Effect of the Addition of Bivalent Ions on Electrochemical Lithium-Ion Intercalation at Graphite Electrodes

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Abstract

Electrochemical lithium-ion intercalation/de-intercalation at a graphite electrode were studied in propylene carbonate-based electrolyte solutions containing both lithium bis(trifluoromethanesulfonfyl)amide and magnesium bis(trifluoromethanesulfonfyl)amide salts by using lithium/graphite cell, and the influence of the salt concentration was investigated. In the higher concentration electrolyte solutions, reversible lithium-ion intercalation/de-intercalation at the graphite electrodes occurred. In contrast, only the exfoliation of graphite occurred in the lower concentration electrolyte solutions. The threshold ratio of the magnesium salt (Mg2+/Li+ = 0.9) was lower than that of the calcium salt (Ca2+/Li+ = 1.1).

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Electrochemical intercalation/de-intercalation of lithium ions at graphite electrodes is a negative electrode reaction that occurs in lithium-ion batteries (LIBs). Ethylene carbonate (EC) is an essential solvent for commercialized LIBs principally due to its high dielectric constant and its ability to form a stable solid electrolyte interphase (SEI). Owing to the relatively high melting point of EC (34°C), the low-temperature performance of LIBs requires improvement if they are to be used as power sources for electric vehicles in cold areas. One way to improve the low-temperature performance of LIBs is to replace EC with another solvent such as propylene carbonate (PC), which has a lower melting point of ~49°C. However, it is well known that intercalation/de-intercalation of lithium ions into/from graphite electrodes in common PC-based electrolyte solutions does not occur.1 According to the Besenhard model,2 this intercalation failure mechanism can be explained briefly as follows; PC-solvated lithium ions co-intercalate into graphite2,3 and PC-solvated lithium ions are reduced by one electron reaction and gas evolution occurs.4 During this process, exfoliation of graphite continues to occur. As a result, lithium ions do not intercalate into the graphite electrodes. The stable intercalation/de-intercalation of lithium ions into/from graphite electrodes in EC-based electrolyte solutions occurs due to the SEI formed from the products of reductive decomposition of EC on graphite electrodes. However, in common PC-based electrolyte solutions without additives, the effective SEI was not formed on graphite. Thus, one possible way to achieve lithium-ion intercalation in PC-based electrolyte solutions is the addition of substances whose reductive decomposition products form an SEI.1–3 In contrast to reports that focus on the SEI, we have focused on the impact of the structure of solvated lithium ions on electrochemical lithium-ion intercalation into graphite electrodes in PC-based electrolyte solutions.10–16 Our previous study showed that the reaction that occurred at a graphite electrode in PC-based electrolyte solutions, which was either lithium-ion intercalation or exfoliation, depended on the concentration of the lithium salt10 and that a high concentration of lithium salt enabled successful intercalation without exfoliation of graphite electrodes. Our previous study reported that the structure of solvated lithium ions in PC-based electrolyte solutions was dependent on the concentration of lithium salt by Raman spectroscopy.12 Based on this result, we attributed this successful lithium-ion intercalation behavior to the different structure of solvated lithium ions in PC-based electrolyte solutions and suggested that when the PC-solvation number of the solvated lithium ion is decreased, lithium ions can intercalate. Furthermore, we have previously reported that lithium-ion intercalation in PC-based electrolyte solutions is facilitated by the addition of calcium salt.13–15 This behavior was also attributed to the decreased PC-solvation number of the solvated lithium ions. This decrease in PC-solvation number is caused by the strong interaction between PC and calcium ions, which is due to the higher Lewis acidity of calcium ions than lithium ions. The strength of the interaction between PC and the cation is dependent on the Lewis acidity of the cation. Therefore, we focused on this aspect of the electrochemical system. Magnesium ions are bivalent (like calcium ions) and have a smaller ionic radius than calcium ions. In addition, magnesium-ion intercalation at graphite electrodes has not been observed; therefore, magnesium ions are expected to be electrochemically inactive in lithium-ion intercalation systems. It is thought that magnesium ions have a higher Lewis acidity than calcium ions and, thus, should act as an effective additive in PC-based electrolyte solutions. In this study, the effect of magnesium-ion addition was investigated and compared with calcium-ion addition on lithium-ion intercalation to demonstrate the concept of electrolyte design based on the Lewis acidity of added cations.

