



Short communication

Dynamic *in situ* fourier transform infrared measurements of chemical bonds of electrolyte solvents during the initial charging process in a Li ion battery



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HIGHLIGHTS

- Solvation/desolvation and SEI formation at a graphite electrode during the initial charging process were investigated.
- We developed dynamic *in situ* FTIR measurement by applying a diamond ATR crystal.
- The measurement elucidated the change in the chemical bond of the electrolyte solvents in Li/electrolyte/graphite/Cu cell.
- The measurement also revealed the contribution of a vinylene carbonate additive to the electrolyte solvent reduction.

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ABSTRACT

Solvation/desolvation and the solid electrolyte interphase (SEI) formation at a graphite electrode during the initial charging process were investigated using *in situ* Fourier transform infrared spectroscopy (FTIR) measurements. These measurements were developed by applying a diamond attenuated total reflectance (ATR) crystal, which probed the electrolyte solvents at the surface of the graphite electrode and provided successive FTIR spectra with high signal to noise ratio. The charging process was performed in the Li(reference)/electrolyte/graphite(working)/Cu cell at a voltage ranging from 3.2 to 0.0001 V vs. Li/Li⁺. The measurement elucidated the change in the chemical bond of the electrolyte solvents. In an early stage, the amounts of solvated and desolvated solvents changed, providing evidence that the Li⁺ ions were intercalated into the graphite layer. The formation of the Li alkyl carbonate that forms the SEI layer was facilitated toward the end of the charging process. Measurements were also obtained of the electrolyte with a vinylene carbonate additive, and the contribution of the additive to the electrolyte solvent reduction was investigated.

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1. Introduction

The solid electrolyte interphase (SEI) on a graphite electrode plays important roles in the function of Li ion batteries; it prevents electrons from meeting Li⁺ ions at the graphite surface during the charging process, and also prevents electro deposition which would severely deteriorate the battery performance [1]. In particular, the SEI formed during at the initial charging and discharging processes is known to be responsible for the battery's performance [2,3]. It has been reported that the SEI consists of organic and inorganic compounds; organic compounds such as Li alkyl

carbonate were deposited on inorganic compounds such as LiF that were deposited on the surface of the graphite through the decomposition of electrolyte salts (for instance, LiBF₄ and LiPF₆) [4–6].

The organic compounds of the SEI were formed through the reduction and decomposition of electrolyte solvents [7–9]. During the charging process, Li⁺ ions (emitted from cathode active materials) were solvated, diffused toward the graphite electrode by the electric field, desolvated at the surface of the graphite, and finally intercalated into the graphite layers [7,10]. The structure of the solvated solvents has also been investigated. For example, a theoretical calculation revealed that one Li⁺ ion was coordinated to ethylene carbonate (EC) and dimethyl carbonate (DMC) molecules [11]. In order to understand the formation of the organic SEI, it is

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necessary to investigate the change in the chemical bonds of the electrolyte solvents at the surface of the graphite electrode during the initial charging process. Numerous approaches have been widely performed; however, it has been found that X ray photo electron spectroscopy (XPS), widely used for the SEI analysis, provides little information on organic SEI and no information on the solvents [5,6]. Moreover, as the technique is performed under a vacuum, it only provides *ex situ* information. Although nuclear magnetic resonance (NMR) provides organic information on the solvents and can be performed during charging, it is unable to probe the solvents at the surface of the graphite electrode, only providing total information on the solvents [9,12].

Many effort investigations of the interface between the electrode and electrolyte solvents employing *in situ* Fourier transform infrared (FTIR) spectroscopy have been performed in order to understand the change in the electrolyte solvents [11,13–17]. However, they were conducted on metal electrodes such as Au, Pt, and Li due to various difficulties. To our knowledge, few *in situ* FTIR measurements have been obtained at the surface of graphite electrodes during the charging and discharging processes. For instance, infrared reflection absorption spectroscopy (IRAS) provides a tiny intensity of reflected light, demanding an increased signal to noise (S/N) ratio to analyze the signals by means of subtractively normalized interfacial FTIR Spectroscopy (SNIFTIRS) [13,17]. Since SNIFTIRS provides the difference spectrum between the sample and reference spectra, it neglects the peak shift. The attenuated total reflectance (ATR) FTIR technique has also been applied to *in situ* FTIR measurements; this method commonly uses a Ge crystal because its high refractivity gives a high S/N ratio spectra [13,17]. However, Ge reacts with Li to form an alloy around 0 V vs. Li/Li⁺ during the charging process, leading to failure of the *in situ* FTIR measurements.

