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Lithium polymer cell assembled by in situ chemical cross-linking of ionic liquid electrolyte with phosphazene-based cross-linking agent

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ABSTRACT

Ionic liquid-based cross-linked gel polymer electrolytes were prepared with a phosphazene-based cross-linking agent, and their electrochemical properties were investigated. Lithium polymer cells composed of lithium anode and $LiCoO_2$ cathode were assembled with ionic liquid-based cross-linked gel polymer electrolyte and their cycling performance was evaluated. The interfacial adhesion between the electrodes and the electrolyte by in situ chemical cross-linking resulted in stable capacity retention of the cell. A reduction in the ionic mobility in both the electrolyte and the electrode adversely affected discharge capacity and high rate performance of the cell. DSC studies demonstrated that the use of ionic liquid-based cross-linked gel polymer electrolytes provided a significant improvement in the thermal stability of the cell.

1. Introduction

Secondary lithium metal polymer batteries are being developed for high energy density power sources, because the lithium metal offers a very high specific capacity (3860 mAh g^{-1}) [1], which is more than ten times that of the currently used carbon anode. In these batteries, gel polymer electrolytes containing a large amount of organic liquid electrolyte exhibit high ionic conductivities exceeding 10^{-3} S cm^{-1} at room temperature, which is necessary for battery applications [2,3]. However, highly flammable organic solvents in the gel polymer electrolytes can cause fire or explosions in the event of short circuit or abuse. At present, ionic liquids are considered as one of the safest electrolytes to substitute for organic solvents used in lithium batteries [4–10]. Ionic liquids have several advantages over organic solvents: negligible vapor pressure, non-flammability, high oxidative stability and thermal stability. A good example of ionic liquid is 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (BMP-TFSI), which exhibits wide electrochemical stability and high ionic conductivity [11–17]. Since it is easily decomposed on the negative electrode at a positive potential relative to that of Li/Li$^+$, a small amount of solid electrolyte interphase (SEI)-forming additives should be added in order to form an electrochemically stable SEI on the electrode [17–19].

In this work, the cross-linked gel polymer electrolytes based on an ionic liquid containing SEI-forming additive were synthesized for applications in lithium polymer batteries with enhanced safety. BMP-TFSI was chosen as the ionic liquid, and vinylene carbonate (VC) was selected as the SEI-forming additive. In order to induce in situ chemical cross-linking reaction in the cell, a new phosphazene-based cross-linking agent with multiple oligo (ethylene oxide) acrylate functional groups was synthesized and used in the chemical cross-linking reaction. The electrochemical characteristics of the cross-linked gel polymer electrolytes based on ionic liquid are investigated, and the electrochemical performances of lithium polymer cells composed of lithium anode, cross-linked gel polymer electrolyte and lithium-cobalt oxide cathode are evaluated. More attention will be paid to the influence of the content of cross-linking agent on cycling performance of the lithium polymer cells.

2. Experimental

2.1. Synthesis of phosphazene-based cross-linking agent

Methacryloyl chloride (Aldrich, 97%) and 3,4-dihydro-*2H*-pyran (Aldrich, 97%) were distilled from anhydrous magnesium sulfate under vacuum onto molecular sieves. Hexachlorocyclotriphosphazene (99%), diethylene glycol (99%), pyridinium *p*-toluenesulfonate (99%) and sodium hydride dispersion in mineral oil (99%) were purchased from Aldrich. A cross-linking agent, hexakis(methacryloyl ethoxyethoxy) cyclotriphosphazene

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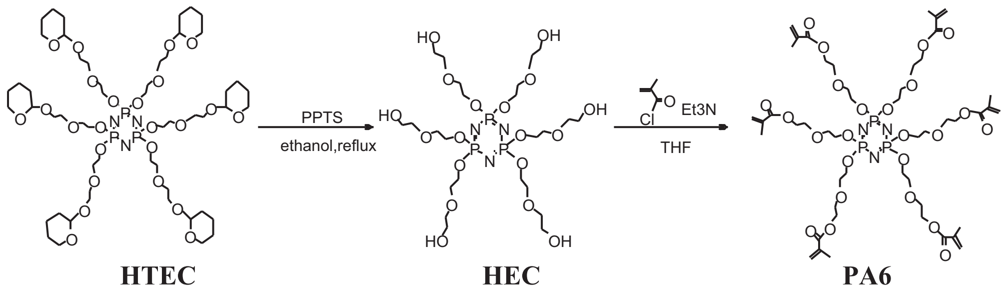

Fig. 1. Synthetic routes of star shaped cyclotriphosphazene cross-linking agent (PA6).

