

Lithium Polymer Batteries Assembled with *In situ* Cross-Linked Gel Polymer Electrolytes Containing Ionic Liquid

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Abstract: Chemically cross-linked gel polymer electrolytes containing ionic liquid were prepared and their electrochemical properties were investigated. Lithium polymer batteries composed of a lithium anode and a $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode were assembled using an *in situ* cross-linked gel polymer electrolyte and their cycling performances were evaluated. The optimum content of the cross-linking agent to ensure both high initial discharge capacity and good capacity retention of the lithium polymer battery was found to be about 4 wt%.

Keywords: cross-linking, cycling performance, gel polymer electrolyte, ionic liquid, lithium polymer battery.

Introduction

Rechargeable lithium polymer batteries using lithium metal as an anode material are one of the most attractive candidates for high energy density power sources in portable electronic devices, electric vehicles, and energy storage systems because the lithium metal offers the largest specific capacity ($\sim 3,860 \text{ mAh g}^{-1}$) as an active electrode material.¹ However, safety issues surrounding lithium polymer batteries must be addressed before they can be widely utilized, especially in large capacity applications, since highly flammable organic solvents in the gel polymer electrolytes can cause fire or explosions in the event of a short circuit or abuse. In the quest to develop a non-flammable electrolyte system, ionic liquids have been extensively studied and are recognized as one of the safest electrolytes in energy conversion devices such as lithium batteries and electrochemical capacitors.²⁻⁹ Ionic liquids have attractive properties including negligible vapor pressure, low flammability, high ionic conductivity, and high thermal stability. Ionic liquids are generally composed of organic ions that may undergo almost unlimited structure variations, and the selection of cation and anion has a drastic effect on their physicochemical properties.⁵⁻⁷ For lithium battery applications, great attention has been paid to ionic liquids composed of pyrrolidinium cations and bis(trifluoromethanesulfonyl) imide anions due to their reasonably wide electrochemical stability and high ionic conductivity.¹⁰⁻¹⁵ However, these ionic liquids easily decompose on the negative electrode at a positive potential relative to that of Li/Li^+ , which results in the formation of an unstable solid electrolyte interphase (SEI) on the electrode.

One of the most efficient ways to form an electrochemically stable SEI is to use SEI-forming additives such as vinylene carbonate (VC), ethylene carbonate (EC), fluoroethylene carbonate (FEC), and 1,3-propane sultone (PS), which tend to decompose on the anode surface before reductive decomposition of the ionic liquid during charging.¹⁶⁻²¹ Gel polymer electrolytes have been actively studied and developed for application in rechargeable lithium batteries.²²⁻²⁵ In this work, the ionic liquid electrolyte containing SEI-forming additive was encapsulated in the cross-linked polymer network, because the poor mechanical strength of physically gelled polymer electrolytes can lead to internal short-circuit and safety hazard in practical lithium batteries. Various inorganic materials such as LiCoO_2 , LiNiO_2 , LiMn_2O_4 , $\text{LiNi}_x\text{Co}_y\text{Mn}_{1-x-y}\text{O}_2$, and LiFePO_4 have been developed and applied as the cathode material in lithium polymer batteries. Among these materials, $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ is of particular interest as an active cathode material because of its high capacity, good structural stability and relatively low cost.²⁶⁻³⁰

With the goal of developing high energy density lithium batteries with improved safety, we assembled lithium polymer batteries composed of a lithium anode, an ionic liquid-based cross-linked gel polymer electrolyte and a $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode, and evaluated their cycling performances. In this work, 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide (BMP-TFSI) was chosen as the ionic liquid, and vinylene carbonate (VC) was selected as the SEI-forming additive. The cross-linked gel polymer electrolytes were synthesized by *in situ* chemical cross-linking in the cells, and the effect of the cross-linking agent content on the electrochemical performance of the cells was investigated.

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Experimental

Synthesis of Cross-Linked Gel Polymer Electrolytes.

