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

Project ES215

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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 will address these issues with a development of advanced in-situ vibrational spectroscopies, sum frequency generation (SFG) and a new type of attenuated total reflection (ATR) Fourier transform infrared spectroscopy. Using these new tools, we will focus on determining the failure modes of an operating Si/Li electrochemical system for vehicular applications.

MILESTONES

(Q1) Develop method to attach Si nanostructures to the electrode substrate used in our spectro-electrochemical cell (Dec. 13). Ongoing

(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). Ongoing

(Q3) Determine role of the Si nanostructure on the SEI formation structure and properties (Jun. 14). Ongoing

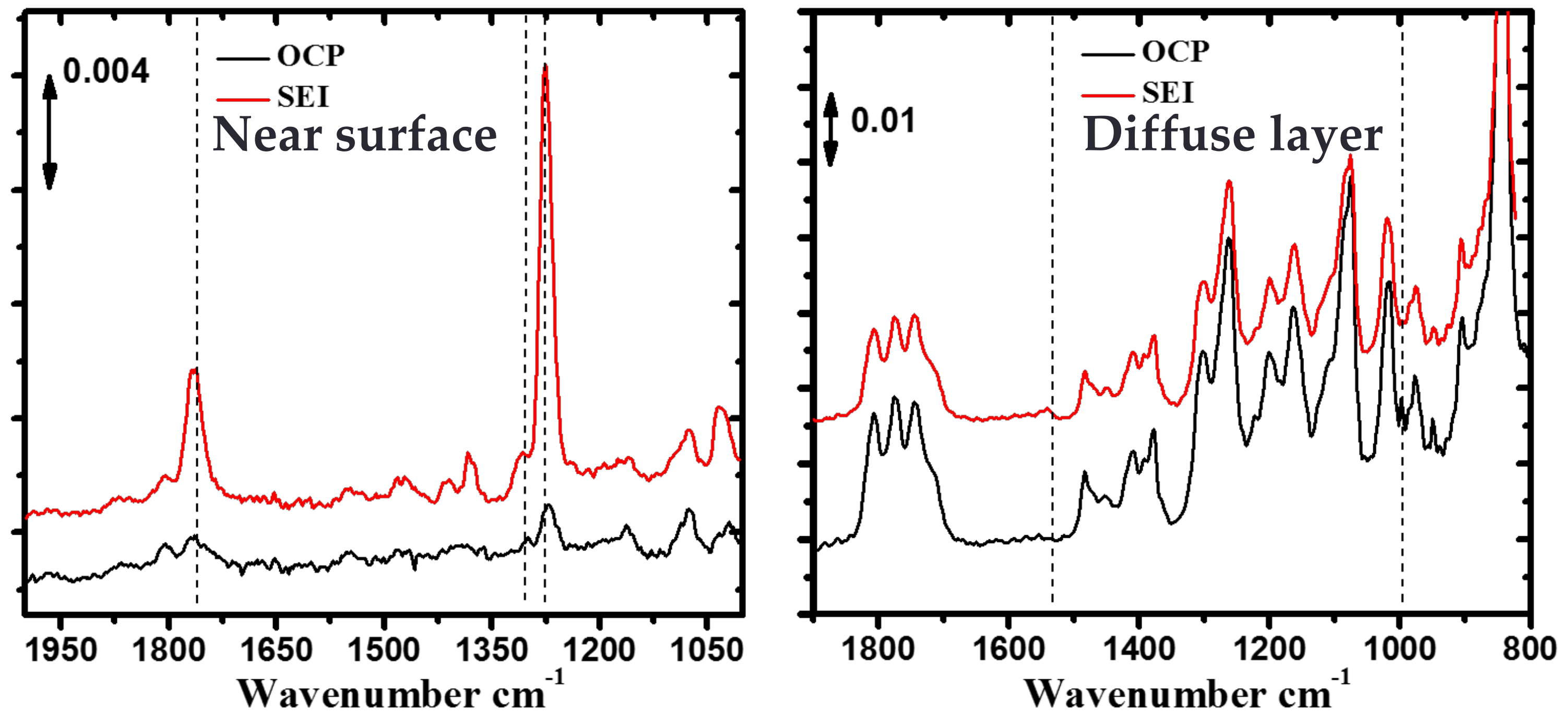
(Q4) Feasibility of surface functionalization to improve SEI properties. Criteria: Functionalize a model Si anode surface and determine how SEI formation is changed (Sep. 14). Ongoing

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, 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.



