

Effect of Counter Anions on Solid Electrolyte Interphase Formation on Graphite Electrodes in Propylene Carbonate-based Electrolyte Solutions

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ABSTRACT

Herein, the effect of counter anions on the formation of a solid electrolyte interphase (SEI) in a propylene carbonate (PC)-based electrolyte solution was investigated. Although the reversible capacities were different, reversible intercalation and de-intercalation of lithium ions occurred in the graphite negative electrode in the PC-based electrolyte solutions containing 1 M LiClO₄, LiPF₆, LiBF₄, and LiCF₃SO₃ at low temperature (-15°C). This indicated that the surface films acted as an effective SEI to suppress further co-intercalation and decomposition reactions at low temperature. However, the SEIs formed at the low temperature were unstable in 1 M LiPF₆ and LiBF₄/PC at room temperature (25°C). On the other hand, increasing reversible capacity was confirmed in the case of LiCF₃SO₃/PC at room temperature, because the SEI formed at the low temperature was still maintained. These results suggest that counter anions are an important factor to consider for the formation of effective SEIs in PC-based electrolyte solutions.

Keywords : Graphite, SEI, Propylene carbonate, Anion, Lithium ion batteries

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1. Introduction

An effective surface film for lithium intercalation and de-intercalation, termed as the “solid electrolyte interphase” (SEI), is required at graphite negative electrodes in lithium-ion batteries (LIBs) [1-4]. The effective SEI exhibits only ionic conductivity with insulating electrons that enable reversible intercalation and de-intercalation of lithium ions into/from the graphite negative electrodes at an extremely low potential (0.25-0.0 V vs. Li⁺/Li); these constitute the main negative electrode reactions in LIBs [5-8]. Thermodynamically, most organic electrolyte solutions become unstable before the lithium intercalation reaction in graphite negative electrodes, and have to be reductively decomposed [1-4, 9]. Therefore, an effective SEI is of urgent need, in order to

suppress the decomposition of the electrolyte solutions and enable facile lithium intercalation into graphite kinetically.

Propylene carbonate (PC), which has a low melting point (-49°C), is an attractive organic solvent from the viewpoint of the wide operating temperature of LIBs [10]. However, in PC-based electrolyte solutions, continuous decomposition and co-intercalation of solvated lithium ions occur at the graphite negative electrode, instead of lithium intercalation, owing to unsuccessful formation of an effective SEI [11-14]. In our previous research, we found that an effective SEI can be formed at the graphite negative electrodes by controlling the concentration and temperature, even when using pure PC as a solvent [15-17]. The results indicated that SEI formation at the graphite negative electrodes was affected by the solvation structure of lithium ions in PC-based electrolyte solutions. In general, in concentrated electrolyte solutions, the interaction between lithium ions and anions is strengthened and leads to the formation of various ion pairs such as solvent-separated ion pairs, contact ion pairs, and aggregates [18,19]. The observation

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that lithium intercalated with graphite at a low temperature in PC-based electrolyte solutions led us to conclude that the solvation structure of the lithium ions was altered at low temperatures, as compared to that at room temperature [17]. This was attributed to the low solubility of lithium cations at low temperatures and their strong interactions with the counter anions that in turn led to weaker interactions between the lithium cations and PC solvent in comparison to those at room temperature. Thus, the counter anions exerted their influence on the solvation environment of lithium ions at low temperatures. Since the formation of the SEI is greatly dependent on the solvation environment, it is imperative to investigate the effect of various solvation environments. Although the influence of counter anions on the solvation structure has been established, the effect of anions on SEI formation has not been clearly understood yet. Therefore, their effect on the formation of an effective SEI at graphite negative electrodes should be investigated in detail.

In this study, we investigated the effect of counter anions on the formation of a SEI in PC-based electrolyte solutions at low temperature (-15°C). Additionally, the stability of the SEI film formed in the PC-based electrolyte solutions containing different lithium salts was investigated at room temperature.

