

# In situ FTIR spectra at the Cu electrode/propylene carbonate solution interface

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## Abstract

In situ Fourier transform infrared spectroscopy (FTIR) spectra measurements were obtained for a Cu electrode/solution of lithium perchlorate in propylene carbonate (PC). The dependence of potential on the concentration of PC in the vicinity of the electrode was investigated. The bands due to free PC and PC solvated to lithium ions in the solution were distinguished by the single reflection attenuated total reflection (ATR) spectra. In the FTIR spectra, the reversible change in the concentration of free PC and solvated PC in the diffuse double layer was observed to be accompanied by a change in potential. As the potential decreased, the free PC concentration increased, while the concentration of the PC solvated to lithium ions decreased. Thus, it can be concluded that the equilibrium shifts from  $\text{Li}^+(\text{PC})_4$  to  $\text{Li}^+(\text{PC})_3 + \text{PC}$  as the potential decreases. Furthermore,  $\text{Li}^+(\text{PC})_3$  orientates itself so that it is parallel to the electrode surface.  
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**Keywords:** Propylene carbonate; Solvation; IRAS; Cu electrode

## 1. Introduction

The interfacial phenomena between electrodes and non-aqueous electrolyte solutions are very important for research and development of rechargeable lithium ion batteries. However, the surface reactions during the charging and discharging phases are complicated by irreversible reactions, formation of a solid-electrolyte interphase (SEI), and the co-intercalation of solvent. Fourier transform infrared spectroscopy (FTIR) is a useful method for analyzing interfacial phenomena. The surface reaction of graphite electrode in many nonaqueous electrolyte solutions has been investigated using both in situ and ex situ FTIR spectroscopy [1–5].

On the other hand, it is well known that when lithium ions are solvated using nonaqueous organic solvents [6–14], the solvents affect the reduction potential and the subsequent decomposition reactions. When considering rechargeable lithium ion batteries, it is important to understand the behavior of species solvated to lithium ions during the charging and discharging phases.

In order to investigate these complex phenomena, the charge and discharge reactions must be separated from the other reactions. Furthermore, a place to observe the phenomenon must be chosen. The electrode reactions need to be classified into those that are reversible and those that are irreversible. As well, the reactions must be classified whether the reaction occurs on the surface of the electrode, near the surface of the electrode, or in the bulk. Of note, the copper that is used in a lithium secondary battery acts as the conductor.

In this study, a copper electrode/solution of lithium perchlorate in a propylene carbonate (PC) system, in which the charging and discharging reactions do not occur, was chosen, and the behavior of PC solvated in  $\text{Li}^+$  at the interface between a copper electrode and the PC solution was examined using in situ FTIR spectroscopy.

## 2. Experimental

Propylene carbonate and battery grade 0.1–1.5 M  $\text{LiClO}_4/\text{PC}$  solutions (Tomiyama Pure Chemical Industries) were used as provided by the company. The electrolyte contained less than 50 ppm of water. The spectro-electrochemical cell used was a two-electrode system. A copper disc with a diameter of 10 mm and a purity of 99.99% was used as the working electrode.

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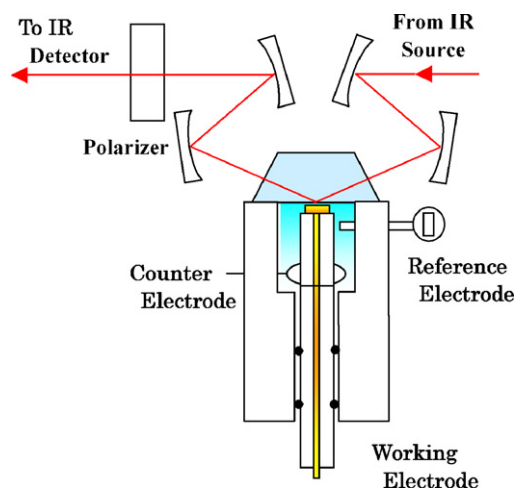


Fig. 1. Optical geometry and the spectro-electrochemical cell.

Lithium foils were used as the reference and counter electrodes. The spectro-electrochemical cell was made of Teflon and had a prismatic BaF<sub>2</sub> window beveled at 65°. The working electrode was pushed against the window. All chemicals were treated in a N<sub>2</sub> gas box.

The spectroscopic measurements were performed using a SPX200 (JEOR) equipped with a liquid nitrogen-cooled MCT detector (Judson). A modified attenuated total reflection (ATR) attachment and a polarizer were also used, as shown in Fig. 1. The spectra were recorded with 500 interferograms (4 cm<sup>-1</sup> resolution) at each potential. Potential control and current measurement were accomplished with an H-501 potentiostat (Hokuto Denko Co.) connected to a personal computer. The user-created electrochemical measurement program was used to run the electrochemical equipment. The procedure was done as follows: (1) the potential was set to a sample potential, and both the p- and s-polarized IRA spectra were measured at this potential; (2) the working potential moved to 2.5 V (versus Li<sup>+</sup>/Li), and both the spectra were measured. This procedure was repeated as the sample potential was changed from 2 to 0.01 V. All of the experiments were performed at room temperature.

