NREL
NATIONAL RENEWABLE ENERGY LABORATORY

Surface analysis of the Silicon SEI

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Silicon Electrolyte Interface Stabilization Focus Group

National Renewable Energy Laboratory

2018 DOE VTO Annual Merit Review

June 20, 2018

Project ID: BAT347

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

Overview

Timeline

- October 1st 2016 - September 30st 2019.
- Percent complete: 40%

Budget

- Funding for FY 18: $3900K

Barriers

- Development of PHEV and EV batteries that meet or exceed the DOE and USABC goals
  - Cost, Performance and Safety

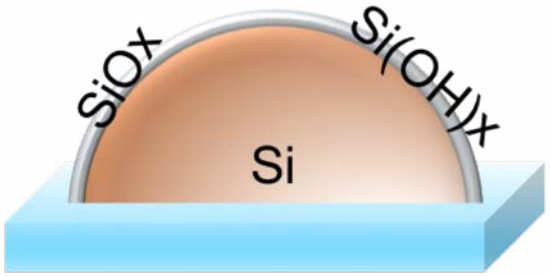
Partners

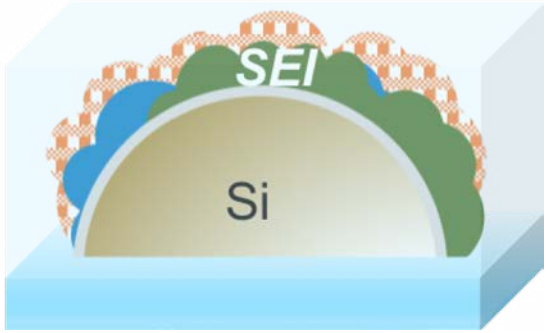
- Five Laboratory Team lead by NREL:
  - Sandia National Laboratory
  - Argonne National Laboratory
  - Oak Ridge National Laboratory
  - Lawrence Berkeley National Laboratory
- UC Berkeley
- Colorado University Boulder
- Colorado School of Mines
- University of Rhode Island

Relevance

The solid-electrolyte-interface (SEI) layer determines the reversibility, cycling performance, and safety of lithium-ion battery.

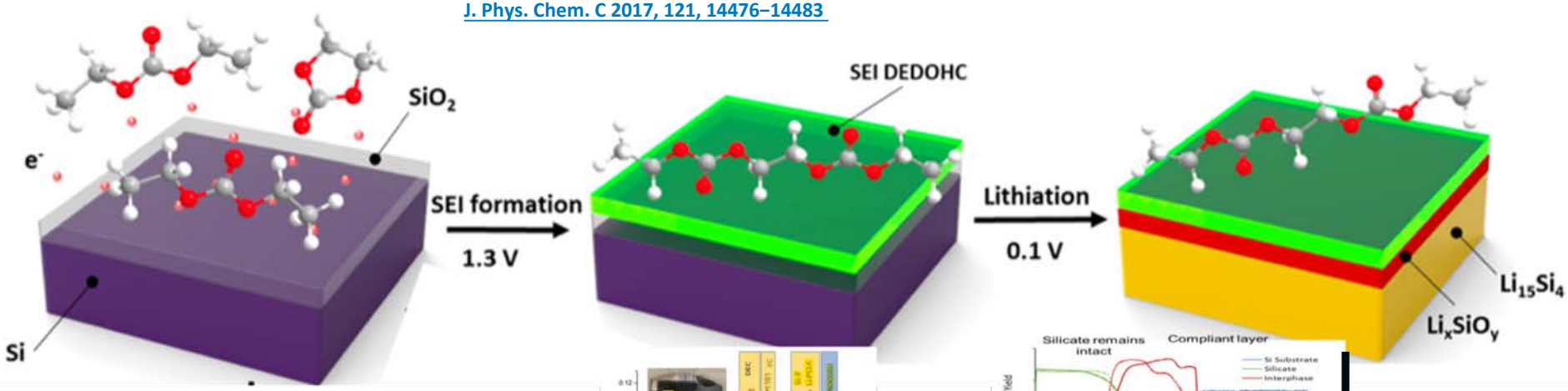
- **The multi-lab research program utilizes advanced characterization/diagnosis techniques to**
  - **Identify the surface composition of Si materials;**
  - **Understand the electrochemical and chemical reactions between the surface species and the electrolyte;**
  - **Investigate the electrochemical-mechanical coupling and its impact on the formation of SEI.**



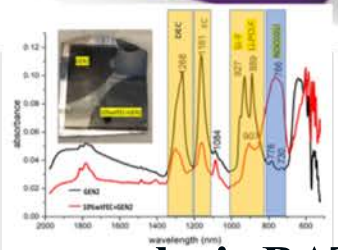


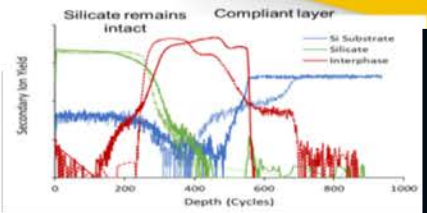
Chemical Reactivity vs Electrochemical Reactivity

J. Phys. Chem. C 2017, 121, 14476–14483



Chemical Reactivity of Silicon
Project ID BAT345

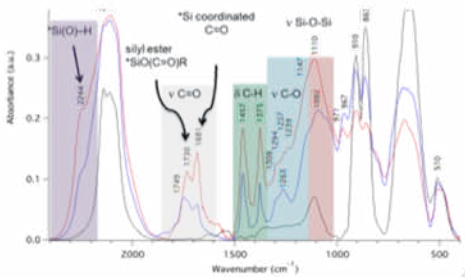


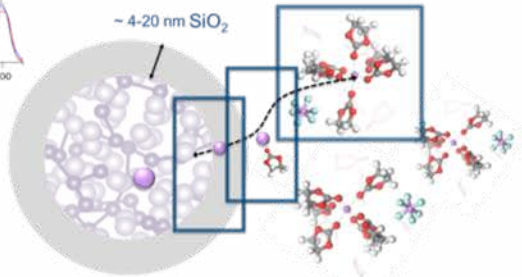


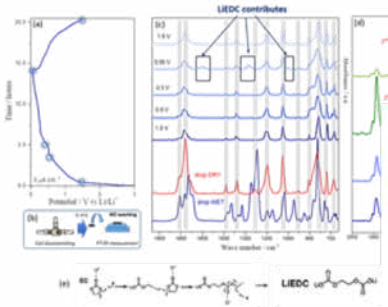
Surface analysis BAT347

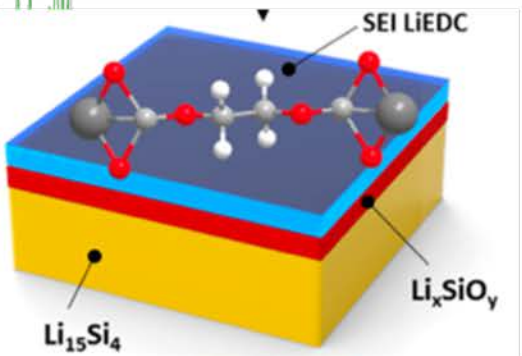
Role of Li Silicates BAT348

Spectro-electrochemistry BAT346









Predicting and Understanding Novel Electrode
BAT344

Milestones FY18

Overarching Mission: Develop a stable SEI layer for Silicon Anodes to enable the use of intermetallic anodes for lithium ion batteries.

Quarter 1 Milestone:

- Have completed the selection and characterization (XPS, SIMS, IR, and Raman), including determination of the surface termination chemistry and impurity levels, of the SEISta model research samples to be used by all members of the team in FY18.

Quarter 2 Milestone:

- Have characterized (XPS, SIMS, IR, and Raman) the surface chemistry and composition of the SEISta model research samples after contact with the electrolyte, before cycling, including the nature of the electrolyte decomposition products.

Quarter 3 Milestone:

- Completed characterization (electrochemistry, IR and Raman) of the early stage silicon electrolyte interphase formation on the SEISta model research samples, specifically by establishing and demonstrating a procedure for quantitatively measuring the solubility of SEI on silicon surfaces.

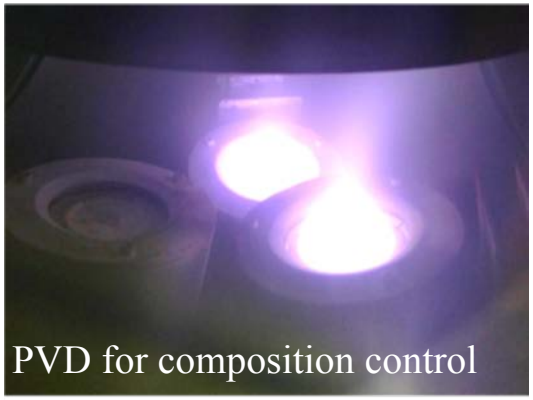
Quarter 4 Milestones:

- Established and demonstrated a procedure for measuring the growth rate of silicon SEI components at fixed potentials and during cycling.
- Have determined how the physical properties of the silicon electrolyte interface are influenced by the nature of the silicon surface on the SEISta model samples.

