The Li ion battery's electrolyte solvation dynamics in operando condition near the electrode

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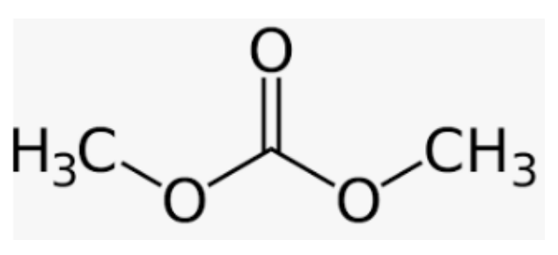
Abstract

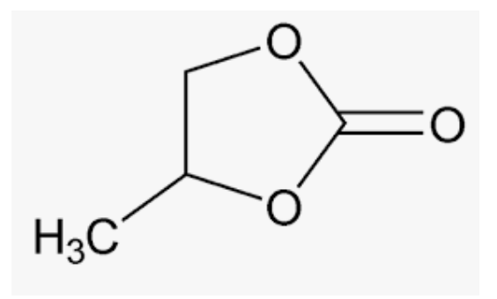
Electrolyte is one of the main components of lithium ion batteries, which acts as transport channels for lithium ions and is closely related to battery performance such as charge rate, capacitance, stability, and safety. Since the performance of these batteries is determined by the microscopic properties of solvent molecules or lithium salts, understanding the solvation dynamics at the molecular level is very important and necessary. In the currently commercialized lithium ion battery, the electrolyte is formed by dissolving a lithium salt in a mixed organic solvent of cyclic carbonate and linear carbonate. The cyclic carbonate has a high dielectric constant to stabilize the Li cation, and the linear carbonate has low viscosity to help transport the Li cation. Many previous studies have dealt with bulk state electrolyte which is not applied electric potential. However, it is very important and necessary to observe the solvation dynamics in operando condition to understand the operation mechanism of the lithium ion battery. To do that, A home-built spectro-electro-chemical cell capable of measuring the spectrum while applying potential to the electrolyte was fabricated. As a result of FT-IR measurements on various electrolytes with home-built spectro-electro-chemical cell, it was observed that the electrolyte have a different solvation dynamics than the bulk electrolyte.

DiMethly Carbonate



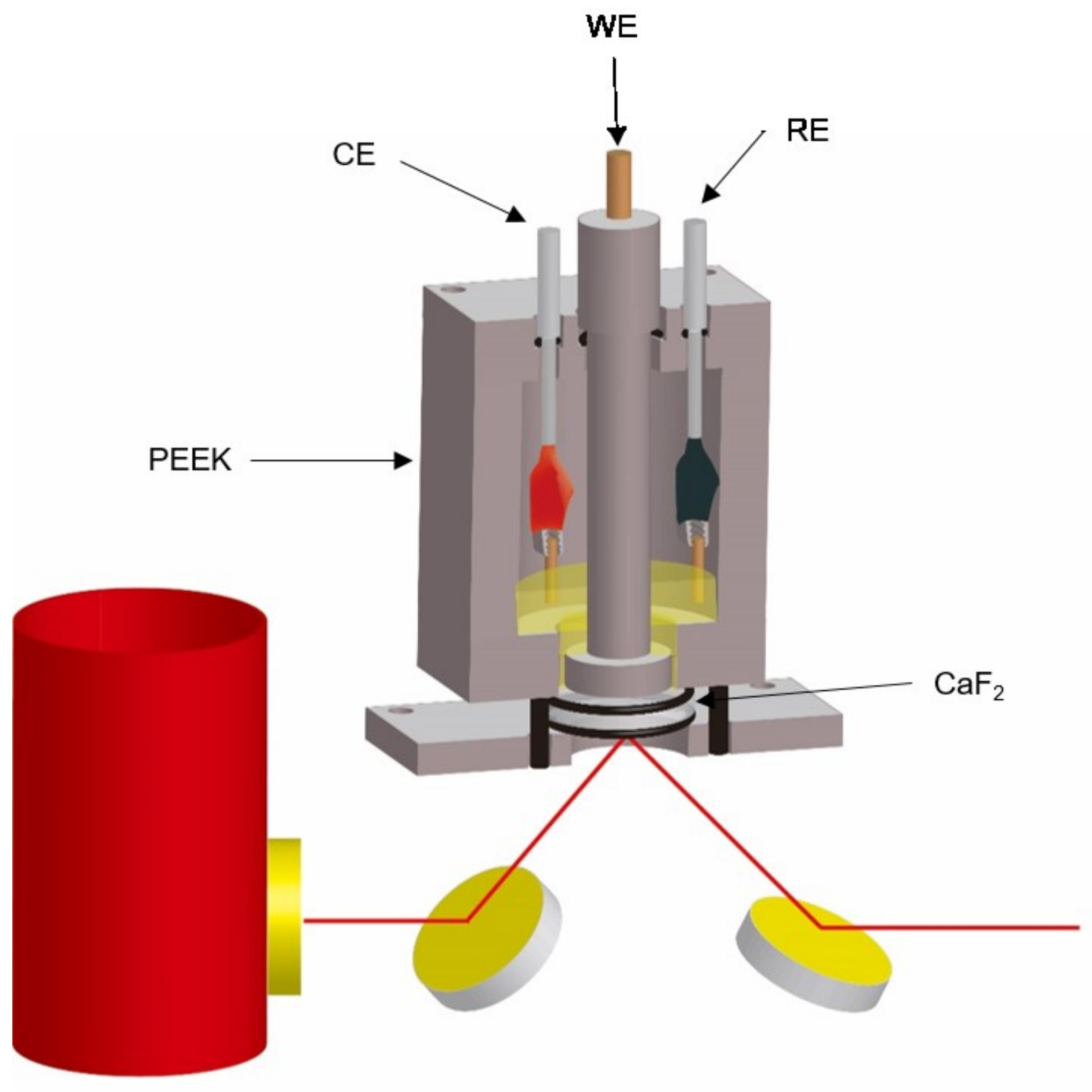
Linear carbonate
Low viscosity
Low dielectric constant

