron tunneling ($T = e^{-40}$).

Electron tunneling barrier: $\Delta E_t = E_g(SEI) - \Phi(SEI) + \Phi(electrode)$

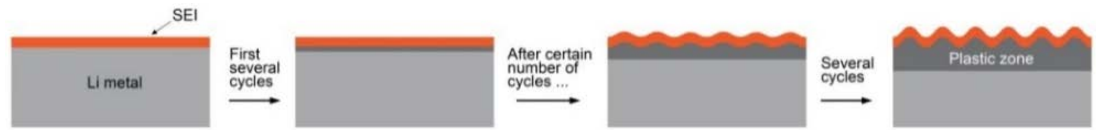
	GGA		HSE06	
Component	ΔE_t **(eV)**	d^* **(nm)**	ΔE_t **(eV)**	d^* **(nm)**
Li_2CO_3	1.78	3.02	4.1	2.00
LiF	3.98 [16]	2.03	6.26	1.62
Li_3PO_4	3.49	2.16	5.91	1.66

Accomplishment 5: revealed the potential SEI failure mechanisms

Analytical solutions based on continuum mechanics analyses provide scaling laws for the critical current density as functions of system parameters (e.g., modulus mismatch, thickness ratio, etc.).

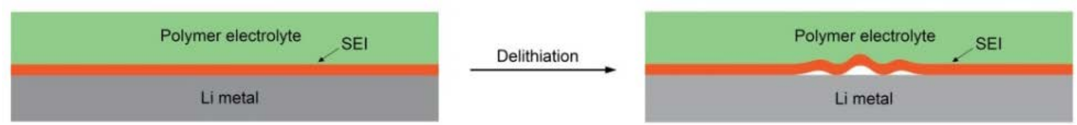
(A) Ratcheting-induced wrinkling

$$I_{crit} \propto \frac{[E_{Li}(1-\nu_{SEI}^2)]^{2/3}}{[E_{SEI}(1-\nu_{Li}^2)]^{5/3}} \cdot Y_{Li}$$



(B) Pop-up delamination

$$I_{crit} \propto \sqrt{\frac{E_{poly}(1-\nu_{SEI}^2)}{E_{SEI}} \frac{h_{SEI}}{h_{poly}}}$$



(C) Crack-driven delamination

$$I_{crit} \propto \sqrt{\frac{(1-\nu_{SEI}^2)}{E_{SEI}} \frac{\Gamma_{int}}{h_{SEI}}}$$

Critical material properties:

- Modulus mismatch
- Yield strength
- Interfacial strength
- Adhesion energy
- Fracture toughness
- Delamination toughness
- Viscoelastic properties
- …

Failure Criteria:

- Energy release rate
- Plastic ratcheting
- Critical length
- Critical thickness
- …

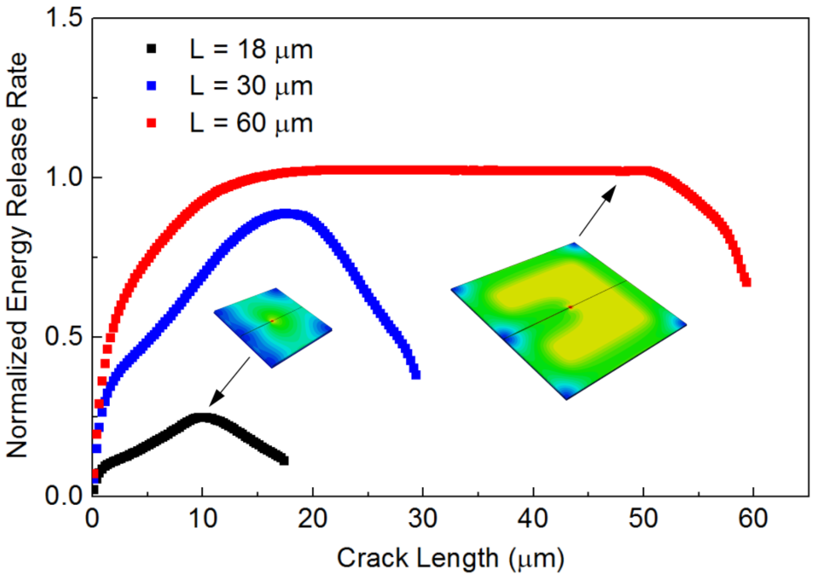
Design space:

