



Functional binders for reversible lithium intercalation into graphite in propylene carbonate and ionic liquid media

Shinichi Komaba^{a,*}, Naoaki Yabuuchi^a, Tomoaki Ozeki^a, Koji Okushi^a, Hiroharu Yui^b, Kozo Konno^b, Yasushi Katayama^c, Takashi Miura^c

^a Department of Applied Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

^b Department of Chemistry, Tokyo University of Science, 1-3 Kagurazaka, Shinjuku, Tokyo 162-8601, Japan

^c Department of Applied Chemistry, Faculty of Science and Technology, Keio University, 3-14-1 Hiyoshi, Kohoku, Kanagawa 223-8522, Japan

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ABSTRACT

Poly(acrylic acid) (PAA), poly(methacrylic acid) (PMA), and poly(vinyl alcohol) (PVA), which have oxygen species as functional groups, were utilized as a binder for graphite electrodes, and the electrochemical reversibility of lithium intercalation was examined in PC medium and ionic liquid electrolyte, lithium bis(trifluoromethanesulfonyl)amide dissolved in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (BMP-TFSA). Columbic efficiency of 75–80% with more than 300 mAh g⁻¹ was achieved upon first reduction/oxidation cycle in both electrolytes using these binding polymers, which were significantly improved in comparison to a conventional PVdF binder (less than 45% of columbic efficiency for the first cycle). For the graphite-PVdF electrode, co-intercalation and/or decomposition of PC molecules solvating to Li ions were observed by the electrochemical reduction, resulting in the cracking of graphite particles. In contrast, the co-intercalation and decomposition of PC molecules and BMP cations for the first reduction process were completely suppressed for the graphite electrodes prepared with the polymers containing oxygen atoms. It was proposed that the selective permeability of lithium ions was attained by the uniform coating of the graphite particles with PAA, PMA, and PVA polymers, because the electrostatic interaction between the positively charged lithium ions and negatively charged oxygen atom in the polymer should modulate the desolvation process of lithium ions during the lithium intercalation into graphite, showing the similar functions like artificial solid-electrolyte interphase.

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1. Introduction

Recently, the demand for the large-scale lithium-ion batteries is rapidly grown for plug-in type hybrid and pure electric vehicles. Graphite, which can deliver more than 350 mAh g⁻¹ of rechargeable capacity with very low operating voltage close to Li, is the promising negative electrode material for the large-scale applications because of the low material cost. Electrochemical performance of the negative electrodes for the lithium-ion batteries is significantly influenced by the difference in the interface between electrolyte and active materials, which can be modified by the electrochemical formation of a passivation layer during first reduction process, so-called solid-electrolyte interphase (SEI). The electrochemical intercalation of lithium ions into the graphite particles with high reversibility cannot be achieved without SEI. Ethylene carbonate (EC) based solution is often used as an electrolyte for

the lithium-ion batteries with the graphite negative electrode. EC is necessary to form the stable SEI during the first reduction process at the graphite/electrolyte interface, which allows the reversible lithium intercalation into the graphite electrode. In contrast, for propylene carbonate (PC) media, the stable SEI cannot be formed by the electrochemical reduction. PC molecules are continuously decomposed at the graphite surface without the formation of passivation layer. Moreover, lithium ions solvated with PC molecules are partly intercalated (without desolvation process of PC), resulting in the cracking of the graphite particles and loss of the electrochemical reversibility as the electrode material [1].

One of the authors has studied the electrochemical molecular sieving effect of the polyion complex (PIC) consisting of bridged polyanions/polycations for enzyme-immobilized electrodes [2,3]. The molecular sieving property can be designed and controlled by the proper combination between the polyanions and polycations with different framework structures. It has been expected that such electrochemical sieving effect of PIC can be also utilized for the lithium intercalation, because, from the microscopic point of view,

* Corresponding author. Tel.: +81 3 5228 8749; fax: +81 3 5228 8749.

