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Cycling Performance of $Li_4Ti_5O_{12}$ Electrodes in Ionic Liquid-Based Gel Polymer Electrolytes

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We investigated the cycling behavior of $Li_4Ti_5O_{12}$ electrode in a cross-linked gel polymer electrolyte based on non-flammable ionic liquid consisting of 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl) imide and vinylene carbonate. The $Li_4Ti_5O_{12}$ electrodes in ionic liquid-based gel polymer electrolytes exhibited reversible cycling behavior with good capacity retention. Cycling data and electrochemical impedance spectroscopy analyses revealed that the optimum content of the cross-linking agent necessary to ensure both acceptable initial discharge capacity and good capacity retention was about 8 wt %.

Key Words : Anode, Ionic liquid, Gel polymer electrolyte, Lithium-ion battery, $Li_4Ti_5O_{12}$

Introduction

Lithium-ion batteries have become the dominant power sources for portable electronic devices, electric vehicles and energy storage systems due to their high energy density and long cycle life. However, serious safety issues surrounding such batteries need to be resolved before they can be widely utilized, especially in large capacity applications. Unfortunately, the highly flammable organic solvents commonly used in lithium batteries could cause fires or explosions in the event of a short circuit or abuse. In the search for non-flammable electrolytes, ionic liquids have been recognized as one of the safest because they are non-flammable, exhibit high thermal stability and negligible vapor pressure even at elevated temperatures.[1-3] Various materials such as lithium metal, carbon, $Li_4Ti_5O_{12}$, Si and Sn have been tested as anode materials in ionic liquid-based cells.[4-16] Among these materials, $Li_4Ti_5O_{12}$ is considered to be promising, because it exhibits good reversibility with regard to the intercalation/deintercalation of lithium ions and shows no structural changes during charge-discharge cycling. Furthermore, additional improvements in safety are expected since the high operating voltage of $Li_4Ti_5O_{12}$ does not allow for the growth of lithium dendrites. Reale *et al.* reported the electrochemical behavior of the $Li_4Ti_5O_{12}$ electrode in pyrrolidinium-based ionic liquids at 40 °C.[13] The ionic liquid electrolytes in the study were found to be irreversibly decomposed on the electrode at a potential that was positive relative to that of the Li/Li^+, which resulted in the formation of an unstable solid electrolyte interphase (SEI) on the electrode. One way to solve these problems is to use a small amount of organic solvent such as vinylene carbonate (VC), ethylene carbonate (EC), and fluoroethylene carbonate (FEC) as an additive, which forms an electrochemically stable SEI before the reduction of the ionic liquid electrolyte.[15]

With the goal of developing a non-flammable ionic liquid-based gel polymer electrolyte for lithium-ion polymer batteries with $Li_4Ti_5O_{12}$ anode, we prepared cross-linked polymer electrolytes containing 1-butyl-1-methylpyrrolidinium bis(trifluoromethanesulfonyl)imide (BMP-TFSI) by *in-situ* chemical cross-linking. In this work, the electrochemical performances of $Li_4Ti_5O_{12}$ electrodes in ionic liquid-based gel polymer electrolytes are presented. More attention will be paid to the influence of the content of cross-linking agent on cycling performance of $Li_4Ti_5O_{12}$ electrodes.

Experimental

Synthesis of Ionic Liquid-based 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 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(trifluoromethanelsulfonyl) imide (LiTFSI, Sigma Aldrich) in BMP-TFSI. Anhydrous VC was added to the IL electrolyte at a concentration of 10 wt %. Poly(ethyleneglycol) dimethacrylate (PEGDMA, $M_n = 550$, Sigma Aldrich) and *t*-amyl peroxypivalate (Luperox 554M75, Seki Arkema Co., Ltd.) were used as a cross-linking agent and an initiator, respectively. In order to control the cross-linking density, the cross-linking agent was added at different concentrations (2, 4, 6, 8, 10 wt %) into the ionic liquid electrolyte. The cross-linked gel polymer electrolyte was then prepared by radical reaction of homogeneous precursor solution consisting ionic liquid electrolyte, cross-linking agent and initiator at 90 °C for 20 min. The synthesis of ionic liquid-based cross-linked gel polymer electrolytes was carried out in an argon filled glove box.