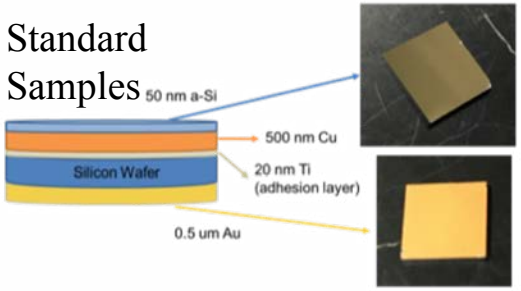
Approach

Integrated Synthesis and Characterization

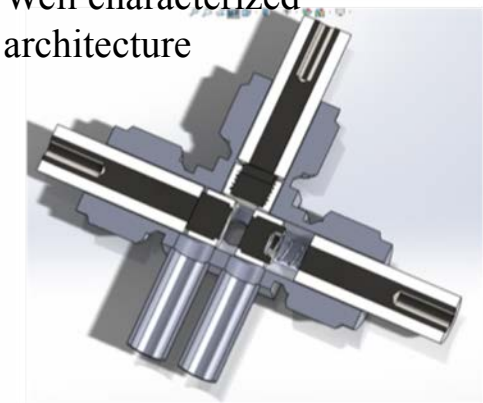
- Standardize the Silicon samples
  - 50nm silicate/50nm Si/500nm Cu/650um D-Si/500nm Au
  - Si amorphous thin film
  - Si wafer model samples with standard cleaning protocol_
- Parallelize Analysis across compositions to look for differences
  - Use easy to assemble architectures for sample recovery
  - Standardize Test Cell for reproducibility
- ***Multimodal characterization technique***
  - Chemical reactivity (Gabe Veith, BAT 345)
  - Spectroelectrochemistry (Robert Kostecki, BAT 346)
  - Surface analysis of SEI (Chunmei Ban, BAT 347)
  - Stability of lithium silicate and its interaction with SEI (Chris Apblett, BAT 348)
  - Electrolyte reactivity and its implication for SEI formation (Kristin Persson, BAT 344)


PVD for composition control

Standard Samples



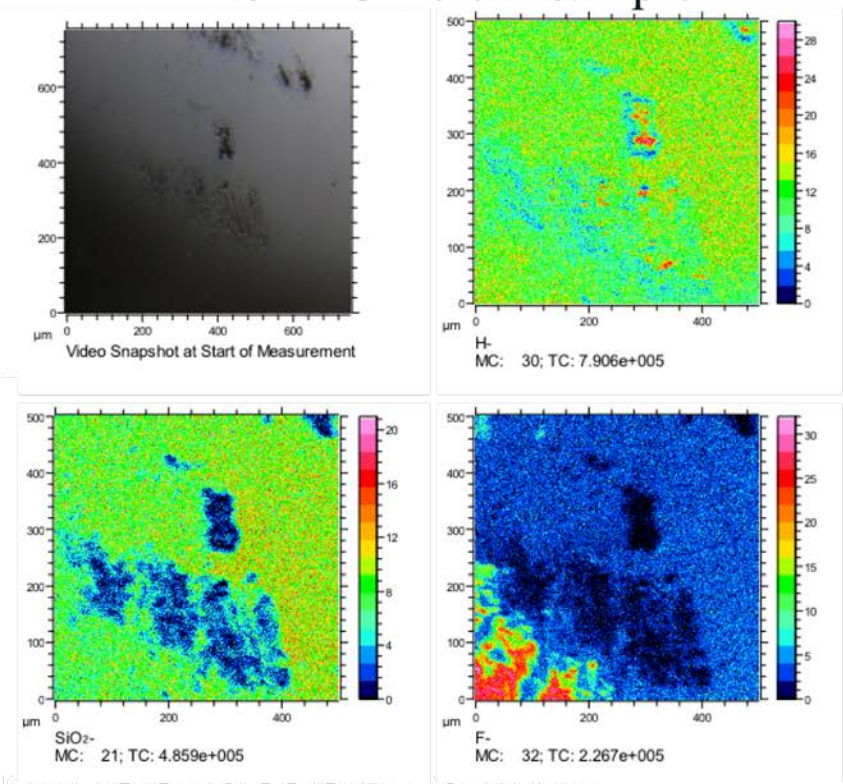
Well characterized architecture



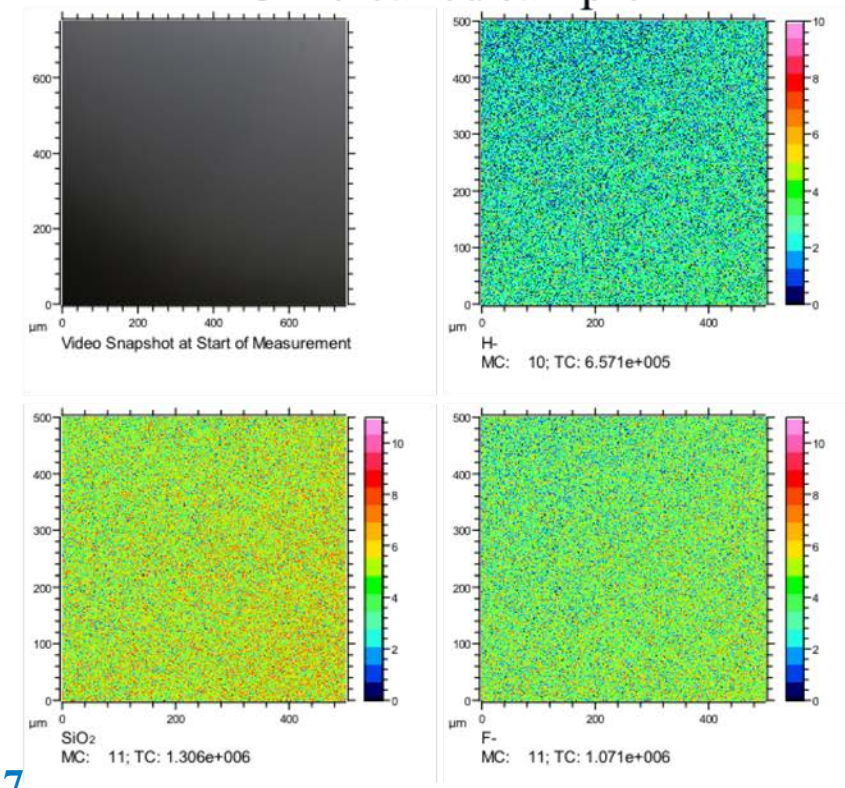
Technical Achievements
Standard Cleaning Schedule for Silicon Model Samples

1. Degrease: remove organic residue off the substrate
2. Particle/organic strip (RCA-1: DI H2O: NH4OH:H2O2, 5:1:1)
3. Ionic clean (RCA-2: DI H2O: HCl:H2O2, 6:1:1)
4. Rinse and dry
5. package

Non-RCA clean sample



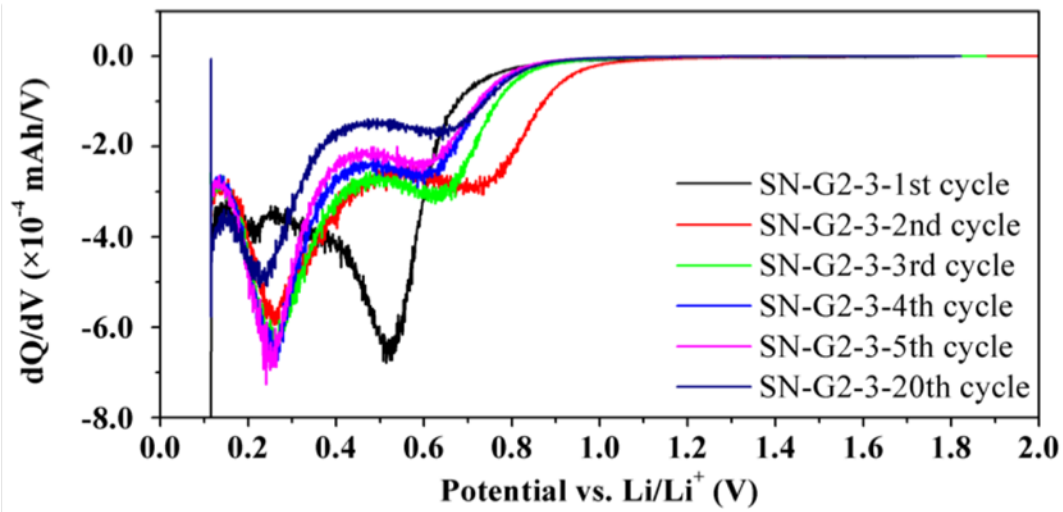
RCA cleaned sample



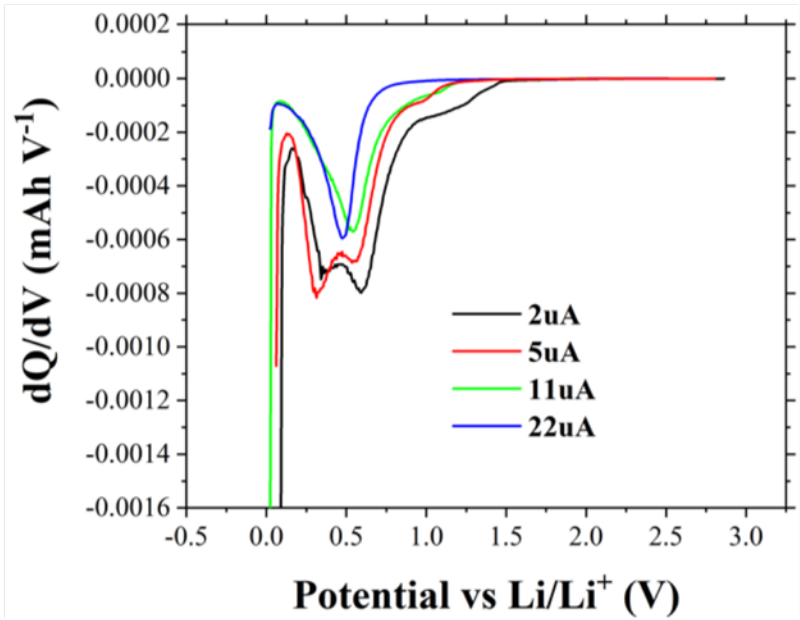
Technical Achievements
Standard Electrochemical Analysis for Si Electrodes

Experiment: Focus on early-stage reduction of electrolyte

- Galavanostatic reduction to 0.12V and then rest 5 hours
- Gen2: 1.2 M LiPF6 in 3:7 EC:EMC (weight ratio)

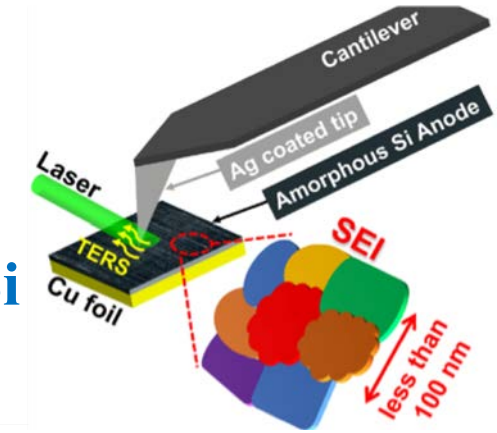


- Reduction reaction occurs at every reduction process. The surface of Si samples can not be easily passivated.
- Reduction of electrolyte can be limited by either kinetic or diffusion control.