E-mail address: komaba@rs.kagu.tus.ac.jp (S. Komaba).

the PIC layer could play the role like artificial SEI to assist the desolvation process of PC-solvated Li^+ ions at the electrolyte/electrode interface because of the molecular size effect of lithium ions vs. relatively large solvating Li^+ -PC. Thus the research was aimed at achieving reversible lithium intercalation/deintercalation into the graphite electrode coated with the PIC in the pure PC electrolyte solution, in other words, the graphite particles coated with the pre-formed SEI. After our efforts for the three years, reversible electrochemical lithium intercalation/deintercalation into the graphite electrodes in the PC media has been unpredictably found by the coating of poly(acrylic acid) (PAA) binder [4], which is one of the polyanions and often used as the component of PIC [2,3]. The graphite electrode coated by PAA binder can be reversibly cycled without the co-intercalation and decomposition of PC molecules as well as the EC/DMC solution [4–6]. It should be noted that PAA can serve as the surface coating layer and also as a binder for the graphite particles.

In this paper, we report the effect of the surface modification of the graphite electrode by the functional polymers of PAA and analogous polymers, such as poly(vinyl alcohol) (PVA), and poly(methacrylic acid) (PMA) having similar framework structures with PAA. We also briefly describe that such PAA coating on the graphite particles enables to improve reversibility of lithium intercalation in the ionic liquid-based electrolyte solution. From these results, we will discuss the factor affecting the electrochemical activity of the graphite electrodes in relation to the role of the polymer binders.

2. Experimental

Reagent grade graphite powders (average particle size; 3 or 10 μm) were used as the active material. PAA (MW: 720,000, Aldrich) PMA (MW: 100,000, Polyscience Inc.), PVA (polymerization degree: 3100–3900, hydrolyzation degree: 86–90%, Wako Pure Chemical Industries), and PVdF were used as a binder. For preparation of working electrodes, the graphite powders were mixed with the binder of PVdF (10 wt%), PAA (15 wt%), PMA (15 wt%), or PVA (5 wt%) in N-methylpyrrolidone (NMP). In the case of PVA, the binder was dissolved in NMP at high temperature (ca. 90 °C) to make a PVA-NMP solution prior to use. This polymer solution was mixed with graphite at room temperature. The amount of the polymer was optimized to obtain higher capacity of the graphite electrodes. Thus obtained slurry was coated onto a nickel mesh as a current collector. The electrodes were dried at 120 °C in vacuum prior to use. The electrolytes used were 1 mol dm⁻³ LiClO_4 in EC:DMC (1:1 by volume), 1 mol dm⁻³ LiClO_4 in PC, and 1 mol dm⁻³ lithium bis(trifluoromethanesulfonyl)amide (LiTFSa) in 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (BMP-TFSA). Battery grade lithium metal foil was used as a counter electrode. Three-electrode beaker type cells were assembled in an argon filled glove box, whose dew point was kept lower than -80 °C. Galvanostatic reduction and oxidation of the graphite electrodes in Li cells at a rate of 50 mA g⁻¹ in organic solvent and 20 mA g⁻¹ in ionic liquid-based electrolyte were carried out between 0.0–2.0 V vs. Li/Li^+ at 25 °C.

Surface of the electrodes was observed by a scanning electron microscope (SEM, S-5000, Hitachi) after the electrochemical cycling. Infrared (IR) spectra of interface between the graphite electrodes and PAA with electrolyte solution were collected by Nicolet 8700 FT-IR, Thermo Fisher Scientific. For the IR spectroscopy, PAA film was prepared without graphite electrode by casting on Cu foil and dried at 120 °C in vacuum prior to use.

3. Results and discussion

3.1. In PC electrolyte solution

We examined three polymers of PAA, PMA, and PVA, which can be used as both surface modifier and binder. The structures of the polymers are illustrated in Fig. 1 with a conventional polymer binder of PVdF for comparison. Not only monomer unit structure but also polymeric conformation are important factors for the battery use [5]. Representative first reduction and oxidation curves of the graphite powder electrodes prepared with these polymers operated at a rate of 50 mA g⁻¹ are shown in Fig. 2. For the graphite-PVdF electrode, voltage plateau of 0.8 V is observed for

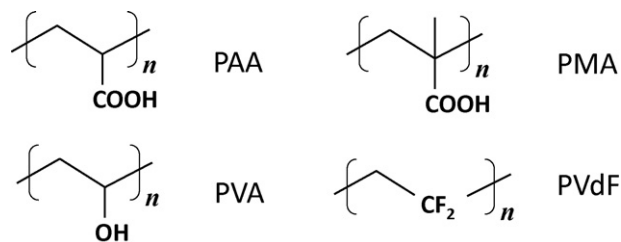


Fig. 1. Molecular structures of the binders used in this study: poly(acrylic acid) (PAA), poly(vinyl alcohol) (PVA), poly(methacrylic acid) (PMA), and conventional binder of poly(vinylidene fluoride) (PVdF).