- Coating thickness
- Coating modulus
- Coating toughness
- Interfacial strength
- Adhesion energy
- Electrolyte composition
- …

Expected results from continuum Analysis

I. Modeling and analysis of key failure modes

Example: Energy release rate calculation



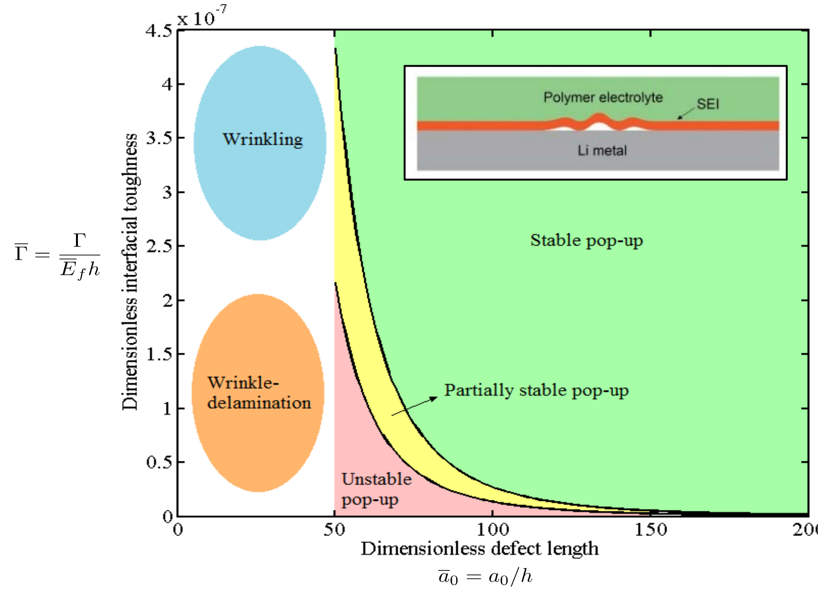
Crack propagates if energy release rate (*G*) exceeds material fracture toughness (*Γ*):

$$G = -\frac{\partial \Pi}{\partial A} = -\frac{\partial (U - F)}{\partial A} \geq \Gamma$$

By designing the coating thickness and modulus, we will identify ways to control the maximum energy release rate and hence suppress the crack propagation.

II. Failure diagram and design space

Example: an estimated failure map for pop-up delamination



Failure diagram will provide valuable information for experimental design, such as:

a) Key parameters governing the failure mechanisms;
b) Critical values of these parameters to induce each failure mode;
c) “Dangerous” region where SEI is unstable;
d) Design space in which SEI failure is suppressed.
e) …

Responses to Previous Year Reviewers' Comments

- **New project started on 10/1/2016.**
- **Not reviewed last year.**

Collaborations and Coordination with Other Institutions

Dr. Wanli Yang (LBNL)	Apply advanced synchrotron to understand the failure mechanism of Li metal with different artificial SEI layers;
Dr. Chongmin Wang, Dr. Jie Xiao (PNNL)	Investigate the stability of artificial SEI on Li using *in-situ* TEM; Advanced electrolyte additives;
Prof. Zhongwei Chen (U. Waterloo)	Advanced electrode architecture;
Dr. Teddy Huang (Bruker)	In-situ electrochemical AFM and nanomechanics characterization.

