



**Analysis of Film Formation Chemistry on Silicon
Anodes by Advanced in-situ and operando
Vibrational Spectroscopy
Project ID ES215**

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Overview

Timeline

- 2013
- 2014
- 2015

Barriers

- High energy density Si anodes have large irreversible capacity, which is mainly due to electrolyte reduction.
- Solid electrolyte interface (SEI) is not stable on the surface with repeated cycling.

Budget

- FY 200K

Partners

- Chunmei Ban (NREL)
- Gao Liu (LBNL)

Objectives

- Understand the composition, structure, and formation / degradation mechanisms of the solid electrolyte interface (SEI) on the surfaces of Si anodes during charge / discharge cycles by applying advanced *in situ* vibrational spectroscopies.
- Determine how the properties of the SEI contribute to failure of Si anodes in Li ion batteries in vehicular applications.
- Consequently, new electrolyte additives and/or surface modification methods will improve Si anode capacity loss and cycling behavior.

Milestones

- (Q1) Develop method to attach Si nanostructures to the electrode substrate used in our spectro-electrochemical cell (Dec. 13). **Completed**
- (Q2) Determine the oxidation and reduction potentials, as well as, products of at least one electrolyte additive provided by Guo Liu's group (Mar. 14). **Completed**
- (Q3) Determine role of the Si nanostructure on the SEI formation structure and properties (Jun. 14). **Completed**
- (Q4) Feasibility of surface functionalization to improve SEI properties. Criteria: Functionalize a model Si anode surface and determine how SEI formation is changed (Sep. 14). **Completed**

Technical Approach

- Model Si anode materials (single crystals, polycrystalline films, and nanostructures) are studied using baseline electrolyte and promising electrolyte variations.
- Combination of *in situ* and *operando* vibrational spectroscopies are used to directly monitor the composition and structure of electrolyte reduction compounds formed on the Si anodes.
- Pre-natal and post-mortem chemical composition is identified using X-ray photoelectron spectroscopy.
- The Si films and nanostructures are imaged using scanning and transmission electron microscopies.

Accomplishments

- Developed a method to fabricate Si micro/nanostructures to an electrode substrate that can be used in our spectroelectrochemical cell.
- Determined the role of the Si micro/nanostructure on electrolyte reduction chemistry.
- Determined the oxidation and reduction potentials and products of the additives FEC and VC.