the first reduction process, which is a characteristic feature of the graphite electrodes in PC; co-intercalation of solvated lithium ions and decomposition of PC molecules. Since the reactions observed at the voltage plateau are irreversible electrochemical reactions, the columbic efficiency upon first cycle is lowered less than 45% for the graphite-PVdF composite electrode. In contrast, the PAA, PMA, and PVA polymer binders completely suppress the irreversible electrochemical reactions even at 0.8 V, resulting in the much improved columbic efficiency (approximately 75–80%) during the first cycle. The PAA binder shows the best columbic efficiency among three polymers examined in this experimental condition. The first oxidation capacity of 355 mA h g⁻¹ was achieved with PAA binder, corresponding to the almost theoretical capacity of the graphite electrode (372 mA h g⁻¹) assumed the formation of LiC_6 , with satisfactory capacity retention as previously described [5,6]. In addition, long-term stability of these binders is excellent, and optimized graphite-PAA electrode can retain the rechargeable capacity for the more than 100 cycles without capacity loss, which will be reported in the future.

The change in the particle morphology of the graphite electrodes prepared with PAA and PVdF was observed by SEM after the first cycle. Fig. 3 compares the changes in the electrode morphology observed in LiClO_4 dissolved in either EC/DMC or PC solution. Agglomerated deposits appear for both electrodes prepared with PVdF (Fig. 3a) and PAA (Fig. 3b) cycled in EC/DMC solution. However, the clear difference for the amount of deposits on the electrodes is noted. Formation of such deposits is evident for the graphite-PVdF electrode compared with the graphite-PAA electrode, corresponding to the difference in the length of voltage plateau observed at 0.8 V during the first cycle for both elec-

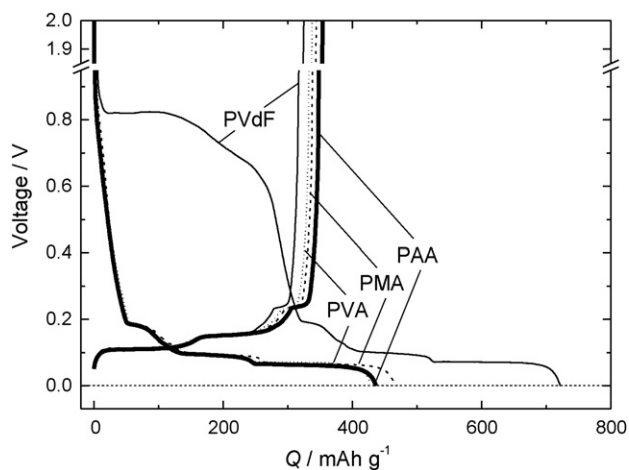


Fig. 2. First reduction and oxidation curves of graphite electrodes in 1 mol dm⁻³ LiClO_4 dissolved in pure propylene carbonate (PC) solution at a rate of 50 mA g⁻¹. The graphite electrodes were prepared with different polymers, i.e., PAA, PMA, PVA, and PVdF.

