

Study on Dynamic Behavior of Diethyl Carbonate Electrolyte on Lithium Metal Surface Using *In Situ* FTIR Spectroscopy

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A dynamic behavior of diethyl carbonate electrolyte on lithium with a surface film, such as a solvent penetration into the surface film and a chemical reaction with lithium, was firstly detected by using *in situ* FTIR spectroscopy.

Lithium metal is very attractive as an anode material for rechargeable lithium batteries, due to its theoretical high energy density. However, the reversibility during discharge and charge cycles is not adequately high for a practical use in rechargeable lithium batteries. This is due to an instability of lithium metal in nonaqueous electrolytes, which is related to chemical reactions of lithium metal with various components involved in electrolytes. Therefore, many studies have been performed to investigate the surface reactions of lithium in nonaqueous electrolytes. In these studies, lithium metal electrodeposited on substrate electrodes or *in situ* cut lithium rod has been used as working electrodes.¹⁻⁷ On the other hand, lithium foils will be used in practical rechargeable lithium batteries. A stability of the lithium foils in nonaqueous electrolytes has been studied using an x-ray photoelectron spectroscopy (XPS) and other spectroscopic methods.⁸⁻¹¹ The lithium foils are usually covered with the surface film which influences surface reactions occurring on the lithium foils. Some phenomena combined with the surface film have been proposed using *ex situ* techniques.⁸⁻¹¹ In this study, an *in situ* measurement was applied to investigate the surface reactions on the lithium foils in diethyl carbonate electrolytes containing LiClO₄ or LiPF₆. From our previous XPS studies, it has been shown that a small amount of HF in LiPF₆ electrolytes strongly influences the surface reactions on lithium, resulting in a formation of a new different surface film on lithium which is seriously related to the stability of the lithium foils in nonaqueous electrolytes.^{12, 13} However, there is no *in situ* observation on the surface reactions of lithium. In this study, we firstly measured a dynamic phenomena of the surface reactions on the lithium foils using an *in situ* Fourier Transform Infrared (FTIR) Spectroscopy.

The *in situ* FTIR spectroscopy has been performed using a special cell, as shown in Figure 1. NaCl was used as a IR window. The cell configuration corresponds to an external reflectance mode.¹⁴ In order to obtain high quality spectra, lithium foils were pressed to the IR window by using a spring coil. A reflectivity of the lithium foils is very important to a quality of the spectrum. Lithium foils which were obtained from HONJO METAL Co. and their surfaces were still like a mirror, were suitable for the FTIR measurement in the external reflectance mode. A surface film on lithium foils depends on conditions of the preparation conditions. The lithium foil used in this study was fully covered with Li₂CO₃, LiOH, and Li₂O, as shown in Figure 1. This result was obtained by using a XPS analysis. The as-received lithium foil was used in *in situ* FTIR spectroscopy. Therefore, the electrolytes firstly contact to the surface film, when the lithium foil is put into electrolytes. Electrolytes (diethyl carbonate (DEC) containing 1.0 mol dm⁻³ LiClO₄ or LiPF₆) were purchased from Mitsubishi Chemicals Company. LiPF₆ electrolyte contains 20~30 ppm H₂O and a small amount of HF. LiClO₄ electrolyte contains 20~30 ppm H₂O.

An amount of electrolyte penetrated into the surface film and an

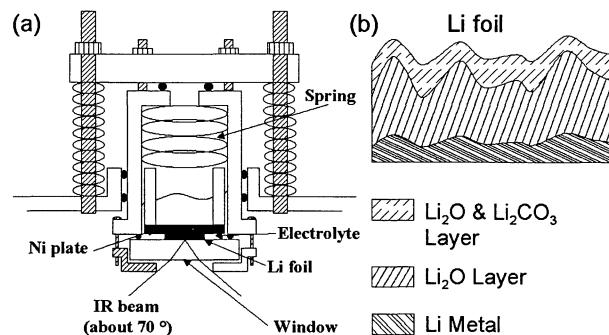


Figure 1. Schematic illustrations of (a) *in situ* FTIR cell with NaCl IR window and (b) the surface film on the lithium foil before the immersion.

amount of organic compounds formed on the lithium foil were not enough to be detected by a standard absorption, reflection, or transmission spectra. Therefore, differential spectra were calculated from two reflectance spectra at two different immersion times. The reflectance spectra were measured at each 10 min interval. A previous spectrum was used as a reference spectrum. The effect of the absorption by the DEC electrolyte bulk in the thin layer cell is minimized by the calculation of the differential spectrum. Peaks in Figures 2 and 3 show the intensity change for one absorption peak between two different times, so that they show an increase or a decrease of chemical species between two different immersion times. Upward and downward peaks appeared in these figures correspond to a disappearance and a formation of chemical species, respectively.