Conclusions

- We have established a flexible coating system for developing well-controlled Li film electrode and solid electrolyte as the protective coatings.
- A comprehensive in-situ diagnostic tools have been developed or adapted from our previous work to investigate the coupled mechanical and chemical degradation.
- Preliminary results show Li metal has very complicated mechanical behaviors, including the viscoelastic creeping behavior.
- The potential failure modes of SEI on Li metal have been proposed, which provided the correlation between the critical current density and SEI fracture.

Publications and presentations

- Wang, Y. and Y.-T. Cheng, A nanoindentation study of the viscoplastic behavior of pure lithium. Scripta Materialia, 130 (2017): 191-195.
- Qinglin Zhang, Lei Han, Jie Pan, Zhi Chen, and Yang-Tse Cheng, Chemically stable artificial SEI for Li-ion battery electrodes, Appl. Phys. Lett. 110, 133901 (2017)
- Yikai Wang and Yang-Tse Cheng, “Determining viscoplastic properties of lithium metal by nanoindentation,” 2017 Materials Research Society Spring Meeting & Exhibit, Phoenix, Arizona, April 17-21, 2017.
- X. Xiao, Towards high cycle efficiency of electrode materials for next generation of lithium ion batteries. Battery Congress, May 7, 2017, Novi, Michigan
- B. W. Sheldon, Mechanical Degradation and Optimization of Solid Electrolyte Interphases in Li Ion Batteries, Society of Engineering Science Annual Meeting, University of Maryland, October, 4, 2016.
- B. W. Sheldon, Stress Evolution and Degradation Mechanisms at Interfaces in Energy-Related Ceramics, Electronic Materials and Applications 2017 (American Ceramic Society), Orlando, FL, January 20, 2017.
- B. W. Sheldon, Mechanical Degradation and Optimization of Solid Electrolyte Interphases in Li Ion Batteries, TMS Annual Meeting, San Diego, CA, March, 2, 2017.
- Yue Qi, Modeling of the Interface and Interphases in Li-ion batteries, Department of Chemical & Biological Engineering, Drexel University, Dec 2016
- Yue Qi, Multi-component and Multi-functional Protection coating for high capacity anodes (Li and Si), 2017 MRS spring meeting, April 18, 2017
- Ravi Kumar, Direct In-Situ Observations of the Chemo-Mechanical Stability of the Solid Electrolyte Interphase (SEI) on Silicon Anodes, MRS Fall meeting, December, 2016

Remaining challenges and barriers

- Understanding the impact of multi-components in SEI layer on the Li transport and current density distribution along the interface between SEI and Li metal.
- Understanding the impact of mechanical properties of SEI layers and protective coatings on the microstructure evolution of Li metal electrode during Li plating and stripping process.
- Lack of reliable approach to characterize the interfacial fracture strength between SEI and Li Metal.
- What are the critical properties of protective coatings on Li metal which can effectively suppress the dendrite and improve the cycle efficiency?

Future plans

- Link the knowledge obtained from in-situ experiments with the long-term electrochemical tests: Develop isotope exchange and ToF-SIMS approach to trace Li microstructure evolution, and the results will be correlated with the SEI mechanical properties to predict desired SEI properties, with special focus on the SEI/Li interface
- Initiate predication of mechanical and transport properties of SEI components and compare with experimental data: The joint DFT and DFTB methods and parameters to balance the computation needs (speed, size and accuracy) in simulating the charge transfer step at the Li/SEI/electrolyte interface.
- Tailor SEI chemistry and perform property predictions at QM and MD levels to investigate structure-chemistry-property relationship of SEI on Li and the impact on Li plating and striping underneath.

Any future work is subject to change based on funding levels.

Acknowledgements

- Tien Duong and Aaron D. Yucon for program management.
- Dr. Qinglin Zhang, Kai Guo, Yikai Wang, Ravi Kumar for the experimental and simulation work.
- Dr. Mei Cai and Dr. Yang Li for helpful discussion.