2. Experimental

Charge and discharge measurements were carried out using a three-electrode cell of the beaker type. Natural graphite powder (Kansai Coke and Chemicals Co., NG-7) was used as a working electrode. A slurry was prepared by mixing natural graphite (90 wt.%) and polyvinylidene fluoride (10 wt.%) in *N*-methyl-2-pyrrolidone. The slurry was coated on copper foil and dried at 80°C under vacuum for the working electrode. Lithium foil was used as the counter as well as reference electrode. PC-based solutions containing LiClO_4 , LiPF_6 , LiBF_4 , and LiCF_3SO_3 (1.0 M salt concentration) were used as the electrolyte solutions. LiClO_4 dissolved in a 1:1 (by volume) mixture of ethylene carbonate (EC) and diethyl carbonate (DEC) (EC + DEC) was used for comparison between the PC- and EC-based electrolyte solutions. All charge and discharge measurements were performed between 0.0 and 3.0 V, with 37.2 mA g^{-1} of constant current (0.1 C) at 25 or -15°C

under argon atmosphere.

Raman spectra of the PC-based electrolyte solutions were acquired at 25 and -15°C using a portable Raman spectroscopy system (Deltanu, Inspector Raman).

3. Results and Discussion

3.1 Charge and discharge properties at low temperature in EC- and PC-based electrolyte solutions

Fig. 1 shows the charge and discharge profiles of natural graphite (NG-7) at low temperature (-15°C) in EC + DEC and PC containing 1 M LiClO_4 . In general, the EC-based electrolyte solutions provided an effective SEI with small irreversible capacity at room temperature, thereby enabling lithium intercalation

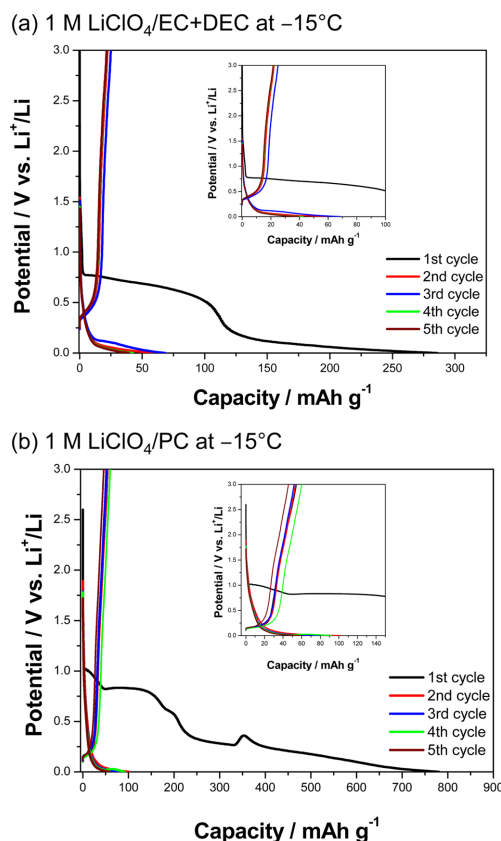


Fig. 1. Potential profiles of natural graphite (NG-7) in 1 M LiClO_4 / (a) EC+DEC (1:1, vol. ratio) and (b) PC at low temperature (-15°C). C-rate: 0.1 C. The inset is a magnified view of the potential profile.

and de-intercalation, and reversible capacity comparable with the theoretical capacity (372 mAh g^{-1}) at the graphite negative electrodes [5,9,20]. However, at low temperature, there was a large irreversible capacity during the first cycle in the EC-based electrolyte solution, in addition to the small reversible capacity of ca. 25 mAh g^{-1} (Fig. 1a). In our previous study, it was found that the co-intercalation and decomposition reactions of solvated lithium ion take place between 1.0 and 0.5 V within/on the graphite negative electrode, and it is these irreversible reactions that are responsible for forming the SEI in the EC-based electrolyte solution at a low temperature [21]. Moreover, large overpotentials related to lithium intercalation and de-intercalation were also confirmed at 0.1 and 0.35 V, respectively, which were attributed to the decreasing ionic conductivity caused by the high melting point of EC (36°C) [10]. Hence, the reversible capacity largely decreased at low temperature than at room temperature.

