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Short communication

Cycling performance of a lithium-ion polymer cell assembled by in-situ chemical cross-linking with fluorinated phosphorous-based cross-linking agent

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ABSTRACT

Lithium-ion polymer cells composed of a carbon anode and a $LiCoO_2$ cathode are assembled with a gel polymer electrolyte cured by in-situ chemical cross-linking with novel cross-linking agents. The strong interfacial adhesion between the electrodes and the porous polyethylene membrane by the chemical cross-linking results in the stable capacity retention of the cell. However, a reduction in the ionic mobility in both the electrolyte and the electrodes adversely affects the high rate performance of the cell. These results imply that proper control of the cross-linking density in the cell is imperative for achieving good capacity retention and high rate performance of the cell.

1. Introduction

Lithium-ion polymer batteries that utilize gel polymer electrolytes have been widely developed for applications in portable electronic devices, hybrid electric vehicles, and load-leveling systems. Attempts to obtain gel polymer electrolytes consisting of a polymer, an aprotic solvent and a lithium salt have been producing materials with high ionic conductivity and electrochemical stability [1–7]. Although the ionic conductivities of such gel polymer electrolytes usually exceed $10^{-3}\,\mathrm{S\,cm^{-1}}$ at ambient temperature, their mechanical strength is not good. The insufficient mechanical strength of gel polymer electrolytes is one of the most critical deficiencies preventing their use in practical lithium batteries. In order to overcome this problem, a microporous polyolefin membrane has been employed as a dimensional support so as to enhance the mechanical strength of gel polymer electrolytes [8–15]. The impregnation of a gel polymer electrolyte into the pores of a membrane has mainly been carried out through dipping and in-situ polymerization. In all related studies, the inclusion of a polyolefin membrane offered improved protection against internal short circuits when compared to the use of a gel polymer electrolyte alone. In addition, the membrane helped reduce the overall thickness of the electrolyte when compared with the gel polymer electrolyte. In our recent work, cross-linked gel polymer electrolytes, supported by a microporous polyethylene membrane have been investigated for application in lithium-ion polymer batteries [15,16]. An electrolyte solution containing a cross-linking agent has been injected into the lithium-ion cell and gelation was carried out by heating the cell. With the aim of improving the capacity of the cell, a new fluorinated phosphorous-based cross-linking agent has been synthesized and applied for assembling the lithium-ion polymer cells. In this paper, the cycling performance of lithium-ion polymer cells assembled by in-situ chemical cross-linking with the new cross-linking agent is presented and discussed.

2. Experimental

2.1. Synthesis of the fluorinated phosphorous-based cross-linking agent

1H,1H,8H,8H-Perfluoro-3,6-dioxaoctan-1,8-diol (Exfluor Research Co., FTG) and acryloyl chloride (TCI. Co.) were used as-received. Phosphorous oxychloride (Aldrich, 99%) was purified by vacuum distillation prior to use. The fluorinated phosphorous-based cross-linking agent was synthesized by the reaction procedure, shown in Scheme 1. FTG (100 g, 0.34 mol) and triethylamine (41.29 g, 0.41 mol) were dissolved in anhydrous tetrahydrofuran (200 ml) at 0 °C under a flow of nitrogen. Acry-

