Functional interface of polymer modified graphite anode

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ABSTRACT

Graphite electrodes were modified by polyacrylic acid (PAA), polymethacrylic acid (PMA), and polyvinyl alcohol (PVA). Their electrochemical properties were examined in $1 \, mol \, dm^{-3}$ $LiClO_4$ ethylene carbonate:dimethyl carbonate (EC:DMC) and propylene carbonate (PC) solutions as an anode of lithium ion batteries. Generally, lithium ions hardly intercalate into graphite in the PC electrolyte due to a decomposition of the PC electrolyte at ca. 0.8 V vs. Li/Li^+, and it results in the exfoliation of the graphene layers. However, the modified graphite electrodes with PAA, PMA, and PVA demonstrated the stable charge–discharge performance due to the reversible lithium intercalation not only in the EC:DMC but also in the PC electrolytes since the electrolyte decomposition and co-intercalation of solvent were successfully suppressed by the polymer modification. It is thought that these improvements were attributed to the interfacial function of the polymer layer on the graphite which interacted with the solvated lithium ions at the electrode interface.

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1. Introduction

Graphite exhibits a high specific capacity (theoretically $372 \, mAh \, g^{-1}$), low working potential close to that of lithium metal anode, and superior cycling performance as negative electrode of Li ion cells [1–4]. When graphite was used as the active material, the irreversible capacity inevitably appears at the initial cycle because the reductive decomposition of electrolyte occurs at electrolyte/graphite interface during the initial charge step including the formation of a passivation layer, so-called solid electrolyte interphase (SEI). The SEI layer plays an important role in reversible lithium intercalation into graphite. The SEI effectively suppresses the decomposition of electrolyte and the co-intercalation of solvent molecules, which allows the lithium intercalation into graphite. The kinetics of lithium intercalation are predominantly determined by the SEI, because lithium ions in an electrolyte must go through the SEI layer accompanied with the complex process of desolvation of solvated lithium ions [3,5,6].

Typical electrolyte solutions for lithium ion batteries are ethylene carbonate (EC)-based solutions. The EC-based electrolyte is difficult to use at low temperature as EC has very high melting point (ca. 37 °C), therefore, EC has to be mixed with a low melting point solvent, for example, dimethyl carbonate (DMC), diethyl carbonate, ethylmethyl carbonate, etc. On the other hand,

propylene carbonate (PC) freezes at much lower temperature of −49 °C, so that higher ionic conductivity than the EC-based electrolyte can be achieved at low temperature [7]. The application of the PC electrolyte is able to improve the low temperature performance of lithium ion batteries. However, the PC electrolyte has an essential problem, that is, lithium ions solvated with PC molecules co-intercalate into crystalline graphite, and it causes the exfoliation of graphene layers and the continuous decomposition of the PC electrolyte. These different lithium intercalation properties in the EC and PC electrolytes depend on their SEI forming ability. In the EC-based electrolyte, the stable SEI is formed during the first charge, and it enables the reversible lithium intercalation/deintercalation. On the contrary, the suitable SEI is not formed in the PC electrolyte. As previously reported, the electrochemical lithium intercalation properties of graphite anode in the PC based electrolyte were improved by dissolving film-forming additives into electrolyte, for example, 12-crown-4 [8], vinylene carbonate [9,10], chloroethylene carbonate [11], ethylene sulfate [12], and so on. These additives are decomposed at higher potential than that of the PC decomposition and lead to the formation of the suitable SEI to pass only lithium ion without solvents.

Recently, we reported that the modification of graphite by polyacrylic acid and alkali polyacrylates suppressed the decomposition and co-intercalation of PC molecules [13,14]. In this report, we investigate and compare the new interface modifiers such as polyacrylic acid (PAA), polymethacrylic acid (PMA), and polyvinyl alcohol (PVA) not only to bind graphite powders but also to mod-

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ify the electrode surface in comparison with the conventional polyvinylidene fluoride (PVdF) binder.

2. Experimental

Reagent grade natural graphite (particle size ca. 3 μm in diameter), 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. Battery grade lithium foil, EC, DMC, PC, and $LiClO_4$ were used without any further purification and treatment.

