

Analysis of film formation chemistry on silicon anodes by advanced in-situ and operando vibrational spectroscopy

Project
ES215

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Gabor A. Somorjai^{1,2}

⁽¹⁾Materials Sciences Division, Lawrence Berkeley National Laboratory, Berkeley CA 94720
⁽²⁾Department of Chemistry, University California, Berkeley CA 94703

ABSTRACT

Major efforts are under way to develop novel materials that provide higher battery capacity for increased driving distances of electric vehicles. A high capacity alternative to graphitic carbon anodes is Si, which stores 3.75 Li per Si versus 1 Li per 6 C yielding a theoretical capacity of 4008 mAh/g versus 372 mAh/g for C.

Unfortunately, this high capacity comes at a cost: the Si anodes exhibit excessive irreversible capacity loss and short cycling lifetime. The irreversible capacity loss is believed to be caused by lattice expansion accompanying lithiation that is followed by particle cracking, continued reduction of electrolyte and formation of solid electrolyte interphase (SEI) on freshly exposed surface. Detachment of the SEI from the Si surface occurs even when the potential region of cycling is restricted to produce a degree of expansion similar to that of graphite.

These observations suggest that the SEI on Si is not intrinsically passivating and that the chemistry of the SEI on the Si surface is different from that of the SEI on graphite. Nonetheless, there are no studies to date suggesting that the SEI on Si is significantly different than that on graphite.

The uncertainty regarding composition, structure, and formation and degradation mechanisms of the SEI is in general due to the poor interfacial sensitivity obtained using conventional spectroscopies. We address these issues with a development of advanced in-situ vibrational spectroscopy, sum frequency generation (SFG), probing the solid / liquid interface. Using these surface sensitive tools, we focus on determining the failure modes of an operating Si/Li electrochemical system for vehicular applications.

MILESTONES

(Q1) Modifying the SFG apparatus in order to obtain high-resolution SFG spectra of amorphous Si anode and electrolyte interface. (Oct-15)

(Q2) Obtaining SFG spectra under dynamic potentials (-0.01 V, 0.5 V and 1.0 V vs Li/Li⁺) of 1 M LiPF₆ in ethylene carbonate (EC) w/o diethyl carbonate (DEC) in order to probe the SEI formed on amorphous silicon anodes.

(Q3) Go/No-Go: Can we distinguish between the various SEI products in the C-H stretch mode (2800 – 3200 cm⁻¹)? If not proceed to conventional C-O region (1700 – 1800 cm⁻¹). (Q3)