(PA6) was synthesized through two steps, as depicted in Fig. 1. Monoprotected diethylene glycol and hexakis(tetrahydropyran-2-yloxy)ethoxyethoxy cyclotriphosphazene (HTEC) were prepared according to procedures in the literature [20,21]. Pyridinium *p*-toluenesulfonate (1.576 mmol) was added to a solution of HTEC (1.576 mmol) in absolute ethanol (100 mL). The reaction mixture was stirred under N_2 and monitored by TLC using a solution of ethyl acetate and methanol. The solution was concentrated and chromatographed on a short pad of silica gel to get hexakis(ethoxyethanol)cyclotriphosphazene (HEC). To a solution of HEC (0.9 g, 1.18 mmol) and triethylamine (Et_3N, 3 mL) in THF (100 mL), methacryloyl chloride (2.22 g, 21.2 mmol) was added drop-wise from a syringe. The mixture was stirred at 30 °C overnight and $HCl{\cdot}Et_3N$ salts were removed by filtration. The resulting compound was purified by column chromatography (silica gel; with DCM/MeOH) to afford a pale yellow PA6 (0.97 g, 70.32%). ^1H NMR ($CDCl_3$), δ (ppm): 6.12 (s, 1H), 5.57 (s, 1H), 4.27 (t, 2H), 4.07 (t, 2H), 3.73 (t, 4H), 1.94 (s, 3H). ^{13}C NMR ($CDCl_3$), δ (ppm): 167.10, 135.92, 125.65, 69.84, 68.95, 64.88, 63.66, 18.14. ^{31}P NMR ($CDCl_3$), δ (ppm): 18.26 (s).

2.2. Preparation of gel polymer electrolytes

BMP-TFSI was purchased from Chem Tech Research Incorporation and was used after drying under a vacuum at 100 °C for 24 h. The water content in BMP-TFSI after vacuum drying was determined to be 8 ppm by Karl Fisher titration. The ionic liquid electrolyte was prepared by dissolving 1.0 M lithium bis(trifluoromethanesulfonyl) imide (LiTFSI, Aldrich) in BMP-TFSI. Anhydrous VC was added to the ionic liquid electrolyte at a concentration of 10.0 wt.%. PA6 and *t*-amyl peroxypivalate (Seki Arkema) as a thermal radical initiator were added into the ionic liquid electrolyte to prepare a precursor electrolyte solution. In order to control the cross-linking density, the cross-linking agent (PA6) was dissolved at different concentrations (0, 2, 4, 6 and 8 wt.%). The cross-linked gel polymer electrolyte was then prepared by a radical-initiated reaction of the homogeneous precursor electrolyte solution at 90 °C for 20 min. The temperature for thermal curing of PA6 was set to be 90 °C for efficient radical polymerization, and the reaction was completed within 20 min at that temperature, irrespective of content of cross-linking agent.

2.3. Electrode preparation and cell assembly

The cathode was prepared by coating the N-methyl pyrrolidone(NMP)-based slurry containing $LiCoO_2$ (Japan Chemical), poly(vinylidienefluoride)(PVdF) and super-P carbon (85:7.5:7.5 by weight) on an aluminum foil. The thickness of the electrodes after roll pressing ranged from 50 to 60 μm. The anode consisted of a 100 μm-thick lithium foil that was pressed onto a copper current collector. The lithium polymer cell was assembled by sandwiching the polypropylene (PP) separator (Celgard 2400) soaked with a precursor electrolyte solution between the lithium anode and the $LiCoO_2$ cathode. The cell was then enclosed in a metalized plastic bag and was vacuum-sealed. All assemblies of the cells were carried out in a glove box filled with argon gas. After the cell assembly, the cells were kept at 90 °C for 20 min in order to induce in situ thermal curing of the precursor electrolyte solution within the cell.