For preparation of working electrodes, the graphite powders were mixed with a binder of PVdF (10 wt%), PAA (15 wt%), PMA (15 wt%), or PVA (5 wt%) in N-methylpyrrolidone. 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 capacities of graphite. The slurry thus obtained was coated onto nickel mesh. The electrodes were dried at 120 °C in a vacuum state prior to use. The electrolytes were 1 mol dm^{-3} $LiClO_4$ in EC:DMC (1:1 by volume) and 1 mol dm^{-3} $LiClO_4$ PC. Three-electrode beaker type cell was assembled in argon filled grove box whose dew point was lower than −80 °C. Galvanostatic charge and discharge tests of the graphite electrode at 50 mA g^{-1} were carried out between 0.0 and 2.0 V vs. Li/Li$^+$ at 25 °C. To check the electrochemical stability of the polymers, Cu foils were coated with PAA, PMA, and PVA by using the polymer dissolved N-methylpyrrolidone solutions without graphite. Cyclic voltammetry (CV) was performed between 0.0 and 2.0 V at a sweep rate of 1 mV s^{-1}.

Electrode surface was observed by scanning electron microscopy (SEM) and X-ray photoelectron spectroscopy (XPS)
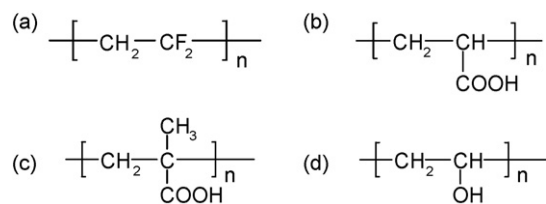

Fig. 1. Structures of polymers used as binder for graphite powder electrodes, (a) PVdF, (b) PAA, (c) PMA, and (d) PVA.

which were employed Al Kα as the incident X-rays, and depth profiling of XPS spectra was made by argon ion beam sputtering.

3. Results and discussion

Fig. 1 compares structures of the polymer binders. The modifiers used here, PAA, PMA, and PVA, have oxygen containing functional groups, that is, PAA and PMA have the carboxyl group, and PVA has hydroxyl group. Using these polymers as a binder, we were able to fabricate graphite powder electrodes like the conventional PVdF–graphite electrodes. Fig. 2 shows SEM images of the modified graphite electrodes before cycling. In all pictures, plate-like graphite particles were distinguishable. After the electrode fabrication with PAA, PMA, and PVA, graphite particles were bound and uniformly modified by polymer. The interfacial functionality was modified by the polymer as mentioned below.

To evaluate electrochemical stability of the polymers a CV measurement was performed in 1 mol dm^{-3} $LiClO_4$ EC:DMC. A working electrode was a copper foil coated with PAA film without graphite. Fig. 3 shows cyclic voltammogram at the first cycle. There is a pair
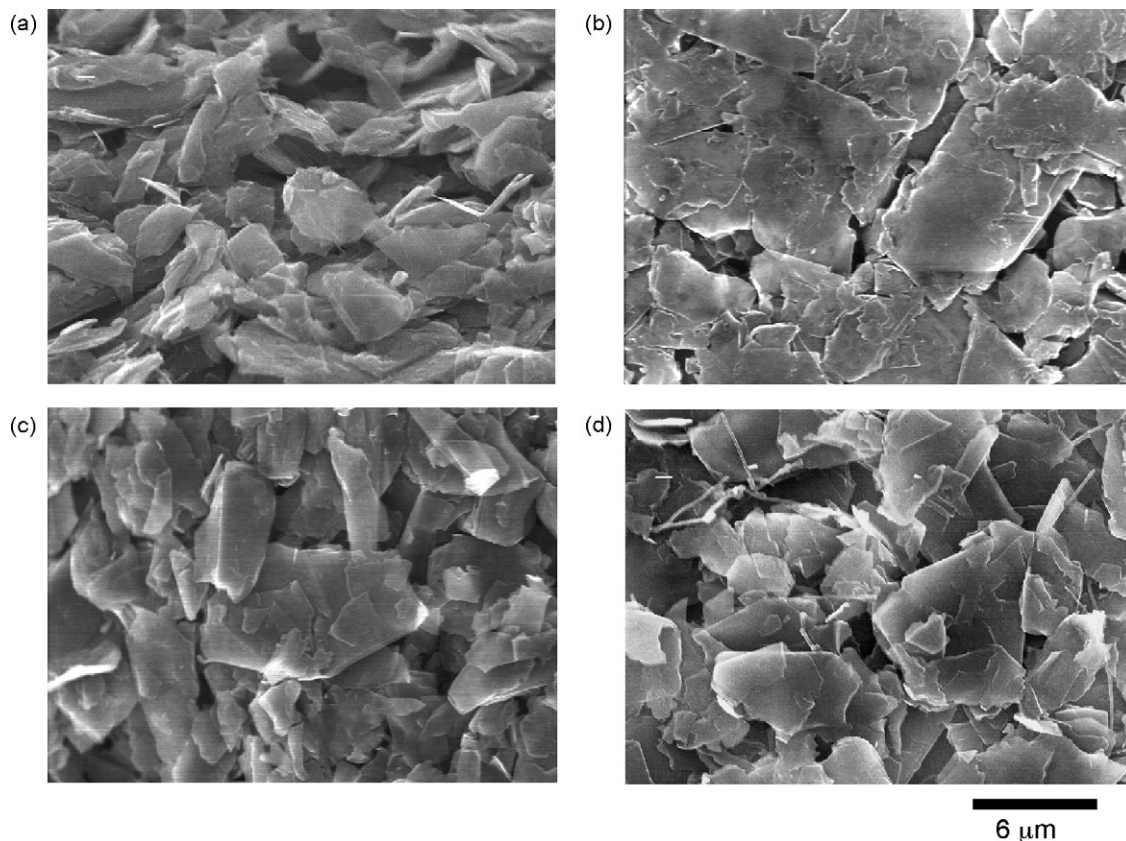