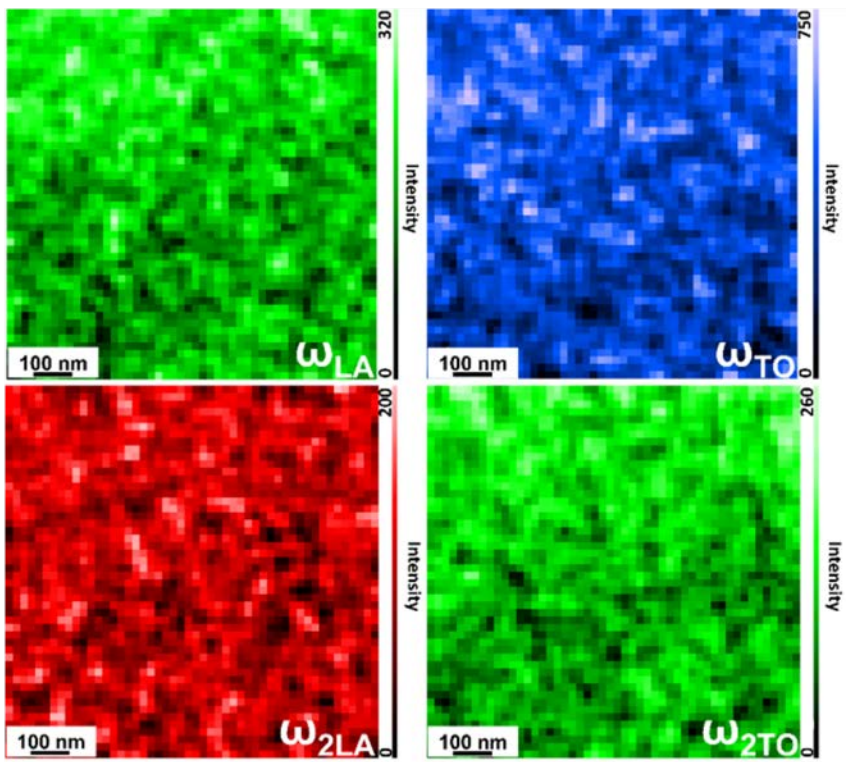
Technical Achievements
Surface Structure via Tip Enhanced Raman Spectroscopy

Use Tip Enhanced Raman spectroscopy (TERS) to obtain vibrational fingerprints of surface species at nanoscale spatial resolution (BAT 345 and 346)

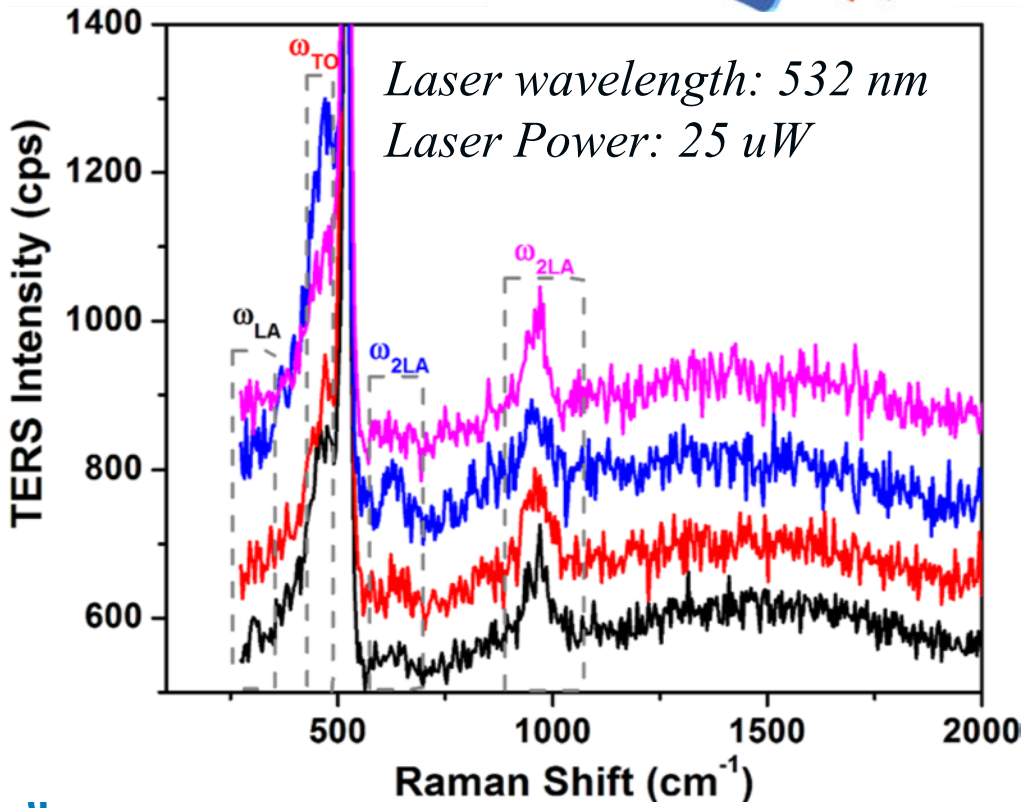


Heterogenous distribution of the lattice mode of a-Si

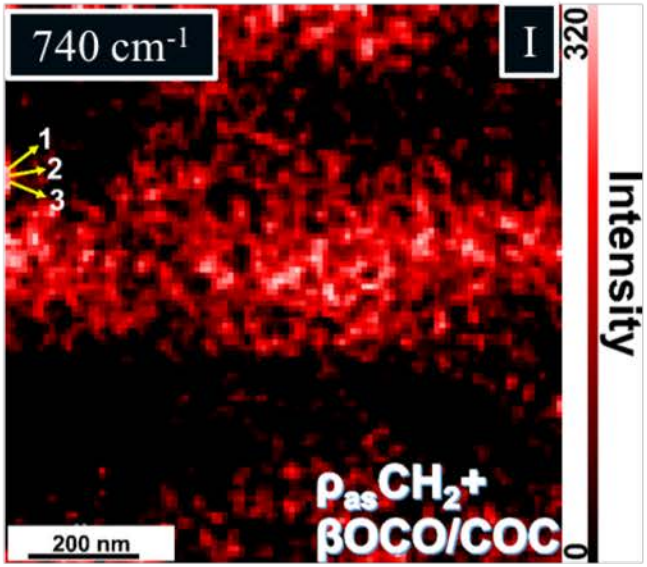
TERS mapping of pristine a-Si

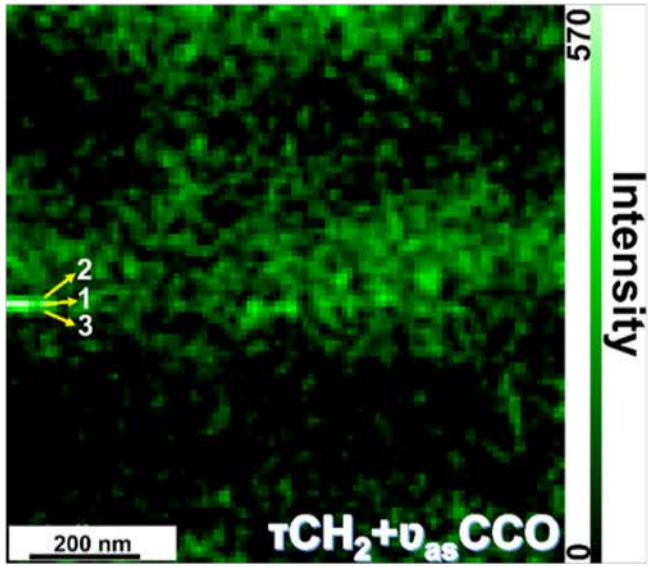


TERS spectra



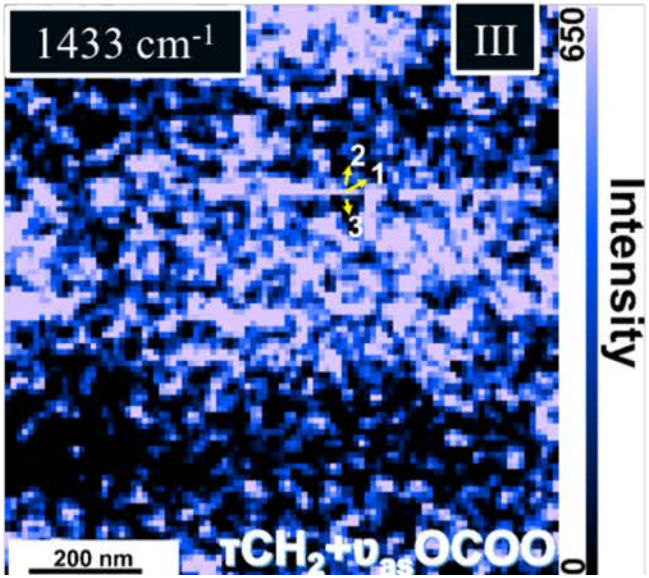
Technical Achievements
Probing the Nanoscale Heterogeneity of SEI