An attenuated total reflectance (ATR) sampling accessory (Spectra Tech) was employed for the single reflectance ATR measurements of the PC solution with different concentrations of LiClO<sub>4</sub>, with a ZnSe trapezoidal prism used as the infrared window. The angle of incidence was set to 65°.

Density functional theory (DFT) calculations were performed for the optimized geometries of free PC and PC solvated to lithium ions, using information about the transition dipole moment of a vibration mode. We used the Becke-style three-parameter density functional method (B3LYP) in combination with the 6-31G(d) polarized basis set [15,16]. The harmonic frequency values computed at the B3LYP/6-31G(d) level are known to systematically overestimate vibrational frequency, hence, it is usual to scale the frequencies predicted at the B3LYP/6-31G(d) level by an empirical factor of 0.9613 [17,18]. For the computational method, DFT (B3LYP) was performed using GAUSSIAN 98. The reference conditions in the simulation of Δ*G*<sup>0</sup> were set to 273.15 K and 1.00 atm.

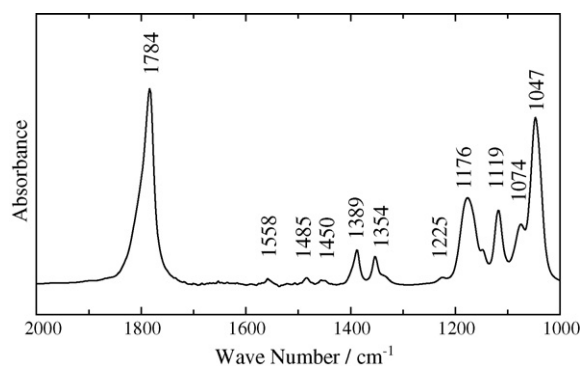


Fig. 2. Single reflection ATR spectrum of propylene carbonate.

### 3. Results and discussion

#### 3.1. Single reflection ATR spectra

Fig. 2 shows the PC spectrum observed using the single reflection ATR measurement. The intensity of the 1784 cm<sup>-1</sup> band was strong. However, using this method, the shape of the band did not have any absorption saturation. Table 1 shows the band assignments and the calculated band frequencies for PC. The main bands at 1784, 1389 and 1354 cm<sup>-1</sup> are assigned to the stretching vibration of C=O, the scissoring vibration of CH<sub>3</sub>, the wagging vibration of O-CH<sub>2</sub>, and the bending vibration of the ring, along with the symmetric bending vibration of CH<sub>3</sub>. The calculated frequencies correspond to isolated molecules. Nevertheless, the frequencies are consistent with the experimental values, except for the stretching vibration of C=O. It seems that the mode of the stretching vibration of C=O is strongly affected by interactions with other molecules.

Fig. 3 shows the single reflection ATR spectra for PC with different concentrations of LiClO<sub>4</sub>. New bands at 1765, 1404, 1362 and 1200 cm<sup>-1</sup> first appeared for a 0.5 M solution of LiClO<sub>4</sub> and increased in intensity as the concentration of LiClO<sub>4</sub> increased. The differential ATR spectrum between PC solutions with and without 1 M LiClO<sub>4</sub> is shown in Fig. 3. Upward and downward bands are clearly observed. The position of the downward bands agrees with the spectrum for PC without LiClO<sub>4</sub>.

It has been reported that the interaction between the solvent and ClO<sub>4</sub><sup>-</sup> in a nonaqueous electrolyte solution is very weak [6,19]. The solvation process of lithium ions in PC and ethylene carbonate was determined using Raman, nuclear magnetic resonance, and impedance spectroscopy. When Li<sup>+</sup>(PC)<sub>4</sub> complex molecules are solvated, the first ionic shell is affected for low lithium ion concentration [7]. Therefore, the upward bands observed in this experiment are assigned to the vibration mode of PC molecules solvated to the Li<sup>+</sup> ions. The main bands due to solvation are listed in Table 1. The original bands at 1389 and 1354 cm<sup>-1</sup> are shifted to 1408 and 1362 cm<sup>-1</sup> towards the high frequency end, while the band at 1784 cm<sup>-1</sup> is shifted to 1765 cm<sup>-1</sup> towards the low frequency end. Furthermore, Table 1 shows the vibration frequencies of Li<sup>+</sup>(PC)<sub>4</sub> that were calculated. For the calculated vibration frequencies of Li<sup>+</sup>(PC)<sub>4</sub>, the mode of ν<sub>Ring</sub>, CH<sub>3</sub>(sy), δCH<sub>3</sub>(sc) and O-CH<sub>2</sub>(wa) shift to the higher frequency end of the spectrum due to the free PC

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