6 μm

Fig. 2. SEM images of graphite electrodes with (a) PVdF, (b) PAA, (c) PMA, and (d) PVA as binder.
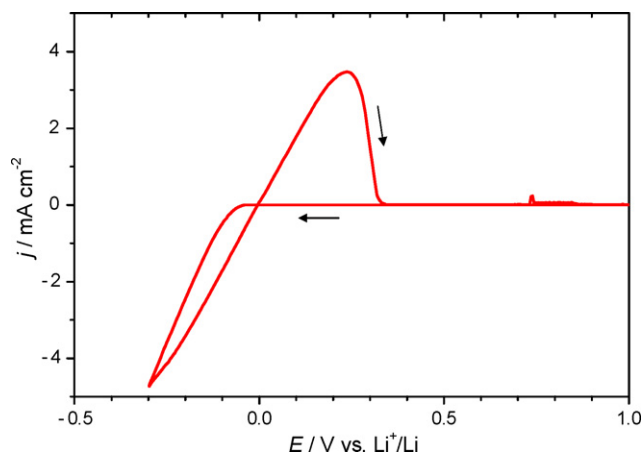
Fig. 3. Cyclic voltammogram of a PAA coated Cu foil at 1 mV s^{-1}.

Fig. 4. Initial charge and discharge curves of graphite electrodes with various binders in 1 mol dm^{-3} LiClO$_4$ EC:DMC electrolyte at 50 mA g^{-1}.

of redox currents, indicating lithium-metal deposition/dissolution around 0 V vs. Li+/Li. Since no additional current flowed in the voltammogram except for lithium deposition/dissolution, PAA would be electrochemically stable as a polymeric binder for negative electrode when lithium intercalation into graphite occurs around 0 V vs. Li/Li$^+$. In the case of PMA and PVA, the similar stability was confirmed by the voltammetry. In addition, we checked that these polymers are sufficiently insoluble in order to bind graphite powders in the EC:DMC or PC electrolyte. Consequently, these polymers were used as a binder of graphite electrodes to investigate the effect of polymer structures and functional groups on the graphite anode performance.

Fig. 4 shows the initial charge and discharge curves of graphite anodes at 50 mA g^{-1} in 1 mol dm^{-3} LiClO$_4$ EC:DMC electrolyte. Several reversible plateaus appeared in the region between 0.3 and 0.0 V vs. Li$^+$/Li, corresponding to the stage structures of Li intercalated graphite. These plateaus appeared in the both charge and discharge curves at the similar potential with the similar capacities, indicating the reversible intercalation of lithium. Although the shapes of the four discharge curves were quite similar, the charge curves were different around 0.8 V. In case of PVdF electrode, there was an obvious plateau that means the decomposition of electrolyte and formation of SEI at 0.8 V. This reaction led the irreversible capacity. However, the irreversible capacity was remarkably reduced by using PAA, PMA, and PVA as a binder. The
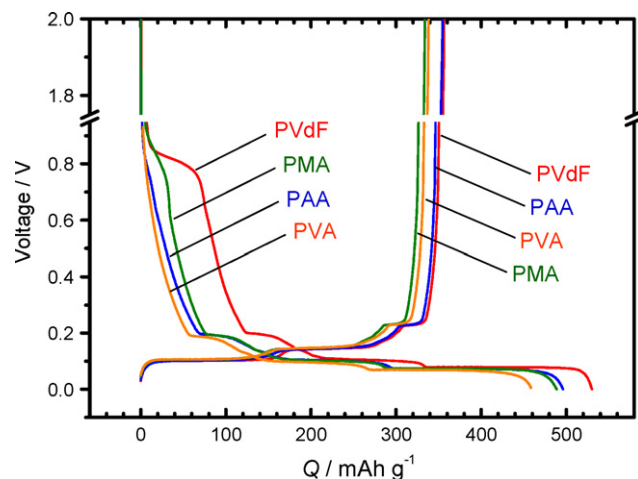
coulombic efficiencies at initial cycle are 67.2%, 71.5%, 68.3%, and 73.8% for PVdF, PAA, PMA, and PVA, respectively. It is probable that the suppressive effect was due to the electrolyte/electrode interface modification by the polymers.