Propylene Carbonate

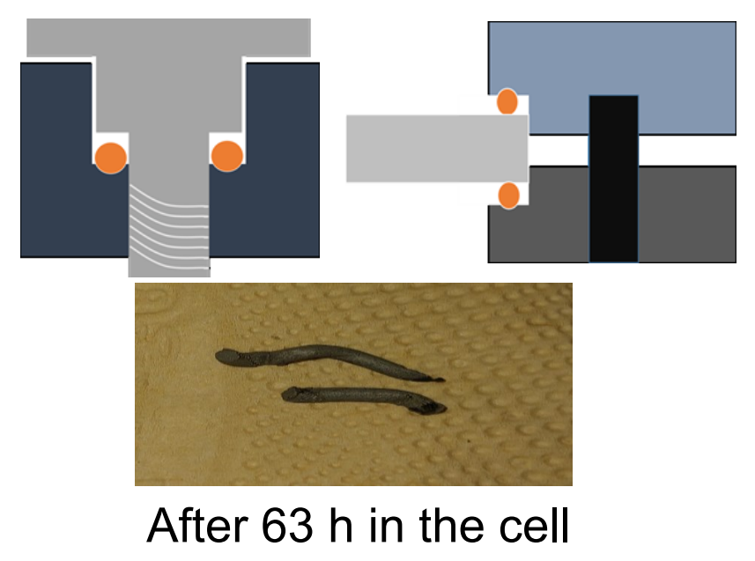


Cyclic carbonate
High viscosity
High dielectric constant

Home-built in-situ Spectro-Electro-Chemical cell

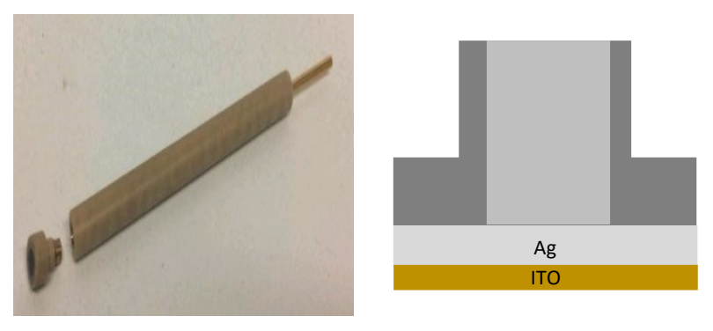


3 electrode system
Reflection geometry

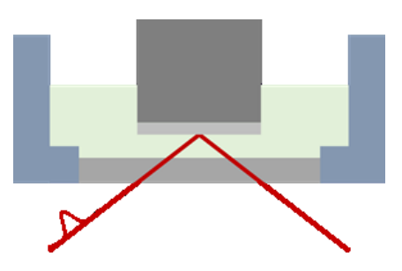


Li is easily oxidized, when exposed to air. Blocking the inside of cell from ambient air by using Viton O-ring

When checked with a multi meter, conductivity was maintained.