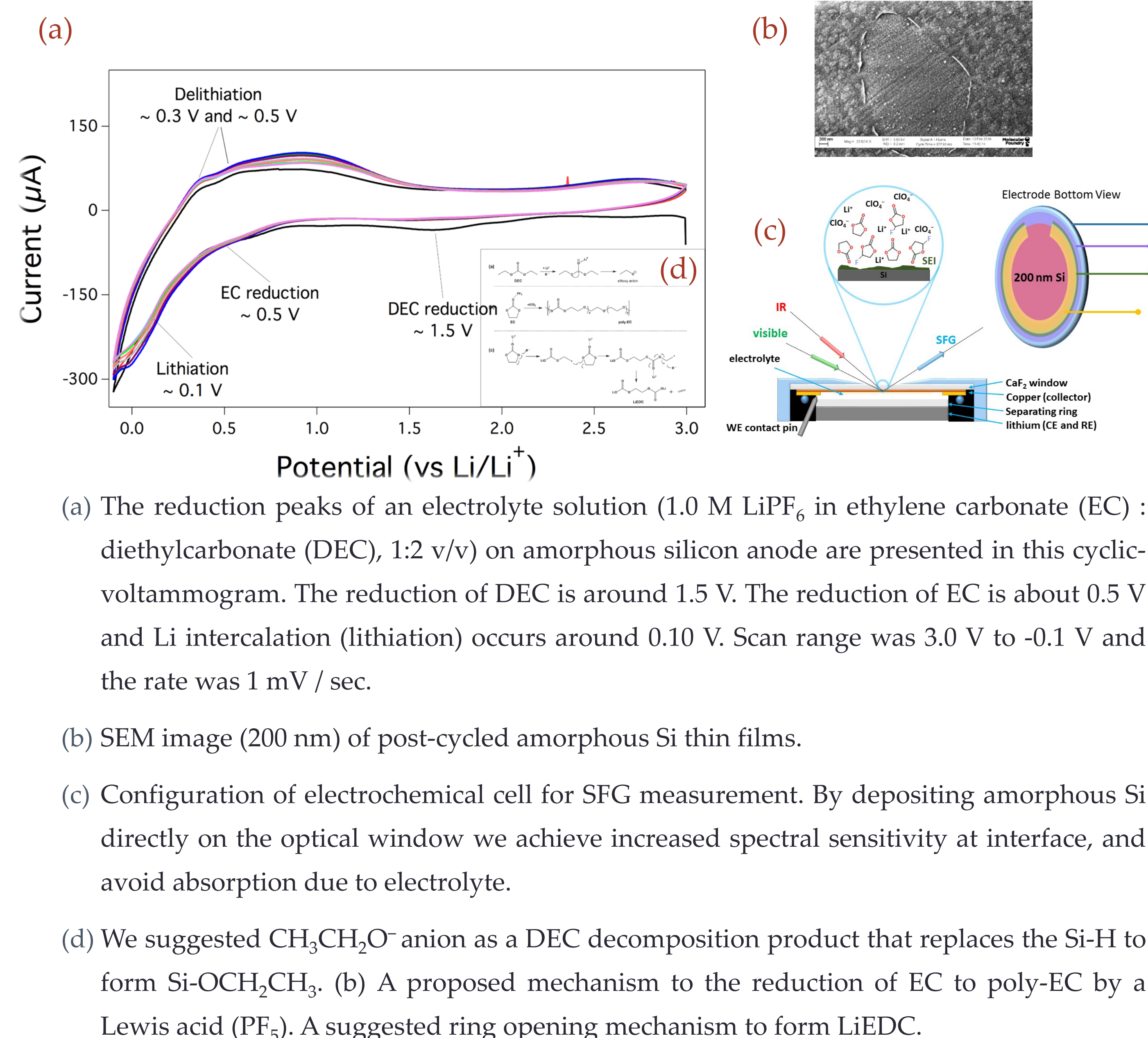
(Q4) Preforming fs-SFG measurement in tandem with cyclic-voltammetry in order to find the ring opening kinetics of EC. (Q4)

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.

TECHNICAL APPROACH

- Model Si anode materials (single crystals and amorphous thin films) are studied using baseline electrolyte and promising electrolyte variations.
- Combination of under reaction conditions sum frequency generation (SFG) vibrational spectroscopy is 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 amorphous Si (a-Si) films and are imaged using scanning and transmission electron microscopies.
- Dividing the SFG spectra emphasizes the appearance or trend of vibrational peaks that are less clear in a regular SFG scan since in most cases the SFG from the Si/SEI is interfered with the SFG generated from the Si substrate.