Fig. 5 shows the variations of the capacities and efficiencies of the polymer modified graphites. The high discharge capacities were maintained over 30 cycles with satisfactory efficiencies for any electrodes in the EC:DMC electrolyte. The modification of graphite with the polymers did not suffer the reversibility and cycleablitiy of the lithium intercalation/deintercalation at all. The cycle performances were not significantly different among four electrodes.

Fig. 6 compares the electrode morphologies after the initial charge–discharge cycle. White deposits in micrometer size were dispersed on the surface of graphite as seen in Fig. 6, and they should be formed by the electrolyte decomposition. These particles should consist mainly of lithium carbonate [16]. Compared to the PAA, PMA, and PVA modified electrodes, a larger number of deposits appeared on the surface of the PVdF electrode. On the surface of the modified graphite, there are fewer amounts of the deposits, suggesting that the decomposition of electrolyte was suppressed by the PAA, PMA and PVA modifier.

The same electrochemical tests were carried out in the PC electrolyte as shown in Fig. 7. In the case of the PVdF electrode, a
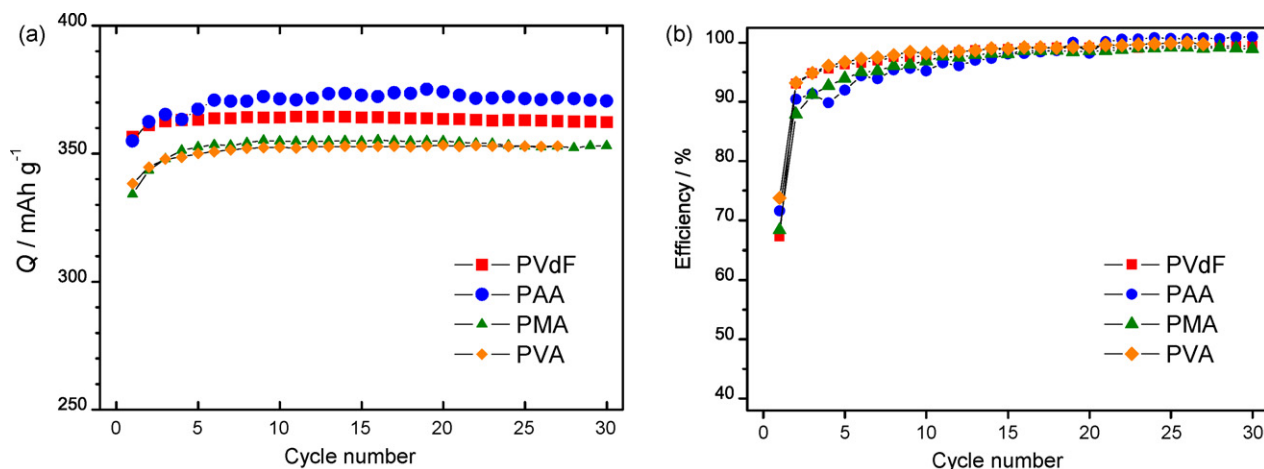