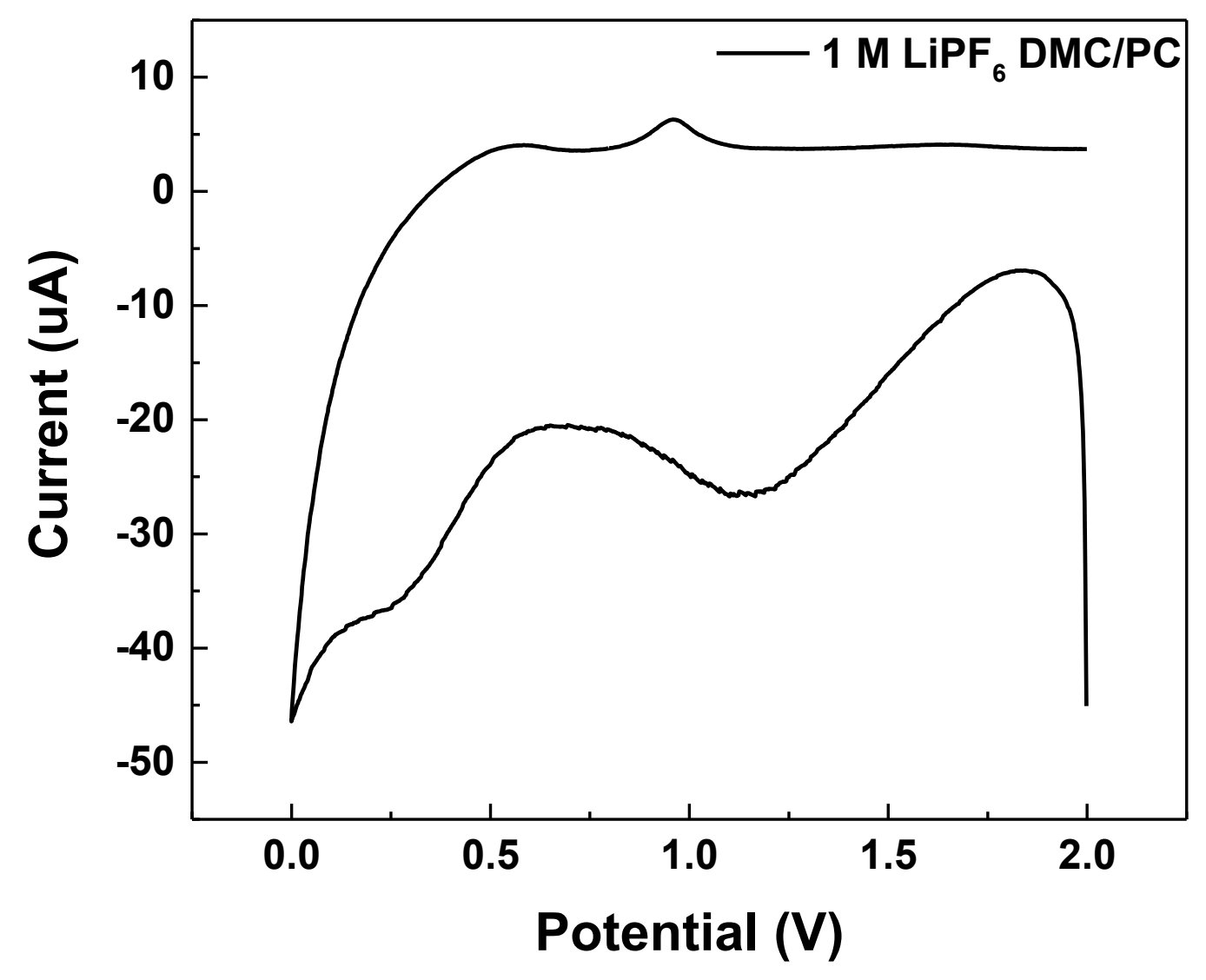


Easily changeable to other electrode material by removable head

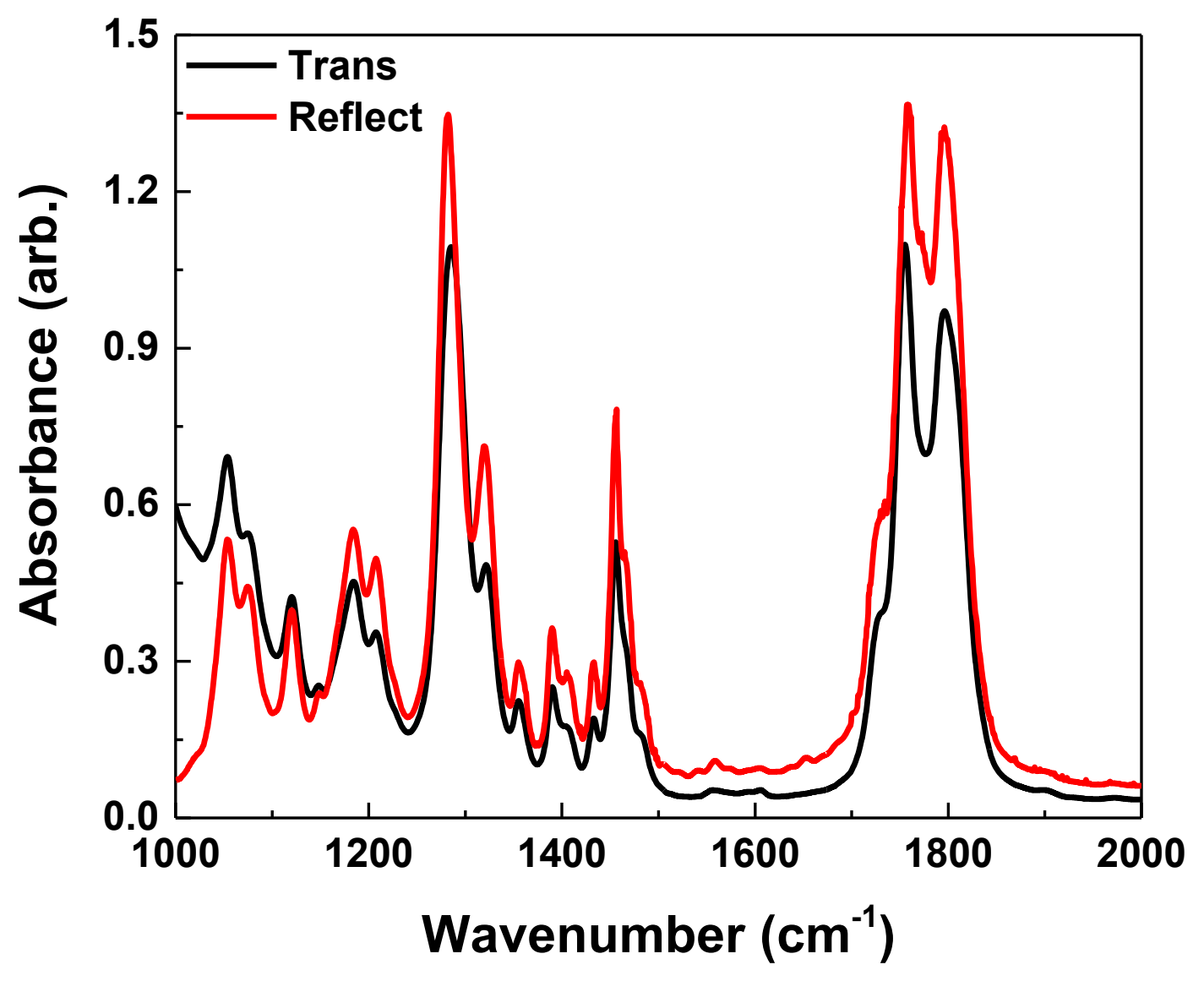


To avoid the CO peak saturation,
Sample path length ≪ 1 μm
Observation of electrolyte near the electrode

CV data & spectrum of 1 M $LiPF_6$ in DMC/PC(1:1 v%) for cell performance test



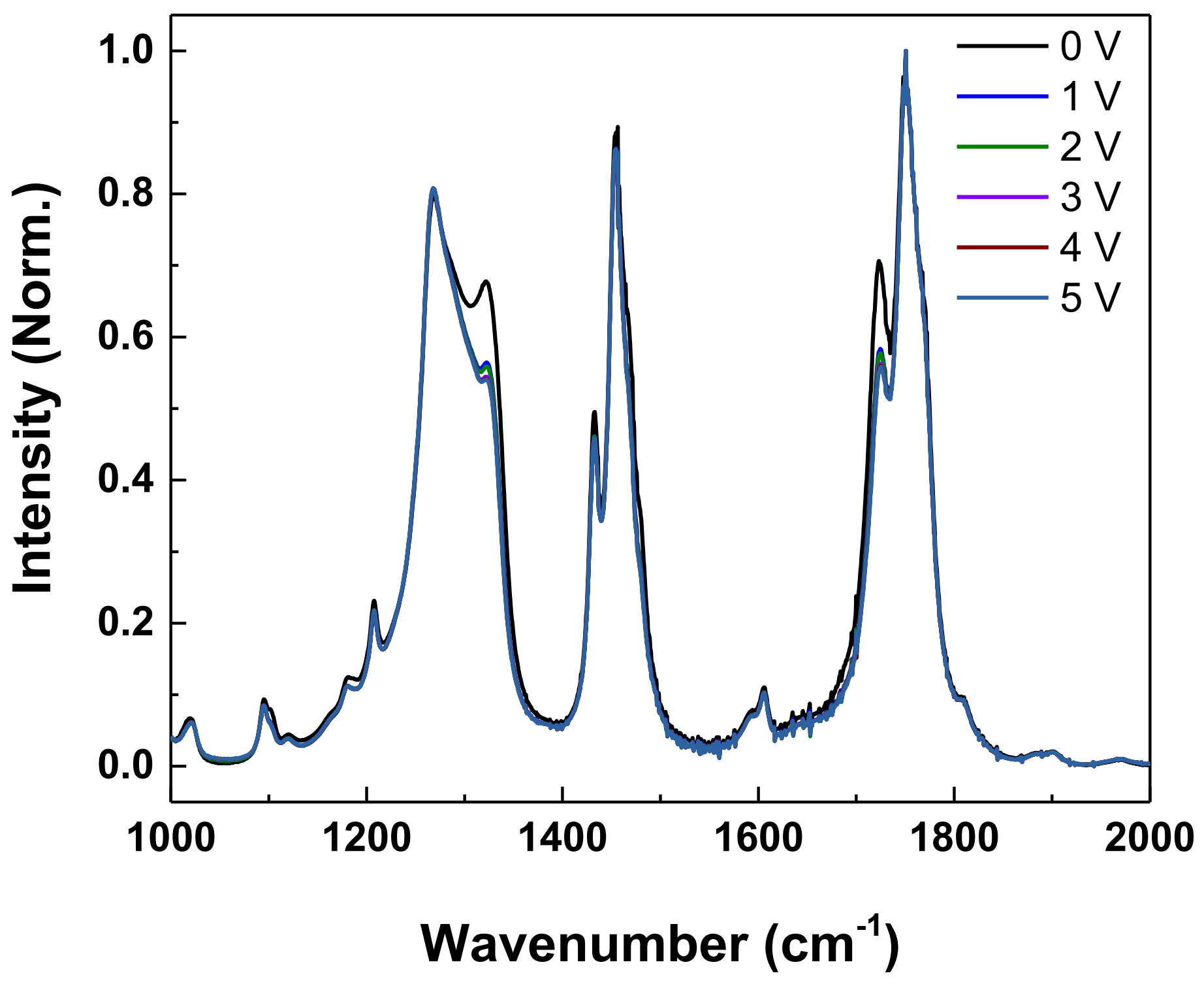
Peak around 0.25 V : lithiation
Peak around 1 V : de-lithiation
Peaks related to charging / discharging process are observed