2.4. Electrical measurements

Linear sweep voltammetry (LSV) was performed in order to investigate the electrochemical stability of the cross-linked gel polymer electrolytes on a stainless steel working electrode with lithium metal as the counter and reference electrodes. The measurements were carried out at a scanning rate of 1.0 mV s^{-1}. AC impedance measurements were performed using a Zahner Elektrik IM6 impedance analyzer over a frequency range of 1 mHz to 100 kHz with an amplitude of 10 mV. Each sample was allowed to equilibrate for at least 2 h at each temperature before the measurements. Charge and discharge cycling tests of the cells were conducted at a constant current density of 0.2 mA cm^{-2} over a voltage range of 3.0–4.2 V using battery testing equipment (WBCS 3000, Wonatech) at 55 °C. In the differential scanning calorimetry (DSC) experiments, the cells were fully charged to 4.2 V after 50 cycles and were disassembled in a dry room. Approximately 5 mg of the cathode was scraped from the current collector and hermetically sealed in a stainless steel pan, where measurements were taken at a heating rate of 1 °C min^{-1}.

3. Results and discussion

Ionic liquid electrolytes with and without VC in this study were confirmed to be non-flammable, as reported earlier [17]. Before applying the precursor electrolyte solution into the cell, gel formation was confirmed by performing chemical cross-linking with different contents of the cross-linking agent. All precursor electrolyte solutions containing cross-linking agent became non-fluidic due to the formation of a three-dimensional polymer network, indicating that PA6 with multiple oligo(ethylene oxide) acrylate functional groups is very effective to induce the thermal cross-linking reaction of the ionic liquid electrolyte.

Fig. 2 shows the temperature dependence of ionic conductivities of the ionic liquid electrolyte and cross-linked gel polymer electrolytes. The ionic conductivities of the cross-linked gel polymer electrolytes decreased with increasing PA6 content at all temperatures. The cross-linking reaction causes an increase in the resistance for ion transport due to the formation of three-dimensional networks, which results in a decrease of the ionic conductivity with increasing cross-linking density. The ionic conductivities increased with increasing temperature due to enhancement of the ionic mobility at high temperature.

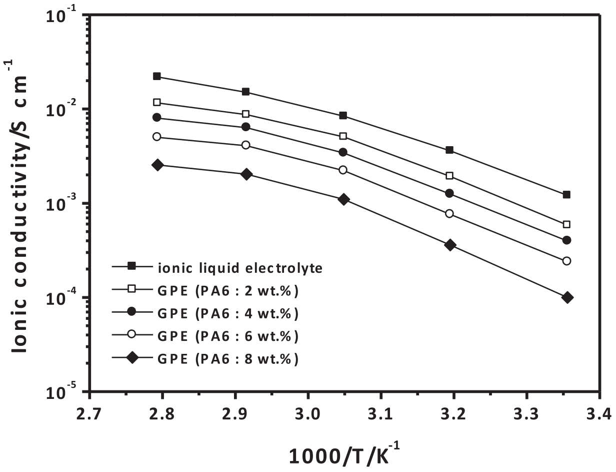

Fig. 2. Temperature dependence of ionic conductivities for ionic liquid electrolyte and cross-linked gel polymer electrolytes.