Fig. 5. Variation in (a) discharge capacities and (b) coulombic efficiency of graphite electrodes with four binders in 1 mol dm^{-3} LiClO$_4$ EC:DMC.
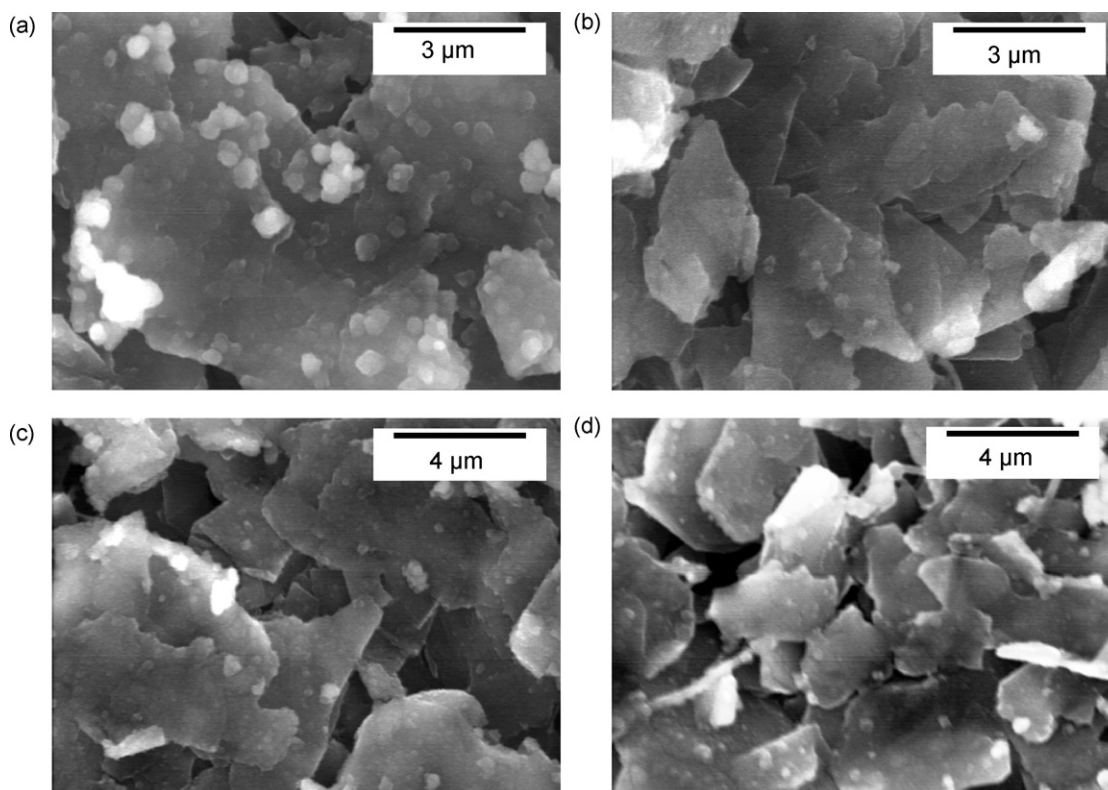
Fig. 6. SEM images of graphite electrodes with (a) PVdF, (b) PAA, (c) PMA, and (d) PVA binders after the first cycle in 1 mol dm^{-3} LiClO$_4$ EC:DMC.

long plateau appeared around 0.8–0.6 V during the initial charge process, and it was not observed during discharge. In the PC electrolyte, it is generally known that this irreversible reaction is due to the massive co-intercalation and decomposition of PC molecules, which resulted in the exfoliation of graphite. As a result, the PVdF electrode showed poor coulombic efficiency, 45.0%, at the first cycle. However, the PAA, PMA, and PVA electrodes did work in the PC electrolyte without the plateau at 0.8 V as well as the EC:DMC electrolyte as described in Fig. 4. We obtained the higher coulombic efficiencies of 81.1%, 73.8%, and 78.8% for the PAA, PMA, and PVA electrodes, respectively. Since the potential variation agrees with the formation of the lithium–graphite stage structures, there were no doubts that the reversible lithium intercalation/deintercalation
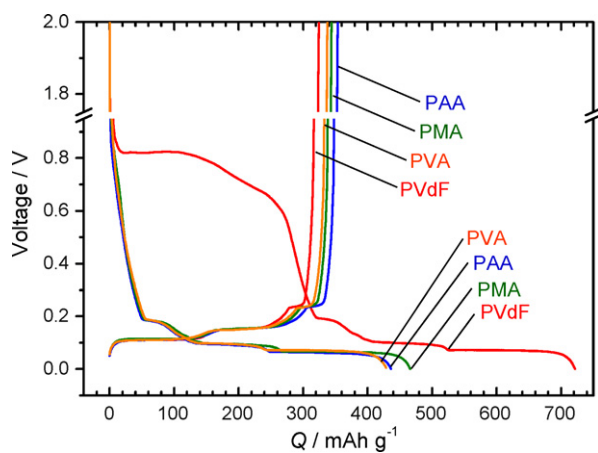
was achieved in the PC electrolyte. The PVdF electrode showed the lower discharge capacity, but it works in the PC electrolyte, which might be due to the size effect of graphite particles. According to [15], when graphite material consists of fine particles, the graphite electrode works as intercalation host even in the PC electrolyte.

