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Anion receptor-coated separator for lithium-ion polymer battery

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Abstract Anion receptor-coated separators were prepared by coating poly(ethylene glycol) borate ester (PEGB) as an anion receptor and poly(vinyl acetate) (PVAc) as a good adhesive material towards electrodes onto microporous polyethylene (PE) separators. Gel polymer electrolytes were fabricated by soaking them in an liquid electrolyte, 1 M LiPF$_6$ in EC/DEC/PC (30/65/5, wt.%). As the weight ratio of PEGB to PVAc in a coating layer increased, gel polymer electrolytes showed higher cationic conductivity and electrochemical stability. The cationic conductivity and electrochemical stability of the gel polymer electrolyte based on coated separator with PVAc/PEGB (2/5, weight ratio) could reach 2.8×10^{-4} S cm^{-1} and 4.8 V, respectively. Lithium-ion polymer cells (LiCoO$_2$/graphite) based on gel polymer electrolytes with and without PEGB were assembled, and their electrochemical performances were evaluated.

Keywords PEG-borate ester · Anion receptor · Coated separator · Gel polymer electrolyte · Lithium-ion polymer battery

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Introduction

Anion receptors have recently been considered as a good component in the electrolytes for lithium secondary batteries, since they can form stable complexes with anions, and thereby enhance electrochemical and thermal stability of anions by suppressing the decomposition reaction of anions [1, 2]. They can also contribute to the increase of lithium ion transference number and dissociation fraction of lithium salt [3, 4]. These anion receptors have been used as an additive for liquid electrolytes [1–4] or a plasticizer or polymer matrix for polymer electrolytes [5–7]. In the former case, only small amounts of anion receptors with low molecular weight could be used in order not to increase the viscosity of liquid electrolytes. On the other hand, oligomers such as poly(ethylene glycol)-borate esters (PEGB) with various chain length could be introduced to polymer electrolytes because the viscosity of polymer electrolytes was not as important as that of liquid electrolytes. However, polymer electrolytes containing anion receptors as plasticizer or polymer matrix have not been commercialized due to their poor mechanical strength.

In order to give polymer electrolytes mechanical strength, separator-supported polymer electrolytes were manufactured by coating polymer electrolytes upon a microporous separator, and thereby could be commercialized as lithium-ion polymer batteries [8–10]. In this work, with this concept, new gel polymer electrolytes based on anion receptor-coated separator were prepared, and the influence of anion receptor on the transference number and electrochemical stability was investigated. In addition, the electrochemical performances of lithium-ion polymer cells composed of LiCoO$_2$/graphite were evaluated.

Experimental

Synthesis of PEGB

PEGB was synthesized by the dehydrocoupling reaction of poly(ethylene glycol) methyl ether (Mn=2,000, n=45, Aldrich) and BH_3/tetrahydrofuran (THF) complex solution (1 M, Aldrich) as described in Fig. 1 [11]. The produced PEGB was dried in a vacuum oven at 100°C for 24 h to remove residual THF and kept in a glove box. ^{1}H-NMR and Fourier transform infrared spectroscopy (FT-IR) were used to characterize the structure of PEGB.

Preparation and characterization of anion receptor-coated separators

Coating solutions were prepared by dissolving an appropriate amount of PEGB and poly(vinyl acetate) (PVAc, Mw= 500,000, Aldrich) with different weight ratios (7/0, 5/2, 4/3, 3/4, 2/5) in methanol. A microporous PE separator (Asahi-Kasei, thickness 20 μm) was immersed in each coating solution, and then taken out and left to evaporate the solvent at room temperature. After evaporation of the solvent, the coated separator was dried under vacuum for 24 h to remove the residual solvent and water trace. The thickness of coating layer was found to be about 5 μm. The surface morphology of separators was investigated by scanning electron microscopy (SEM) using the Philips SEM 535 M.

Preparation of lithium-ion polymer cells with gel polymer electrolytes based on coated separators

The gel polymer electrolytes were prepared by soaking the coated separators in a liquid electrolyte (1 M $LiPF_6$ in EC/ DEC/PC 30/65/5 wt.%, Cheil Industries), and then sandwiched between $LiCoO_2$ cathode and graphite anode for lithium-ion polymer cells. Both electrodes were also soaked in the same liquid electrolyte before cell assembly in order to fill the pores in the electrodes. The cells were finally packaged in an aluminized polyethylene bag and vacuum sealed in a glove box filled with argon.