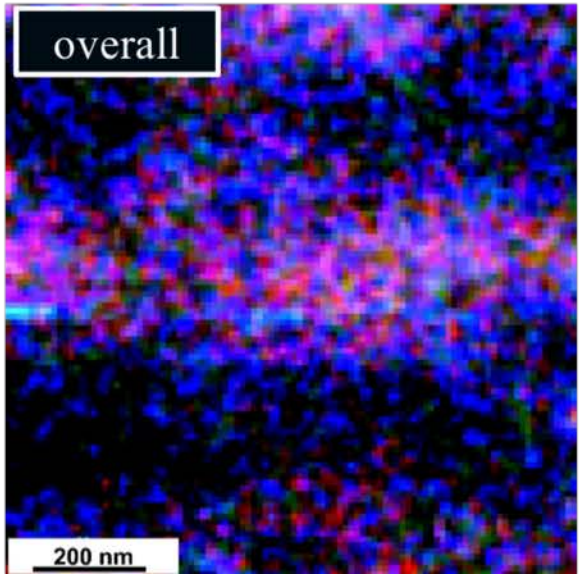


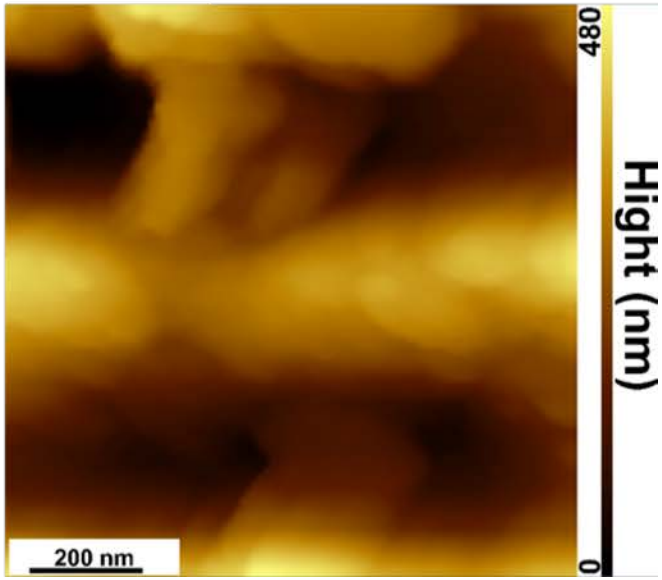


TERS mapping of three random regions on the surface of the 1st-cycled Si electrode.

3 spots 10nm apart selected for TERS spectra (next slide)

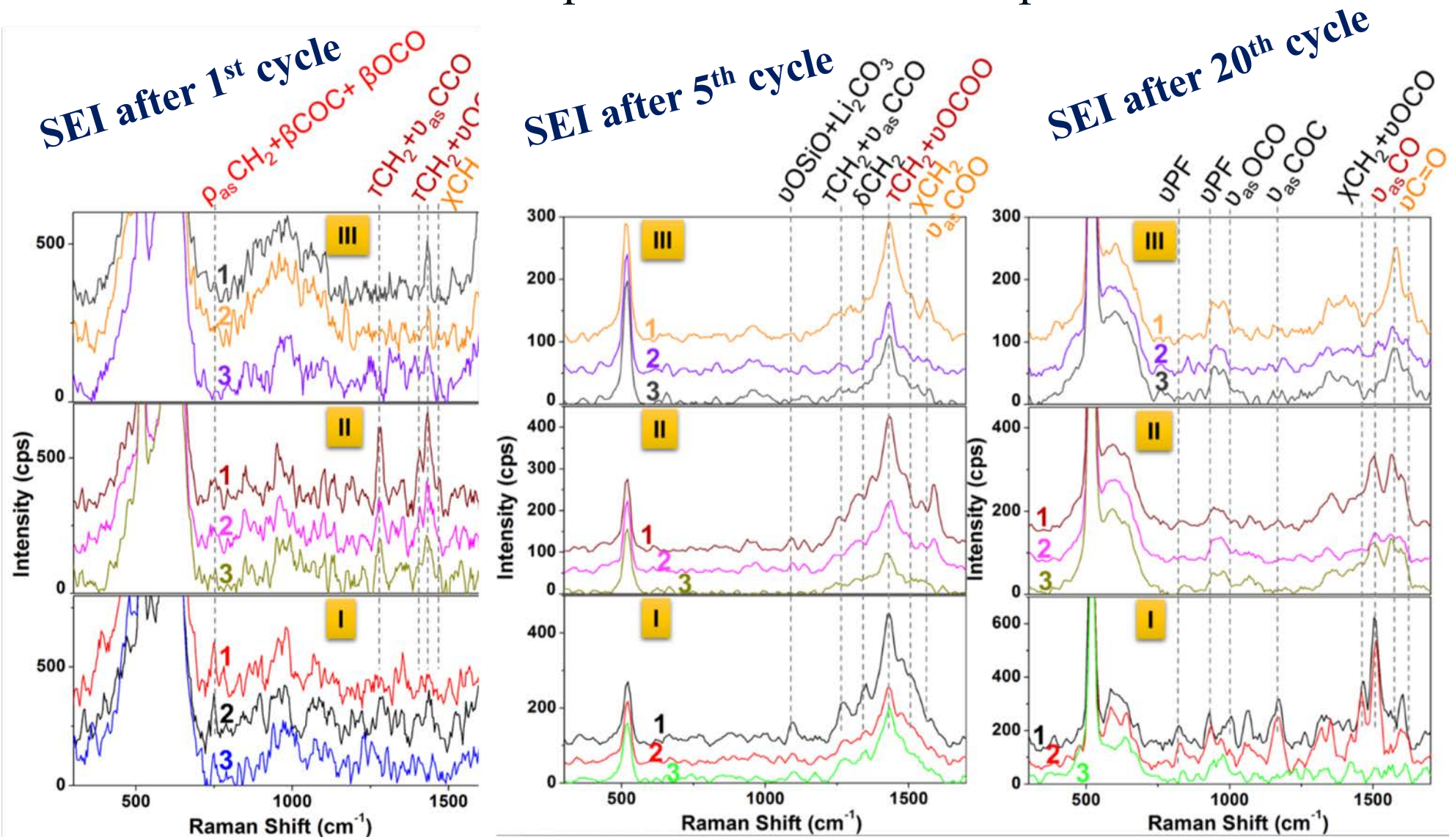




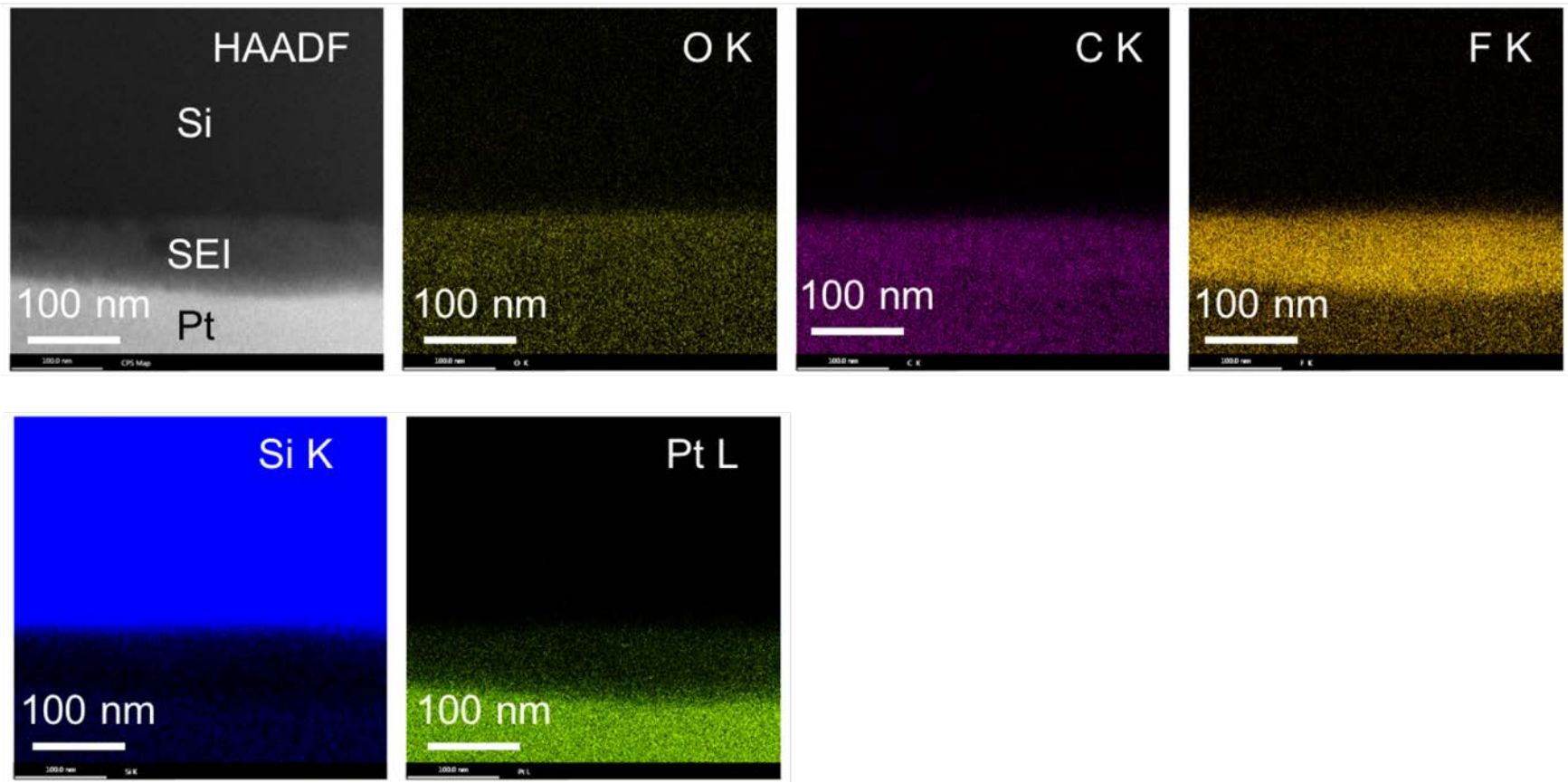


Technical Achievements
Chemical Evolution in the SEI

Raman spectra of the selected spots.