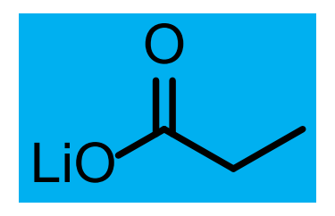
Inner reflection (Kretschmann mode) design could minimize the background signal from electrolyte solvent and thus increase surface sensitivity. Furthermore, by adjusting the incident angle or the ATR media (reflection index), we could analyze both near-surface layer and deep into the diffuse layer regions of the electrolyte.

ACCOMPLISHMENTS

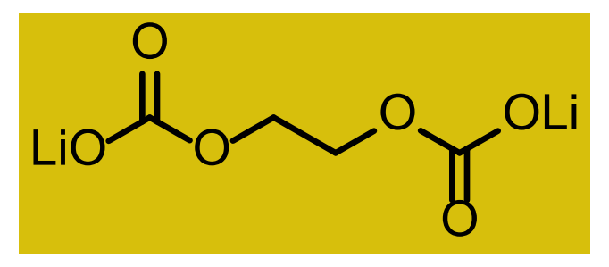
- A novel in-situ ATR-FTIR spectro-electrochemical cell was developed, which provided unprecedented tuning of the depth of probing the vibration al spectra of molecules near the electrode surface.
- Two alternative anode materials were studied, Si and Sn, with Au used as a contrasting "inert" metallic electrode.
- Preliminary results show that Si and Sn surface formed soluble products (diethyl 2,5 dioxohexane dicarboxylate, i.e. DEDOHC) via alkyl and alkoxide radicals; while Au electrode produce more insoluble compounds (lithium ethylene dicarbonate, LiEDC).
- The reduction product dependence on various surface would determine the passivation of solid electrolyte interface, thus affects whether electrolyte reduction will continue.

RESULTS

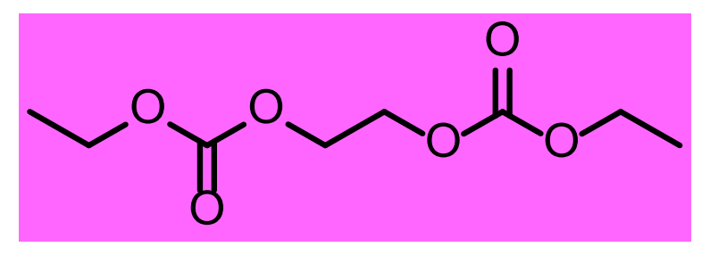
SEI components for Au and Sn Anodes were: **Li-propionate**, **LiEDC**, **DEDOHC**