The electrodes used in this work were fabricated as follows. The anode was prepared by coating a slurry containing 95 wt.% natural graphite and 5 wt.% poly (vinylidene fluoride) (PVdF, Elf Atochem) binder in N-methyl-2-pyrrolidone (NMP, Aldrich) on a copper foil. The cathode slurry consisting of 88 wt.% $LiCoO_2$, 6.8 wt.% Super-P (MMM carbon), and 5.2 wt.% PVdF binder in NMP was cast on aluminum foil. The dried electrodes were roll pressed to enhance both particle contact and adhesion to the current collector foils. The loading amount of cathode active material corresponded to a capacity of 2.4 mAh cm^{-2}.

Electrical measurements

The gel polymer electrolytes based on anion receptor-coated separators were sandwiched between the two stainless steel electrodes to measure ion conductivities. The ionic conductivities were obtained from bulk resistance measured by a.c. complex impedance analysis using a Solartron 1255 frequency response analyzer in combination with a Solartron 1287 electrochemical interface over frequency range of 100 Hz~1 MHz under amplitude of 10 mV. The transference number of lithium cation (t_{Li}) was investigated by means of the potentiostatic polarization measurement [12]. A constant polarization of 10 mV was applied to Li/Li symmetric cells. The transference number was calculated by the relation ($t_{Li} = I_s/I_0$). The electrochemical stability of gel polymer electrolytes was determined by linear sweep voltammetry experiment performed on a stainless steel (SS304) electrode as a working electrode with lithium as a reference electrode at a scanning rate of 2 mV s^{-1}.

The lithium-ion polymer cells (cell size: 2×2 cm^2) were cycled between 3.0 and 4.2 V at a constant current density (0.2C, 0.48 mA cm^{-2}) at room temperature using a TOSCAT-3000U instrument (Toyo System Co. Ltd). The charge process was cut-off at 20% of the initial constant current.

Fig. 1 Synthesis scheme of PEG-borate ester from borane-THF complex solution and poly (ethylene glycol) methyl ether by the dehydrocoupling reaction
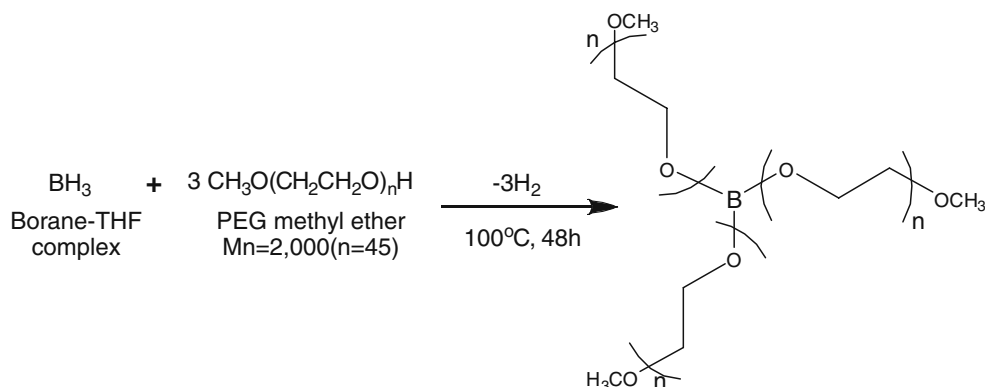
Table 1 Thicknesses, ion conductivities, transference numbers, and cationic conductivities of bare PE separator and coated separators with different PEGB contents in coating layer

Type	PEGB contents in coating layer	Thickness (μm)	σ (S cm^{-1})	Uptake amount (wt.%)[a]	t_{Li}	σ_{Li} (S cm^{-1})[b]
Bare	–	20±0.2	$(8.3\pm0.4)\times10^{-4}$	170±10	0.21±0.04	$(1.7\pm0.4)\times10^{-4}$
Coated	0%	25±0.4	$(11.0\pm0.3)\times10^{-4}$	210±7	0.20±0.03	$(2.2\pm0.3)\times10^{-4}$
	29%	25±0.4	$(9.8\pm0.2)\times10^{-4}$	206±5	0.24±0.03	$(2.4\pm0.3)\times10^{-4}$
	43%	25±0.4	$(9.3\pm0.2)\times10^{-4}$	199±6	0.27±0.03	$(2.5\pm0.3)\times10^{-4}$
	57%	25±0.4	$(8.7\pm0.2)\times10^{-4}$	192±5	0.30±0.03	$(2.6\pm0.3)\times10^{-4}$
	71%	25±0.4	$(8.6\pm0.2)\times10^{-4}$	183±5	0.32±0.03	$(2.8\pm0.3)\times10^{-4}$

