Research Article

Raman Spectroscopy for Understanding of Lithium Intercalation into Graphite in Propylene Carbonated-Based Solutions

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Electrochemical lithium intercalation within graphite was investigated in propylene carbonate (PC) containing different concentrations, 0.4, 0.9, 1.2, 2.2, 2.8, 3.8, and 4.7 mol dm⁻³, of lithium perchlorate, LiClO₄. Lithium ion was reversibly intercalated into and deintercalated from graphite in 3.8 and 4.7 mol dm⁻³ solutions despite the use of pure PC as the solvent. However, ceaseless solvent decomposition and intense exfoliation of the graphene layers occurred in other solutions. The results of the Raman spectroscopic analysis indicated that contact ion pairs are present in 3.8 and 4.7 mol dm⁻³ solutions, which suggested that the presence of contact ion pairs is an important factor that determines the solid electrolyte interphase- (SEI-) forming ability in PC-based electrolytes.

1. Introduction

In commercially available lithium secondary batteries, lithium ions are electrochemically intercalated into and deintercalated from the graphite negative electrode during charging and discharging, respectively. These electrochemical reactions are basically reversible; however, the reversibility depends greatly on the kind of electrolyte solutions. They are highly reversible in ethylene carbonate- (EC-) based solutions containing lithium salts such as LiClO₄, LiPF₆, and LiCF₃SO₃. The discovery of EC-based electrolyte systems is a seminal breakthrough that has enabled the electrochemical preparation of lithium-graphite intercalation compounds (Li-GICs) [1, 2]. On the other hand, propylene carbonate (PC)-based solutions are attractive electrolyte systems owing to their superior ionic conductivities when compared to EC-based solutions at low temperatures [3]. However, it is very difficult to get Li-GICs in PC-based electrolytes because of poor compatibility between graphite and PC [4–6].

In a previous study [7], we reported a simple electrochemical preparation of Li-GICs in PC-based solutions, LiN(SO₂C₂F₅)₂ (LiBETI) dissolved in PC. The work showed that lithium intercalation within graphite from the LiBETI-PC solutions is an electrochemical reaction that strongly

depends on the electrolyte concentration. Lithium ions were intercalated within graphite to form a stage 1 Li-GIC in concentrated LiBETI-PC solutions whereas solvent decomposition or the intensive exfoliation of graphene layers occurred continuously in relatively low-concentration solutions; that is, the poor compatibility between graphite and PC could be improved by increasing electrolyte concentration. However, the details for the effects of electrolyte concentration on lithium intercalation and deintercalation reactions are still unclear. In this study, we performed Raman spectroscopic analysis to know the correlations between electrolyte concentration and interfacial reactions between graphite and PC-based solutions.

2. Experimental

The electrolyte solutions were prepared by dissolving LiClO₄ in PC. All these reagents were purchased from Kishida Chemical Co. and were used as received. The concentrations of LiClO₄ were 0.4, 0.9, 1.2, 2.2, 2.8, 3.8, and 4.7 mol dm⁻³, which correspond to 20:1, 1:9, 1:7, 1:5, 1:4, 1:3, and 1:2, respectively, by the molar ratio of Li⁺ to PC. The water content in each solution was less than 30 ppm, which was confirmed using a Karl-Fischer moisture titrator (Kyoto Electronics

Manufacturing Co., MKC-210). The concentration of all electrolyte solutions is expressed as the molarity of lithium salt (mol dm^{-3}).

Natural graphite powder (The Kansai Coke and Chemicals Co., NG-7) was used for the charge/discharge tests. The test electrode was prepared by coating a mixture of the graphite powder (90 wt%) and a polymeric binder (10 wt%) on copper foil, as described elsewhere [8]. The charge and discharge tests were carried out using conventional three-electrode cells at a constant current of 5.2 mA g^{-1} in an argon-filled glove-box (Miwa, MDB-1B+MM3-P60S) with a dew point below -60°C . Lithium foil was used as the counter and reference electrodes. All potentials are referred to as volts versus Li^+/Li .

Raman spectra of the electrolyte solutions were recorded using a triple monochromator (Jobin-Yvon, T-64000). Excitation was carried out with a 514.5 nm line (50 mW) from an argon ion laser (NEC, GLG2265). The scattered light was collected in a direction of 90° to the incident light.

3. Results and Discussion

In a previous study [7], we used LiBETI-PC solutions of different concentrations as electrolytes, as mentioned in the introduction, to investigate the effects of electrolyte concentration on lithium intercalation into graphite. In the present study, however, LiClO_4 -PC solutions instead of LiBETI-PC solutions were used as electrolytes because a lot more information on ion-solvent or ion-ion interactions which would be expected to have an effect on interfacial reactions between electrode and electrolyte can be obtained from the former solution by Raman spectroscopy. Before the Raman spectroscopic analysis, the charging (lithium intercalation) and discharging (lithium deintercalation) of the graphite electrode was executed in seven LiClO_4 -PC electrolytes of different concentrations: 0.4, 0.9, 1.2, 2.2, 2.8, 3.8, and 4.7 mol dm^{-3} . The graphite electrode showed electrolyte concentration dependence of the electrochemical lithium intercalation reaction in LiClO_4 -PC solutions similar to that observed in LiBETI-PC solutions. Among the electrolytes, the 3.8 and 4.7 mol dm^{-3} solutions were effective for the electrochemical preparation of Li-GICs. No lithium intercalation and deintercalation reactions occurred in the other solutions.