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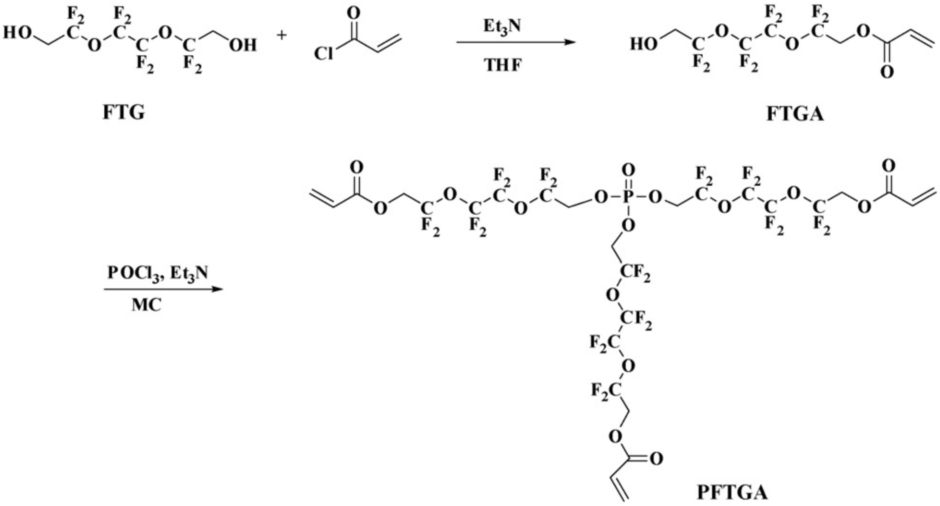

Scheme 1. Synthesis of the fluorinated phosphorous-based cross-linking agent (PFTGA).

loyl chloride (28.06 g, 0.31 mol) in tetrahydrofuran (100 ml) was added dropwise to the solution. After stirring for 12 h, the resulting solution was filtered in order to remove precipitates. The excess solvent was evaporated and the residue was purified by column chromatography (dichloromethane/hexane = 1:1 by volume) so as to obtain a colorless liquid of 2-(2-(1,1-difluoro-2-hydroxyethoxy)-1,1,2,2-tetrafluoroethoxy)-2,2-difluoroethyl acrylate (FTGA) with a 45% yield. FTGA (20 g, 5.74 mmol) and triethylamine (5.81 g, 5.74 mmol) were dissolved in anhydrous dichloromethane (150 ml) at 50 °C under a flow of nitrogen. Phosphorous oxychloride (2.93 g, 1.91 mmol) was then slowly added to this solution using a syringe pump. After stirring at room temperature for 12 h, the resulting reaction mixture was filtered off from the precipitate. The solvent was removed by evaporation and the reaction product was purified by column chromatography using dichloromethane/hexane (1:1 by volume) as an eluent (yield: 65%). The structure and purity of the PFTGA were confirmed by ^{1}H NMR, ^{13}C NMR, and ^{31}P NMR spectroscopy. ^{1}H NMR (300 MHz, $CDCl_3$, ppm): 4.36–4.45 (m, 2H, P–O–CH_2–CF_2), 4.52–4.58 (m, 2H, CF_2–CH_2–O–CHO), 5.95–5.99 (d, 1H, CH_2=CH–), 6.13–6.22 (m, 1H, CH_2=C*H*–), 6.49–6.54 (d, 1H CH_2=CH–). ^{13}C NMR (300 MHz, $CDCl_3$, ppm): 61.05 (3C, CF_2–CH_2–O–CHO), 64.77 (3C, P–O–CH_2–CF_2), 111.32, 113.58, 115.85 (6C, –O–CF_2–CF_2–O–), 117.30, 119.51, 121.80 (3C, –O–CF_2–CH_2–O–CHO), 118.36, 120.57, 122.78 (3C, P–O–CH_2–CF_2–O–), 125.91 (3C, CO–CH=CH_2), 132.30 (3C, CO–CH=CH_2), 163.49 (3C, O–CO–CH). ^{31}P NMR (125 MHz, $CDCl_3$, ppm): −3.13 (*P*–O–CH_2–).