Lithium propionate



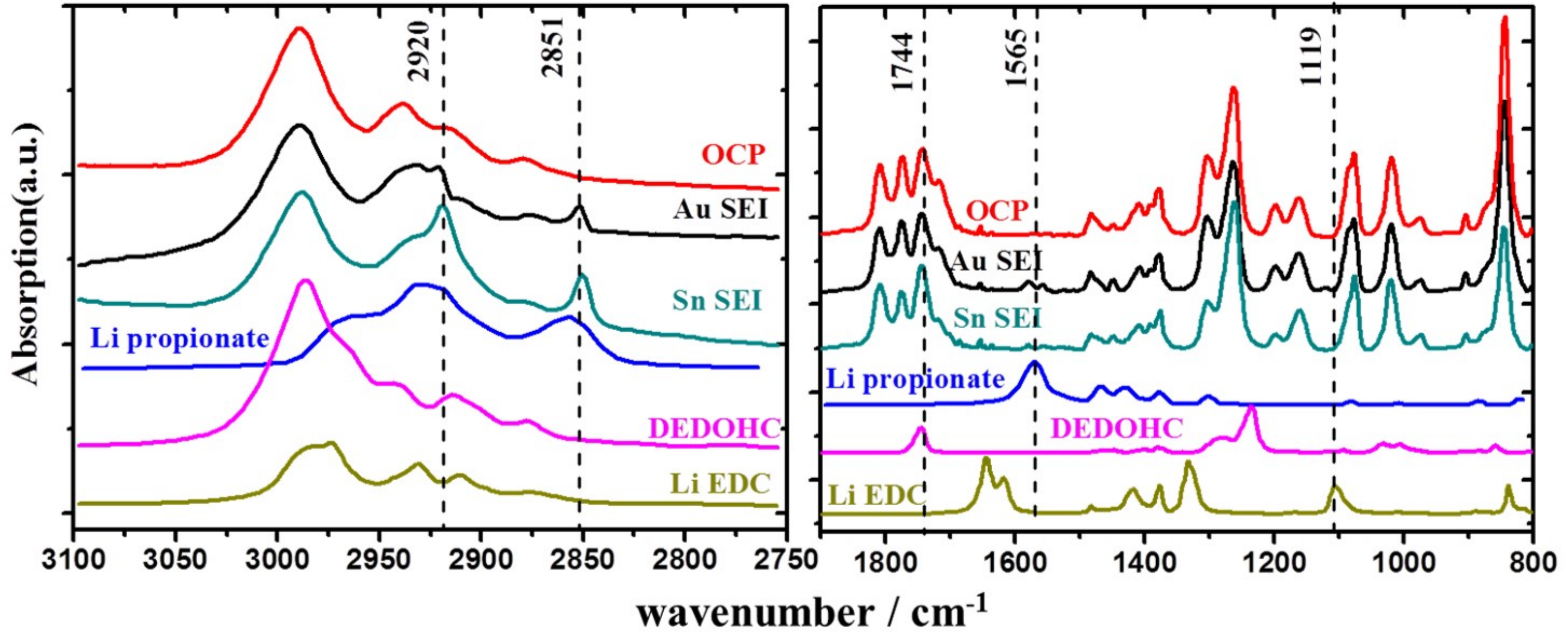
LiEDC
lithium ethyl dicarbonate



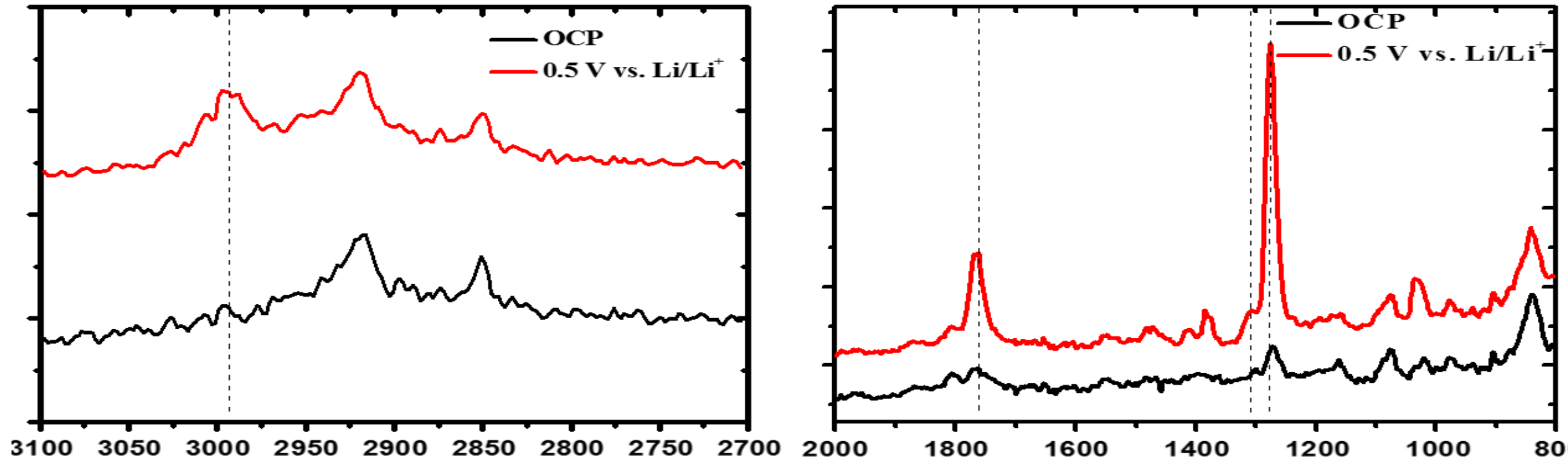
DEDOHC
Diethyl 2,5-dioxahexane dicarboxylate