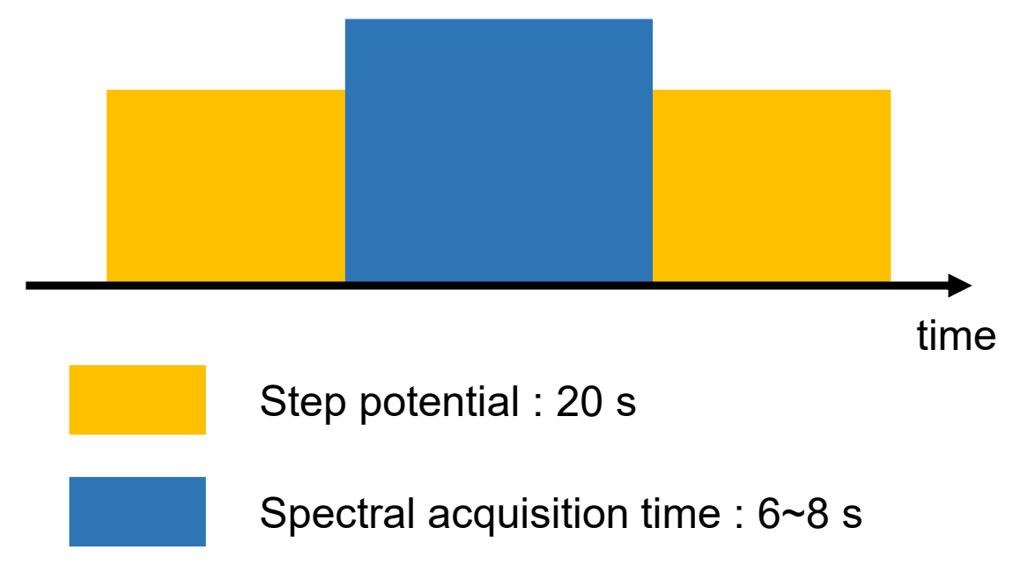
The home built in-situ SEC cell provides the same spectrum as that obtained from transmission cell.
Peaks are not saturated.