In this study, we applied a diamond ATR crystal to the *in situ* FTIR measurement. Diamond is electrochemically inactive during the charging process. We investigated the chemical bond change in the electrolyte solvents at the surface of the graphite in the Li(reference)/electrolyte/graphite(working)/Cu cell. In the initial charging process, the voltage ranged from 3.2 to 0.0001 V vs. Li/Li⁺. At a voltage between 3.2 and 0.5 V, we observed the desolvation of the solvated Li⁺ ions at the surface of the graphite from the high S/N ratio FTIR spectra, which supported the previous reports [7,8,10]. At a voltage between 0.5 and 0.05 V, the solvated and desolvated solvents were nearly constant in amount, which meant that the desolvation balanced the diffusion of the solvated Li⁺ ions. At a voltage between 0.05 and 0.0001 V, we clearly observed the transform of the solvents into the Li alkyl carbonate, suggesting that the organic SEI formation was promoted at the late stages of the initial charging process. We also applied the *in situ* FTIR measurement to the electrolyte with a vinylene carbonate (VC) additive, and clearly showed that the additive prevented the formation of the Li alkyl carbonate at the surface of the graphite electrode.

2. Experimental

2.1. Battery cell fabrication

A graphite electrode was fabricated by a coating slurry of 90% (w/w) graphite and 10% (w/w) PVdF binder in *N* methylpyrrolidone on both sides of a copper foil. The copper foil contained paths of the electrolyte, which allowed us to acquire *in situ* FTIR spectra during the charging and discharging processes. After drying, a graphite electrode disk with a diameter of 14 mm was used as a working electrode. Li foil was employed as both reference and counter electrodes. The graphite and Li electrodes were separated by glass wool and the electrolyte. The electrolyte was composed of battery

grade dimethyl carbonate (DMC), diethyl carbonate (DEC), and ethylene carbonate (EC) (1:1:1 in v/v) with 1.0 M LiPF₆ (UBE industries Ltd.) without further purification. The water contents of DMC, DEC, and EC were less than 20 ppm.

2.2. In situ FTIR measurement

The *in situ* FTIR measurements were performed using an Agilent FTS 7000e FTIR spectrometer equipped with a liquid nitrogen cooled mercury cadmium telluride detector. The spectrometer was equipped with a single reflectance mode of the ATR sampling apparatus (Specac Ltd.) used for the charging and discharging processes, as shown in Fig. 1. The sampling apparatus was covered with a plastic cylinder, which enables the measurement to be performed under inactive conditions without an atmospheric effect. The battery cell was placed on the diamond prism, and then the electrolyte was added into the apparatus in an argon globe box having a dew point lower than -60 °C. After the apparatus was removed from the globe box, it was set into the FTIR spectrometer. The angle of incident light was set to 45°. The measurements were conducted in a kinetics mode at room temperature, and one spectrum was acquired every second. Since the average of the spectra was obtained from a 60 s measurement at each point, the signal intensity was enough large to be analyzed without the spectrum correction. The spectra were recorded at a resolution of 4 cm⁻¹ between 650 and 4000 cm⁻¹, and they were analyzed in detail between 1600 and 1900 cm⁻¹.

It was noticed that a theoretical penetration depth of the incident light ranges from 1.1 μm (1900 cm⁻¹) to 1.3 μm (1600 cm⁻¹). This means that it is necessary to decrease the distance between the diamond crystal and the graphite electrode for probing information in the vicinity of the graphite electrode. Therefore, the cell was pushed against the diamond crystal and the graphite electrode was placed very close to the diamond crystal. Though we were concerned that the electrolyte might be restricted in its diffusion to the graphite electrode because of the narrow space, the electrolyte solution was able to diffuse through the intrinsic surface roughness of the graphite electrode, thereby continuing the electrochemical reaction.

2.3. Estimation of solvation and desolvation from FTIR spectra

In order to distinguish between the solvation and desolvation of the solvents from the FTIR spectra, single mode ATR measurements were conducted on DMC, DEC, and EC, both with and without 1.0 M LiPF₆. Typical spectra obtained from the *in situ* FTIR measurements

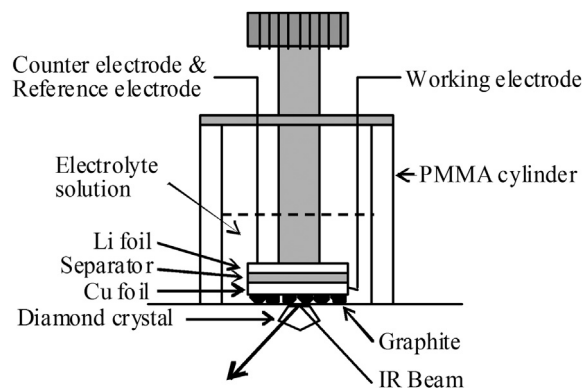


Fig. 1. Schematic illustration of the *in situ* FTIR apparatus. The battery cell was fabricated in the sampling ATR apparatus, where a graphite electrode formed on both sides of the Cu foil that contained paths of the electrolyte.

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