Electrochemistry of electrolyte reduction on Si microstructures

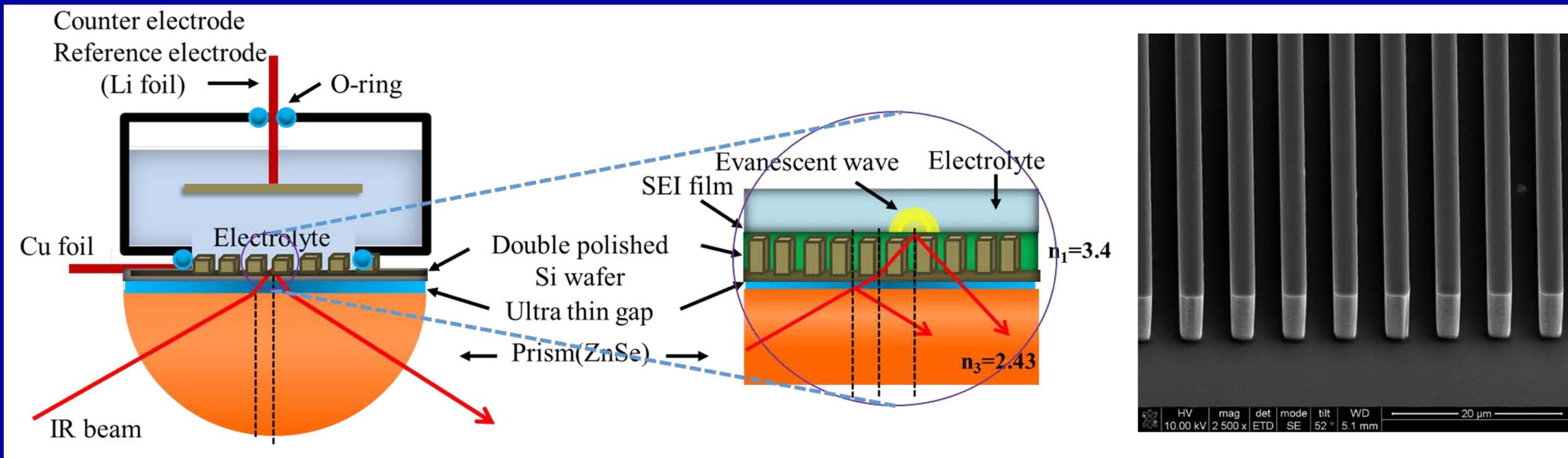


Figure 1. (left) ATR geometry of the in-situ IR spectroelectrochemical cell using a patterned Si microstructure shown at left (10 micron feature size)

Electrochemistry of electrolyte reduction on Si microstructures – continued

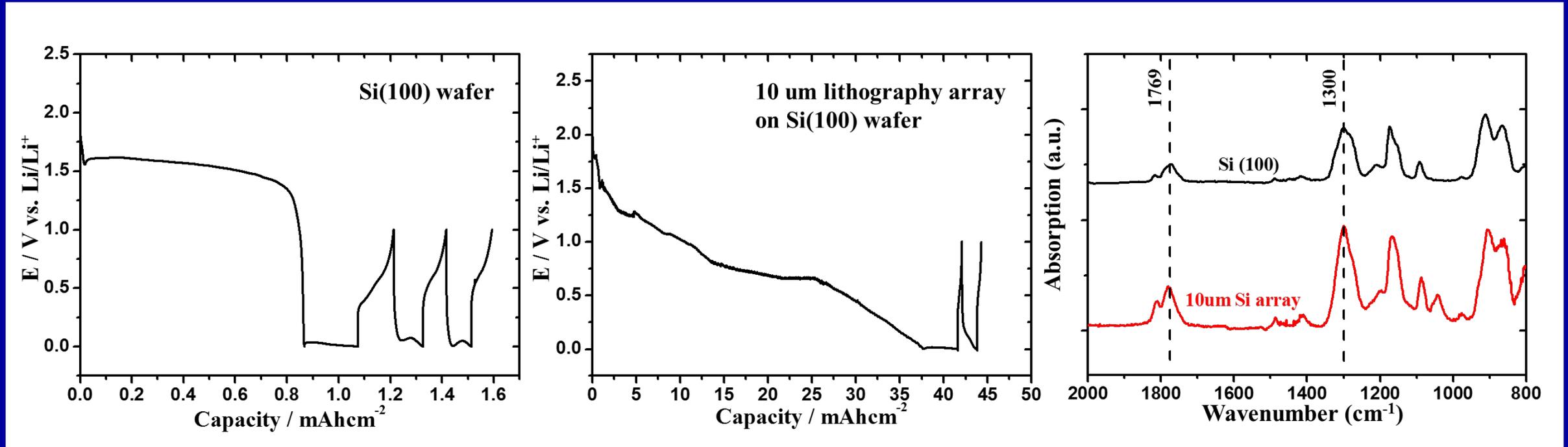


Figure 2. First cycle galvanostatic curve comparison between Si (100) wafer and 10 μm array on Si (100) wafer; ex-situ FTIR spectra of Si (100) wafer and 10 μm array samples after 5 cycles with

- the microstructure of the Si surface does not cause a change in the chemistry of electrolyte reduction and passive film formation.