Experimental

Electrolyte solutions were prepared from lithium bis(trifluoromethanesulfonfyl)amide (LiTFSA), magnesium bis(trifluoromethanesulfonfyl)amide (Mg(TFSA)2), calcium bis(trifluoromethanesulfonfyl)amide (Ca(TFSA)2), and PC, all of which were purchased from Kishida Chemical Co., Ltd. The concentration of LiTFSA in PC was fixed at 1 mol dm−3, and the molar ratios of Mg(TFSA)2 or Ca(TFSA)2 to LiTFSA were 0.7, 0.9, or 1.1. Residual water in the electrolyte solutions was removed using molecular sieves, resulting in water contents below 100 ppm confirmed by means of a Karl-Fischer moisture titrator.

The ionic conductivities of the electrolyte solutions were measured by a two-electrode cell comprising Pt electrodes. Activation energies for ionic conduction were also examined. In addition to ionic conductivities, the viscosities of the electrolyte solutions were also measured. A three-electrode cell was used for cyclic voltammetry and charge and discharge measurements. Hereafter, all potentials are referred to Li/Li+. A composite electrode comprising natural graphite (SNO-15, SEC carbon) and polyvinylidene difluoride (PVdF) at a weight ratio of 9:1 was used as a working electrode. Lithium metal was used for both counter and reference electrodes. Cyclic voltammetry was conducted at 0.1 mV s−1 between 3 V and 0 V. Charge and discharge measurements were carried out at a constant current of 37.2 mA g−1, which corresponds to 0.1C (1C = 372 mA g−1). In this paper, the intercalation process and de-intercalation process are denoted as discharge and charge, respectively. To confirm the presence of intercalates in the graphite electrodes, they were kept at 0 V for 24 h after being discharged to 0 V and analyzed by X-ray diffraction.
(XRD) measurement. To prevent the resulting products from decomposing, the sample was kept in a cell filled with Ar. All electrochemical measurements were performed in an argon-filled glove box.

**Results**

Our previous study on PC-based electrolyte solutions containing both lithium and calcium salts showed that the intercalation behavior depended on the amount of calcium salt added to the electrolyte solution. In the electrolyte solutions containing lithium and calcium salts, electrochemical intercalation of lithium ions occurred when the Ca\(^{2+}/\text{Li}^{+}\) molar ratio was higher than 1.0.\(^{12}\) Here we have conducted the experiments at similar ratios (0.7, 0.9, and 1.1) with a magnesium salt, and studied the dependence of electrochemical behavior on the salt addition.

Figure 1 shows the cyclic voltammograms of graphite electrodes in LiTFSA+Mg(TFSA)_2/PC electrolyte solutions ((a) Mg\(^{2+}/\text{Li}^{+}\) = 0.7, (b) Mg\(^{2+}/\text{Li}^{+}\) = 0.9, and (c) Mg\(^{2+}/\text{Li}^{+}\) = 1.1). As shown in Figure 1a, a large reduction current was observed near 0 V. This is most likely due to lithium metal deposition and dissolution, which proceeds competitively with the reduction of the electrolyte solution. Hence, lithium-ion intercalation did not occur in the electrolyte solution with Mg\(^{2+}/\text{Li}^{+}\) = 0.7. This result is in good agreement with that for the calcium salt. However, for Mg\(^{2+}/\text{Li}^{+}\) = 0.9 and 1.1, clear redox peaks were observed near 0 V, as shown in Figures 1b and 1c. Since magnesium-ion intercalation into graphite electrodes is not known, and magnesium deposition does not occur in these electrolyte solutions, these redox peaks must be due to lithium-ion intercalation/de-intercalation. These results indicate that magnesium salts can act as an additive that enables lithium ions to intercalate into graphite electrodes in PC-based electrolyte solutions, in the same way as calcium salts. Comparing the shape of the cyclic voltammograms for Mg\(^{2+}/\text{Li}^{+}\) = 0.9 and Mg\(^{2+}/\text{Li}^{+}\) = 1.1, the redox peak current was large, and oxidation peak splitting was observed, for Mg\(^{2+}/\text{Li}^{+}\) = 0.9. This peak splitting has been previously reported for slow-scan cyclic voltammograms,\(^{18}\) and indicates that the electrochemical response of Mg\(^{2+}/\text{Li}^{+}\) = 0.9 is faster than that of Mg\(^{2+}/\text{Li}^{+}\) = 1.1. This is most likely due to the difference in ion transport behavior of these electrolyte solutions. The ionic conductivities and viscosities of Mg\(^{2+}/\text{Li}^{+}\) = 0.9 and Mg\(^{2+}/\text{Li}^{+}\) = 1.1 were 1.7 mS cm\(^{-1}\) and 82 mPa s, and 0.96 mS cm\(^{-1}\) and 137 mPa s, respectively. Considering these values, the ion transport in the graphite composite electrode is faster for Mg\(^{2+}/\text{Li}^{+}\) = 0.9, and ion transport properties have a large influence on the electrochemical response. Unlike the calcium salt, lithium-ion intercalation/de-intercalation proceeded in the electrolyte solution with Mg\(^{2+}/\text{Li}^{+}\) = 0.9. In the case of the calcium salt, the threshold ratio for this reaction was Ca\(^{2+}/\text{Li}^{+}\) = 1.1. This is discussed later.