[a] Uptake amount (wt.%)=$(W-W_0)/W_0\times100$

[b] $\sigma_{Li}=\sigma\times t_{Li}$

W and W_0 are the weights of the soaked and dried separators

Results and discussion

Among various anion receptors, PEGB was taken as a coating material for a PE separator because its chain length could be easily controlled by that of reactant, poly(ethylene glycol) methyl ether, as shown in Fig. 1. The chain length of PEGB must exceed the chain entanglement level for dimensional stability of coating layer even in case of being immersed in liquid electrolytes. For higher boron content in gel polymer electrolyte, on the contrary, it is desired that the chain length of PEGB must be as short as possible. With these reasons, PEGB with number average molecular weight (Mn) about 6,000 was synthesized and used in this work. PVAc was selected as a reference coating material due to its good affinity with liquid electrolytes and adhesive property towards electrodes [13]. The compatibility between PEGB and PVAc was confirmed by the existence of one glass transition temperature of PEGB/PVAc blend in DSC thermogram.

The ion conductivities of gel polymer electrolytes prepared by soaking the coated separators in a liquid electrolyte (1 M LiPF$_6$ in EC/DEC/PC 30/65/5 wt.%) are listed in Table 1. It is found that the ion conductivities of gel polymer electrolytes are higher than that of bare separator, which is closely related to the uptake amount of liquid electrolyte into separators. In case of coated separators, as the content of PEGB in the coating layer increases, the ion conductivities of gel polymer electrolytes gradually decrease due to the decrease of uptake amount and the suppression of anion migration. It may be originated from less dense structure of coating layer as shown in Fig. 2 and increase of anion receptor content, respectively. However, the transference numbers of gel polymer electrolytes increase with increase of PEGB
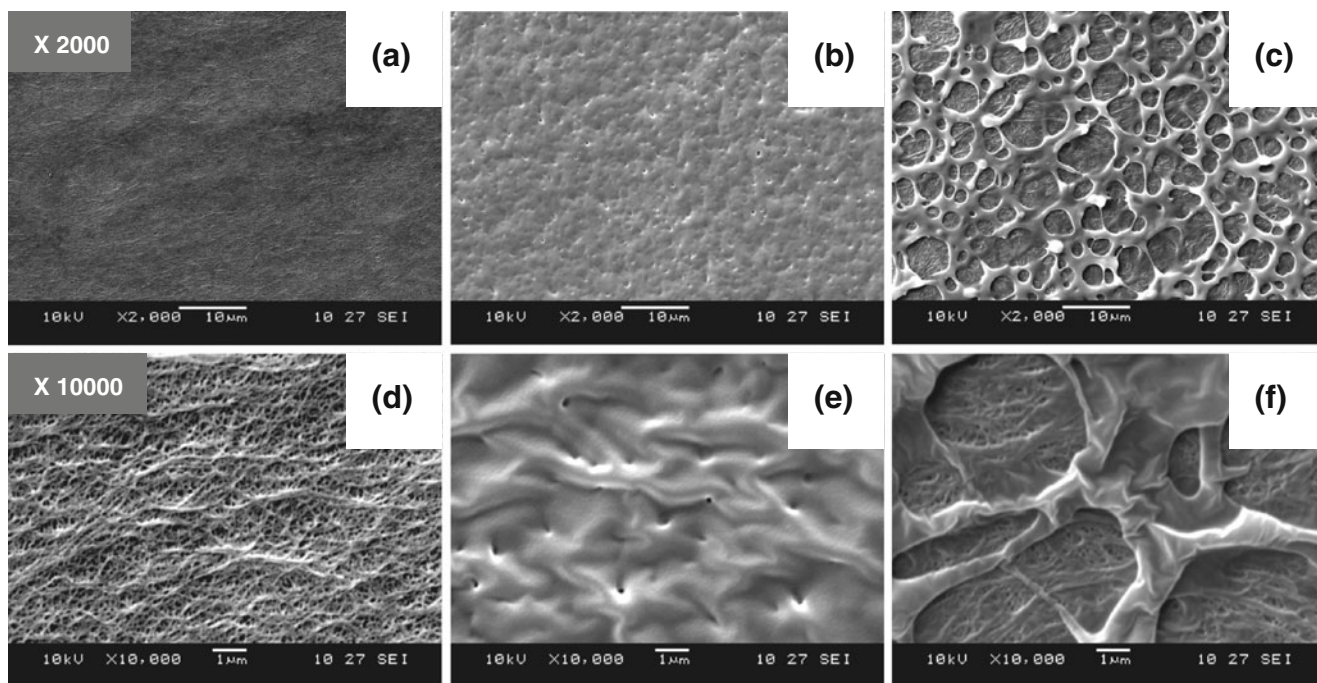