2.2. Preparation of the gel polymer electrolytes and electrodes

In order to accelerate the in-situ chemical cross-linking reaction rate in the cell and to make a homogeneous precursor electrolyte solution, a mixture of PFTGA and trimethylolpropane triacrylate (80/20 by weight) was used as a cross-linking agent. Cross-linking agents and *t*-butyl peroxy-2-ethyl hexanoate (a thermal radical initiator) were added into the liquid electrolyte (1.0 M $LiClO_4$ in ethylene carbonate/dimethyl carbonate, 1/1 by volume). The gel polymer electrolyte was prepared by a radical-initiated reaction of the microporous polyethylene membrane (Asahi Kasei, thickness: 25 μm; porosity: 40%) soaked in a homogeneous precursor electrolyte solution. This precursor solution consisted of the cross-linking agent, a liquid electrolyte, and the thermal radical initiator. The electrolyte was cured at 90 °C for 20 min. In order to control the cross-linking density, the cross-linking agent was dissolved at different concentrations (0, 2.5, 5.0, 7.5, and 10.0 wt%) in the liquid electrolyte. The carbon anode was prepared by coating the N-methyl pyrrolidone (NMP)-based slurry of mesocarbon microbeads (MCMB, Osaka gas), poly(vinylidene fluoride) (PVdF), and super-P carbon (MMM Co.) on a copper foil. The cathode contained $LiCoO_2$ (Japan Chemical), along with the same binder and super-P carbon, which was cast on an aluminum foil. The thickness of the electrodes after roll pressing ranged from 55 to 70 μm, and their active mass loading corresponded to a capacity of approximately 2.9 mAh cm^{-2}.

2.3. Electrical measurements

Linear sweep voltammetry was performed in order to evaluate the electrochemical stability of the gel polymer electrolyte on a stainless steel working electrode. The measurements were carried out at a scanning rate of 1.0 mV s^{-1}, using lithium counter and reference electrodes. To measure the ionic conductivity, AC impedance measurements were carried out using an impedance analyzer over a frequency range of 100 Hz to 100 kHz with an amplitude of 10 mV. The lithium-ion polymer cell was assembled by sandwiching the microporous polyethylene membrane between the carbon anode and the $LiCoO_2$ cathode, which had previously been immersed in the electrolyte solution containing the cross-linking agents and the initiator. The cell was enclosed in a metallized plastic bag, then vacuum-sealed and aged at 90 °C for 20 min in order to induce in-situ thermal curing. Cell assembly was carried out in a dry box filled with argon gas. The charge and discharge cycling tests of the lithium-ion polymer cells were conducted using battery test equipment at 25 °C.

3. Results and discussion

Before applying the cross-linking agents into the cell, gel formation was confirmed by performing chemical cross-linking with different contents of the cross-linking agent. Fig. 1 shows images of the gel polymer electrolytes cured by different amounts of the cross-linking agent. Gelation was not detected for the electrolyte system cured by 2.5 wt% of the cross-linking agent. This result suggests that the content of the cross-linking agent should be higher than 2.5 wt% in the liquid electrolyte in order to induce thermal chemical cross-linking effectively in the cell.

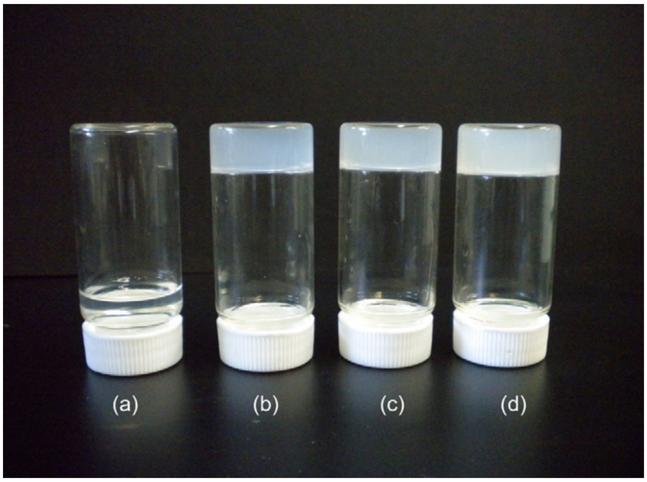

Fig. 1. Images of gel polymer electrolytes cured by different amounts of cross-linking agent. (a) 2.5 wt%, (b) 5.0 wt%, (c) 7.5 wt%, (d) 10.0 wt%.