Interestingly, in the PC-based electrolyte solution, a reversible capacity of ca. 50 mAh g^{-1} was obtained below 0.25 V corresponding to the lithium intercalation and de-intercalation reactions at low temperature (Fig. 1b). This result suggested that an effective SEI was formed, which hindered further co-intercalation and decomposition reactions during the first cycle at low temperature. Moreover, the electrochemical performance in terms of the reversible capacity at low temperature improved when the PC-based electrolyte solution was used instead of the EC-based electrolyte solution.

3.2 Effect of counter anions on the formation of a SEI at low temperature in PC-based electrolyte solutions

Charge and discharge tests were carried out to investigate the effect of counter anions on the formation of a SEI at -15°C in PC-based electrolyte solutions containing LiPF_6 , LiBF_4 , and LiCF_3SO_3 (Fig. 2). A large irreversible capacity, which was attributed to solvent co-intercalation and electrolyte decomposition, was confirmed during the first cycle in all cases. However, the irreversible reaction was suppressed and the potential dropped toward the lithium intercalation potential during the first cycle. Hence, reversible intercalation and de-intercalation reactions of lithium ions took place below 0.25 V after the first charge process, suggesting the formation of

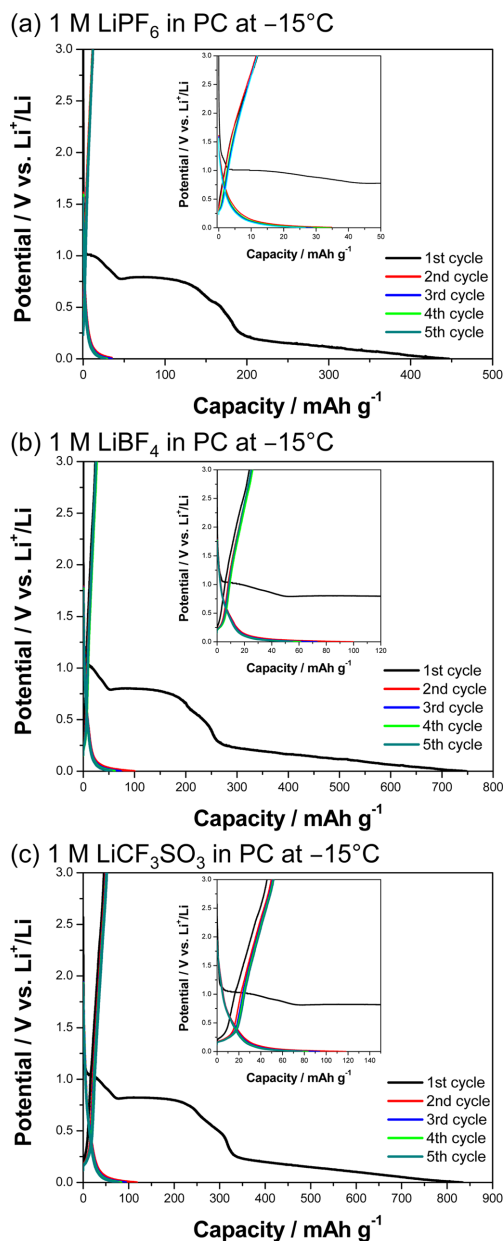


Fig. 2. Potential profiles of natural graphite (NG-7) in PC-based electrolyte solutions containing 1 M (a) LiPF_6 , (b) LiBF_4 , and (c) LiCF_3SO_3 at low temperature (-15°C). C-rate: 0.1 C. The inset is a magnified view of the potential profile.

an effective SEI on the graphite negative electrode in these electrolyte solutions at -15°C . Although effective SEIs were formed for the reversible reactions on graphite at low temperature, the reversible capacities