Electrode Preparation and Cell Assembly. Anatase TiO_2 prepared by a hydrothermal method was used to synthesize the $Li_4Ti_5O_{12}$.[17] High purity $TiCl_4$, urea and ammonium sulfate were first mixed into a water-ethanol mixture submerged in an ice water bath. The mixed solution was transferred to a Teflon-lined autoclave and heated to 120 °C for 24 h. After incubation, the resulting slurry was filtered and washed with ethanol. The obtained powder was vacuum-dried and sintered at 400 °C for 5 h in air. $Li_4Ti_5O_{12}$ was then synthesized from mesoporous anatase TiO_2 combined with Li_2CO_3 (molar ratio of Li/Ti is 0.4) and calcined at 900 °C for 20 h under air. The $Li_4Ti_5O_{12}$ electrodes were prepared by coating an *N*-methyl pyrrolidone (NMP)-based slurry of $Li_4Ti_5O_{12}$, PVdF, super-P carbon and KS-6 carbon (80:10:5:5) onto a copper foil. In the present study, carbon mixtures of super-P and KS-6 were used to obtain the better electric contact between $Li_4Ti_5O_{12}$ particles and current collector. The thickness of the electrode was about 40 μm after roll pressing. The lithium electrode was prepared by pressing lithium foil (Cyprus Foote Mineral Co., thickness: 100 μm) onto a copper current collector. The Li/$Li_4Ti_5O_{12}$ cell was assembled by sandwiching the polypropylene separator (Celgard®2400, thickness: 25 μm) soaked with a precursor electrolyte solution between the lithium and the $Li_4Ti_5O_{12}$ electrode. The cell was then enclosed in a metalized plastic bag and vacuum-sealed. After the cell assembly process, the cells were kept at 90 °C for 20 min in order to induce *in-situ* thermal curing within the cell. All cell-assembly was carried out in an argon-filled glove box.

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 counter and reference electrodes of lithium metal. The measurements were carried out at a scanning rate of 1.0 mVs^{-1}. In order to measure the ionic conductivities of gel polymer electrolytes, AC impedance measurements were performed using a Zahner Electrik 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 2 hr at each temperature before measurements. The self-extinguishing time (SET) was measured to quantify the flammability of the mixed electrolyte, as described in previous literature.[16,18] Briefly, SET was obtained by igniting the pre-weighed electrolytes soaked in an inert glass-fiber wick, followed by recording the time it took for the flame to extinguish. Charge and discharge cycling tests of the cells were conducted at a constant current density of 0.06 mA cm^{-2} (0.1 C rate) over a voltage range of 1.0-3.0 V with battery testing equipment (WBCS 3000, Wonatech) at 55 °C.

Results and Discussion

Before applying ionic liquid-based cross-linked gel polymer electrolytes into the cell, gel formation was confirmed by performing a chemical cross-linking reaction with different cross-linking agent content. Figure 1 shows images of the ionic liquid-based cross-linked gel polymer electrolytes, which are cured by different amounts of the cross-linking agent. Gelation was not detected for the ionic liquid electrolyte systems cured by 2 wt % and 4 wt % of the cross-linking agent. This result suggests that the content of the cross-linking agent should be higher than 6 wt % in the ionic liquid electrolyte to induce the thermal chemical cross-linking reaction effectively in the cell. Accordingly, the content of cross-linking agent was chosen to be higher than 6 wt % for further studies.

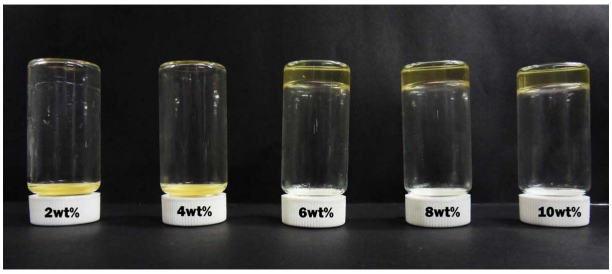

Figure 1. Images of cross-linked gel polymer electrolytes cured with different amounts of cross-linking agent.