Technical Achievements
Cross-Section Morphology of the SEI



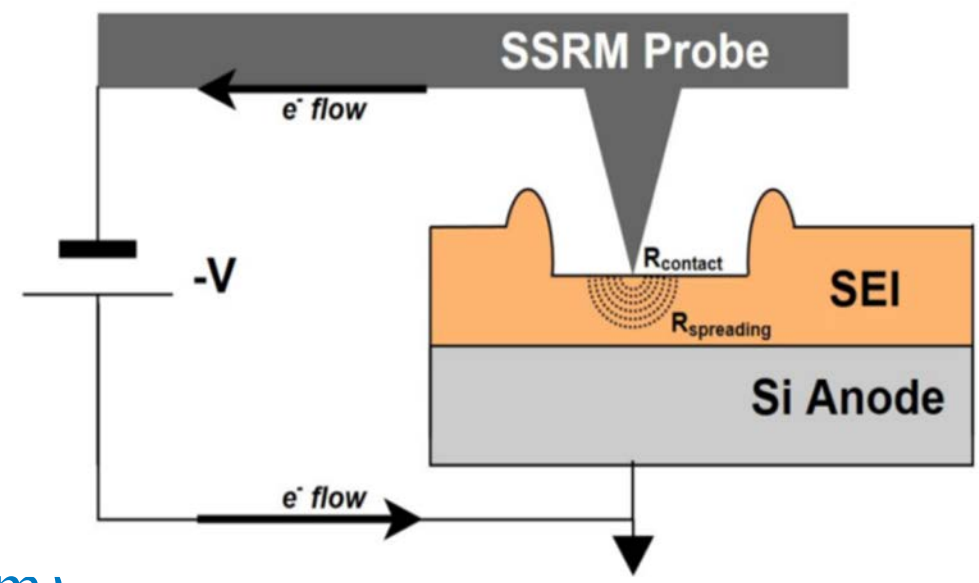
STEM high angle annular dark field imaging (HAADF),

Energy dispersive x-ray spectroscopy (EDS) elemental mapping

Technical Achievements
Electrical Conductivity Measurements

Scanning Spread Resistance Microscopy (SSRM) Measurement

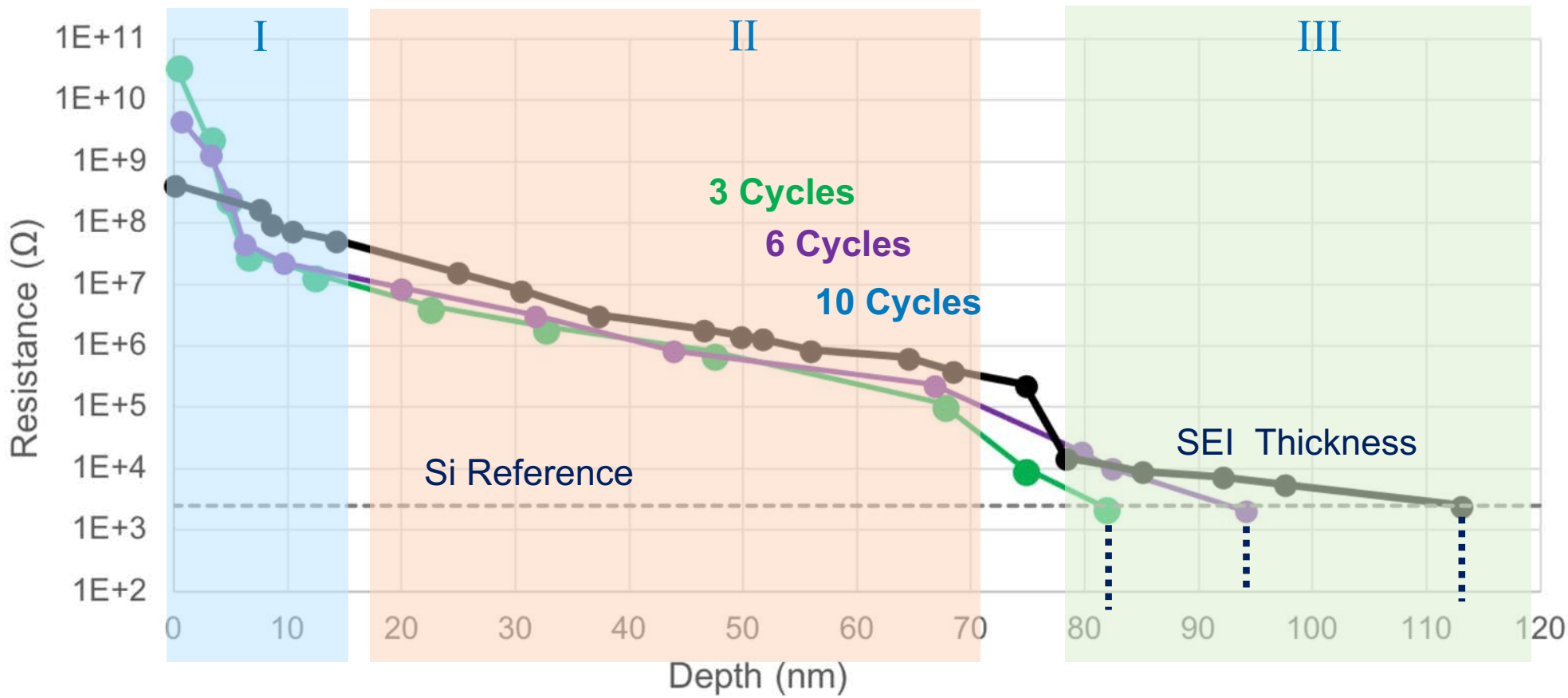
- Operating in a contact mode, when applying a voltage bias between the probe tip and the sample base;
- Measuring the current response, to obtain the resistance. The relationship between the resistivity and the resistance is shown below:
- $R = \frac{\rho}{4a} + R_{barrier}(\rho)$



  - R =measured resistance (Ω)
  - ρ = resistivity (Ω·cm)
  - a = electrical probe radius (nm)

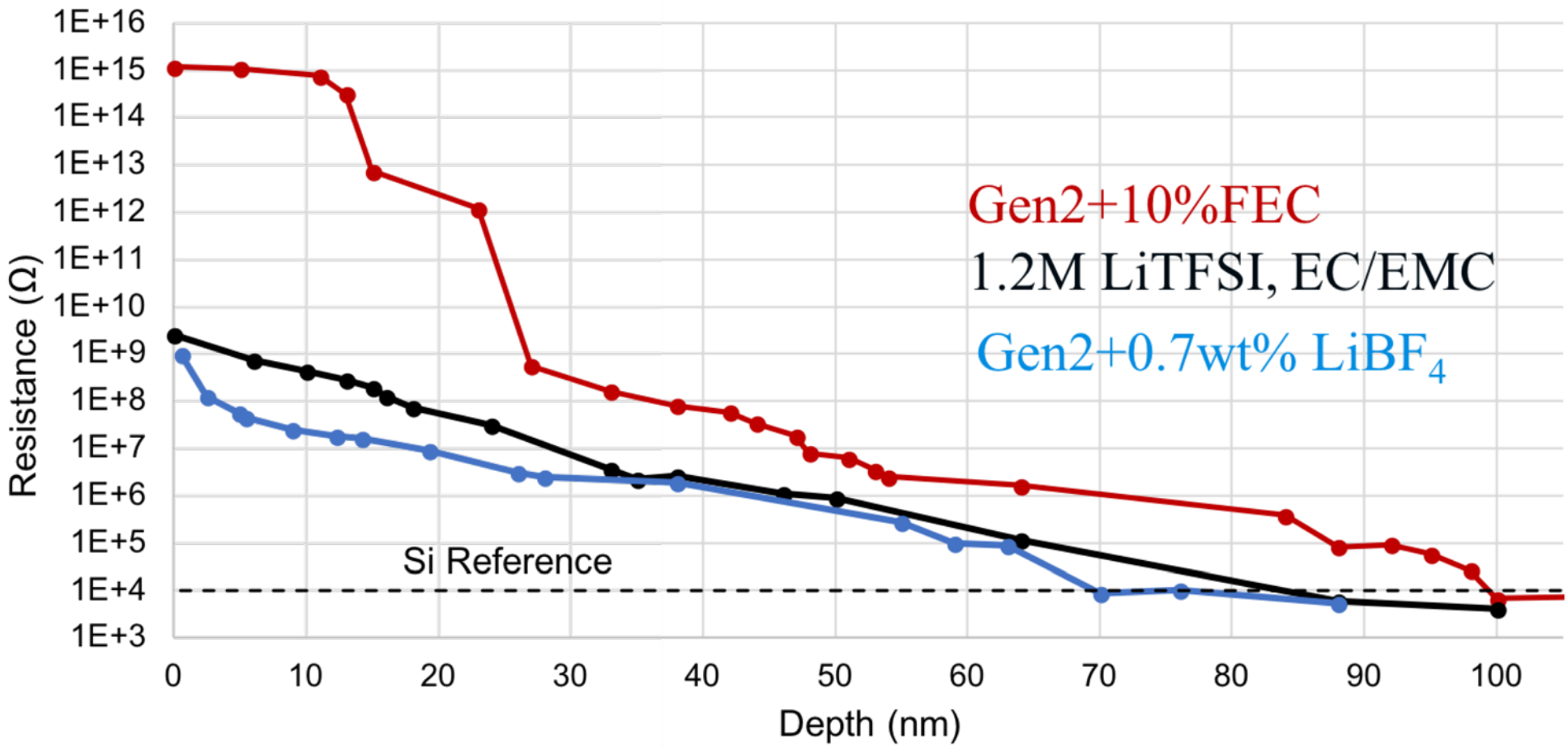
Technical Achievements
SEI Resistance Depth Profile

