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# In situ FTIR study of the Cu electrode/ethylene carbonate + dimethyl carbonate solution interface

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## Abstract

The interfacial phenomena between Cu electrode and solution of lithium perchlorate in ethylene carbonate (EC)–dimethyl carbonate (DMC) have been investigated using in situ reflection absorption Fourier transform infrared (FTIR) spectroscopy and single reflection ATR–FTIR spectroscopy. The ATR spectra confirmed the bands due to free EC and DMC and the molecules solvated to lithium ions in the solution. The bands due to the result of the interaction between $ClO_4^-$ and DMC in the mixture solution also appeared in the ATR spectra. In the FTIR spectra, the potential dependence on the concentration of EC and DMC in the vicinity of the Cu electrode was observed. It was understood that the reversible changes in the concentration of free EC and DMC and solvated EC and DMC in the diffuse double layer take place with changing in potential. As the potential decreased, the free EC and DMC concentrations increased, while the concentration of the EC and DMC solvated to lithium ions decreased. Thus, it can be concluded that the equilibrium shifts from $Li^+(EC)_2(DMC)_2$ to $Li^+(EC)_2(DMC)$ + DMC or $Li^+(EC)(DMC)_2$ + EC as the potential decreases. The bands due to $(CH_2OCO_2Li)_2$ and $CH_3OCO_2Li$ were observed for an irreversible reaction.

*Keywords:* Ethylene carbonate; Dimethyl carbonate; Solvation; IRAS; Cu electrode

## 1. Introduction

The interfacial phenomena between electrodes and nonaqueous electrolyte solutions are very important for the research and development of rechargeable lithium ion batteries. However, the surface reactions during the charge and discharge phases are complicated by irreversible reactions, the formation of a solid–electrolyte interphase (SEI), and the co-intercalation of solvent. Therefore, the nonaqueous solvent/electrode interface has yet to be sufficiently characterized. It is well known that when lithium ions are solvated using nonaqueous organic solvents [1–9], the reduction potential is affected and subsequent decomposition reactions occur. When considering rechargeable lithium ion batteries, it is important to understand the behavior of the species solvated to the lithium ions during the charge and discharge phases.

Fourier transform infrared (FTIR) spectroscopy is a useful method for analyzing interfacial phenomena. Electrode surface reactions in many nonaqueous electrolyte solutions have been investigated using both in situ and ex situ FTIR spectroscopy [10–14].

In our previous study of the propylene carbonate (PC)/Cu electrode system, the solvation of PC to lithium ions was clearly confirmed from single reflection ATR–FTIR spectral measurements, and stable structures of $Li^+(PC)_3$ and $Li^+(PC)_4$ were estimated in the $LiClO_4$-containing electrolyte solution [15]. Thus, the following reversible reaction was expected to reach equilibrium:

$$Li^+(PC)_3 + PC \leftrightarrows Li^+(PC)_4 \quad (1)$$

It was found that the concentration of solvated PC in the diffuse double layer depends on the electrode potential. It seems that the equilibrium between solvated PC and free PC shifts in the diffuse double layer as the electrode potential changes, due to the change in the potential gradient of the diffuse double layer. A decrease in the concentration of solvated PC and an increase in the concentration of free PC is caused when reaction (1) proceeds to the left. As a result, a decrease in the solvated PC band intensities is observed. It was determined that the stability

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of $Li^+(PC)_4$ and $Li^+(PC)_3$ in the diffuse double layer depends on the potential gradient.

The behavior of the solvation complex is directly related to the form of lithium ions present at the electrode surface, as well as the mechanism of the charge/discharge reaction. Therefore, more research and a greater understanding of these electrode surface phenomena and reaction mechanisms is required for the development of new rechargeable lithium ion batteries.

In order to investigate these complex phenomena, the charge and discharge reactions must be separated from the other reactions, and the electrode reactions need to be classified as reversible or irreversible. In addition, the reaction must be classified according to whether the reaction occurs on the electrode surface, near the electrode surface, or in the bulk. In this study, a system consisting of a Cu electrode in a solution of lithium perchlorate in an ethylene carbonate–dimethyl carbonate (EC + DMC) mixture, in which charge/discharge reactions do not occur, was selected. Lithium perchlorate was chosen as the support electrolyte for comparison with the previous research using the PC electrolyte. The behavior of EC and DMC solvated to lithium ions at the interface between the Cu electrode and the mixed solution was examined using in situ FTIR spectroscopy.