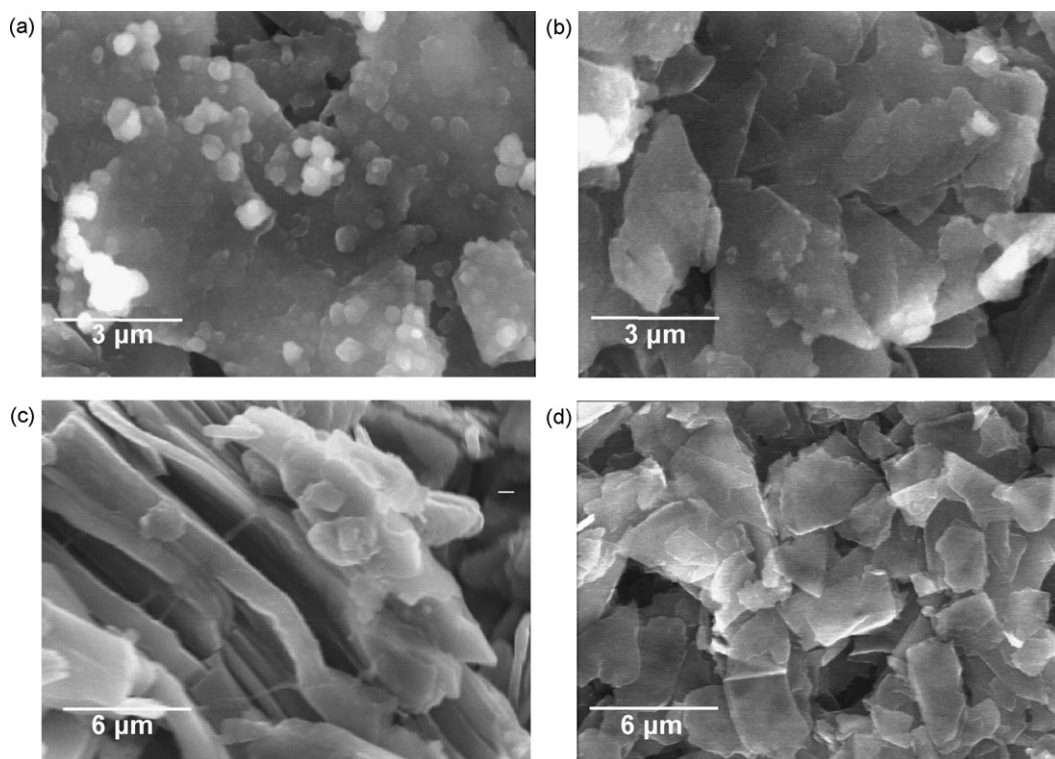


Fig. 3. SEM images of graphite electrodes prepared with (a) PVdF, or (b) PAA after the first cycle in $1 \text{ mol dm}^{-3} \text{ LiClO}_4 \text{ EC/DMC}$ (1/1 by volume) electrolyte, and (c) PVdF or (d) PAA after the first reduction/oxidation cycle in $1 \text{ mol dm}^{-3} \text{ LiClO}_4 \text{ PC}$.

trodes, in fact approximately 50 mAh g^{-1} of irreversible voltage plateau observed for the graphite-PVdF electrode in EC/DEC was reduced to less than 15 mAh g^{-1} for the graphite-PAA electrode (not shown). The difference in the electrode morphology changes becomes more evident when both electrodes are cycled in the pure PC electrolyte solution. The solvating PC molecules are co-intercalated with lithium into the graphite and are decomposed for the graphite-PVdF electrode, generating many cracks [1] in the graphite particles, especially for the large graphite particles (Fig. 3c). Such cracks in the graphite particles cannot be confirmed for the graphite particles coated with the PAA binder in Fig. 3d, which is in good agreement with Fig. 2.

In order to study the mechanism on improvement of the electrochemical reactivity of graphite-PAA electrode in PC solution, ATR/FTIR spectra were collected at the interface between PAA film casted on Cu foil and PC solution with or without LiClO_4 as a lithium salt. The spectra shown in Fig. 4 were collected as a function of time from 30 to 600 s after contact between PAA film and PC solution. Fig. 4a shows highlighted ATR/FTIR spectra ranged from 1500 to 1900 cm^{-1} , which were collected at the interface between PAA film and PC solution without lithium salt. In this region, three signals from the PC molecule and PAA polymer can be observed: (1) a strong absorption band at 1795 cm^{-1} , which can be assigned into $>\text{C}=\text{O}$ in the PC molecule, (2) weak absorbance from carboxylic acid functional group ($-\text{COOH}$ in the PAA polymer) at 1717 cm^{-1} , and (3) relatively weak absorbance at 1630 cm^{-1} , which is originated from the hydrogen bonding formation between two carboxylic acid groups to bridge the PAA polymer main chains. The absorbance from the PC molecules decreases as a function of time, whereas the absorbance bands originated from the PAA polymers increases. This observation suggests that the PAA polymer is partly swelling by gelling with PC solvent as a function of time.