BMP-TFSI was purchased from Chem Tech Research Incorporation and was used after drying under vacuum at 100 °C for 24 h. The water content remaining in the 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, Sigma Aldrich) in BMP-TFSI. Anhydrous VC was added to the ionic liquid electrolyte at a concentration of 10 wt%, as a SEI-forming additive. Poly(ethyleneglycol) dimethacrylate (PEGDMA, $M_n=550$, Sigma Aldrich) and *t*-amyl peroxyvalate (Luperox 554M75, Seki Arkema) were used as the cross-linking agent and initiator, respectively. In order to control the cross-linking density, the cross-linking agent was added to the ionic liquid electrolyte at different concentrations (2, 4, 6, 8, and 10 wt%). The cross-linked gel polymer electrolyte was prepared by radical reaction of the microporous polypropylene (PP) separator (Celgard®2400, thickness: 25 μm) soaked with a homogeneous precursor solution consisting of ionic liquid electrolyte, cross-linking agent and initiator at 90 °C for 70 min.

Electrode Preparation and Cell Assembly. $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ powders were synthesized by a co-precipitation method, as described previously in detail.²⁸ The cathode was prepared by coating the *N*-methyl pyrrolidone (NMP)-based slurry containing $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, poly(vinylidene fluoride) (PVDF), and super-P carbon (85:7.5:7.5 by weight) on an aluminum foil. The electrode thicknesses ranged from 50 to 60 μm after roll pressing, and active mass loading corresponded to a capacity of about 1.6 mAh cm^{-2} . 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 PP separator soaked with a precursor electrolyte solution between lithium anode and $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode. The cell was then enclosed in a metalized plastic bag and vacuum-sealed. All assemblies of the cells were carried out in a glove box filled with argon gas. After the cell assembly process, the cells were kept at 90 °C for 70 min in order to induce *in situ* thermal curing of the precursor electrolyte solution within the cell. The *in situ* cross-linking enabled to the separator firmly bond both electrodes together in the cell, as shown in Figure 1.

Measurements. Linear sweep voltammetry (LSV) was performed in order to investigate the electrochemical stability of the ionic liquid-based 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} . In order to determine the ionic conductivities of the gel polymer electrolytes supported by the microporous PP separator, AC impedance measurements were performed using a Zahner

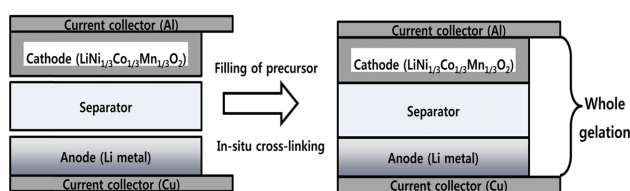


Figure 1. Schematic diagram of lithium polymer battery before and after *in situ* chemical cross-linking of a precursor electrolyte solution.

Elektrik IM6 impedance analyzer over a frequency range of 10 Hz 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 0.32 mA cm^{-2} (0.2 C rate) over a voltage range of 3.0–4.3 V using battery testing equipment (WBCS 3000, Wonatech) at 55 °C. In the differential scanning calorimetry (DSC) experiments, the cells were fully charged to 4.3 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} . In order to investigate the flammable behavior of ionic liquid electrolyte solution, an inert glass-fiber wick was soaked with the electrolyte solution, and it was ignited with flame source for 10 s. The electrolyte was judged to be non-flammable if the electrolyte never ignited during the testing, or if the ignition of electrolyte ceased when the flame source was removed.³¹

Results and Discussion

The flammability of the ionic liquid electrolyte with and without VC was investigated. None of the ionic liquid electrolytes showed any combustion, which means all the ionic liquid electrolytes are non-flammable. Before applying the ionic liquid-based cross-linked gel polymer electrolyte into the $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell, gel formation was visually confirmed by performing a chemical cross-linking reaction with different cross-linking agent contents. Figure 2 shows images of the ionic liquid-based cross-linked gel polymer electrolytes cured with different amounts of the cross-linking agent. Clearly, the electrolyte becomes non-fluidic due to the formation of three-dimensional polymer networks after cross-linking. However, complete gelation was not detected for the ionic liquid electrolyte systems cured by 2 wt% cross-linking agent. This result suggests that the content of the cross-linking agent should be greater than 2 wt% in the ionic liquid electrolyte to effectively induce the thermal chemical cross-linking reaction in the cell.