The ionic conductivity of the gel polymer electrolytes supported by a porous PE membrane was measured as a function of cross-linking agent content; the results are shown in Fig. 2. The ionic conductivity of the liquid electrolyte was measured to be 7.9 mS cm^{-1}. The PE membrane soaked in the liquid electrolyte exhibited a reduced ionic conductivity of 0.56 mS cm^{-1}, because the presence of the PE membrane increased the effective resistance of the electrolyte. The ionic conductivities of the gel polymer electrolytes cured by the cross-linking agent decreased as cross-linking agent content increased. This result suggests that ionic motion is restricted with increasing cross-linking density.

The electrochemical stability of the gel polymer electrolytes was evaluated by linear sweep voltammetric measurements. Fig. 3 shows the linear sweep voltammetry curves of the cells prepared with either the liquid electrolyte or the chemically cross-linked gel polymer electrolytes cured by different amounts of the cross-linking agent. A rapid rise in current was observed at about 5.0 V vs. Li/Li$^+$ for the liquid electrolyte. The current continued to increase as the potential was swept. This behavior was associated with oxidative decomposition of the liquid electrolyte. On the other hand, the electrochemical oxidation of the cross-linked gel polymer electrolytes occurred in a slightly higher potential region than that of the liquid electrolyte, indicating that the electrochemical stability of the electrolyte was improved by chemically cross-linking the liquid electrolyte.

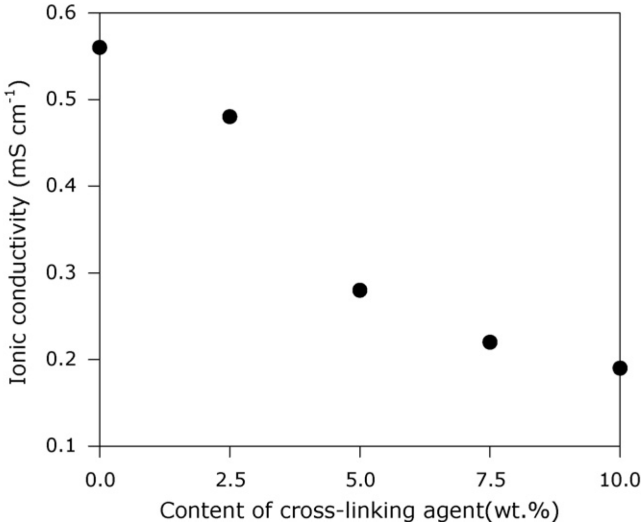

Fig. 2. Ionic conductivities, as a function of the content of cross-linking agent, of gel polymer electrolytes supported by a PE membrane.

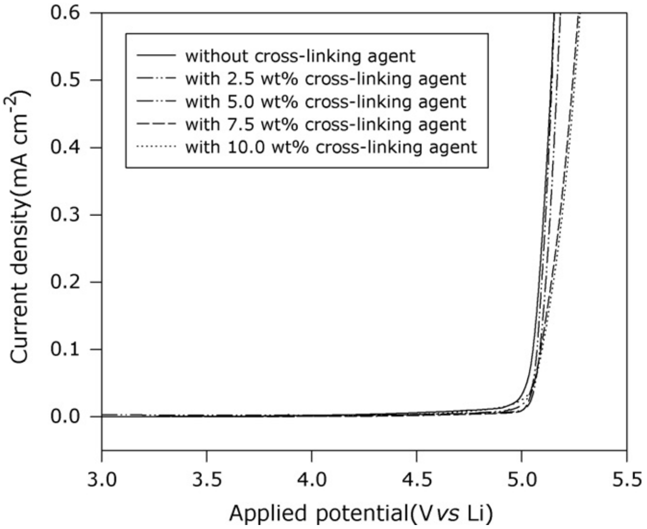

Fig. 3. Linear sweep voltammetry curves of cells prepared with liquid electrolyte and cross-linked gel polymer electrolytes (scan rate: 1 mV s^{-1}).