Fig. 4b shows the variation of the absorbance as a function of time at the interface between the PAA and PC containing the lithium salt ($1 \text{ mol dm}^{-3} \text{ LiClO}_4$). The change in the absorbance band shape

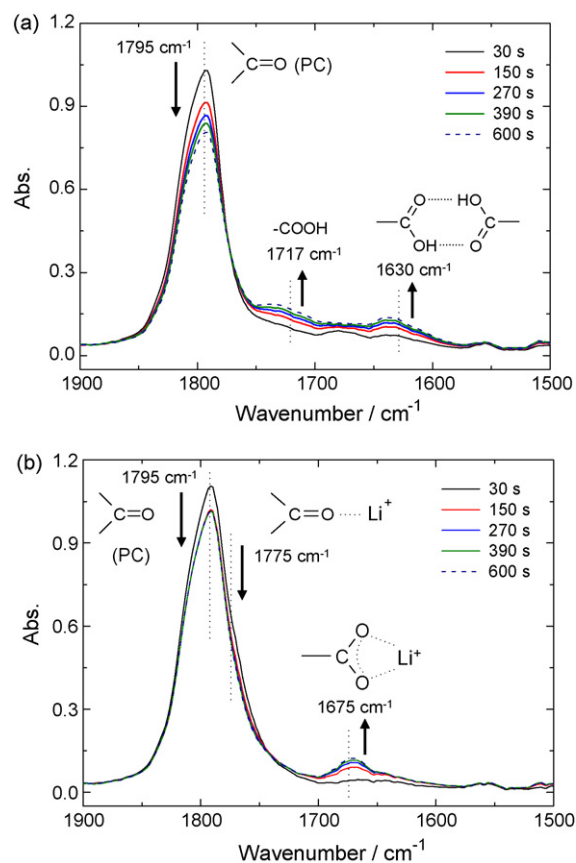


Fig. 4. The variation of ATR/FTIR spectra collected at the interface between the PAA film and (a) pure PC solvent (lithium salt free) and (b) $1 \text{ mol dm}^{-3} \text{ LiClO}_4 \text{ PC}$ solution as a function of time.

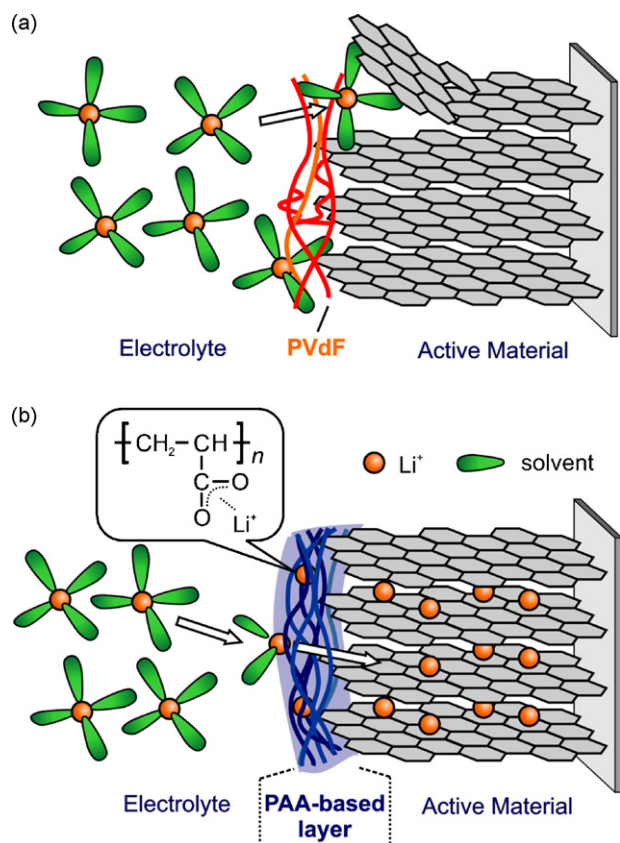


Fig. 5. Schematic illustrations of the interface between graphite and lithium ion containing PC solution as an electrolyte solution; (a) PVdF- and (b) PAA-graphite electrode. See the text in detail.

at 1795 cm^{-1} is observed. This band can be deconvoluted into two bands at 1795 cm^{-1} and at 1775 cm^{-1} , which were assigned into $>\text{C}=\text{O}$ originated from free PC and solvating PC to the lithium ions, respectively. This was supported by the dependence of the peak ratio on lithium concentration. Absorbance of the two bands is weakened within a shorter period of time ($<150\text{ s}$), suggesting partial gelling of PAA film with LiClO_4 PC solution. In addition, a new band appears at 1675 cm^{-1} , and its absorbance increases as a function of time. This band can be assigned to lithium carboxylate ($-\text{COOLi}$). It is speculated that (a) protons in carboxylic acid functional groups in the PAA polymer are ion-exchanged by lithium ions in the electrolyte solution, and then intermolecular hydrogen bonding between carboxylic acid groups would be lost, leading to the partial modulation of the polymer chain conformation, and (b) carboxylate groups in the PAA polymer and solvated Li ions are possibly interacting directly each other.