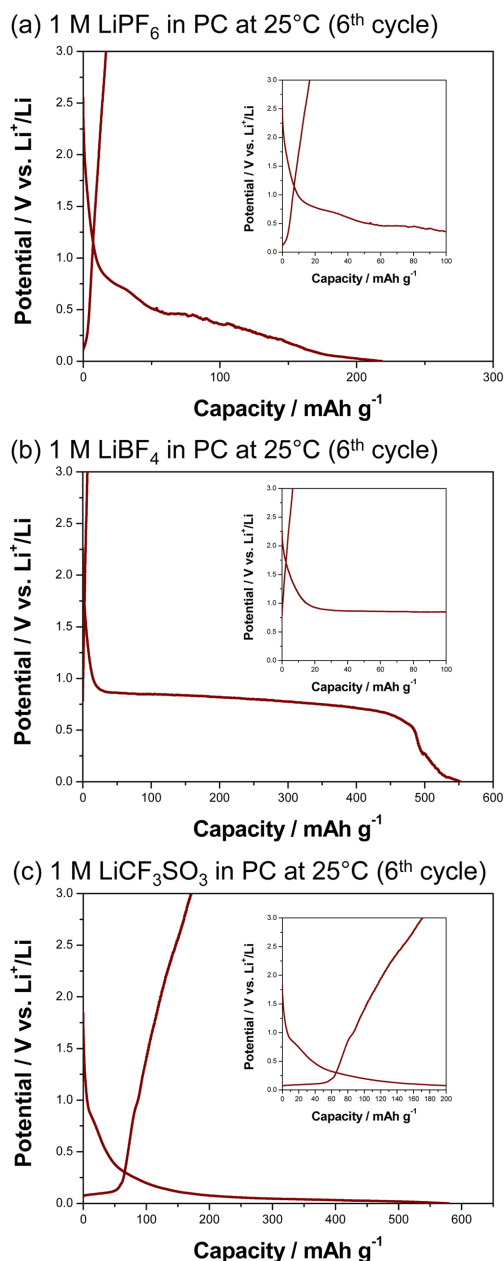


Fig. 3. Potential profiles of natural graphite (NG-7) in PC-based electrolyte solutions containing 1 M (a) LiPF_6 , (b) LiBF_4 , and (c) LiCF_3SO_3 at room temperature (25°C) after five cycles at -15°C . C-rate: 0.1 C. The inset is a magnified view of the potential profile.

were significantly different among the electrolyte solutions. This suggests that the formation of an SEI is affected by the types of counter anions.

The electrochemical cells cycled at low temperature were moved to a room-temperature environment, and charge/discharge tests were performed at room temperature in order to investigate the stability of the SEI formed after five cycles at low temperature in these electrolyte solutions (Fig. 3). The charge and discharge properties of the graphite electrode were significantly different at room temperature among the electrolyte solutions. A large irreversible capacity related to the co-intercalation and decomposition of solvated lithium ions was observed in the PC-based electrolyte solutions containing LiPF_6 and LiBF_4 . (Fig. 3a, b). Moreover, continuous co-intercalation and decomposition reactions occurred at approximately 0.9 V in LiBF_4/PC , which led to the irreversibility, owing to graphite exfoliation. These results indicate that the SEI formed at low temperature was not effective for the suppression of further co-intercalation and decomposition reactions at room temperature in LiPF_6 and LiBF_4/PC . On the other hand, the cell potential rapidly dropped to the lithium intercalation potential with a small irreversible capacity, and lithium intercalation and de-intercalation reactions took place in addition to an increase in the reversible capacity in 1 M $\text{LiCF}_3\text{SO}_3/\text{PC}$ (Fig. 3c). Here, the SEI formed at low temperature acts as an effective SEI even at room temperature. In general, the CF_3SO_3^- anion interacts more strongly with the lithium ion in the electrolyte solutions because of its stronger association strength than PF_6^- and BF_4^- anions [22]. Hence, the interaction between the lithium ion and PC molecules becomes weaker in 1 M $\text{LiCF}_3\text{SO}_3/\text{PC}$ as compared to other electrolyte solutions at low temperature and this leads to good electrochemical properties with an effective SEI. Thus, counter anions have a demonstrable influence on the formation of a SEI in PC-based electrolyte solutions at low temperature.