## 2. Experimental

Battery grade EC and DMC and EC + DMC (1:1 v/v) with and without 0.1 M or 1.0 M $LiClO_4$ (Tomiyama Pure Chemical Industries) were used as provided by the company. The water content in each electrolyte solutions was less than 20 ppm. The spectro-electrochemical cell used was a three-electrode system, as shown in Fig. 1. A copper disc with a diameter of 10 mm and a purity of 99.99% was used as the working electrode. Lithium foils were used as the reference and counter electrodes. The spectro-electrochemical cell was made of Teflon and had a prismatic $BaF_2$ window beveled at 65° [15]. The working electrode was pushed against the window. All chemicals were treated in a glove box.

The FTIR measurements were performed using a spectrometer (SPX200 JEOR) equipped with a liquid nitrogen-cooled MCT detector (Judson). A modified attenuated total reflection (ATR) attachment and a polarizer were also used. The spectra were recorded with 500 interferograms (4 $cm^{-1}$ resolution) at each potential. Potential control and current measurement were accomplished with a potentiostat (H-501 Hokuto Denko) 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 waited for that the irreversible reduction current disappeared and, both the p- and s-polarized infrared reflection–absorption (IRA) spectra were measured at this potential; (2) the working potential moved to 2.5 V (vs. $Li^+/Li$), and both the spectra were measured. This procedure was repeated as the sample potential was changed from 2 to 0.1 V. All of the experiments were performed at room temperature.

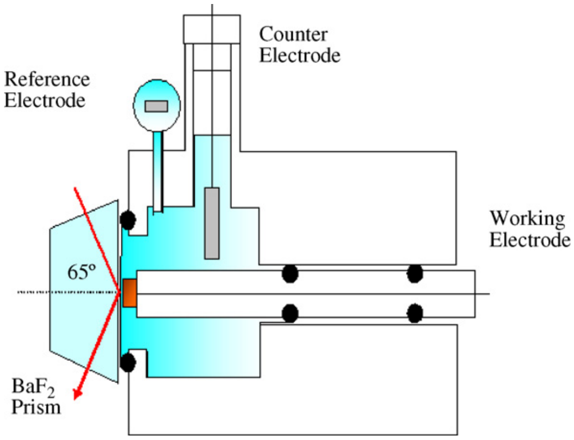

Fig. 1. Schematic illustration of spectro-electrochemical cell.

An ATR sampling accessory (Spectra Tech) was employed for the single reflectance ATR–FTIR measurements of the EC + DMC solution with and without $LiClO_4$, 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 3-parameter density functional method (B3LYP) in combination with the 6-31G(d) polarized basis set [16,17]. 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 [18,19]. For the computational method, DFT (B3LYP) was performed using GAUSSIAN 98 [20]. The reference conditions in the simulation of $\Delta G°$ were set to 273.1 K and 1.00 atm.

## 3. Results and discussion

### 3.1. Single reflection ATR spectra

Single reflection ATR–FTIR measurements were carried out for the individual electrolyte solutions in order to assign bands due to EC and DMC. Fig. 2 shows the spectra of EC in the presence and absence of 1 M $LiClO_4$ and the ATR–FTIR difference spectrum. Table 1 shows the band assignments and the calculated band frequencies for EC molecules. The main bands at 1481, 1390, 1155, and 1067 $cm^{-1}$ are assigned to the scissoring and wagging vibrations of $CH_2$, and the stretching vibrations of C–O. The bands corresponding to the C=O stretching vibration mode of the EC molecule are observed at 1770 and 1796 $cm^{-1}$. Originally, the stretching mode of C=O in EC is composed of a single band. In a previous study, two intense bands were observed for pure EC at 1796 and 1770 $cm^{-1}$ with similar intensities [21]. The 1770 $cm^{-1}$ band has been attributed to C=O stretching, and the 1796 $cm^{-1}$ band to the overtone of the ring breathing mode at 889 $cm^{-1}$. 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.