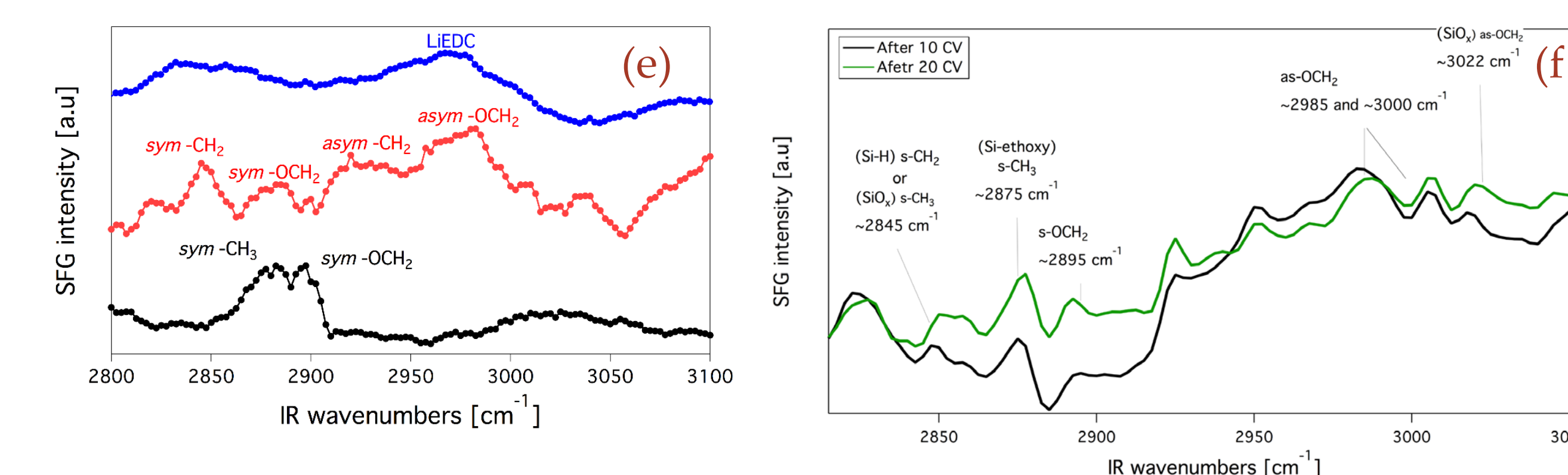


ACCOMPLISHMENTS

- A novel in-situ solid / liquid spectro-electrochemical sample preparation and sum frequency vibrational spectroscopy apparatus was developed. These provide unprecedented tuning of the depth of probing the vibrational spectra of molecules near the electrode surface.
- SFG vibrational spectroscopy spectra suggest that amorphous Si surface formed both soluble and insoluble (Si-CH₂CH₃) products.
- The reduction product dependence on various surface would determine the passivation of solid electrolyte interface, thus affects whether electrolyte reduction will continue.