The potential profiles of natural graphite powder during the first charging and discharging cycles in 2.8 and 3.8 mol dm^{-3} solutions are shown in Figure 1 (potential profiles obtained in the other solutions are not shown here). It is well known that the electrochemical intercalation of lithium into graphite mainly occurs at potentials below 0.25 V [9–11]. There was no charge capacity at the potential profile obtained in 2.8 mol dm^{-3} solution. In contrast, the charge capacity corresponding to lithium intercalation was recorded at potentials below 0.25 V in 3.8 mol dm^{-3} solution. Potential plateaus observed at 0.170, 0.080, and 0.045 V during charging and 0.135, 0.180, and 0.255 V during discharging in Figure 1(b) are direct evidence of lithium intercalation and deintercalation. The potential plateaus can be assigned to reversible stage transformations between Li-GICs of different stage numbers.

FIGURE 1: (a) Charge and discharge curves in the first cycle of natural graphite powder (NG-7) in 2.8 and 3.8 mol dm^{-3} LiClO_4 dissolved in PC. (b) Magnified view of panel (a).

The above results demonstrate that the solid electrolyte interphase- (SEI-) forming ability of LiClO_4 -PC electrolytes is greatly dependent on the concentration of LiClO_4 . The following two possibilities can be considered as the reason for SEI formation on graphite surface to form Li-GICs in high-concentration solutions. First, it may be due to the structural changes in solvated lithium ions as the concentration increases, because the electrolyte decomposition and exfoliation of graphene layers at around 0.8 V in the 2.8 mol dm^{-3} solution are originated from the intercalation of solvated lithium ions [12]. The structural changes may lower the potential of solvated lithium ions to be intercalated into graphite, resulting in forming an SEI by the decomposition of electrolyte below 0.8 V. Second, a new chemical species may have been produced in high-concentration solutions, resulting in their decomposition to form an SEI.

The ion-solvent interactions between lithium ions and PC molecules were investigated by laser Raman spectroscopy

TABLE 1: Mole fraction of solvated PC molecules and charge-discharge behaviors of graphite in LiClO_4 -PC solutions.

Concentration (mol dm^{-3})	Charging-discharging	Mole fraction of solvated PC
4.7	Success	0.91
3.8	Success	0.82
2.8	Failure	0.63
2.2	Failure	0.52
1.2	Failure	0.36
0.9	Failure	0.26
0.4	Failure	0.05

to confirm the first possibility. Figure 2 shows the Raman spectra of pure PC and LiClO_4 -PC solutions of different concentrations in the wavenumber range of 660 to 800 cm^{-1} . The vibrational spectroscopy of PC in this frequency region provides useful information on the interactions between lithium ions and PC molecules [13–17]. In pure PC, the strong band at 712 cm^{-1} is assigned to the symmetric ring deformation mode of free PC molecules [13]. The shape of this band became less symmetric and a new band appeared at around 723 cm^{-1} . The intensity of the new band increased with an increase in the concentration of LiClO_4 whereas the intensity of the band from free PC decreased. This indicates that the new band is originated from the interaction between PC molecules and lithium ions and is assigned to the symmetric ring deformation mode of solvated PC [13–15]. The band from free PC almost disappeared in 3.8 and 4.7 mol dm^{-3} solutions, indicating that most of PC molecules solvate lithium ions in the solutions. The mole fraction of the solvated PC molecules in each solution was obtained from the integrated intensities of the free or solvated PC bands (Table 1). Curve fitting was performed to separate each band. The 82 and 91% of PC molecules were solvated to lithium ions in 3.8 and 4.7 mol dm^{-3} solutions, respectively, where an effective SEI was formed on graphite.

Figure 2 and Table 1 clearly show that there are structural changes in solvated lithium ions as the concentration changes. The solvation number of lithium ions in LiClO_4 -PC solution is expected to decrease with an increase in the concentration of the lithium salt. Such a difference in the solvation number may result in suppressing the intercalation of solvated lithium ions and their decomposition occurring at around 0.8 V in the 2.8 mol dm^{-3} solution or the solvated lithium ions may be intercalated at lower potentials than 0.8 V, resulting in forming an SEI by the decomposition of electrolyte below 0.8 V. If this assumption is correct, an SEI may be generated when the electrode potential is forced to step to a lower potential than 0.8 V in a short time. This is because the intercalation of solvated lithium ions is suppressed by the formation of an SEI although the two reactions are competing at the low potential. However, such an effective SEI was not formed, as shown in Figure 3.