The charge and discharge profiles of lithium/graphite cells in 1 mol dm\(^{-3}\) LiTFSA/PC with salt addition at molar ratios of Mg\(^{2+}/\text{Li}^{+}\) = 1.1 and 0.9 are shown in Fig. 2. When the molar ratio is Mg\(^{2+}/\text{Li}^{+}\) = 1.1, the potential continued to descend to 0.3 V where plateaus were observed, and reached at 0 V during the discharge process, as shown in Fig. 2a. These plateaus below 0.3 V were also observed during the charge process of the graphite electrode, which suggests that the reaction is reversible. The voltage profile resembles that for the intercalation/de-intercalation of lithium ions into/from graphite in PC-based electrolytes containing the calcium salt.\(^{12}\) Although the irreversible capacity at the 1st cycle was large (about 350 mA h g\(^{-1}\)), the reversible capacity at the 1st cycle was about 350 mA h g\(^{-1}\), which is very similar to the theoretical capacity, and the reversible capacity at the 2nd cycle was almost the same as that of the 1st cycle. These results show that the exfoliation of graphite by the co-intercalation of PC-solvated lithium ions did not occur significantly and the consecutive reduction of the electrolyte solution occurred during discharge process. Hence, it is considered that the formed SEI did not adequately suppress the reductive decomposition of electrolyte solution at the surface of the graphite. When the ratio is Mg\(^{2+}/\text{Li}^{+}\) = 0.9, the reversible capacities of the 1st and 2nd cycles were both 20 mA h g\(^{-1}\), and these values are quite low, as illustrated in Fig. 2b. Therefore, the formed SEI did not adequately suppress the exfoliation of graphite. As a result, the large irreversible capacity due to the decomposition of electrolyte solution was also observed. The morphologies of the SEI obtained in Mg\(^{2+}\) - or Ca\(^{2+}\)-containing electrolyte solutions are currently under investigation in our group using in-situ scanning probe microscopy, and will be reported in due course.

We confirmed the lithium-ion intercalation with XRD measurement. The typical XRD patterns of graphite electrodes kept at 0 V in the electrolyte solutions with molar ratios of Mg\(^{2+}/\text{Li}^{+}\) = 1.1 and 0.9 are shown in Fig. 3. Peaks due to the Cu substrate are denoted as ‘Cu’. The interlayer distance of pristine graphite is 0.335 nm and it presents a peak at 26.6°. However, the resulting products exhibited no peak at 26.6°, suggesting that pristine graphite did not remain in the resulting
products. The peaks at $2\theta$ and $49^\circ$ are attributed to a graphite intercalation compound (GIC). The interlayer distance obtained from these two peaks was calculated to be 0.37 nm. The interlayer distance for C-Li-C is reported to be 0.370 nm; thus, we identified the resulting product as a stage 1 Li-GIC. The resulting GIC was gold in color, which is consistent with the known color of stage 1 Li-GICs.