In-situ FT-IR spectrum

Electrolyte near the electrode



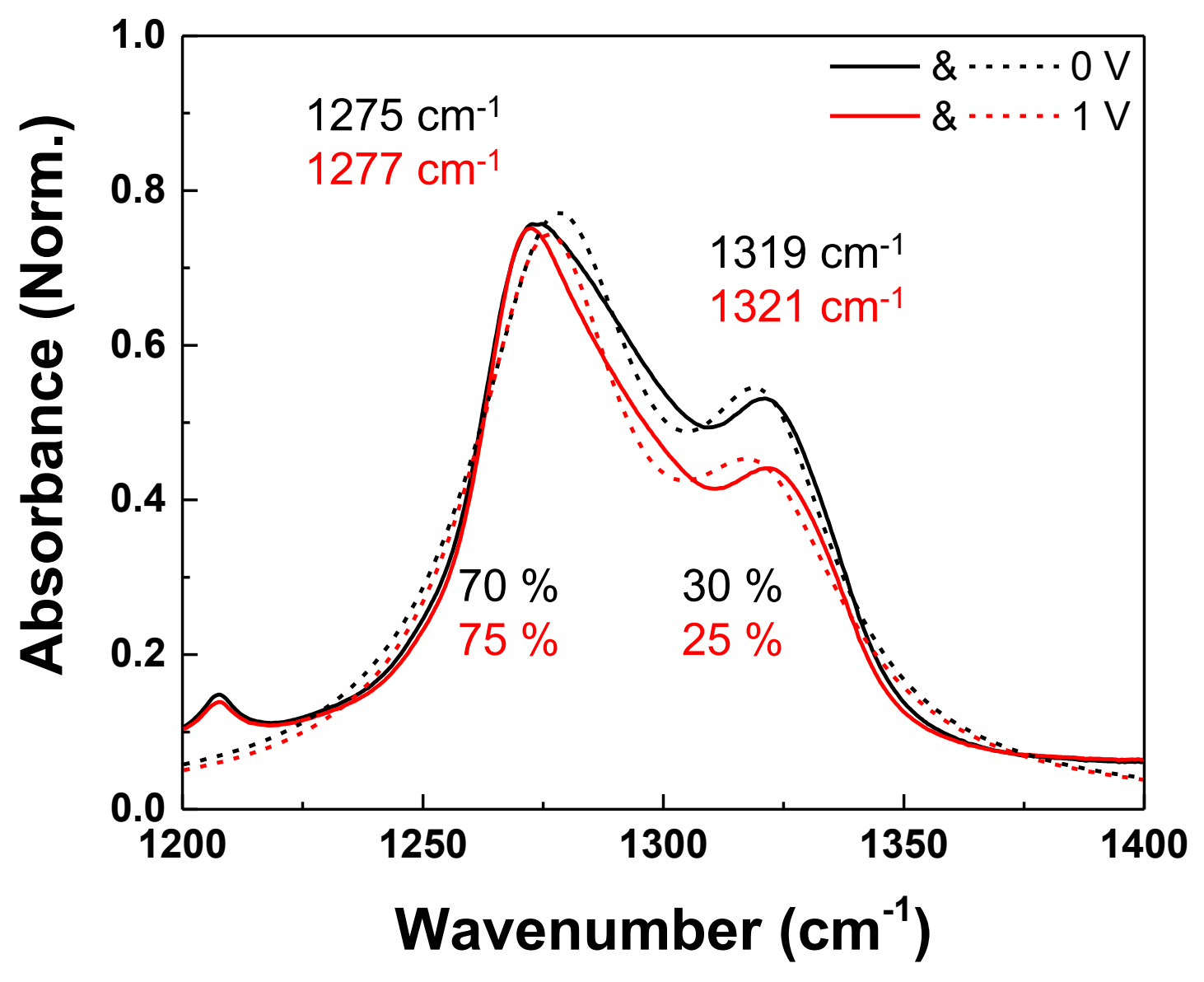
How to obtain in operando spectrum



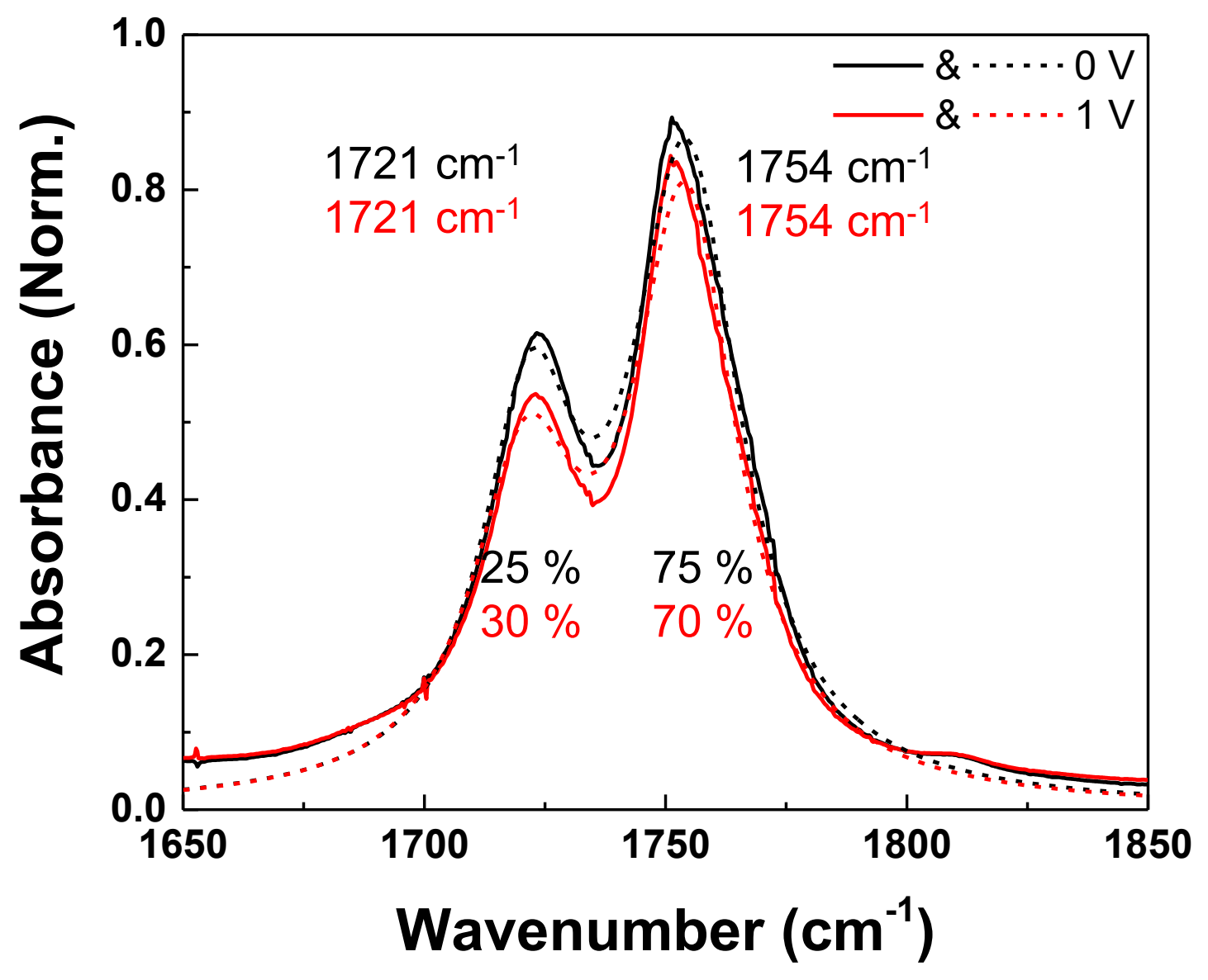
Apply the step potential of the desired value longer than the spectral acquisition time.

The spectrum is normalized by CH_3 peak at near the 3000 cm^{-1} & fitted w/ Lorentz profile.