Figure 3 shows the ionic conductivity of the ionic liquid-based cross-linked gel polymer electrolytes supported by PP

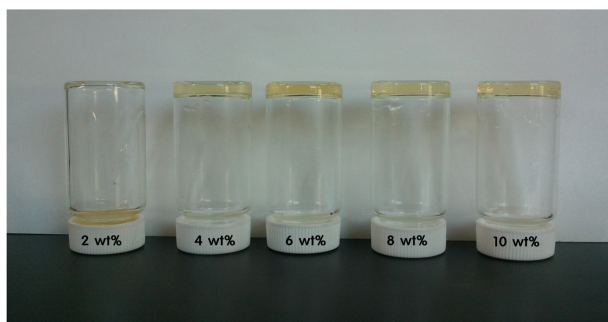


Figure 2. Photographs of ionic liquid-based gel polymer electrolytes cured with different amounts of cross-linking agent.

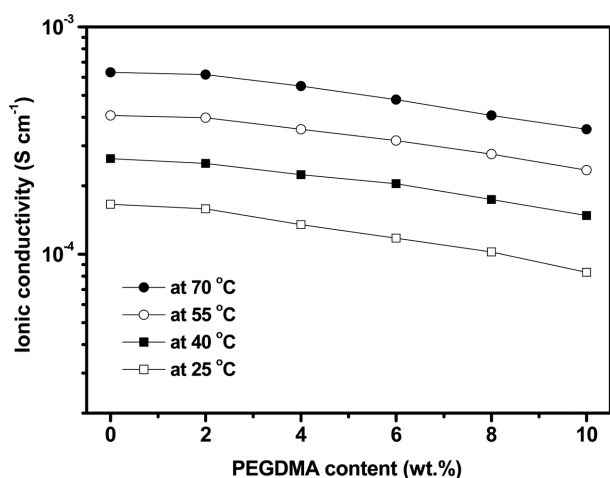


Figure 3. Ionic conductivities of the ionic liquid-based gel polymer electrolytes supported by PP separator, as a function of the cross-linking agent content.

separator, as a function of the cross-linking agent content. The ionic conductivity of the gel polymer electrolytes decreased with increasing cross-linking agent 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 conductivity increases with increasing temperature due to enhancement of the ionic mobility.

LSV curves of the ionic liquid-based cross-linked gel polymer electrolytes are shown in Figure 4. The LSV results of ionic liquid electrolyte without VC are also included to emphasize the effect of VC. In the cathodic scan shown in Figure 4(a), the BMP-TFSI without VC was reductively decomposed around 1.6 V vs. Li/Li⁺, as previously reported.³² In case of ionic liquids with VC, the cathodic current starts to increase around 1.7 V vs. Li/Li⁺, irrespective of the PEGDMA content. 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 reduction peak associated with BMP-TFSI indicates that the