I= 22 μA cm-2; 1-0.01V EC:EMC (3:7 by wt.) + 1.2M $LiPF_6$



I: Organic-rich regime
II: inorganic-rich regime
III: SEI-Si mixed regime

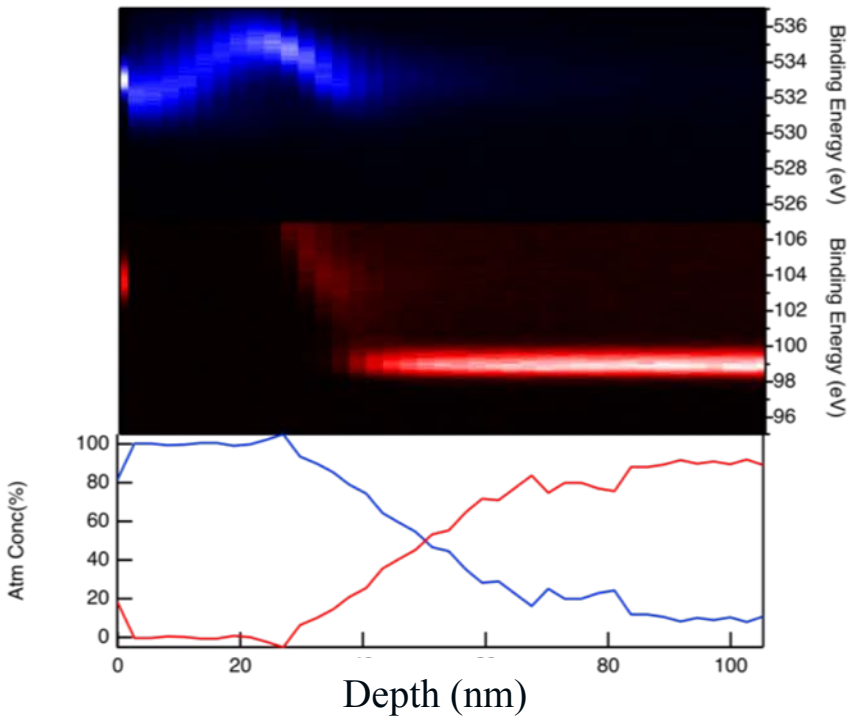
Technical Achievements
SEI Resistance Depth Profile



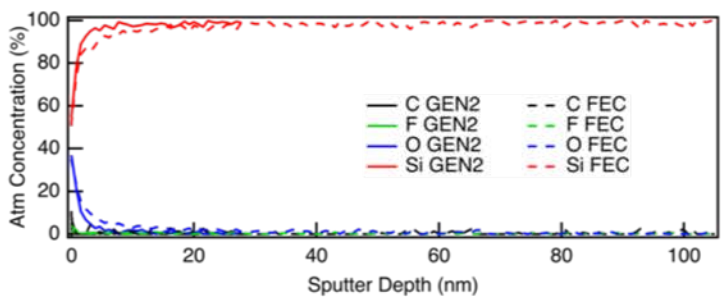
I= 22 μA cm-2; 1-0.01V
3 cycle

Technical Achievements
Electrolyte Etching during Early-Stage SEI Formation

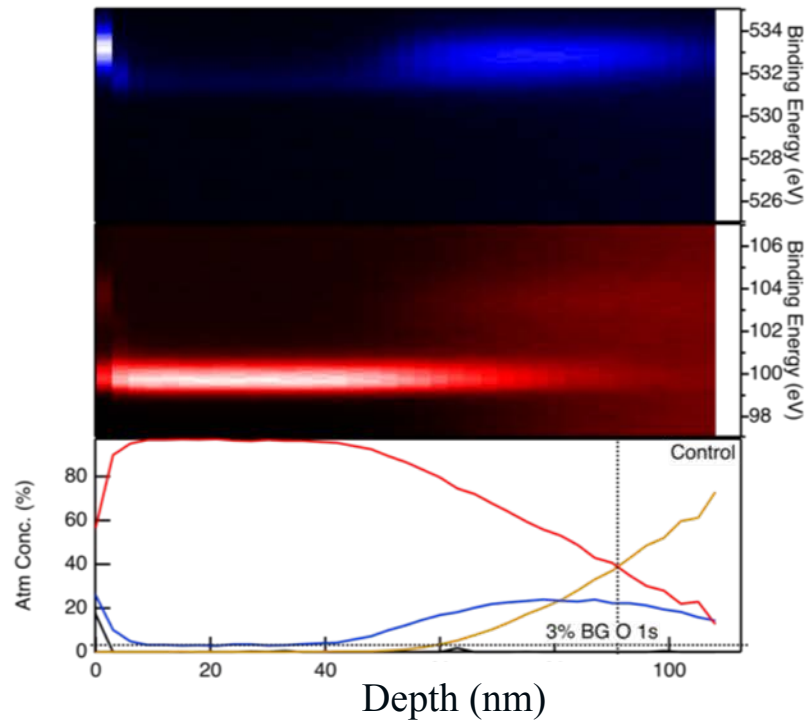
SEISta 50 nm Controlled SiO_2



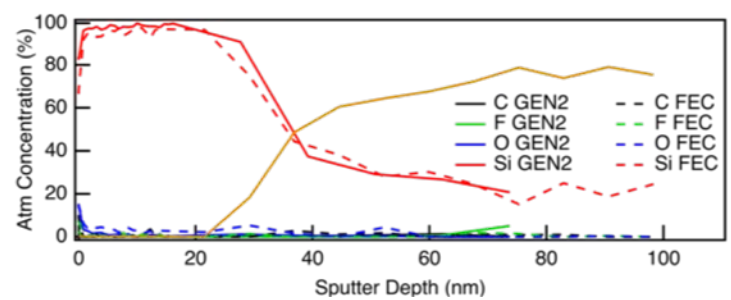
After electrolyte contact



Thin Film Si on Cu

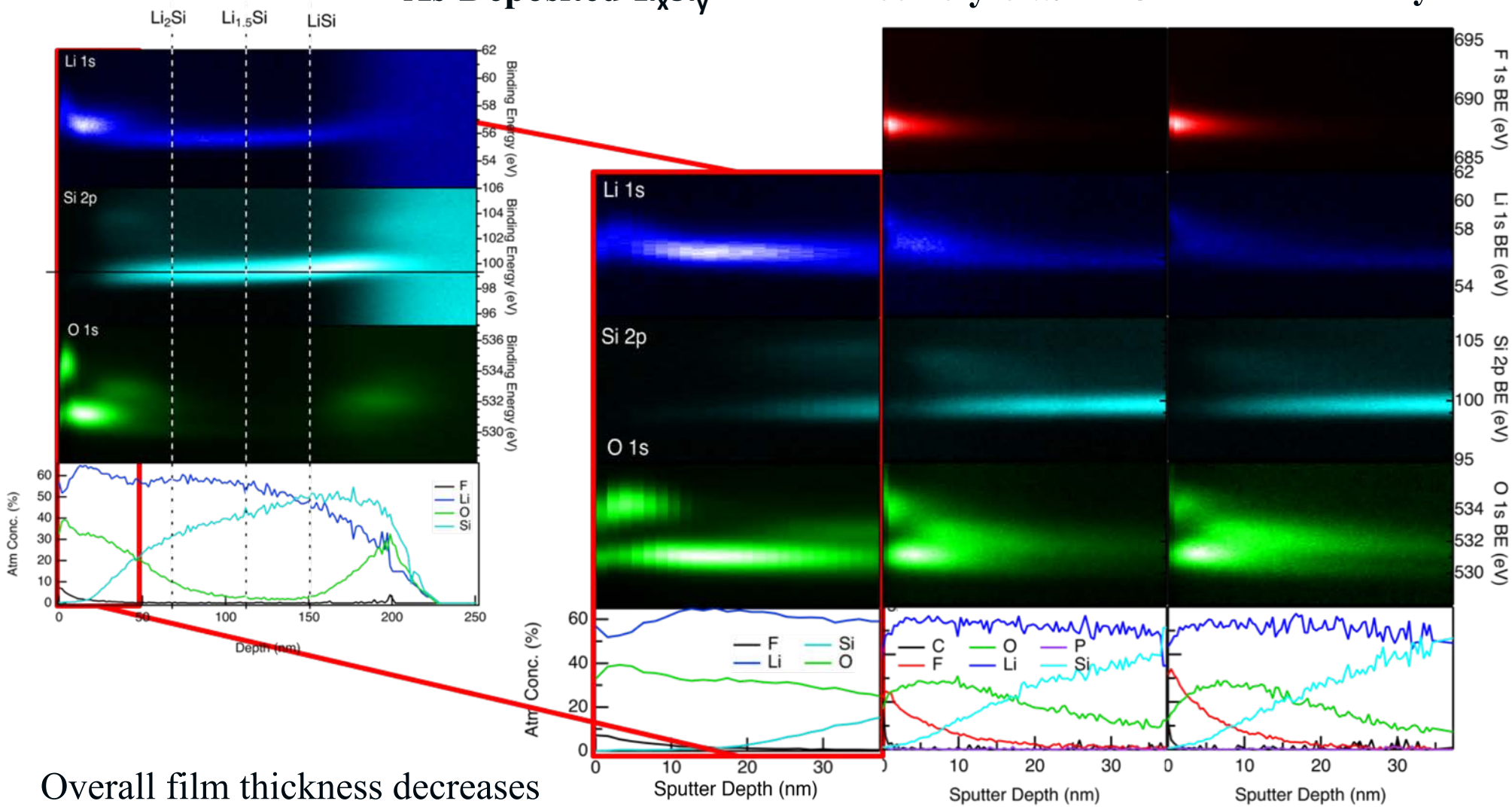


After electrolyte contact



Technical Achievements
Electrolyte Etching of Li_xSiy

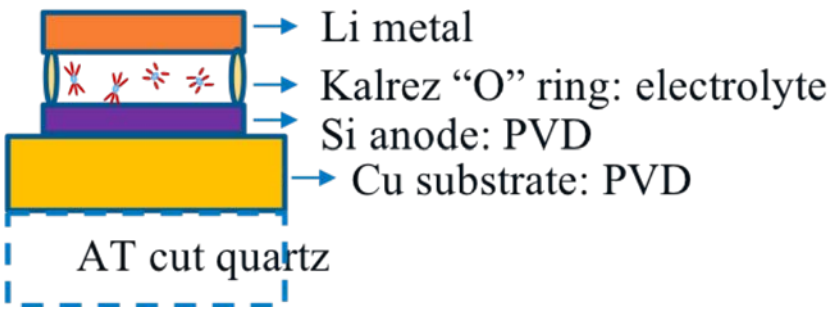
As-Deposited Li_xSi_y **Electrolyte w/ FEC** **Gen2 Electrolyte**