From the above results, Fig. 5 shows schematic illustrations of the plausible interface structure between PC-based electrolyte and the conventional graphite-PVdF in comparison to the graphite-PAA electrode. There is general consensus that PC solution cannot bring about the formation stable SEI layer, indicating that graphite cannot be covered by the SEI for the reduction process. The PVdF polymer binds the graphite particles, and the particle surface is only partly covered by PVdF [7] because of crystallization and bundle formation of PVdF main chains. It is noted that the PC solution is permeated easily through PVdF-graphite electrode, suggesting that solvating PC molecules continuously supplied to the surface of graphite particles from the bulk of electrolyte. This causes the large irreversible capacity shown in Fig. 2. Moreover, co-intercalation of the solvated Li^+ ions results in the cracking of the graphite particles as mentioned in Fig. 3c.

On the other hand, the PAA polymer binder covers uniformly graphite particles, like glue, as was confirmed by X-ray photoelectron spectroscopy [6] and is amorphous in dried state unlike PVdF. In addition, the polyacrylate is partly gelled by the PC solution and entrapped as a part of SEI layer as drawn in Fig. 5b. Note that the solvated lithium ions, which are positively charged species, can interact with unshared electron pairs localized at negatively polarized oxygen of the carboxylate group such as $-\text{COOLi}$ and $-\text{COOH}$. The strongly solvated lithium ions by PC could be also affected by the electrostatic interaction between Li^+ ions and the oxygen atoms in PAA-based SEI. This is considered to be a similar manner to lithium complexation in a poly(ethylene oxide)-based solid electrolyte, in which ether oxygen atoms coordinate to the lithium ions as is known generally [8]. Similar complexation between lithium ions and crown ethers was also reported [9]. It appears from our consideration that negatively polarized oxygen atoms in the conventional SEI formed in EC based electrolyte must interact with solvated lithium ions, accelerating the desolvation process and lithium intercalation into graphite. This is also consistent with the fact that the electrochemical reversibility of graphite electrodes in PC solution is improved with different polymers having the negatively polarized oxygen, i.e., PMA and PVA as well as PAA. From these considerations, we propose that the functionality of polymer binders, containing the negatively polarized lone pairs at oxygen atom of functional groups in these polymers, induces the analogous properties to that of SEI, so-called artificial SEI. In other words, the polymer coating would act as a passivating layer. The detailed experimental study on the specific role of these polymers having the functionality for the electrochemical properties is currently under way in our group.

3.2. In ionic liquid-based electrolyte

In the previous section, we demonstrated that PAA binder shows the beneficially unique effect on the lithium intercalation into the graphite in PC solution. It is interesting to note that the surface modification enables reversible lithium intercalation even in ionic liquid-based electrolytes. Fig. 6 shows the molecular structures of anionic/cationic species of BMP-TFSA forming molten salt at room temperature, ionic liquid, which was used in this study as an electrolyte [10,11]. First galvanostatic reduction/oxidation curves of the graphite electrodes (artificial graphite; average particle size of $10\text{ }\mu\text{m}$) prepared with PVdF or PAA polymer binder are shown in Fig. 7. As can be clearly seen in Fig. 7, the voltage is gradually lowered from 0.8 to 0.2 V for the graphite-PVdF electrode, whereas the voltage quickly drops down to less than 0.2 V for the graphite-PAA electrode. By comparing reduction and oxidation capacity, large irreversible capacity ($>100\text{ mAh g}^{-1}$) was confirmed for the graphite-PVdF electrode with a short voltage plateau at 1.0 V for the oxidation process. The graphite-PAA electrode can deliver more than 300 mAh g^{-1} at a rate of 20 mA g^{-1} , which is much larger reversible capacity compared with the graphite-PVdF electrode (ca. 140 mAh g^{-1}). The origin of the voltage plateau was examined by XRD for the graphite electrodes pre-

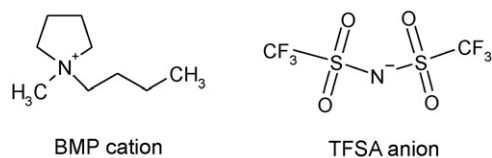


Fig. 6. The structure of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)amide (BMP-TFSA) as an ionic liquid electrolyte used in this study.