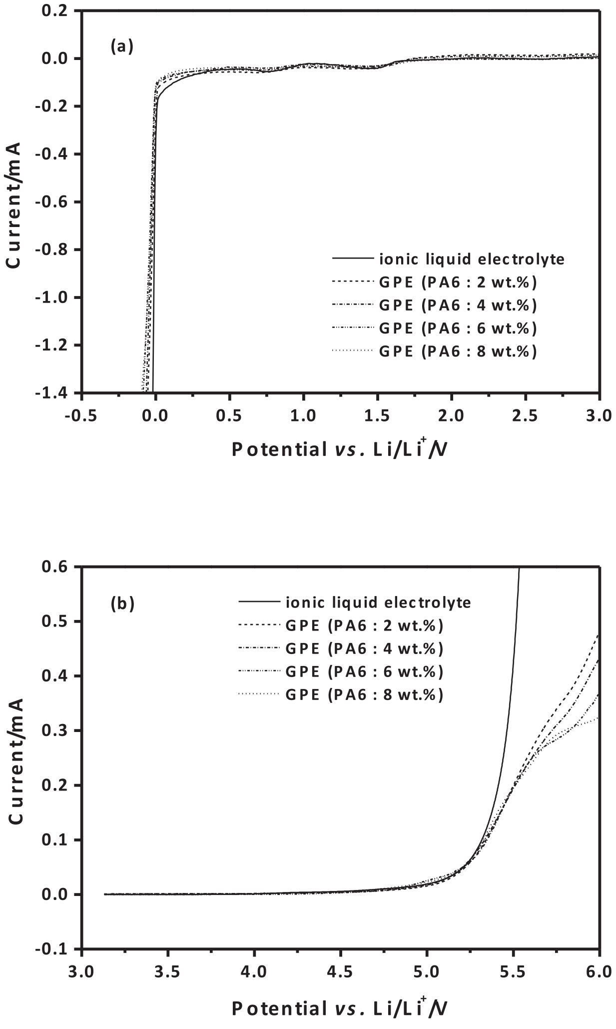

Fig. 3. Linear sweep voltammograms of the ionic liquid-based gel polymer electrolytes cured with different amounts of cross-linking agent: (a) cathodic and (b) anodic scans. In this figure, GPE is an abbreviation for gel polymer electrolyte.

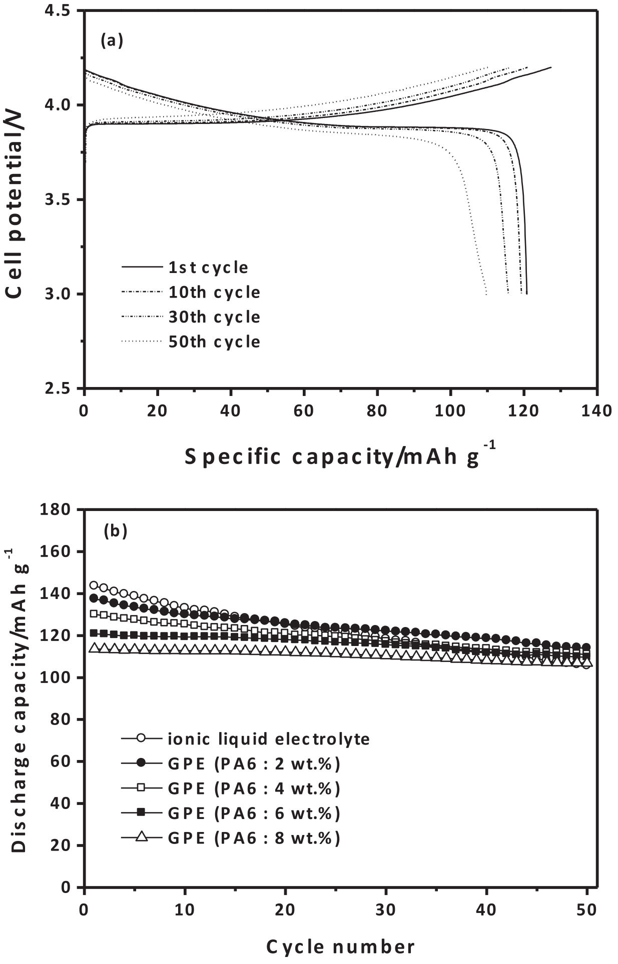

Fig. 4. (a) Charge and discharge curves of the Li/$LiCoO_2$ cell assembled with the gel polymer electrolyte cured by 6 wt.% cross-linking agent, and (b) discharge capacities as a function of cycle number for the Li/$LiCoO_2$ cells assembled with gel polymer electrolytes cured with different amounts of cross-linking agent.