O-C-O asymmetric stretching



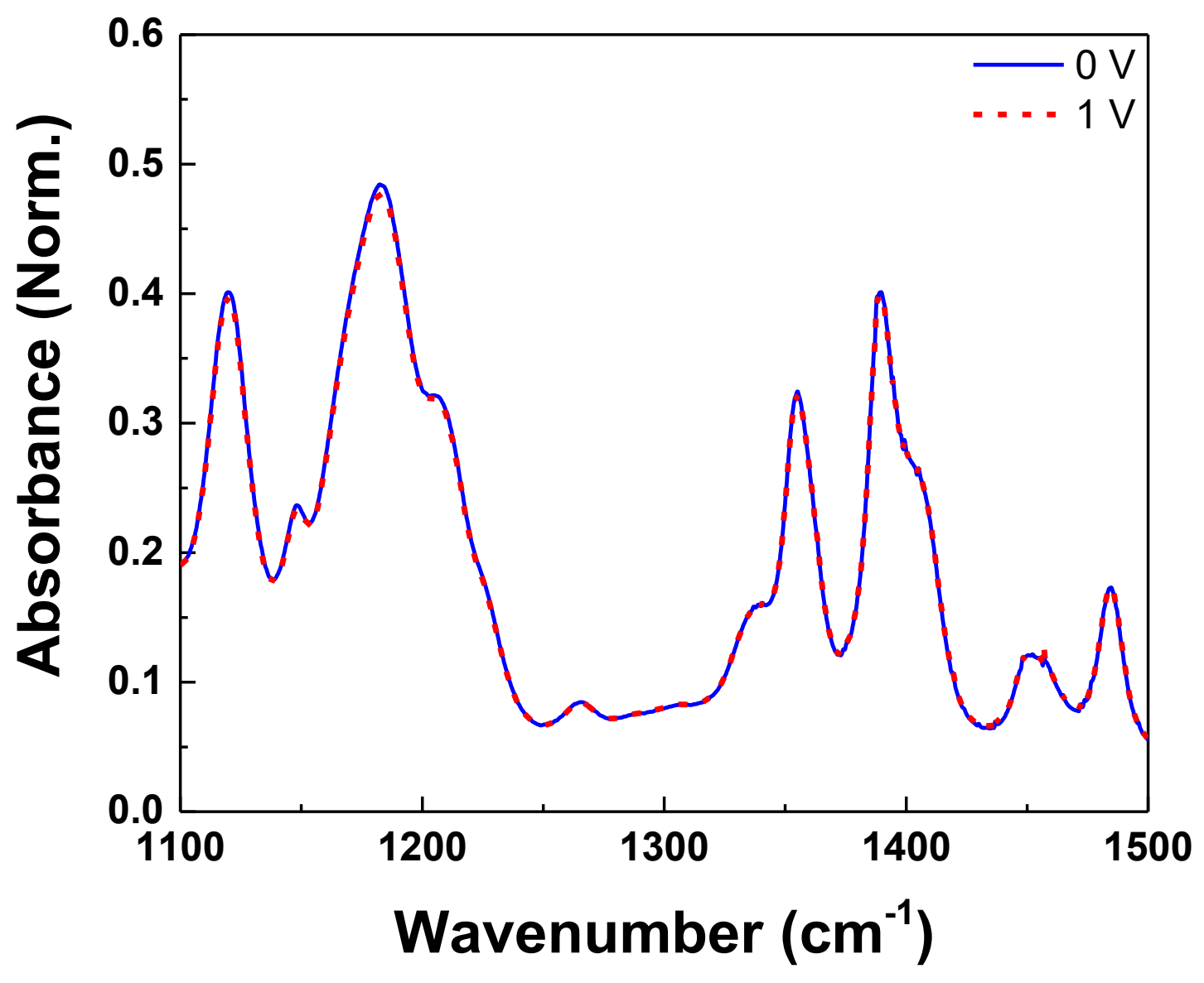
C=O stretching



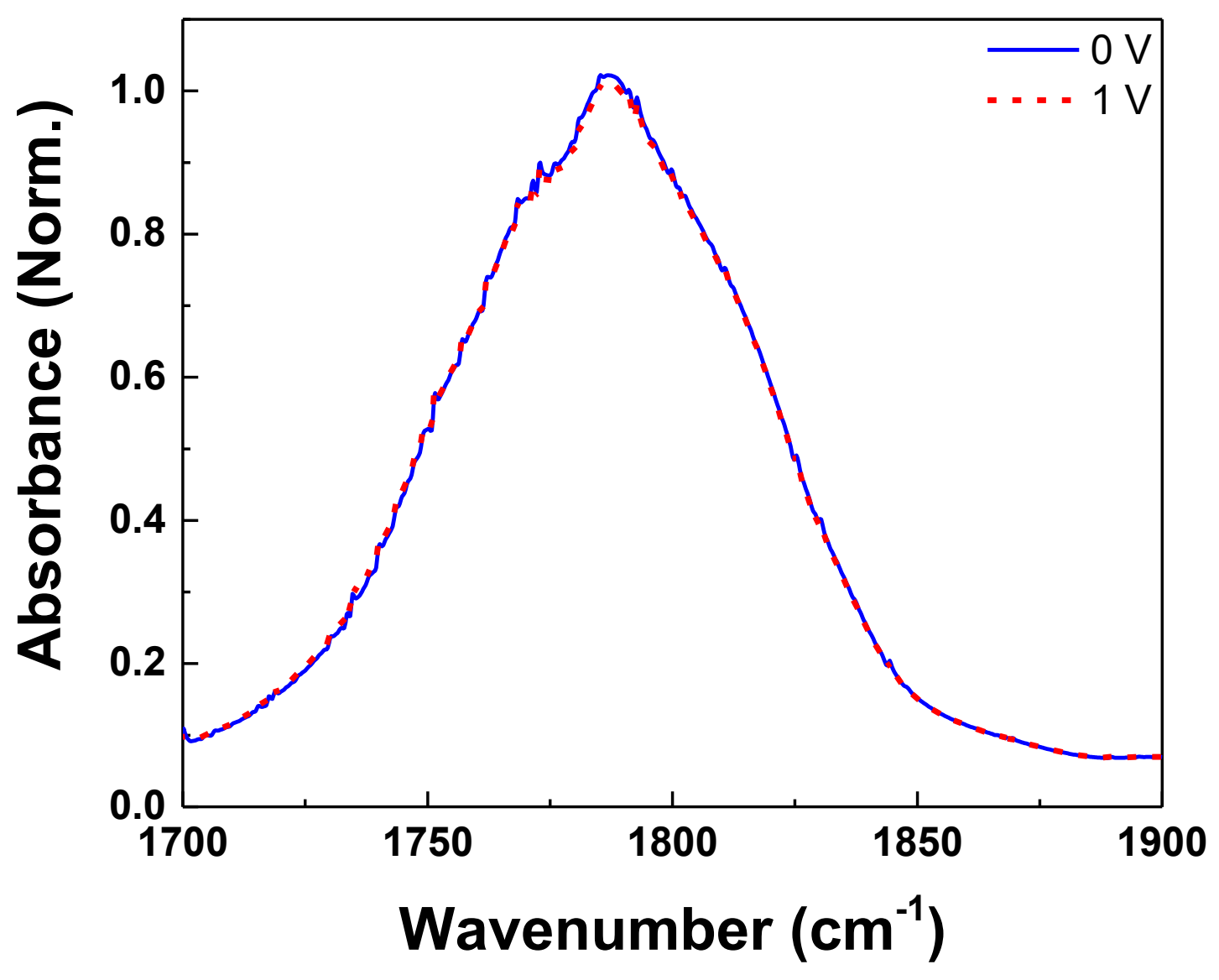
The FT-IR spectrum of 1 M $LiPF_6$ in DMC with electric potential.

When the potential is applied, the amplitude ratio of shoulder peaks related to Li ion interaction decreased by 5 %.