Then, we investigated the relation between the electrochemical behavior and physicochemical properties of the electrolyte solutions. Figure 4 shows the temperature dependence of the ionic conductivities of LiTFSA and Mg(TFSA)$_2$ and Ca(TFSA)$_2$/PC electrolyte solutions. All electrolyte solutions exhibited Arrhenius-like behavior, facilitating calculation of the activation energies for ionic conduction, which are presented in Table I with viscosities. The ionic conductivities decreased with increasing $M$(TFSA)$_2$ concentration due to the increase of viscosities, and the activation energies increased with increasing $M$(TFSA)$_2$ concentration. This is due to the increased ion-ion interaction at higher concentrations. From this data, one may think that the magnesium ion is smaller than that of the calcium ion, but large activation energies have an influence on the lithium-ion intercalation behavior at higher concentrations. From this data, one may think that the magnesium ion is smaller than that of the calcium ion,20 affording a higher charge density than the calcium ion (i.e., a higher Lewis acidity, as described in the Introduction). Thus, the interaction with PC is stronger for magnesium ions. Another important factor is the steric hindrance between solvating molecules, since the volume of the first solvation shell would be different for magnesium ions and calcium ions. The coordination number of magnesium ions and calcium ions in coordination compounds has been reported to be 6 and 6–8, respectively. However, since these values were obtained from crystalline compounds we cannot directly apply the values to the solvation structures. Differences in the repulsion between solvating molecules is also important, as highlighted by the solvation preference of N, N-dimethylformamide (DMF) and N, N-dimethylacetamide (DMA) for magnesium and calcium ions, respectively. While calcium ions prefer to be solvated by DMA, which possesses a higher donor number than DMF, magnesium ions prefer DMF, which is not as bulky as DMA. Thus, the interaction between PC and bivalent ions is also affected by repulsions between the solvating molecules. Another factor to be considered is the difference in the degree of dissociation of the salt. The percentage of dissociation varies with the cation, as reported for $M$(ClO$_4$)$_2$/acetonitrile solutions ($M$ = Ca, Mg). The percentage of calcium ions that were dissociated from the anion was less than 10% of the total calcium ion concentration, even when the molality was 0.3 mol dm$^{-3}$, and most of the calcium ions existed as contact ion pairs or triplet ions. In contrast, the percentage of dissociated magnesium ions was more than 60% at the same molality. This underlines the importance of the interaction between cation and anion, and shows that the coordination sites of calcium ions tend to be more occupied by anions than those of magnesium ions, which lowers the number of available coordination sites on calcium ions for solvent molecules than is expected from the coordination number of un-complexed calcium ions alone. Considering these factors, high Lewis acidity and a high degree of dissociation increase the solvation number of magnesium ions, and large steric hindrance decreases it.
Figure 4. Temperature dependence of ionic conductivities of electrolyte solutions.

Table I. Activation energies for ionic conduction and viscosities of electrolyte solutions.

| Ratio (M²⁺/Li⁺) | 0.9 | 1.0 | 1.1 |
|----------------|-----|-----|-----|
| $M^2+$ (cation) | Mg²⁺ | Ca²⁺ | Mg²⁺ | Ca²⁺ | Mg²⁺ | Ca²⁺ |
| $E_a$ /kJ mol⁻¹  | 16  | 28  | 27  | 32  | 29  | 33  | 31  |
| Viscosity / mPa s | 9.5 | 82  | 63  | 108 | 79  | 137 | 96  |

The solvation number of magnesium ions is larger than that of calcium ions in LiTFSA+M(TFSA)₂/PC electrolyte solutions, and more PC is released from PC-solvated lithium ions. Therefore, it is thought that the threshold for magnesium ions is lower than that of calcium ions. Thus, we have identified the influence of magnesium and calcium ions as Lewis acids on the structure of solvated lithium ions. The solvent/salt ratio, size of the naked ion, and the degree of salt dissociation are also important for the structure of solvated lithium ions. The number of PC molecules attracted by magnesium and calcium ions from solvated lithium ions is still not clear and is currently under investigation using Raman spectroscopy. However, the separation of PC-solvated magnesium or calcium ions and PC-solvated lithium ions is quite difficult, and we have not yet obtained clear results.

Conclusions

Various amounts of Mg(TFSA)₂ were added to 1 mol dm⁻³ LiTFSA/PC electrolyte solutions. In these electrolyte solutions, the lithium-ion intercalation/de-intercalation at the graphite electrode was investigated by cyclic voltammetry and charge and discharge measurement. Successful lithium-ion intercalation/de-intercalation proceeded in the electrolyte solution with Mg²⁺/Li⁺ = 0.9, indicating that magnesium ions are an effective additive in PC-based electrolyte solutions. The threshold ratio for the magnesium salt was lower than that previously reported for the calcium salt (Ca²⁺/Li⁺ = 1.1). It was also indicated that the formed SEI at the surface of the graphite did not adequately suppress the reductive decomposition of electrolyte solution at higher Mg²⁺ content (Mg²⁺/Li⁺ = 1.1) and the exfoliation of graphite at lower Mg²⁺ content (Mg²⁺/Li⁺ = 0.9). Based on these results, it is proposed that the structure of the solvated lithium ion is affected by the strong Lewis acidity of the magnesium ions, allowing them to attract PC from solvated lithium ions. For this purpose, magnesium ions are favorable in terms of Lewis acidity and dissociation degree, but unfavorable in terms of steric hindrance between solvating molecules because of its small ionic radius.

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