As shown in Fig. 8, the discharge capacities depended on the polymers. The PVdF electrode exhibits the lower discharge capacities which are gradually reduced during the 30 cycles due to the gradual collapse of graphite. On the other hand, it was found that the graphite electrodes modified with PAA, PMA, and PVA demonstrated the higher discharge capacity and satisfactory cycle stability in the PC solution. The discharge capacities were maintained with sufficient efficiencies over 30 cycles for the PAA, PMA, and PVA modified graphite electrodes.

The electrode surface morphology after the initial charge–discharge cycle was observed by SEM in Fig. 9. For the PVdF electrode, the partial exfoliation of graphite was confirmed (marked in Fig. 9a). This corresponds to the appearance of the irreversible plateau at 0.8 V in Fig. 7, i.e. continuous decomposition and co-intercalation of PC molecules. However, the smooth graphite surface was kept after cycling for the PAA, PMA, and PVA, and no obvious deposits and no exfoliation were confirmed from the figures. Therefore, the polymer modification of graphite suppressed the co-intercalation and decomposition of PC molecules, and improved the lithium intercalation property.

The chemical circumstance of the graphite surface after galvanostatic cycling was investigated by XPS as is shown in Fig. 10. Etching the surface by argon ion sputtering for 10 s was carried out to observe the depth distribution. Before etching, hydrocarbon, alkyl carbonate (RCO$_2$Li), and lithium carbonate (Li$_2$CO$_3$) were simultaneously detected from the C 1s XPS spectra. These components were decomposition products of the electrolyte, indeed, it
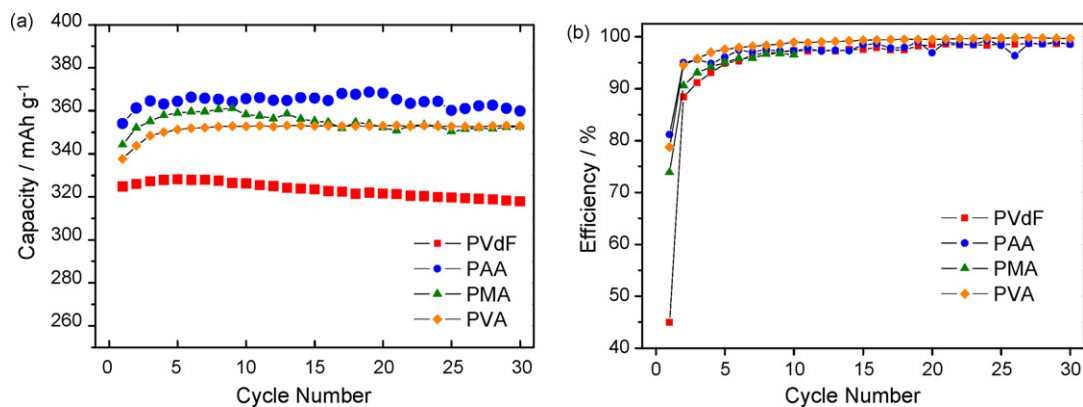

Fig. 7. Initial charge and discharge curves of graphite electrodes with different binders in 1 mol dm^{-3} LiClO$_4$ PC electrolyte.

Fig. 8. Variation in (a) discharge capacities and (b) coulombic efficiency of graphite electrodes with various binders in 1 mol dm^{-3} LiClO$_4$ PC.

was difficult to distinguish the decomposed products and polymers in the spectra because of the similarity of molecular structures. Since the polymer was stable against the electroreduction as mentioned in Fig. 3, the polymer for modification would be entrapped in these components, which gave us the effect to stabilize the SEI and lithium intercalation property.

From the above results, the effects of polymer modification were thought as follows. Generally, the desolvation of lithium ion must occur at the interface when lithium ion in an electrolyte solution intercalates into graphite, and the decomposition of the EC-based electrolyte at graphite electrode results in the irreversible capacity and the SEI formation at the initial reduction. This irreversible capacity was greatly suppressed for the PAA, PMA, and PVA graphite electrode in Figs. 4 and 7. As previously described [17,18], the graphite surface was partly uncovered with PVdF binder. Fig. 11 shows the XPS spectra of graphite electrodes before electrochemical investigation. Clearly, the peak intensity of graphite for the PAA electrode was remarkably weak compared to that of the PVdF electrode. This indicates that the graphite was uniformly covered with the polymers unlike PVdF, that is, the PAA, PMA, and PVA served