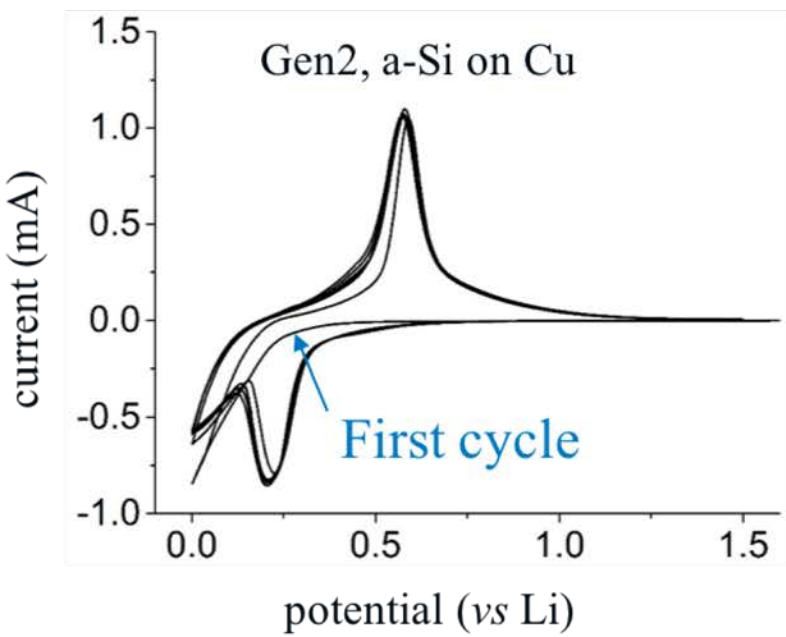


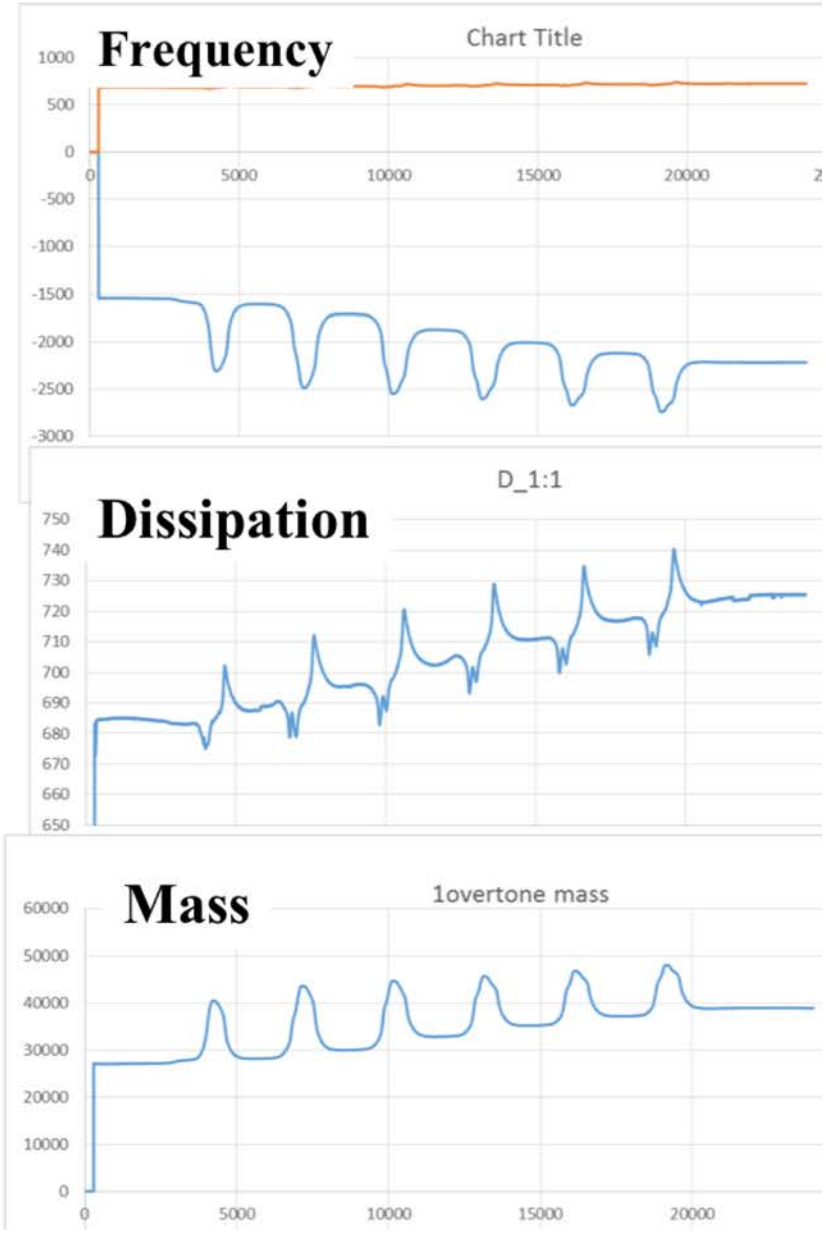
Overall film thickness decreases (200 nm → 75 nm) after contact.

Technical Achievements
Direct Visualization of SEI Formation and Growth

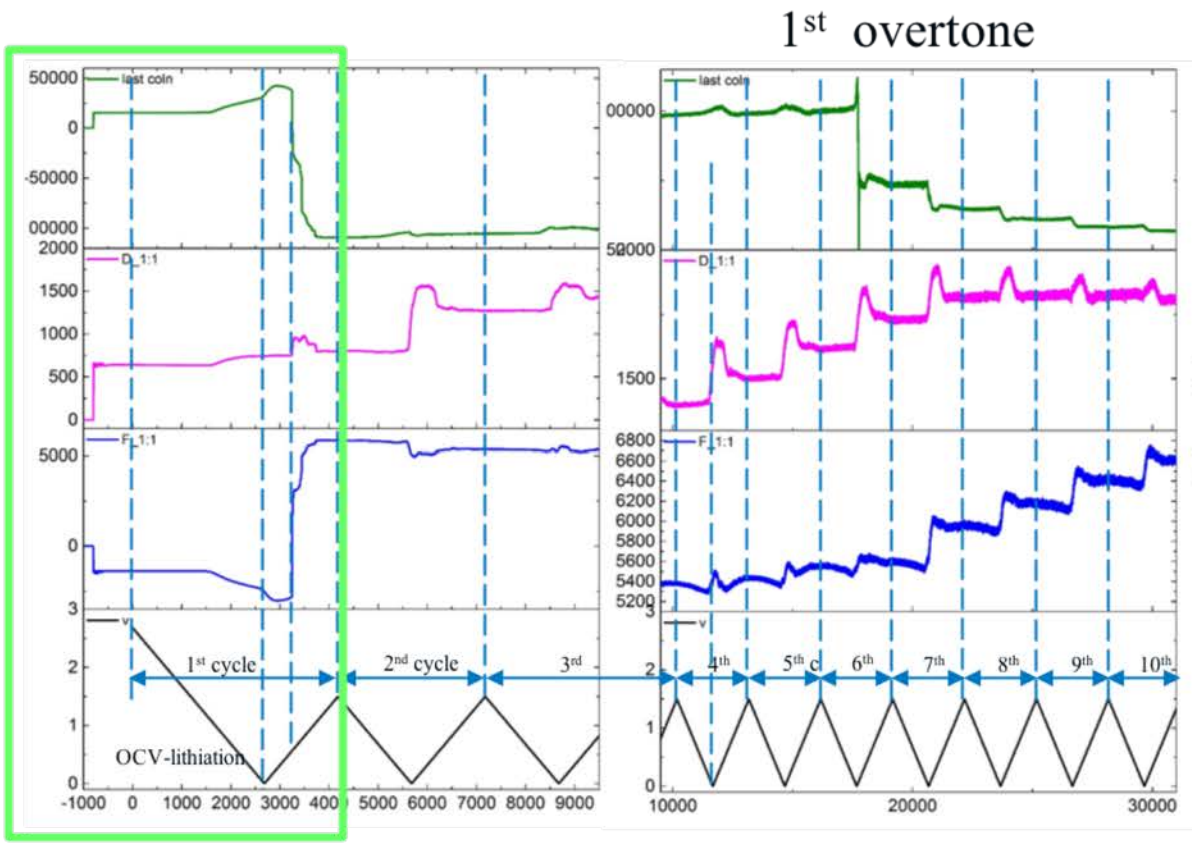
Electrochemical quartz crystal microbalance (EQCM) cell design