RESULTS CONT'D

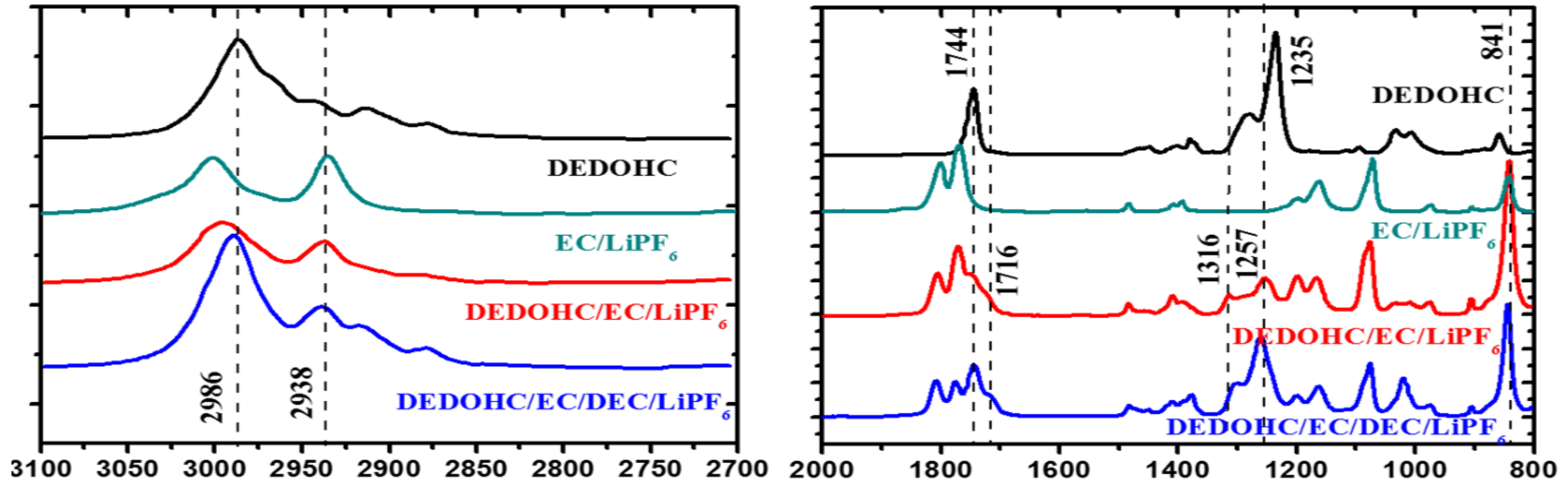
Li-propionate, **LiEDC**, **DEDOHC** FTIR spectra:



The *in-situ* spectra from the near surface region changed when the potential was applied on the Si electrode. Two strong peaks appeared above the electrolyte features, these could be attributed to **DEDOHC.**



DEDOHC reference compound was synthesized and characterized. In order to have better peak assignment of the surface species, DEDOHC spectra under various condition were taken (considering solvation effect).



CONCLUSIONS

Anode	Si	Graphite
SEI compounds	**Lithium propionate** **DEDOHC**	LiEDC Li Oxalate ($Li_2C_2O_4$)
Soluble?	YES	NO
Effect on Cyclibility	Bad	Good

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

FUTURE PLANS

- Fluorinated ethylene carbonate (FEC) was selected as an additive for future studies by SFG and ATR-FTIR.
- Selectively controlling the solvent reduction reactions pathways by surface modification of the Si in order to reduce the solubility of the SEI.