The electrochemical stability of the cross-linked gel polymer electrolytes was evaluated by linear sweep voltammetric measurements. LSV curves of the cross-linked gel polymer electrolytes are shown in Fig. 3(a) and (b), which are obtained from cathodic and anodic scans, respectively. It has been reported that the BMP-TFSI without VC was reductively decomposed around 1.6 V vs. Li/Li$^+$ [22]. In case of ionic liquids with VC, the cathodic current starts to increase around 1.7 V vs. Li/Li$^+$, as shown in Fig. 3(a). This cathodic current can be attributed to the reductive decomposition of VC, which results in the formation of an SEI film on the electrode. The absence of a reduction peak associated with BMP-TFSI indicates that the SEI film formed by VC prevents reductive decomposition of the ionic liquid and kinetically extends its cathodic stability to 0 V vs. Li/Li$^+$. The small and broad reductive peak around 0.8 V vs. Li/Li$^+$ is probably due to LiTFSI impurities and water contamination, as previously reported [23,24]. Beyond this point, the large reductive current observed around 0 V vs. Li/Li$^+$ corresponds to the reductive deposition of lithium onto the electrode. With respect to anodic stability, the thermal curing of the ionic liquid electrolyte by PA6 hardly affected the oxidative stability of the cross-linked gel polymer electrolyte. All of the cross-linked gel polymer electrolytes exhibited oxidative stabilities higher than 5.0 V. Based on these results, it is expected that the ionic liquid-based cross-linked gel polymer electrolytes containing a small amount of VC have suitable electrochemical stability for electrochemical operation of Li/$LiCoO_2$ cells.

Cycling performance of lithium polymer cells assembled with cross-linked gel polymer electrolytes was evaluated. Fig. 4(a) shows the charge and discharge curves of the Li/$LiCoO_2$ cell cured with 6.0 wt.% PA6, which were obtained at a constant current density of 0.2 mA cm^{-2}. The cell delivered an initial discharge capacity of

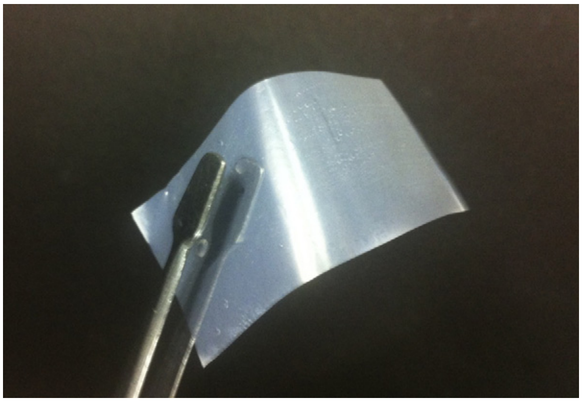

Fig. 5. Photograph of cross-linked gel polymer electrolytes supported by PP separator, which is cured by 6.0 wt.% cross-linking agent.

120.8 mAh g^{-1} based on a $LiCoO_2$ active cathode material, and the discharge capacity of the cell declined to 109.7 mAh g^{-1} after 50 cycles. The decline in the discharge capacity is related to the gradual growth of internal resistance of the cell during repeated cycling. Fig. 4(b) shows the discharge capacities as a function of the cycle number in the cells prepared with ionic liquid electrolyte or ionic liquid-based cross-linked gel polymer electrolytes. As shown in the figure, the initial discharge capacity of the cell gradually decreases with increasing cross-linking agent content, which arises due to the increased resistance for ion migration in both the electrolyte and the $LiCoO_2$ electrode. Accordingly, the initial discharge capacity is the lowest in the cell prepared with the cross-linked gel polymer electrolyte cured by 8 wt.% cross-linking agent. On the other hand, the capacity retention was improved by using the cross-linked gel polymer electrolyte. A large capacity decline in the cell with ionic liquid electrolyte may be related to a gradual exudation of electrolyte solution during cycling, which arises from poor compatibility between the PP separator and ionic liquid electrolyte. Other polymer separators that are compatible with ionic liquid are desirable for improving the cycling stability of ionic liquid-based cell. Upon gelling by thermal curing with the cross-linking agent, the ionic liquid electrolyte becomes a chemically cross-linked gel polymer electrolyte supported by a PP separator, as shown in Fig. 5. This allows effective encapsulation of the ionic liquid electrolyte in the cell as well as promotes good interfacial adhesion between the electrolyte and electrodes, which results in good capacity retention. This presumption can be confirmed from ac impedance measurements of the cells after repeated cycling. Fig. 6 shows the ac impedance spectra of the cells prepared with ionic liquid electrolyte or cross-linked gel polymer electrolytes. After charge and discharge cycles, ac impedance spectra showed a poorly separated semicircle. The overlapped semicircles observed from high to low frequency regions corresponds interfacial resistances, which are related to SEI film resistance and charge transfer process, respectively [25,26]. When comparing the interfacial resistance among the cells, the cells assembled by in situ chemical cross-linking have lower values than ionic liquid electrolyte-based cell. This result can be ascribed to good interfacial adhesion between electrolyte and electrodes, which is essential for efficient charge transport during charge-discharge cycling. However, increasing the content of cross-linking agent results in slight increase of interfacial resistance, which may be due to the suppression of ionic migration in the electrode, though it can promote strong interfacial adhesion between the electrodes and the electrolyte.