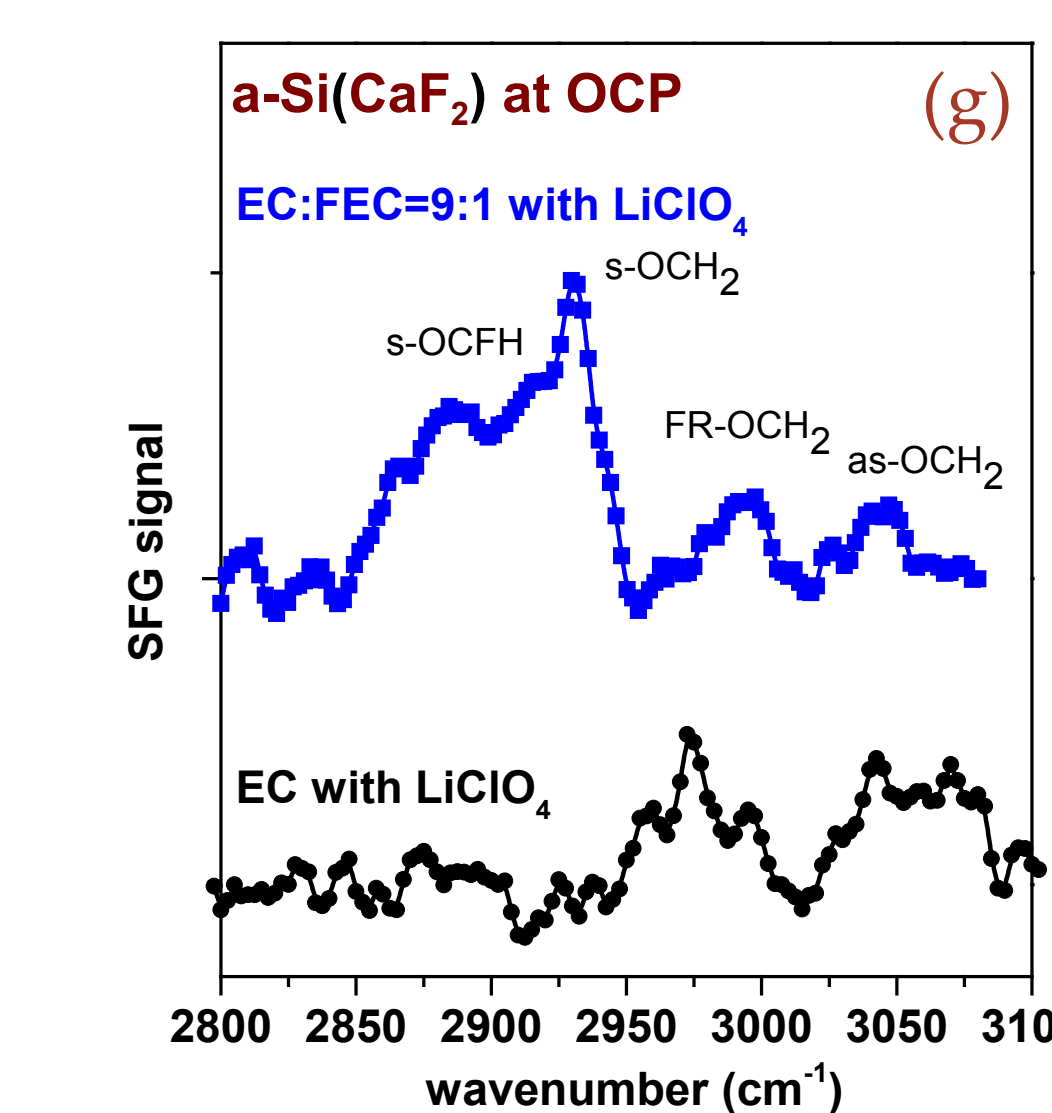
RESULTS

- We have observed that amorphous Si (a-Si) with a native oxide surface termination (Si-O_x) has a mixed SFG spectrum that has both SiO_x and Si-hydrogen (Si-H) features. However, insoluble SEI products such as Si-ethoxy (Si-OCH₂CH₃) features are not clear as in the case of crystalline silicon, Si(100)-H surfaces.



- We show the evolution of SFG signal under reaction conditions of crystalline silicon Si(100)-hydrogen terminated anode. In order to emphasize the evolution of the Si-ethoxy peaks we divided the SFG spectra by their former potentials, as follows: SFG1.1 V ↔ 0.8 V / OCP (black), SFG0.65 V ↔ 0.35 V / SFG1.1 V ↔ 0.8 V (blue), and SFG-0.05 V ↔ 0.1 V / SFG0.65 V ↔ 0.35 V (red). (f) We show the evolution of SFG signal under reaction conditions of amorphous silicon with SiO₂ terminated anode. The SFG spectra were taken at open circuit potential and after 10 (black) and 20 (green) CVs at 3.0 V ↔ -0.1 V, at a scan rate of 1mV / sec.

- We present that addition of fluoroethylene carbonate (FEC) to ethylene carbonate (EC) electrolyte causes great effect on the SEI properties such as: molecular structures at interface and compositions. It is not the chemical nature of FEC that makes it a desired additive but it's ability to improve orientational ordering of EC molecules perpendicularly to the silicon surfaces. The EC molecules now re-oriented upon reduction form the better SEI layer. Hence, it results to remarkably improves discharge capacity retention and coulombic efficiency with FEC additives.



- We probe electrolyte of 1 M LiClO₄: EC (black) and EC:FEC=9:1 mixture (green) on Si anode surface by SFG profiles. The SFG spectra were taken at open circuit potential. Peak assignments are noted in the figure.

CONCLUSIONS

Amorphous Si with a native oxide surface termination has a mixed SFG spectrum that has both Si-O_x (oxide) and Si-H (hydrogen) features. We have observed that FEC on a-Si induces better ordering of the adsorbed EC on the silicon anode and also affects the SEI composition at interface.

FUTURE PLANS

- Selectively controlling the solvent reduction reactions pathways by surface modification of the Si in order to reduce the solubility of the SEI.
- Applying external potentials to reach lithiation and investigate the nature of different SEI compositions for FEC and EC/FEC mixtures with SFG spectroscopy under reaction.