Figure 3 shows chronoamperograms obtained after potential step from 2.9 to 0.3 V in 2.8 and 3.8 mol dm^{-3}

FIGURE 2: Raman spectra of pure PC and LiClO_4 -PC solutions of different concentrations. The concentration of all solutions is expressed as the molality of LiClO_4 (mol dm^{-3}) inside figure.

FIGURE 3: Current-time curves of the natural graphite powder (NG-7) observed in response to the potential step from 2.9 to 0.3 V in (a) 2.8 and (b) 3.8 mol dm^{-3} LiClO_4 dissolved in PC.

solutions. In 2.8 mol dm^{-3} solution, more than 10 times more charge was consumed compared to that consumed in 3.8 mol dm^{-3} solution, and exfoliation of graphene layers was also observed. This indicates that no SEI is formed on graphite by the decomposition of 2.8 mol dm^{-3} solution. The above results demonstrate that a chemical species with the ability to generate an effective SEI is present in 3.8 mol dm^{-3} solution, but not present in 2.8 mol dm^{-3} solution. This, as mentioned earlier, supports the second possibility.

We noted that ion pairs are formed only in concentrated solutions and investigated them by laser Raman spectroscopy. Figure 4 shows the Raman spectra of pure PC and LiClO_4 -PC solutions of different concentrations in the wavenumber

TABLE 2: Mole fraction of ClO_4^- anions and charge-discharge behaviors of graphite in LiClO_4 -PC solutions.

Concentration (mol dm^{-3})	Charging-discharging	Mole fraction		
		Free	Solvent-separated	Contact
4.7	Success	0.02	0.58	0.40
3.8	Success	0.08	0.72	0.20
2.8	Failure	0.22	0.78	0.00
2.2	Failure	0.38	0.62	0.00
1.2	Failure	0.48	0.52	0.00
0.9	Failure	0.55	0.45	0.00
0.4	Failure	1.00	0.00	0.00

FIGURE 4: Raman spectra of pure PC and LiClO_4 -PC solutions of different concentrations. The concentration of all solutions is expressed as the molality of LiClO_4 (mol dm^{-3}) inside figure.

range of 900 to 1000 cm^{-1} . The vibrational spectroscopy of ClO_4^- anions in this frequency region provides useful information on ion pairs. James et al. studied ion-ion-solvent interactions in LiClO_4 -acetone solutions with Raman spectroscopy [18]. They reported that there are four kinds of the symmetrical stretching vibration of ClO_4^- anions in solutions originating from (i) free anions, ClO_4^- (934 cm^{-1}), (ii) solvent-separated ion pairs, Li^+ -solvent- ClO_4^- (939 cm^{-1}), (iii) contact ion pairs, $[\text{Li}^+\text{ClO}_4^-]$ (948 cm^{-1}), and (iv) multiple ion aggregates, $\{\text{Li}^+\text{ClO}_4^-\}_n$ ($n \geq 2$) (958 cm^{-1}). On the basis of this report, curve fitting was performed to separate each band. From the fitting results, the mole fraction of each species was obtained in a manner similar to the method used to obtain Table 1, and the results are shown in Table 2. Among the four kinds of ClO_4^- anions, three species were observed, except multiple ion aggregates, from LiClO_4 -PC solutions. It should be noted that an effective SEI formation and reversible lithium intercalation and deintercalation reactions took place

in 3.8 and 4.7 mol dm^{-3} solutions, in which contact ion pairs are present. In the other solutions, only free anions and solvent-separated ion pairs are present. These results suggest that the presence of contact ion pairs in the electrolyte enhances the SEI-forming ability. On the other hand, ion pairing in LiClO_4 -PC solutions reduces the conductivity of the electrolyte. The maximum ionic conductivity is observed at 1.3 mol dm^{-3} LiClO_4 -PC solution [13]. At a higher concentration the conductivity decreases because of the higher viscosity originating from the formation of ion pairs in the solution. The conductivity appears to have little effect on SEI formation reactions. The detailed interpretation of the direct correlations between the conductivity and the SEI formation reactions is beyond the scope of the present work.

4. Conclusions

This study was conducted to better understand SEI formation reactions occurring at the interface between the graphite electrodes and PC-based electrolyte in lithium secondary batteries. Lithium ions were electrochemically intercalated into graphite in LiClO_4 dissolved in PC by increasing the concentration of LiClO_4 . An effective SEI was formed on graphite in concentrated solutions without the aid of any SEI-forming agents. The results of this study suggest that the presence of contact ion pairs is an important factor that determines the SEI-forming ability in PC-based electrolytes. We are yet to understand the causative reasons for the SEI formation by contact ion pairs and intend to focus our future reports on gaining an understanding of the factors contributing to the electrolyte-concentration dependence of SEI formation in PC-based electrolytes.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

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