The structures of the solvated lithium ions were investigated in the electrolyte solutions at -15 and 25°C . The Raman spectra of the PC-based electrolyte solutions containing LiPF_6 , LiBF_4 , and LiCF_3SO_3 are shown in Fig. 4. In all cases, there was a strong band at approximately 712 cm^{-1} and a shoulder at approximately 730 cm^{-1} at 25°C , which were attributed to the symmetry ring deformation band of free PC and solvated PC with the lithium ions, respectively. However, at -15°C , the band corresponding to free PC shifted to a lower wavenumber,

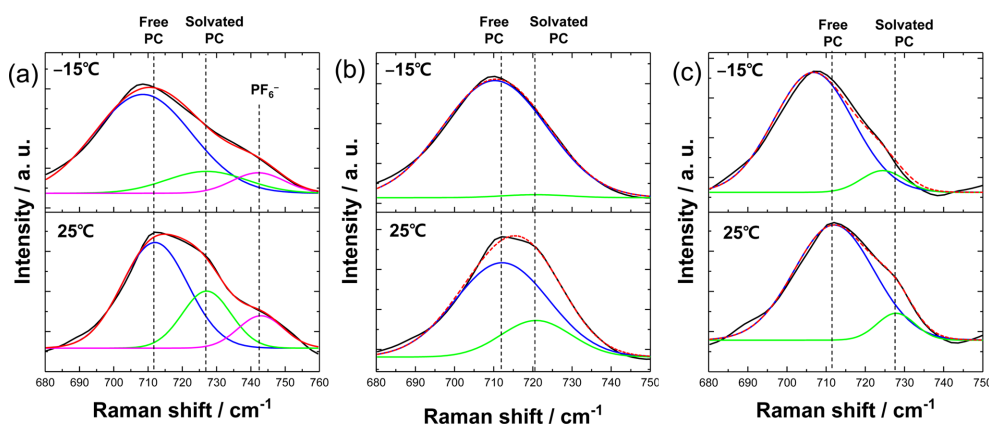


Fig. 4. Raman spectra of the PC-based electrolyte solutions containing 1 M (a) LiPF_6 , (b) LiBF_4 , and (c) LiCF_3SO_3 at 25 and -15°C .

whereas the shoulder corresponding to solvated PC with lithium ions disappeared. These results indicate that the interaction between lithium ions and PC molecules becomes weaker and the solvation structures are changed, compared with that at room temperature [17]. Consequently, the lithium intercalation reaction can occur in the graphite negative electrode at low temperature in PC-based electrolyte solutions, as shown in Fig. 2. It was found that the properties of the SEI formed at low temperature, in terms of its charge and discharge characteristics, were affected by the nature of the counter anions, as shown in Fig. 3; however, the reason for the different properties exhibited by the SEI in PC-based electrolyte solutions containing different counter anions is not yet clear. Nevertheless, the above results suggest that in addition to an appropriate solvent, the choice of a proper anion is also important to form an effective SEI at graphite negative electrodes.

4. Conclusions

In this study, we investigated the effect of various counter anions on the formation of SEI at low temperature in PC-based electrolyte solutions. Reversible lithium intercalation and de-intercalation reactions into/from the graphite negative electrode took place at low temperature, owing to the formation of an effective SEI with weaker interaction between the lithium ions and PC molecules, compared to that at room temperature. Moreover, from

the viewpoint of reversible capacity, better electrochemical performance was obtained in 1 M LiClO_4/PC than in 1 M $\text{LiClO}_4/\text{EC}+\text{DEC}$ (1:1, vol. ratio) at low temperature. However, the properties of the SEI formed at low temperature were significantly different among the PC-based electrolyte solutions containing LiPF_6 , LiBF_4 , and LiCF_3SO_3 . It was found that the SEIs formed at low temperature in 1 M LiPF_6 and LiBF_4/PC were not effective at room temperature and led to further co-intercalation and decomposition reactions. On the other hand, the SEI formed at low temperature in 1 M $\text{LiCF}_3\text{SO}_3/\text{PC}$ was effective even at room temperature. The chemical reaction mechanism for the formation of anion-derived SEIs was also elucidated and the results suggested that the nature of the counter anion is important to obtain an effective SEI in PC-based electrolyte solutions. Furthermore, it was established that SEI formation can be controlled by the addition of suitable anions to the electrolyte solutions. Additional studies on understanding the composition and structure of the anion-derived SEIs are currently underway.