O-C-O asymmetric stretching



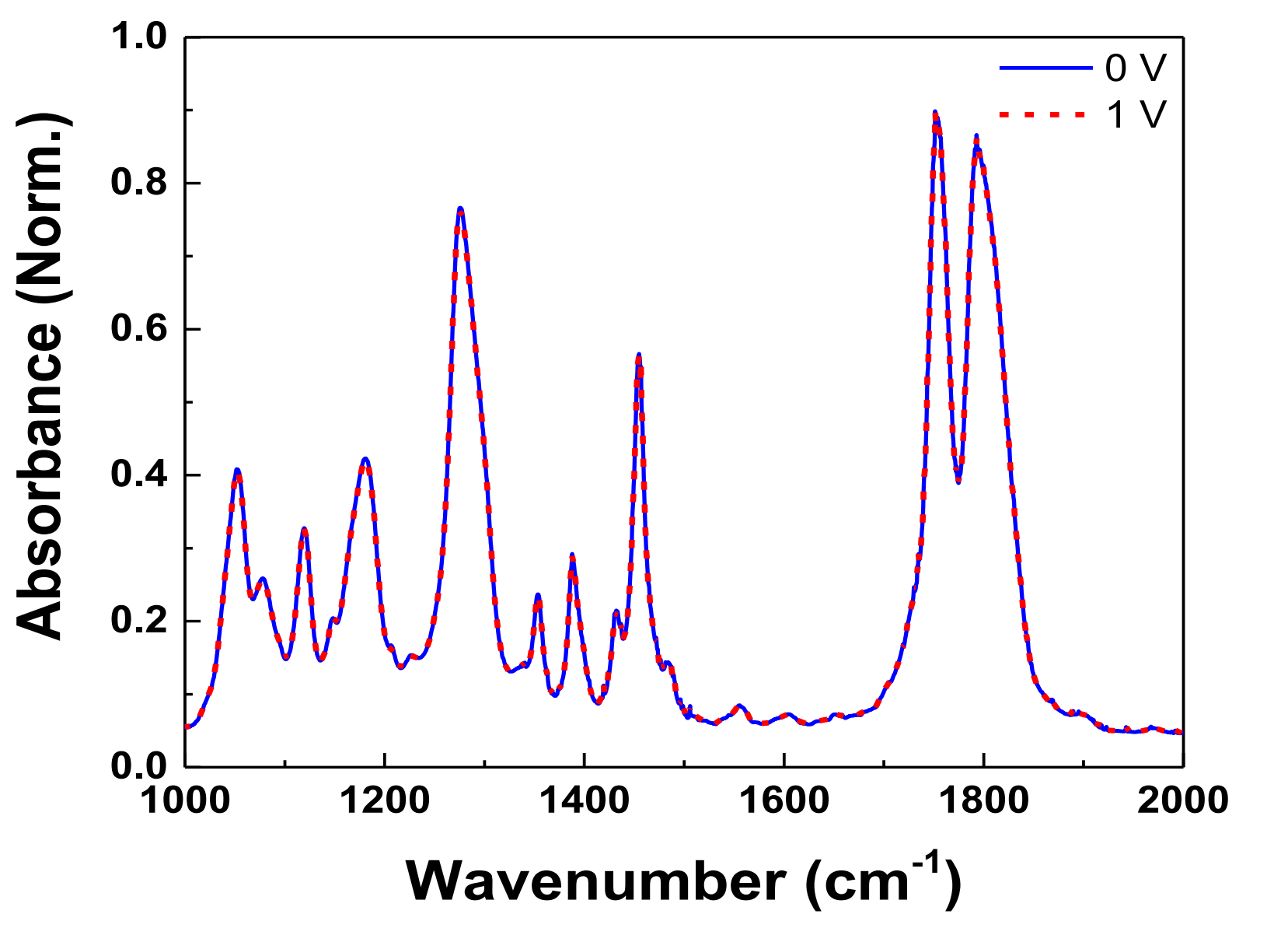
C=O stretching



The FT-IR spectrum of 1 M $LiPF_6$ in PC with electric potential.

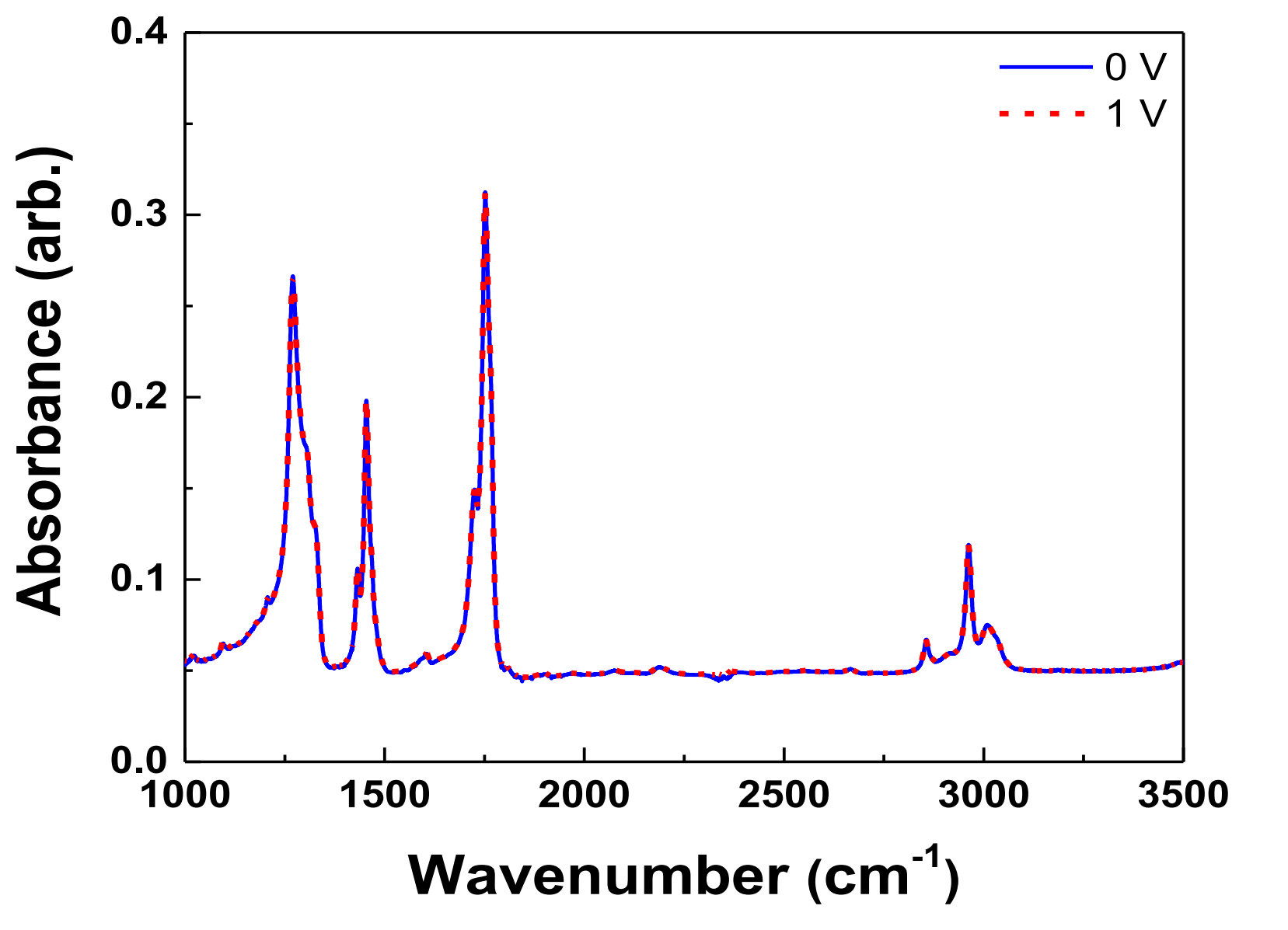
When the potential is applied, the amplitude ratio of shoulder peaks related to Li ion interaction did not changed.