The cycling performance of the lithium-ion polymer cells assembled by in-situ chemical cross-linking was evaluated at 25 °C. The assembled cell was initially subjected to preconditioning cycles with cut-off voltages of 4.2 V for the upper limit and 2.8 V for the lower limit at a rate of 0.1 C (0.29 mA cm^{-2}). After three preconditioning cycles, the cell was charged at a current density of 1.45 mA cm^{-2} (0.5 C rate) up to the target voltage of 4.2 V. This was followed by a constant voltage charge with a decline in the current until a final current of 20% of the charging current was reached. The cell was then discharged down to a cut-off voltage of 2.8 V at the same current density (0.5 C rate). Fig. 4 shows the charge-discharge curves of the 1st, 10th, 50th, 100th and 200th cycle of a lithium-ion polymer cell assembled with the gel polymer electrolyte cured by

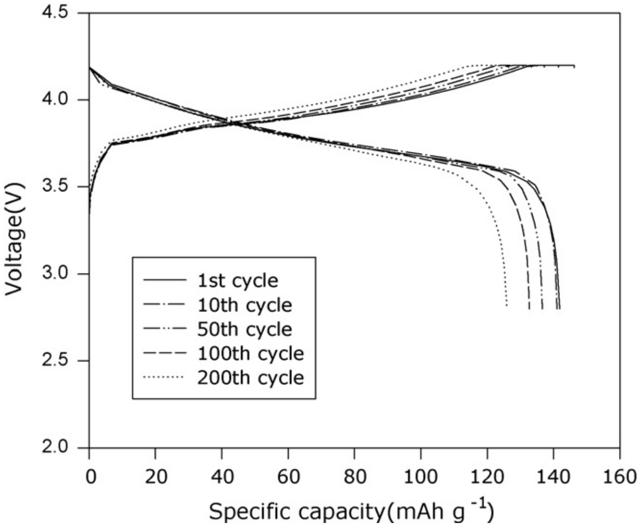

Fig. 4. Charge and discharge curves of a lithium-ion polymer cell assembled with a gel polymer electrolyte cured by 5 wt% of cross-linking agent. Cycling was carried out between 2.8 and 4.2 V at a current rate of 0.5 C and 25 °C.

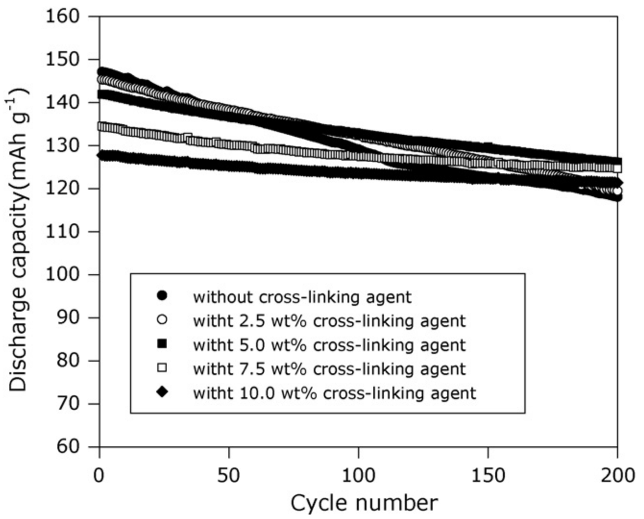

Fig. 5. Discharge capacities, as a function of the cycle number, for lithium-ion polymer cells assembled by in-situ chemical cross-linking with different amounts of cross-linking agent (cut-off: 2.8–4.2 V, 0.5 C rate).

5 wt% of cross-linking agent. The cell had a first discharge capacity of 141.9 mAh g^{-1} based on the $LiCoO_2$ active cathode material. The discharge capacity of the cell declined to 126.1 mAh g^{-1} after 200 cycles, which corresponds to 88.9% of the initial discharge capacity. The coulombic efficiency steadily increased with the cycle number and was maintained above 99.0% throughout cycling after the initial few cycles.