Fig. 2 Surface morphology of **a** PE separator (×2,000), **b** PVAc-coated PE separator (×2,000), **c** PVAc/PEGB (71 wt.% PEGB)-coated PE separator (×2,000), **d** PE separator (×10,000), **e** PVAc-coated PE separator (×10,000), **f** PVAc/PEGB (71 wt.% PEGB)-coated PE separator (×10,000)
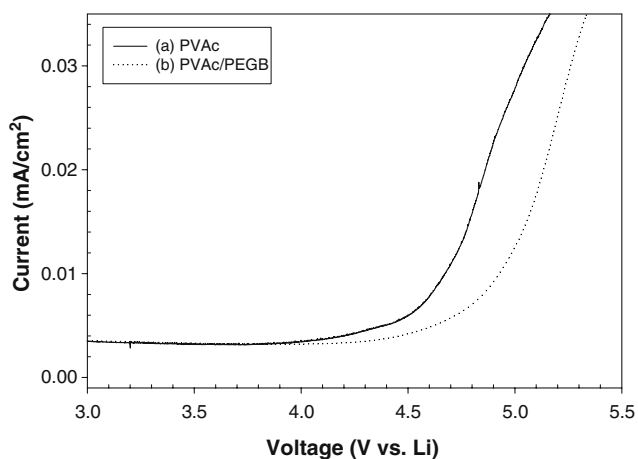
Fig. 3 Linear sweep voltammetry (LSV) curves of the cells with and without PEG borate ester as a coating layer material

Fig. 5 Discharge capacity as a function of cycle number at 0.2C rate for graphite/polymer electrolyte/LiCoO$_2$

content in coating layer. It is because PEGB in the coating layer may function properly as an anion receptor to suppress the migration of anions by forming the stable complexes with anions. As a result, even though gel polymer electrolytes with higher PEGB content showed lower ion conductivities, their cationic conductivities increased with increase of PEGB content due to much enhanced transference number. For the highest cationic conductivity, coated separator based on 71 wt.% PEGB was taken for further electrochemical experiments.

The surface morphology of the bare and coated separators is shown in Fig. 2. It is found that the microporous surface structure of bare separator is completely covered with coating materials in both coated separators. However, the morphology of coating layer in the coated separator with 71 wt.% PEGB became coarse and porous. It may be originated from lower molecular weight of PEGB than those of general polymers and the insufficient solubility of PEGB
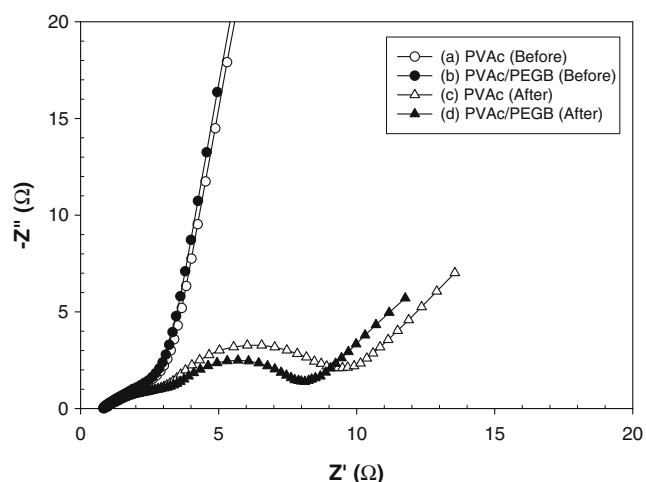