Electrochemistry of additives FEC and VC

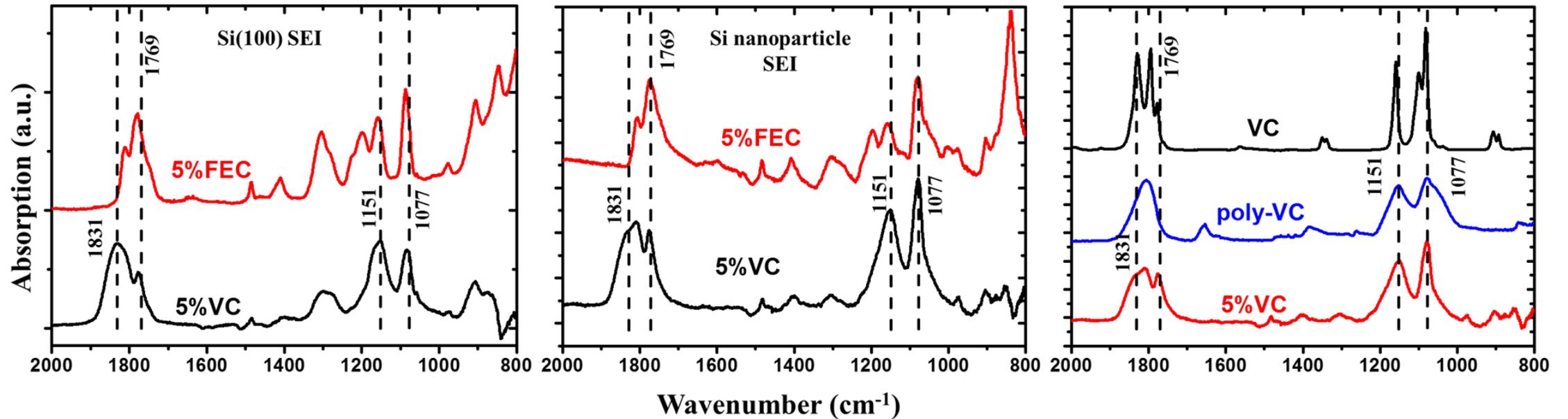


Figure 3. Ex situ ATR-FTIR spectra of Si (100) p-type doped wafer and for Si nanoparticles after 3 CV cycles with 0.1mV/s scan rate (2V-0.01V vs. Li/Li⁺) and rinsing with DMC to remove residual electrolyte.

- Based on the synthesized poly-VC standard spectra, VC additive reduction compound has been assigned to poly-VC or its oligomer.
- FEC were to react under the same pathway as EC to form LEDC, the fluorine ends up exclusively as difluoroethylene.

Summary

On **Si** anodes the main products observed of electrolyte (EC:DEC) reduction are:

1. Lithium propionate ($C_3H_5LiO_2$) – soluble!

2. Diethyl 2,5 dioxohexane dicarboxylate (DEDOHC) – soluble!

} Electrolyte
consumption

• On **graphite** anodes the main products observed of electrolyte (EC:DEC) reduction are:

1. Lithium ethylene dicarbonate (LiEDC) – insoluble.

2. Lithium oxalate – insoluble.

} Electrolyte
preservation

The electrolyte reduction chemistry does not appear to depend on the Si microstructure

An ALD coating by NREL did not appear to alter the electrolyte reduction chemistry

VC and FEC additives have different reduction potentials and different products

Si based anodes require different electrolyte composition from the conventional Li ion electrolyte ubiquitous to graphite anodes.

Future Work

- All Milestones Completed for 2015
- Elucidating chemical reactions at the electrode/electrolyte interface under working conditions by Sum Frequency Generation Vibrational Spectroscopy (SFG-VS)
 - Anode
 - Radical formation
 - Ethylene carbonate ring opening
 - Cathode
 - $\text{Li}_x\text{Mn}_{1.5}\text{Ni}_{0.5}\text{O}_4$ (LMNO)
 - Cathode material surface orientation, *e.g.*, LMNO (112) vs. LMNO(111)
 - Chemical reactions at the cathode electrolyte interface