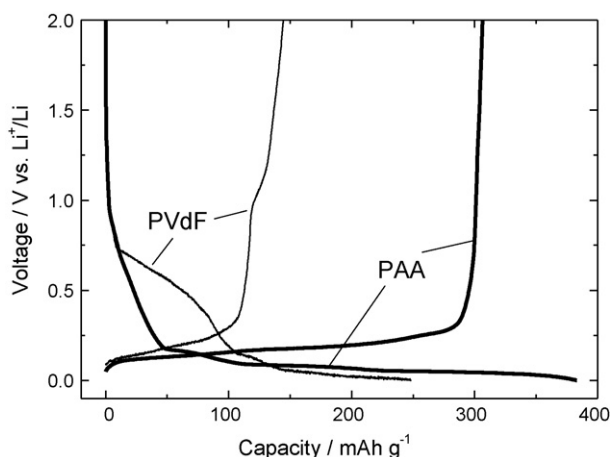


Fig. 7. First reduction and oxidation curves of graphite electrode in 1 mol dm^{-3} LiTFSI BMP-TFSI liquid operated at a rate of 20 mA g^{-1} . The graphite ($10 \mu\text{m}$ size) electrodes were prepared with different polymers, i.e., PAA and PVdF.

pared with both binders. Highlighted XRD patterns of the fully reduced graphite electrodes are shown in Fig. 8. Interlayer distance of the graphite-PVdF is elongated from 0.336 to 0.386 nm, which is much wider interlayer distance than that of 0.369 nm for the first stage lithium intercalated graphite (LiC_6). The result suggests that BMP cations are intercalated into the graphite. It is not surprising result because the concentration of Li and BMP is 1.0 and ca. 3 mol dm^{-3} , respectively. Similar observation with the elongated interlayer distance related to the BMP intercalation can be found in the literature [12]. Since electrochemical potential (vs. Li/Li^+) of the BMP intercalation would be higher than that of lithium intercalation into graphite, it is speculated that the voltage plateau at approximately 1.0 V observed for the oxidation process could be originated from the deintercalation of BMP cations from the graphite.

In contrast, for the graphite-PAA, staging phenomena in relation to the graphite and Li are confirmed by XRD (Fig. 8) and Bragg reflections originated from BMP intercalation cannot be observed, which is also consistent with the galvanostatic reduction/oxidation curves without the additional voltage plateau. The

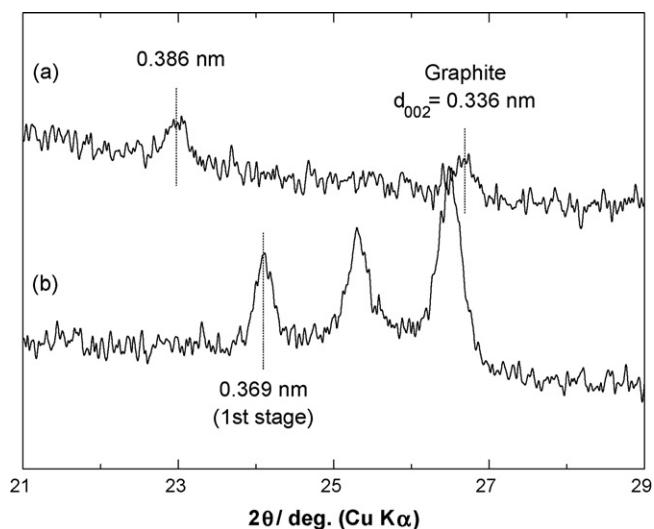


Fig. 8. Highlighted XRD patterns of the fully reduced graphite electrodes prepared with (a) PVdF and (b) PAA polymer binders in BMP-TFSI ionic liquid (1 mol dm^{-3} LiTFSI).