Some peaks were observed at 1020 cm⁻¹, 1260 cm⁻¹, and 1750 cm⁻¹ in Figure 2, when using LiPF₆ electrolyte. These peaks were assigned to stretching vibrations of C-O-C and >C=O in DEC, respectively. Other weak peaks were also assigned to diethyl carbonate. Initially, these peaks appeared in a downward direction, indicating that DEC involved in the surface film increased. Then, these peaks changed to a upward direction, indicating that DEC in the surface film decreased. The DEC electrolyte firstly contacts to the surface film. Therefore, the downward peaks are explained by the penetration of DEC into the surface film during the initial immersion period. The upward peaks reveal the exclusion of DEC from the surface film during the later period. Although the penetration of solvent can occur when the surface film has some pores, the exclusion of solvent may be explained by the chemical composition and structure changes of the surface film. The surface analysis for the final state of the lithium surface has been performed using XPS in our laboratory and has shown that the surface film gradually changes to the thin LiF/Li₂O layer in the later period when LiPF₆ is used as an electrolyte salt.^{8, 9, 11} This process involves two steps. The first step is an etching of the surface film with HF and the second one is an acid-base reaction between Li₂O and HF. The etching process of the surface film results in the disappearance of solvent penetrated into the surface film at the later period. Therefore, the upward peaks observed in Figure 2 reflects the etching process of the

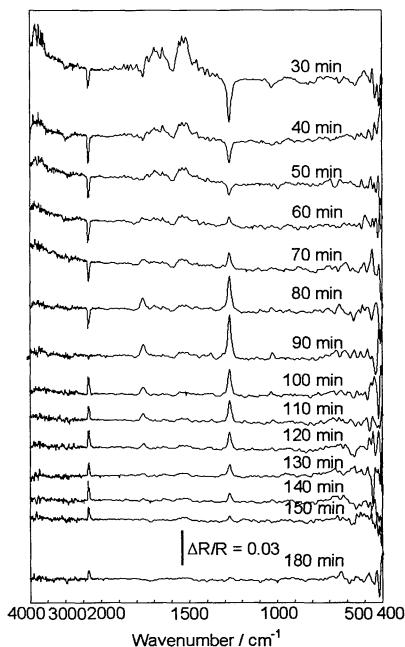


Figure 2. in situ FTIR spectra during the immersion in diethyl carbonate containing $1.0 \text{ mol dm}^{-3} \text{ LiPF}_6$.

surface film. On the other hand, any peaks indicating a formation of new organic compounds on the lithium metal were not observed. This means that DEC penetrated into the surface film during the initial period does not contact to lithium metal. Probably, the formation of $\text{LiF}/\text{Li}_2\text{O}$ layer, which may be highly protective to the penetration of DEC, occurs immediately after the etching process of the surface film.

Figure 3 shows the FTIR spectra obtained for the lithium foil immersed in DEC containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$. These spectra were completely different from those in Figure 2. The different results directly indicate that the dynamic behavior of DEC electrolyte on the lithium foils depends on the type of the electrolyte salt. Most of downward peaks appeared after 20 min immersion are assigned to DEC solvent. This is understood by the penetration of solvent into the surface film, as observed for LiPF_6 electrolyte. New downward peaks appeared after 40 min immersion were mostly assigned to lithium alkoxide or lithium alkylcarbonate. At the same time, upward peaks were also observed at wavenumbers corresponding to DEC. These spectra indicate that DEC solvent penetrated into the surface film, contacts to lithium metal and reacts with lithium metal to form new organic compounds. The simultaneous observation of both downward and upward peaks well reveals the dynamic behavior of DEC solvent on the lithium foil.

When LiPF_6 electrolyte is used, the native surface film is not stable, due to the presence of HF in the electrolyte. As a result of the chemical reaction of HF with the surface film, the surface film on lithium is converted to the $\text{LiF}/\text{Li}_2\text{O}$ film which works as a protective film to the direct reaction of DEC solvent with lithium. According to this dynamic model for LiPF_6 electrolyte on the lithium foil, we obtained the FTIR spectra, as shown in Figure 2. On the other hand, the formation of lithium alkoxide or lithium alkyl carbonate were observed when using LiClO_4 electrolyte. Although the surface film is stable in this electrolyte, DEC solvent easily penetrates into the surface film and contacts to lithium to form new organic compounds in the surface film, resulting in a morphology change of the surface film on lithium which causes a mechanical destruction of the surface film.¹⁰ Therefore, lithium metal is unstable in this electrolyte.

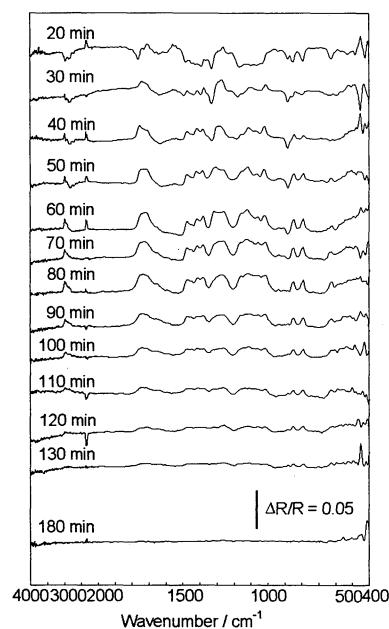


Figure 3. in situ FTIR spectra during the immersion in diethyl carbonate containing $1.0 \text{ mol dm}^{-3} \text{ LiClO}_4$.

In this way, the *in situ* FTIR measurement clearly show that the dynamic behavior of DEC electrolyte on lithium metal strongly depends on the kind of electrolyte salt. This dependence is explained by penetration of electrolyte and chemical reactions of DEC solvent with lithium metal. The most important point to suppress chemical reactions of electrolyte with lithium metal is the conversion of the surface film.

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