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References

- [1] E. Peled, *J. Electrochem. Soc.*, **1979**, *126*(12), 2047-2051.
- [2] J. O. Besenhard, M. Winter, J. Yang, and W. Biberacher, *J. Power Sources*, **1995**, *54*(2), 228-231.
- [3] S.-K. Jeong, M. Inaba, T. Abe, and Z. Ogumi, *J. Electrochem. Soc.*, **2001**, *148*(9), A989-A993.
- [4] D. Aurbach, M. Koltypin, and H. Teller, *Langmuir*, **2002**, *18*(12), 9000-9009.
- [5] Z. Ogumi, and M. Inaba, *Bull. Chem. Soc. Jpn.*, **1998**, *71*(3), 521-534.
- [6] T. Ohzuku, Y. Iwakoshi, and K. Sawai, *J. Electrochem. Soc.*, **1993**, *140*(9), 2490-2498.
- [7] M. Inaba, H. Yoshida, Z. Ogumi, T. Abe, Y. Mizutani, and M. Asano, *J. Electrochem. Soc.*, **1995**, *142*(1), 20-26.
- [8] D. Aurbach, and Y. Ein-Eli, *J. Electrochem. Soc.*, **1995**, *142*(6), 1746-1752.
- [9] K. Xu, *Chem. Rev.*, **2004**, *104*(10), 4303-4417.
- [10] S.S. Zhang, K. Xu, J.L. Allen, T.R. Jow, *J. Power Sources*, **2002**, *110*(1), 216-221.
- [11] M. Inaba, Z. Siroma, Y. Kawatate, A. Funabiki, and Z. Ogumi, *J. Power Sources*, **1997**, *68*(2), 221-226.
- [12] D. Aurbach, B. Markovsky, I. Weissman, E. Levi, and Y. Ein-Eli, *Electrochim. Acta*, **1999**, *45*(1-2), 67-86.
- [13] G.-C. Chung, H.-J. Kim, S.-I. Yu, S.-H. Jun, J.-W. Choi, and M.-H. Kim, *J. Electrochem. Soc.*, **2000**, *147*(12), 4391-4398.
- [14] H.-Y. Song, and S.-K. Jeong, *J. Power Sources*, **2018**, *373*, 110-118.
- [15] S.-K. Jeong, M. Inaba, Y. Iriyama, T. Abe, and Z. Ogumi, *Electrochem. Solid-State Lett.*, **2003**, *6*(1), A13-A15.
- [16] S.-K. Jeong, M. Inaba, Y. Iriyama, T. Abe, and Z. Ogumi, *J. Power Sources*, **2008**, *175*(1), 540-546.
- [17] S.-K. Jeong, H.-Y. Song, S. I. Kim, T. Abe, W. S. Jeon, R.-Z. Yin, and Y. S. Kim, *Electrochem. Commun.*, **2013**, *31*(24), 24-27.
- [18] Y.-S. Kim, and S.-K. Jeong, *J. Spectrosc.*, **2015**, *2015*.
- [19] Y. Yamada, M. Yaegashi, T. Abe, and A. Yamada, *Chem. Commun.*, **2013**, *49*(95), 11194-11196.
- [20] P. Novak, F. Joho, R. Imhof, J.-C. Panitz, and O. Haas, *J. Power Sources*, **1999**, *81*, 212-216.
- [21] S.-K. Jeong, M. Inaba, T. Abe, and Z. Ogumi, *J. Electrochem. Soc.*, **2001**, *148*(9), A989-A993.
- [22] W. A. Henderson, *J. Phys. Chem. B*, **2006**, *110*(26), 13177-13183.