reason for successful intercalation of lithium ions by coating of PAA in ionic liquid, unlike PVdF binder, is considered as follows: (1) the strong electrostatic interaction between Li cations and TFSA anions, forming $[\text{Li}(\text{TFSA})_2]^-$ cluster [13], in ionic liquid, which could disturb the efficient lithium intercalation/deintercalation reaction including charge transfer reactions, is weakened at the graphite electrode/ionic liquid interface due to the negatively polarized oxygen in PAA polymer similarly to the desolvation process of PC as already mentioned and (2) BMP cations, which have lower positive charge density compared with lithium ions, could hardly interact with negatively polarized oxygen in the coated PAA layer, resulting in the preferential intercalation of lithium ions above BMP cations. The cycleability is also improved by the PAA binder. From these observations, we conclude that lithium ions are selectively and reversibly intercalated into the graphite without intercalation of BMP cations by the polyacrylate modifier.

4. Conclusion

We examined that the effect of the surface modification of graphite particles by PAA, PMA, and PVA polymer binders, which have functional groups containing oxygen atoms. It was demonstrated that the graphite electrodes prepared with these polymers can suppress the co-intercalation and decomposition of the solvating PC because of the electrostatic interaction of lithium cation with negatively charged oxygen atoms in uniformly coating polymer, resulting in the highly reversible lithium intercalation/deintercalation in LiClO_4 PC solution. The surface modification by these polymer binders is the beneficial method to improve the electrochemical activity in ionic liquid-based electrolyte solution (e.g., LiTFSI/BMP-TFSA). The PAA polymer layer suppresses BMP cation intercalation into the graphite, resulting in the selective and highly reversible lithium intercalation. It was proposed that electrostatic interaction, between lithium ions in the electrolyte solution and the unpaired electron at negatively polarized oxygen atoms of functional groups in the polymers, modulates the desolvation process of PC from the lithium ion upon the reduction process. We believe that the surface modification of the battery materials by the polymers in this study will be widely applicable to other electrode materials apart from Li intercalation/insertion compounds, e.g., electrochemical lithium alloying and conversion reactions. Further experimental works are in progress in our group to prove the intercalation mechanism.

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References

- [1] D. Aurbach, M. Koltypin, H. Teller, *Langmuir* 18 (23) (2002) 9000–9009.
- [2] T. Osaka, S. Komaba, M. Seyama, K. Tanabe, *Sensors and Actuators B: Chemical* 36 (1–3) (1996) 463–469.
- [3] T. Osaka, S. Komaba, A. Amano, Y. Fujino, H. Mori, *Sensors and Actuators B: Chemical* 65 (1–3) (2000) 58–63.
- [4] F. Mikami, M. Watanabe, S. Komaba, H. Yashiro, N. Kumagai, *The 46th Battery Symposium in Japan*, November 17, 2005, 2D-16, p. 494.
- [5] S. Komaba, K. Okushi, T. Ozeki, H. Yui, Y. Katayama, T. Miura, T. Saito, H. Groult, *Electrochemical and Solid State Letters* 12 (5) (2009) A107–A110.
- [6] S. Komaba, T. Ozeki, K. Okushi, *Journal of Power Sources* 189 (1) (2009) 197–203.
- [7] K.A. Hirasawa, K. Nishioka, T. Sato, S. Yamaguchi, S. Mori, *Journal of Power Sources* 69 (1–2) (1997) 97–102.
- [8] M.A. Ratner, D.F. Shriver, *Chemical Reviews* 88 (1) (1988) 109–124.

- [9] Z.X. Shu, R.S. McMillan, J.J. Murray, *Journal of the Electrochemical Society* 140 (6) (1993) L101–L103.
- [10] D.R. MacFarlane, P. Meakin, J. Sun, N. Amini, M. Forsyth, *Journal of Physical Chemistry B* 103 (20) (1999) 4164–4170.
- [11] Y. Katayama, T. Morita, M. Yamagata, T. Miura, *Electrochemistry* 71 (12) (2003) 1033–1035.
- [12] E. Markevich, V. Baranchugov, G. Salitra, D. Aurbach, M.A. Schmidt, *Journal of the Electrochemical Society* 155 (2) (2008) A132–A137.
- [13] Y. Umebayashi, T. Mitsugi, S. Fukuda, T. Fujimori, K. Fujii, R. Kanzaki, M. Takeuchi, S. Ishiguro, *Journal of Physical Chemistry B* 111 (45) (2007) 13028–13032.