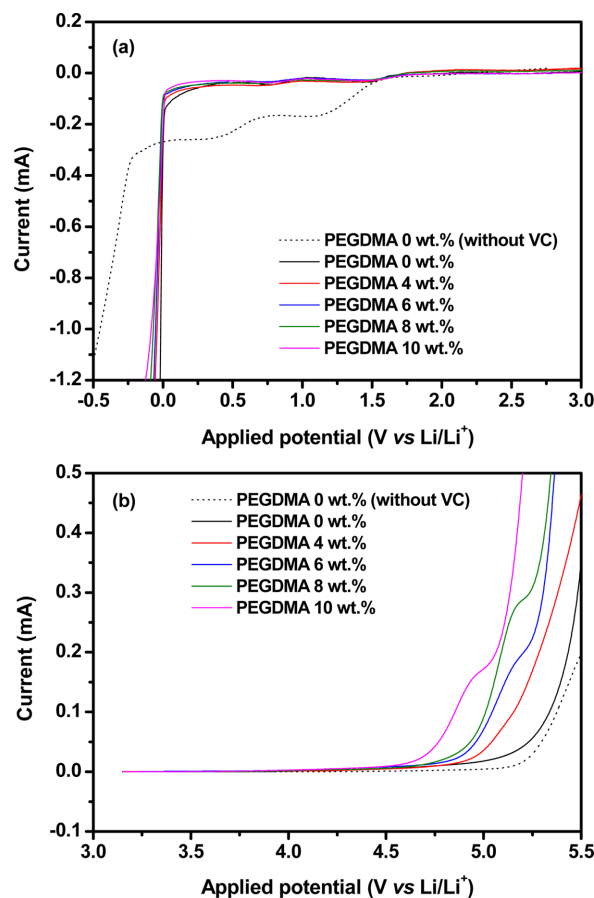


Figure 4. Linear sweep voltammograms of the ionic liquid-based gel polymer electrolytes cured with different amounts of cross-linking agent at a scan rate of 1 mV s⁻¹: (a) cathodic and (b) anodic scans.

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.^{33,34} Beyond this point, the large reductive current observed around 0 V vs. Li/Li⁺ corresponds to the reductive deposition of lithium onto the electrode (*i.e.*, Li⁺+e → Li). With respect to anodic stability, an introduction of VC slightly decreases the oxidation potential of the electrolyte due to the anodic decomposition of VC. The thermal curing of the ionic liquid electrolyte by PEGDMA also decreases the anodic stability of the cross-linked gel polymer electrolyte, which may originate from the oxidative decomposition of PEGDMA itself. Nevertheless, all of the gel polymer electrolytes demonstrated oxidative stabilities higher than 4.6 V, which is essential for high voltage cathode applications. 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 the electrochemical operation of Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cells.

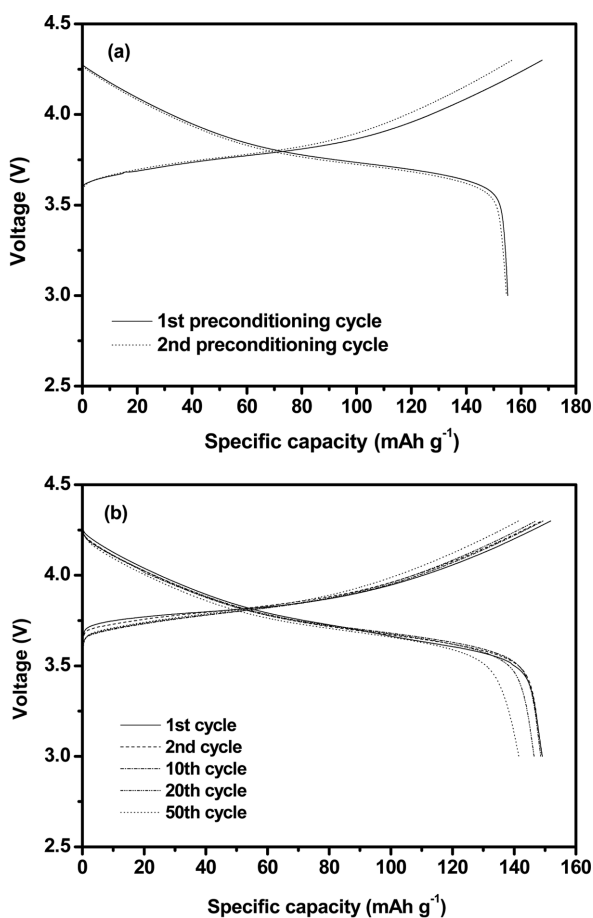


Figure 5. (a) Charge and discharge curves of the Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cell assembled with the gel polymer electrolyte cured by 4 wt% cross-linking agent, which are obtained for initial preconditioning cycles (55 °C, 0.05 C rate), and (b) charge and discharge curves of the Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cell after the preconditioning cycles (55 °C, 0.2 C rate).