Fig. 5 shows the discharge capacity as a function of the cycle number in the cells prepared with the liquid electrolyte and the chemically cross-linked gel polymer electrolytes. It is clear that the cycling characteristics of the cells were dependent on the content of cross-linking agent. As can be seen in the figure, the initial discharge capacity of the cell decreased with increasing content of cross-linking agent. As mentioned earlier, a cross-linking reaction causes an increase in the resistance for ion migration in both the electrolyte and the electrodes. This results in a decrease in the discharge capacity. On the other hand, the capacity retention is improved with an increase in the degree of cross-linking. Compact interfacial contact between the PE membrane and the electrodes is critical for stable capacity retention. Upon gelation of the liquid electrolyte by thermal curing with the cross-linking agent, it becomes a gel polymer electrolyte and serves as an adhesive, chemically bonding the membrane and the electrodes and resulting in good capacity retention.

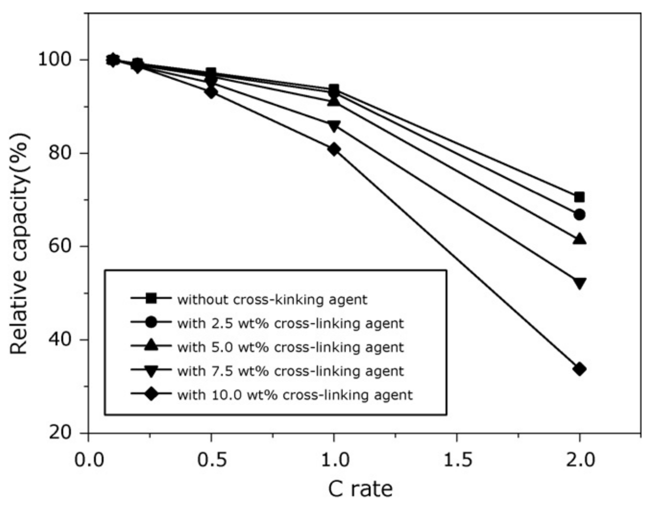

Fig. 6. Relative capacities, as a function of the current rate, of lithium-ion polymer cells assembled with and without cross-linking agent.

The rate capability of the lithium-ion polymer cell prepared with the gel polymer electrolyte cured by different amounts of cross-linking agent was evaluated. The cells were charged to 4.2 V at a constant current of 0.2 C and discharged at different current rates, from 0.1 to 2.0 C. The relative discharge capacities, as a function of the C rate, of lithium-ion cells prepared with the liquid electrolyte and the chemically cross-linked gel polymer electrolytes are compared in Fig. 6. In this figure, the relative capacity is defined as the ratio of the discharge capacity at a specific C rate to the discharge capacity delivered at a 0.1 C rate. It can be seen that the chemical cross-linking of the liquid electrolyte adversely affects the high rate performance. A reduction in the ionic mobility in both the electrolyte and the electrodes occurs as a result of the chemical cross-linking. This reduction hampers charge transport during the electrochemical reaction at both electrodes, even though the chemical cross-linking improves the interfacial adhesion. These results imply that proper control of the cross-linking density in the cell is imperative for achieving good capacity retention and high rate performance of the cell.

4. Conclusions

Lithium-ion polymer cells have been assembled with gel polymer electrolytes cured by in-situ chemical cross-linking with a mixture of fluorinated phosphorous-based triacrylate and trimethylolpropane triacrylate. The ionic conductivities of the gel polymer electrolytes cured by the cross-linking agent decreased as cross-linking agent content increased. However, the cross-linking reaction could promote strong interfacial adhesion between the electrodes and the membrane. As such, cells assembled by in-situ cross-linking exhibited a capacity retention that was more stable. For the cell assembled with the gel polymer electrolyte cured by 5 wt% of cross-linking agent, the discharge capacity was decreased from 142 to 126 mAh g^{-1} after 200 cycles. The chemical cross-linking reduced the ionic motion in both the electrolyte and the electrodes, resulting in a decrease in the discharge capacity at a high current rate. Thus, it can be concluded that a proper control of the cross-linking density in the cell is very important for achieving good capacity retention and high rate performance of the cell.

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