Solvent adsorption on electrode



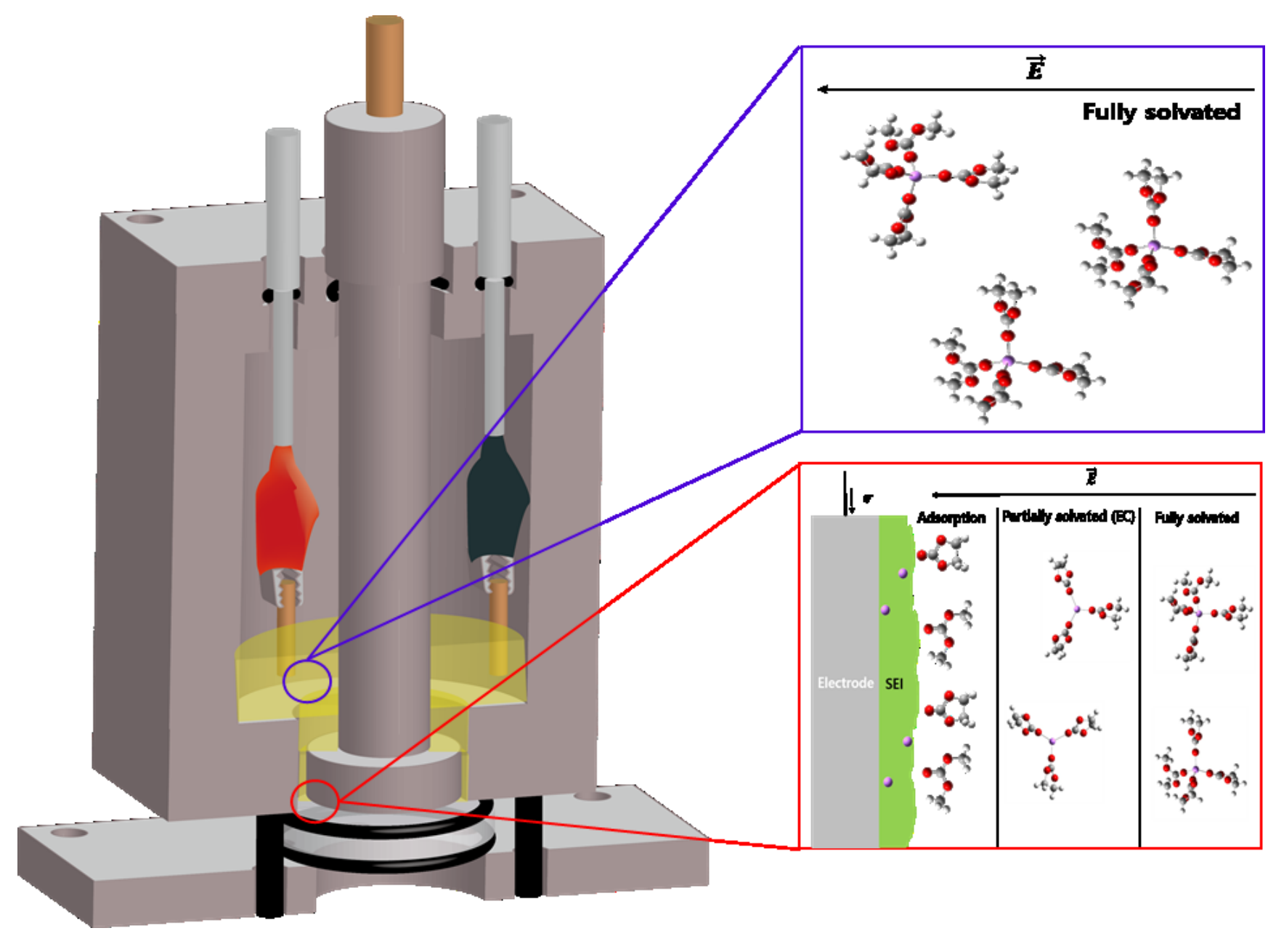
The FT-IR spectrum of DMC/PC(1:1 v%) with electric potential.
When the potential is applied, the spectrum does not changed.

Bulk electrolyte



The FT-IR spectrum of 1 M $LiPF_6$ in DMC with electric potential.
In this case, Ag electrode only acts as a mirror and Pt foil is introduced as a new working electrode.
No spectral changes are observed.

Conclusion



- ✓ The DMC solvent molecule has a low dielectric constant and is weakly bound the to Li ion. Therefore, when the potential is applied, the change in amplitude ratio of shoulder peaks related to Li ion interaction observed is due to the change of the solvation number near the electrode. It has also been found that this spectral change of Li interaction peaks occurs only near the electrode.
- ✓ The PC solvent molecule has a high dielectric constant and is strongly bond to the Li ion. Therefore, the spectral change does not occur even though the potential is applied. It is expected that the PC and the Li ion are strongly bounded in the vicinity of the electrode with electric potential.
- ✓ Many previous papers have reported adsorption of solvent molecules or formation of SEI layers on the electrode (less than 50 nm), but this phenomenon is small compared to the overall sample path length (~ 1 μm). Therefore, spectral changes due to adsorption or SEI formation are difficult to observe in this experiment.
- ✓ The solvation structure near the electrode differs from the bulk state, and this difference is closely related to the dielectric constant of the solvent molecule.

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