In order to evaluate the cycling performance of lithium polymer batteries assembled with ionic liquid-based gel polymer electrolytes, the cells were initially subjected to the preconditioning cycles in the voltage range of 3.0 to 4.3 V at a 0.05 C rate. Figure 5(a) shows the initial charge and discharge curves of the Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cell assembled with ionic liquid-based gel polymer electrolyte cured by 4.0 wt% PEGDMA, which was obtained for initial preconditioning cycles at 55 °C. The discharge capacity obtained at the first cycle was 155.1 mAh g⁻¹ based on LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ active material in the cathode, with a coulombic efficiency of 92.5%. The initial irreversible capacity loss of the cell can be ascribed to irreversible reduction of VC, resulting in the formation of an SEI layer on the electrode. For the second cycle, the coulombic efficiency of the cell increased to 98.7%. This result suggests that the SEI layer formed during the first cycle suppresses any further reductive decomposition of the electrolyte during the second cycle, which leads to a

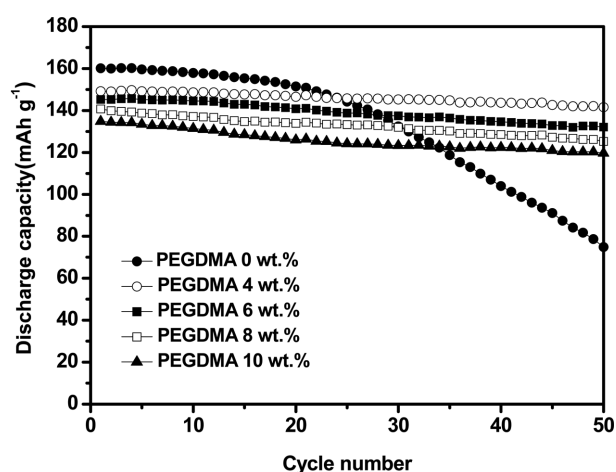


Figure 6. Discharge capacities as a function of cycle number for the Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cells assembled with gel polymer electrolytes cured with different amounts of cross-linking agent (55 °C, 0.2 C rate, cut-off voltage range of 3.0–4.3 V).

reduction of the irreversible capacity loss after the first cycle. After two preconditioning cycles, the cells were cycled over the same cut-off voltage range at a 0.2 C rate. Figure 5(b) presents the charge and discharge curves of the Li/LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ cell cured with 4.0 wt% PEGDMA. The discharge capacity of the cell declined from an initial value of 149.1 to 141.5 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 the repeated cycling.

Figure 6 shows the discharge capacities as a function of the cycle number in the cells prepared with the ionic liquid electrolyte or the ionic liquid-based cross-linked gel polymer electrolytes. The cycling characteristics of the cells were found to depend on the cross-linking agent content. As shown in 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 LiNi_{1/3}Co_{1/3}Mn_{1/3}O₂ electrode. Accordingly, the initial discharge capacity is the lowest in the cell prepared with the cross-linked gel polymer electrolyte cured by 10 wt% cross-linking agent. On the other hand, the capacity retention was significantly improved by using the cross-linked gel polymer electrolyte, irrespective of the cross-linking agent content. A large capacity decline in the cell comprising 0 wt% PEGDMA may be related to gradual exudation of electrolyte solution during cycling, which arising from poor compatibility of PP separator with ionic liquid electrolyte. Upon gelling by thermal curing with the cross-linking agent, the ionic liquid electrolyte becomes a chemically cross-linked gel polymer electrolyte, as previously shown in Figure 2. This allows effective encapsulation of the ionic liquid electrolyte in the cell as well as promoting good interfacial adhesion between the electrolyte and electrodes, which results in good capacity