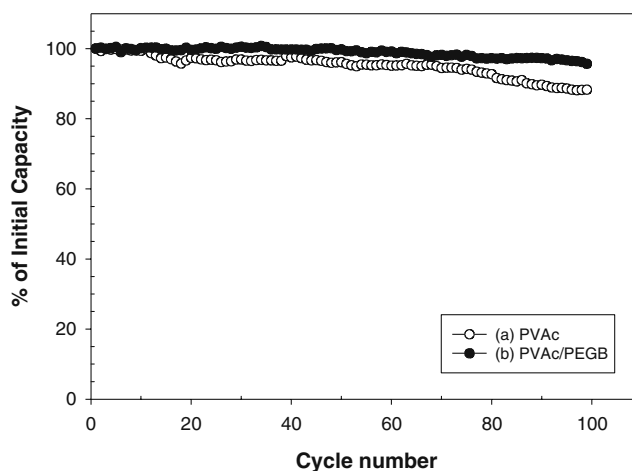Fig. 4 A.c. impedance spectra of graphite/polymer electrolyte/LiCoO$_2$ cell before and after precycling

in methanol. It is well-known that the phase separation between polymer and solvent is accelerated when the solubility of polymer in a solvent is poor and the evaporation rate of solvent is fast [14]. Large solvent-rich regions caused by phase separation during solvent evaporation process are changed to the pores of coating layers.

In order to evaluate the effect of PEGB on electrochemical stabilities of gel polymer electrolytes, linear sweep voltammetry experiments were performed. As shown in Fig. 3, electrochemical stability of gel polymer electrolytes with PEGB in a coating layer could be enhanced to 4.8 V, which was 0.3 V higher than gel polymer electrolyte without PEGB. It is considered that the initiation for the irreversible oxidative decomposition of PF$_6^-$ anions in the gel polymer electrolyte is delayed by the strong complex formation between anion receptors in the coating layer and anions. This interaction has been already confirmed by the previous researches of relative proportion change of free anions with Raman or FT-IR spectroscopy [4, 15]. In general, it is known that the wave number of symmetric stretch band of anions can be changed according to its states (free ion, contact ion pairs, multiple ion aggregates). From both previous literatures, the Raman and FT-IR spectra for the electrolytes showed the concentration of free anion increased with increasing the concentration of the anion receptor. Therefore, it is concluded that anion receptor in a coating layer of separator can also play a proper role in gel polymer electrolytes.

The electrochemical performances of lithium-ion polymer cells with and without PEGB in a coating layer were evaluated by cycle life test and impedance spectroscopy technique. Figure 4 shows the impedance spectroscopy of lithium-ion polymer cells before and after precycling. Before precycling, there is no effect of coating materials on resistances of unit cells. However, after precycling, the total resistance of lithium-ion polymer cell with PEGB is found to be lower

than that of lithium-ion polymer cell without PEGB, even though the initial capacities of both unit cells are similar. This difference is mainly originated from the anodic interfacial resistance at low frequency region, not from the bulk or the cathode interfacial one. When their anodic semicircles are fitted by resistance-capacitance parallel equivalent circuit, the interfacial resistance of lithium-ion polymer cell without PEGB(~8.5 Ω) is about 1.5 times higher than that with PEGB(~5.5 Ω). It means that less resistive solid electrolyte interphase (SEI) layer is formed on the surface of graphite anode of lithium-ion polymer cells with PEGB, since the decomposition of anions can be reduced by the formation of a stable anion and anion receptor complex. It is generally accepted that the decomposition products of anions such as LiF are more resistive than those of organic solvents [16, 17].

The discharge capacities as a function of cycle number of lithium-ion polymer cells with and without PEGB were shown in Fig. 5. The discharge capacity of lithium-ion polymer cell with PEGB retained about 95% of the initial discharge capacity after 100 cycles, on the other hand, that of lithium-ion polymer cell without PEGB about 88%. It is thought that the higher capacity retention ability of lithium-ion polymer cell with PEGB is mainly originated from lower interfacial resistance. Therefore, PEGB in a coated separator can properly function as an anion receptor thereby the electrochemical performance of lithium-ion polymer cell with PEGB can also be enhanced. In addition, this electrolyte system can be more attractive for cathode materials with higher voltage cut-off than 4.2 V.

Conclusions

PEGB, an anion receptor, was successfully introduced as a coating material for a PE separator. Gel polymer electrolytes based on anion receptor-coated PE separator showed higher cationic conductivity and electrochemical stability compared to those based on only PVAc-coated PE separator, which may be originated from the formation of stable complexes between anion receptors and anions. It also contributed to the formation of less resistive SEI layer by suppressing the decomposition reaction of anions on the electrodes. As a result, the cell performance was much improved compared to the cell without PEGB.

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