as glue, therefore, the polymer layers should act as a passivation film like the SEI layer. Even in the PC medium, the polymer layer did suppress co-intercalation and decomposition of PC molecules. It is generally known that small lithium ion in the electrolyte is strongly electrostatically coordinated with unshared electron pairs at the oxygen atoms of carbonate molecules, such as EC and PC. It is reasonable to think that the solvation-like bond is also possible between lithium ion and the polarized oxygen atoms along the coating polymer at the electrolyte/graphite interface, which is the same interaction as the solvation bonding between lithium cation and oxygen of solvent molecules. Generally, a solvation number for lithium cation in the conventional electrolyte solution was determined to be 3 or 4 [19,20]. If lithium ion was solvated with the polarized oxygen atoms of the polymer at the electrode interface, the solvation number of lithium ion with EC or PC molecules should be decreased, which might help the complete desolvation of lithium ion at the interface. As a result, the uniform polymer modification affected the lithium intercalation into graphite, especially, the suppression of the irreversible decomposition and the graphite exfoliation as mentioned above.
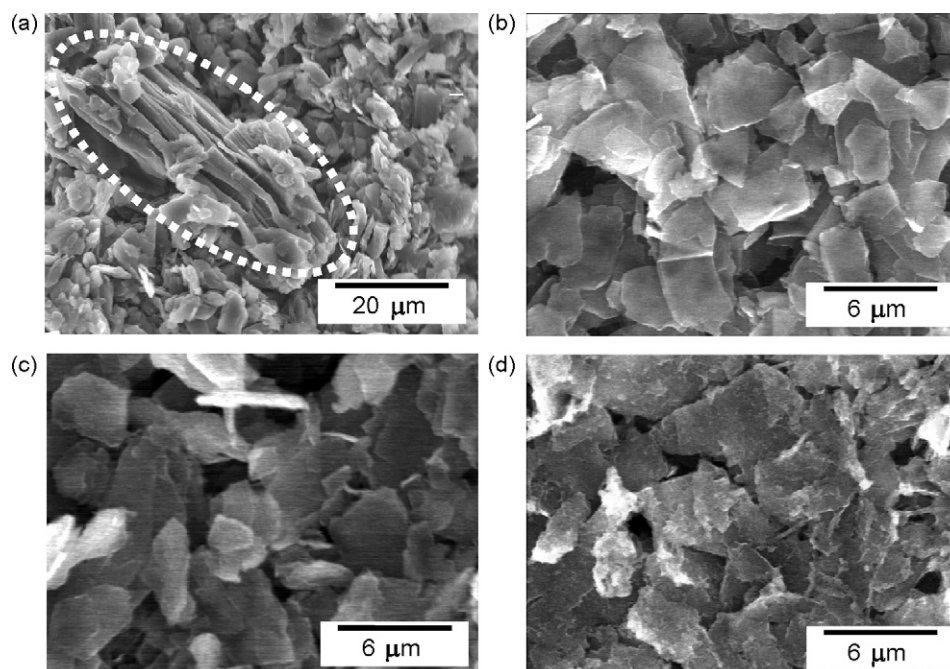

Fig. 9. SEM photos of graphite electrode surface with (a) PVdF, (b) PAA, (c) PMA, and (d) PVA after the first cycle in 1 mol dm^{-3} LiClO$_4$ PC.

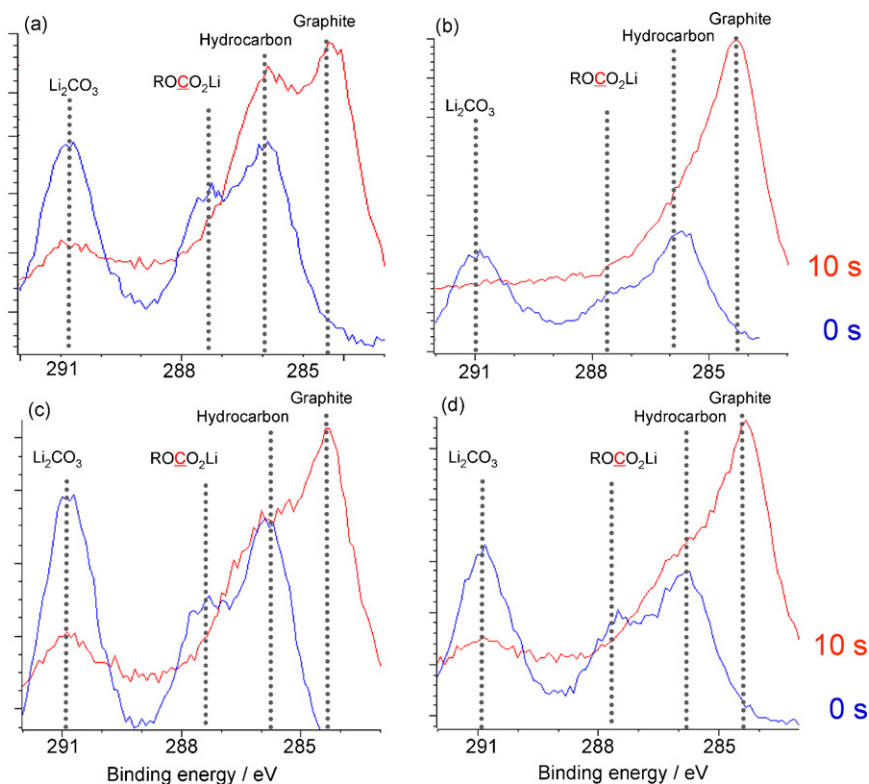**Fig. 10.** Carbon 1s XPS spectra of graphite electrodes with (a) PVdF, (b) PAA, (c) PMA, and (d) PVA binders after the first cycle in 1 mol dm^{-3} LiClO$_4$ PC.