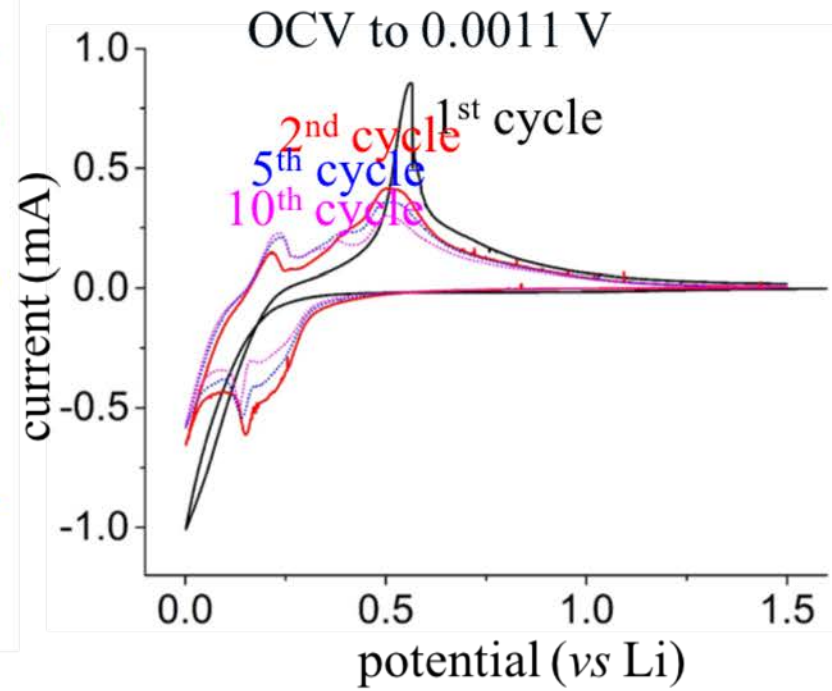






Technical Achievements
Direct Visualization of SEI Formation and Growth





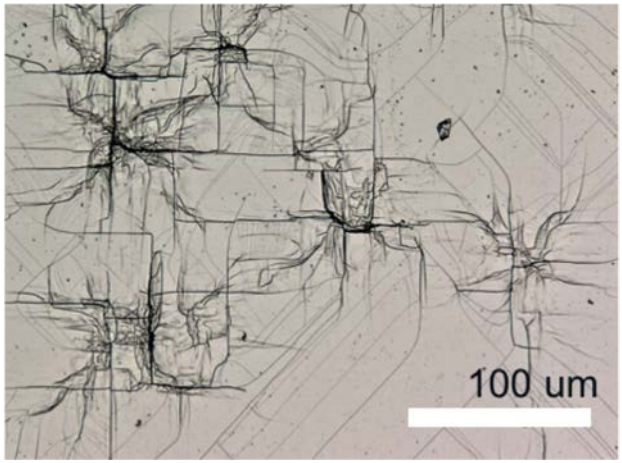
- Weight gained before lithiation, suggesting SEI start formation at high potentials.
- Dissipation increase upon cycle number, indicating film thickening and softening.
- Low dissipation (rigid) observed during lithiation.

Gen2+10% FEC, a-Si thin film on Cu substrate

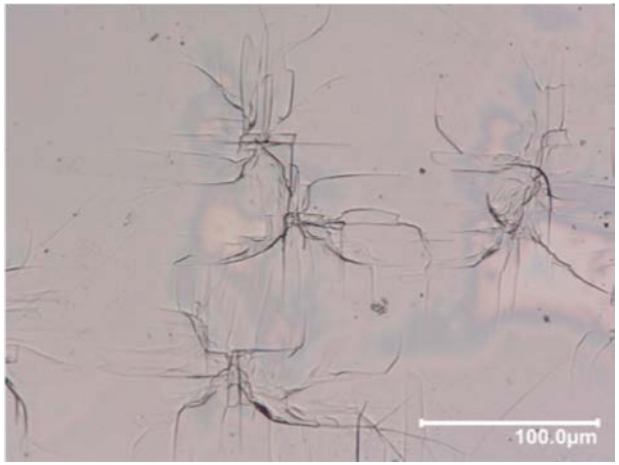
Technical Achievements
Impact of Surface Structure on Properties

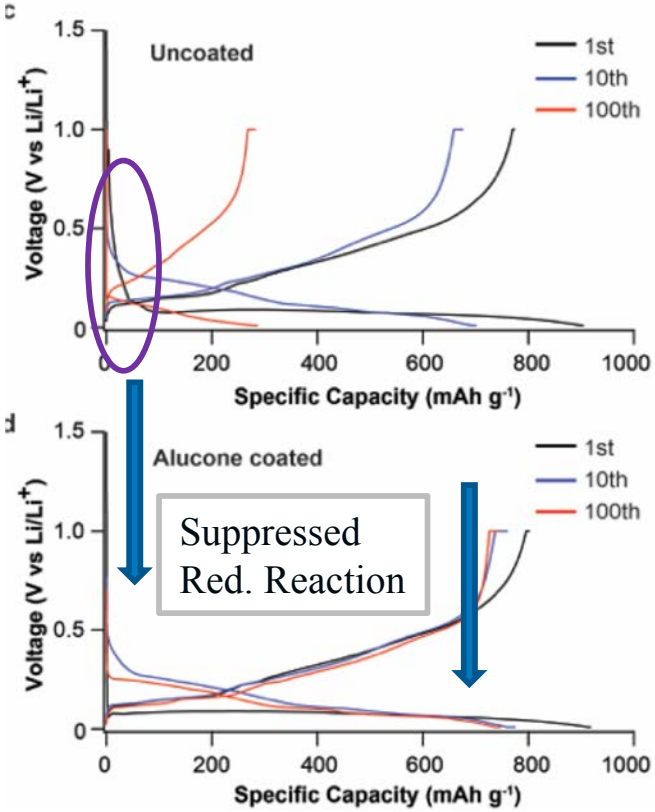
Digital microscopy of the cycled Si-wafer electrodes

Pristine



Alkoxide-modified surface



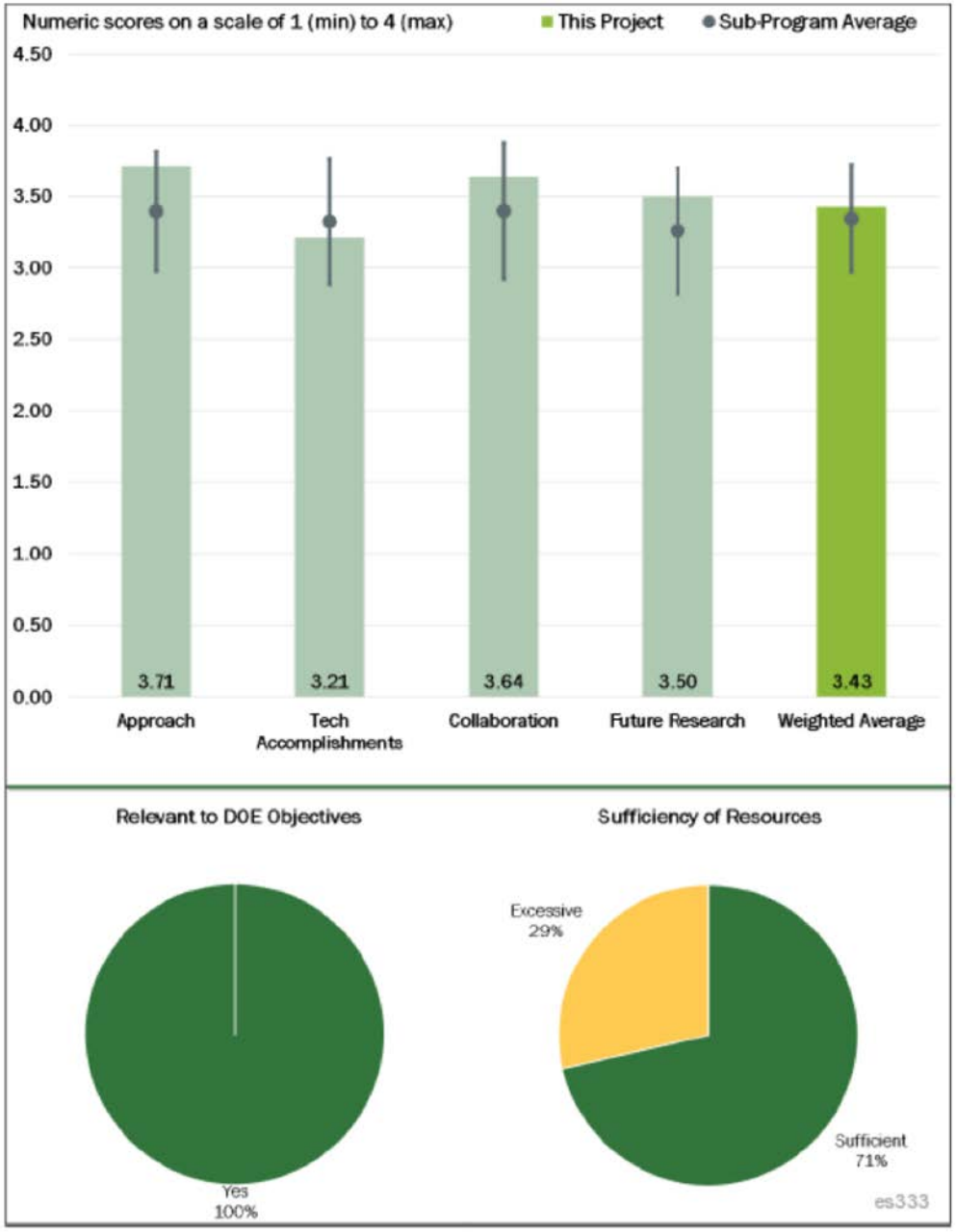


Reversibility improved

- Pristine : Cracks oriented at both <110> and <100> directions.
- Alkoxide-modified surface : Less cracks formed on <110> , cracks oriented at <100> no observed.

Response to Previous Reviewers' Comments

- Covered in BAT 343
- Active exchange of materials within team
- Continued to develop collaborations across program with materials exchanges and analysis of the same samples.
- Standardized test cells and protocols



Contributors and Acknowledgment

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Remaining Challenges and Barriers

- The impact of surface species on the SEI formation and the electrochemical properties;
  - Mitigation strategy: Model samples with identified surface species
- The chemical composition and the physicochemical properties of SEI, as well as the correlation between the structure and properties;
  - Using in-situ and non-destructive advanced characterization techniques
- Decouple the mechanical and electrolyte effects on the formation of SEI;
  - Mitigate the cracks and mechanical disintegration.

Proposed Future Research

- Evaluation of non-passivating behavior of silicon anodes;
  - Preparation of model samples including Si wafer, Si thin film and Si particles;
  - Decouple lithiation current versus corrosion/ passivation current;
  - Designed electrochemical chronamperometry measurements and polarization at selected potentials over a prolonged period of time;
  - Correlate the observed electrochemical behavior with the thickness, composition and structure of the SEI layer and possible presence of soluble compounds in the electrolyte.

Summary

- Developed advanced characterization and diagnosis techniques to measurement conductivity, monitor chemical evolution and structure of the SEI layer on the Si model samples.
  - Nanoscale heterogeneity and chemical evolution of SEI observed via TERS
  - Thickness of SEI and its correlation with electrolyte composition confirmed by using SSRM
  - Electrolyte etching behavior discovered by using XPS depth-profiling data.
  - Impact of surface chemistry on the mechanical and electrochemical properties