Rate capability of the $Li/LiCoO_2$ cells prepared with cross-linked 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 0.1 C and discharged at different current rates, from 0.1 to 2.0 C. Voltage profiles of the cell prepared with the gel polymer electrolyte cured by 6.0 wt.% cross-linking agent are presented in Fig. 7(a). It is found that both average discharge voltage and discharge capacity are decreased on increasing the current rate.

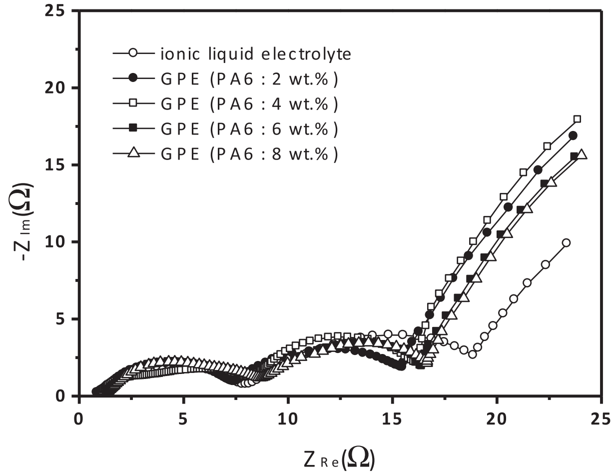

Fig. 6. AC impedance spectra of the $Li/LiCoO_2$ cells assembled with gel polymer electrolytes cured with different amounts of cross-linking agent, which are measured after the repeated 50 cycles.

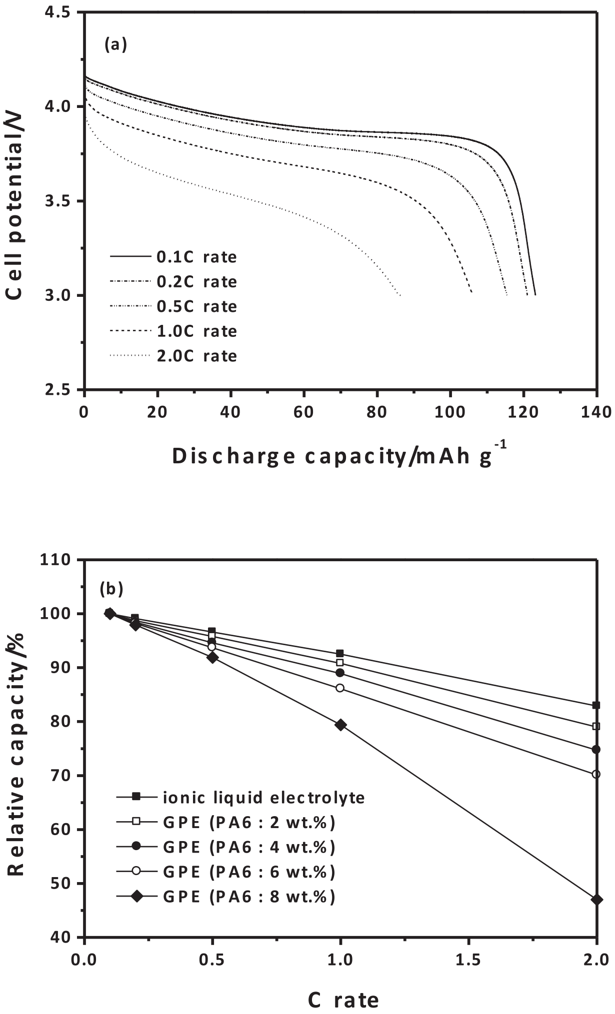

Fig. 7. (a) Discharge profiles of lithium polymer cell cured by 6 wt.% cross-linking agent at different current rates and (b) relative capacities of lithium polymer cells assembled with cross-linked gel polymer electrolyte as a function of the current rate.