In Fig. 12, the initial coulombic efficiencies are compared in the EC:DMC and PC media. For the conventional PVdF–graphite electrode, the efficiency in EC:DMC electrolyte was much higher than that in the PC electrolyte. Contrary, the modified graphite electrode cycled in the PC electrolyte exhibited the higher coulombic efficiency than that in the EC:DMC electrolyte. The difference would depend on the functionality at the interface which resulted from the chemically connected effects of solvent, lithium salt, graphite, and polymer modifiers. Further investigation of the electrolyte/graphite interface is in progress to analyze the interface structure.
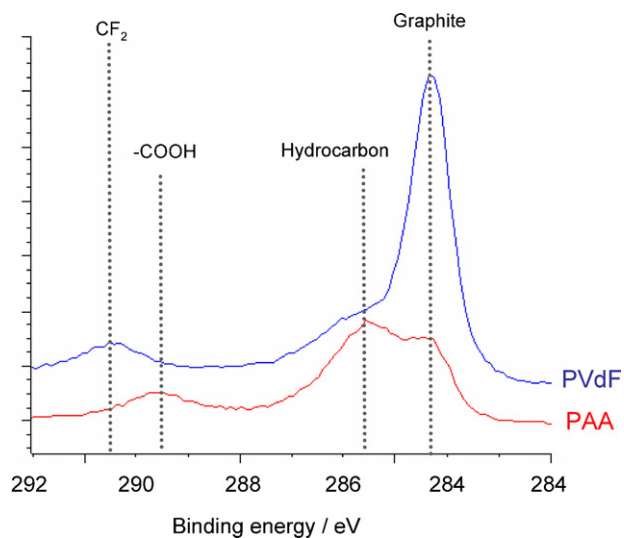

Fig. 11. Carbon 1s XPS spectra of graphite electrodes with PVdF and PAA binders before electrochemical tests.
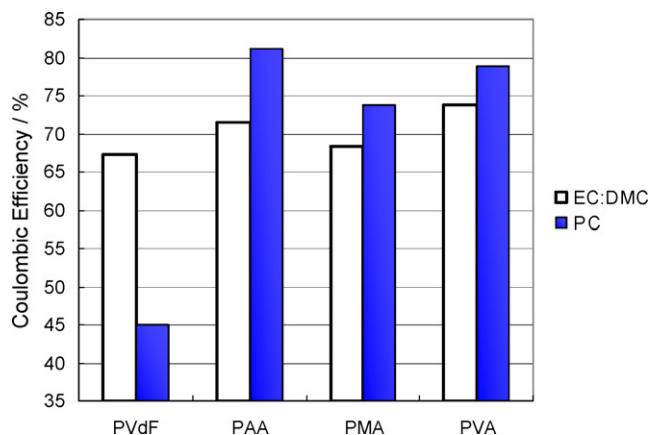

Fig. 12. Comparison of the initial coulombic efficiencies of graphite anodes with various polymer modifications in the EC:DMC and PC electrolytes.

4. Conclusion

The application of PAA, PMA, and PVA as a binder improved the initial coulombic efficiency of graphite anode compared to the PVdF binder in EC:DMC and PC electrolyte. Especially, the decomposition and co-intercalation of the PC electrolyte were not observed from charge–discharge tests in the PC electrolyte. XPS spectra showed the existence of the thin SEI on modified graphite surface, which implies polymers were entrapped in the SEI without their decomposition. The improvements are attributed to characteristic of the polymers and interaction between the oxygen in the polymers and lithium ion. This interaction would change the SEI formation process or desolvation barrier of electrochemical lithium intercalation.

Acknowledgement

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