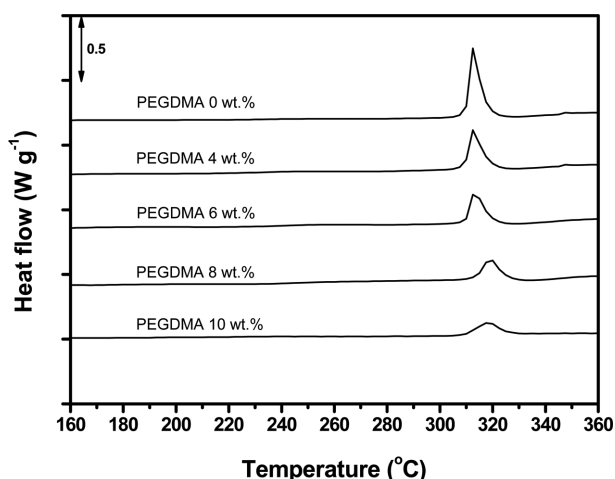


Figure 7. DSC profiles of the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode materials charged to 4.3 V after 50 cycles in the cells assembled with ionic-liquid based gel polymer electrolytes cured with different amounts of cross-linking agent.

retention. The optimum content of the cross-linking agent for efficient cell operation was found to be 4 wt% considering the initial discharge capacity and capacity retention.

The thermal stability of the delithiated (charged) cathode material is very important for battery safety. DSC measurements were performed to evaluate the thermal stability of the fully charged cathode material after repeated cycling in different electrolytes. Figure 7 shows the DSC profiles of the cathode materials charged to 4.3 V, which are obtained after 50 cycles. In this figure, the DSC trace of $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ in the cell prepared with the ionic liquid electrolyte without thermal curing has an exothermic peak with a reaction heat of 213.5 Jg^{-1} at $312.5 \text{ }^\circ\text{C}$. The exothermic peak resulted from electrolyte oxidation caused by released oxygen from $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$, as previously reported.^{21,35} The exothermic heat is much lower than that measured for $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ (584.4 Jg^{-1}) in the cell prepared with a standard liquid electrolyte.²¹ Moreover, the $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ materials in the cell assembled with the cross-linked gel polymer electrolyte had smaller exothermic reaction heat values ranging from 107.5 to 156.7 Jg^{-1} , where the magnitude of the exothermic heat decreased with increasing cross-linking agent content. It was also found that the peak temperature shifted slightly to a higher temperature with increasing cross-linking agent content. These results suggest that the delithiated $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material is less reactive toward the ionic liquid-based cross-linked gel polymer electrolytes, leading to improved thermal stability.

Conclusions

The ionic liquid-based cross-linked gel polymer electrolytes composed of BMP-TFSI and VC were prepared, and their electrochemical properties were investigated. Using

these gel polymer electrolytes, the lithium polymer batteries composed of a lithium anode and a $\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cathode were assembled, and their cycling performances were evaluated at $55 \text{ }^\circ\text{C}$. The optimum content of cross-linking agent to ensure both high initial discharge capacity and good capacity retention of the $\text{Li}/\text{LiNi}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ cell was demonstrated to be about 4 wt%. The cell assembled with the gel polymer electrolyte cured by 4 wt% cross-linking agent delivered an initial discharge capacity of 149.1 mAh g^{-1} and exhibited a good capacity retention (95% after 50 cycles). DSC studies showed that the thermal stability of delithiated $\text{Li}_{1-x}\text{Ni}_{1/3}\text{Co}_{1/3}\text{Mn}_{1/3}\text{O}_2$ material was improved by applying the ionic liquid-based cross-linked gel polymer electrolytes.

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