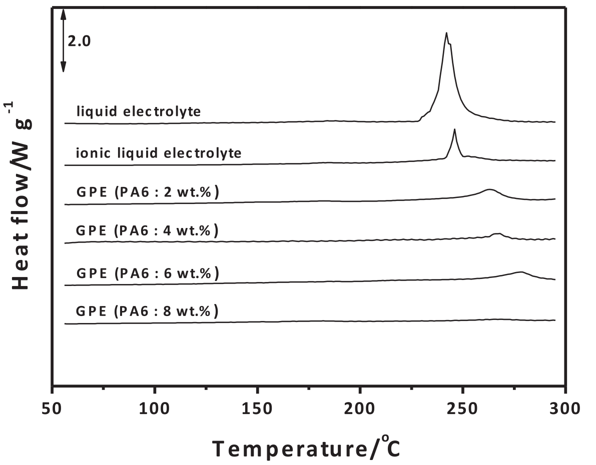

Fig. 8. DSC profiles of the $Li_{1-x}CoO_2$ cathode materials charged to 4.2 V after 50 cycles in the cells assembled with liquid electrolyte, ionic liquid electrolyte and ionic liquid-based cross-linked gel polymer electrolytes.

The discharge capacity is found to drop to 86 $mAh\,g^{-1}$ at 2.0 C rate, which corresponds to 70% of the capacity as delivered at 0.1 C rate. This result is not sufficient for high rate performance, and has to be improved. Fig. 7(b) shows the relative capacities of the $Li/LiCoO_2$ cells prepared with ionic liquid electrolyte and chemically cross-linked gel polymer electrolytes as a function of current rate. It can be seen that the chemical cross-linking of the ionic liquid electrolyte adversely affects the high rate performance. As discussed above, in situ chemical cross-linking with cross-linking agent may suppress the ionic migration in both electrolyte and electrode, even though it promotes interfacial adhesion between electrolyte and electrodes.

DSC measurements were performed to evaluate the thermal stability of the delithiated cathode material after repeated cycling in different electrolyte systems. Fig. 8 shows the DSC profiles of the cathode materials charged to 4.2 V, which are obtained after 50 cycles. A DSC thermogram of $Li_{1-x}CoO_2$ in the standard liquid electrolyte (1.0 M $LiPF_6$ in ethylene carbonate/diethylene carbonate, 5/5 by volume) is also included for comparison. The main exothermic peaks observed between 220 and 300 °C are associated with oxidation reactions of the electrolyte with oxygen released from the charged $Li_{1-x}CoO_2$ lattice [27–29]. The exothermic heat in ionic liquid electrolyte is (72 $J\,g^{-1}$) much lower than that measured for $Li_{1-x}CoO_2$ in the cell prepared with a liquid electrolyte (590 $J\,g^{-1}$). Moreover, the $Li_{1-x}CoO_2$ materials in the cell assembled with the cross-linked gel polymer electrolyte had smaller exothermic reaction, where the magnitude of the exothermic heat decreased with increasing content of cross-linking agent. It was also found that the peak temperature shifted to a higher temperature with increasing cross-linking agent content. These results suggest that the delithiated $Li_{1-x}CoO_2$ material is less reactive toward the ionic liquid-based cross-linked gel polymer electrolytes, leading to improved thermal stability.

4. Conclusions

Ionic liquid-based cross-linked gel polymer electrolytes were prepared with a phosphazene-based cross-linking agent, and their electrochemical properties were investigated. Using these gel polymer electrolytes, the lithium polymer cells composed of a lithium anode and a $LiCoO_2$ cathode were assembled and their cycling performances were evaluated. Both discharge capacity and high rate capability were decreased with increasing cross-linking density, however, the capacity retention was improved by using the cross-linked gel polymer electrolyte. DSC studies showed that the thermal stability of the delithiated $Li_{1-x}CoO_2$ electrode was significantly improved by applying the ionic liquid-based cross-linked gel polymer electrolytes.

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