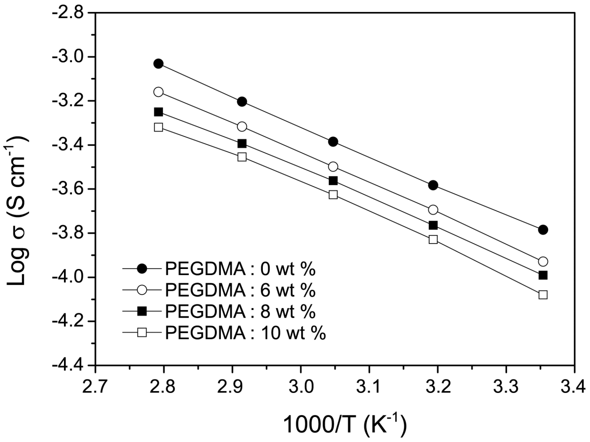

Figure 2. Temperature dependence of ionic conductivities for ionic liquid-based gel polymer electrolytes cured with different amounts of cross-linking agent.

Figure 2 shows the temperature dependence of the ionic conductivity for cross-linked gel polymer electrolytes, as a function of cross-linking agent content. The ionic conductivity of ionic liquid electrolyte before chemical cross-linking (i.e., content of PEGDMA is 0 wt %) is 1.6×10^{-4} S cm^{-1} at room temperature. The ionic conductivities of gel polymer electrolytes decreased with the content of cross-linking agent. 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 in the ionic conductivity with increasing cross-linking density. The ionic conductivity gradually increases with temperature due to the improvement of ionic mobility.

Linear sweep voltammetry curves of the ionic liquid-based gel polymer electrolytes are shown in Figure 3(a) and (b), which are obtained from cathodic and anodic scans, respectively. It has been reported that the ionic liquid electrolyte without VC was decomposed reductively around 1.6 V *vs.* Li/Li^+.[15] In the case of the ionic liquid electrolyte with VC (i.e., content of PEGDMA is 0 wt %), the cathodic current starts to increase around 1.7 V *vs.* Li/Li^+. This peak

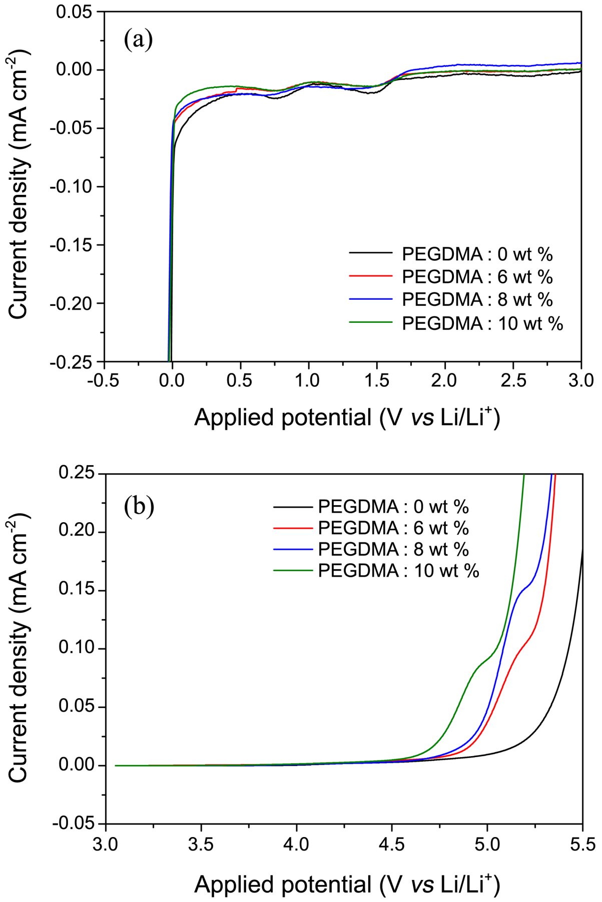

Figure 3. Linear sweep voltammograms of the ionic liquid-based gel polymer electrolytes cured with different amounts of cross-linking agent (scan rate: 1 mV s^{-1}). (a) cathodic scan and (b) anodic scan.

can be attributed to the reductive decomposition of VC, which results in the formation of an SEI film on the electrode. This SEI film prevents further reductive decomposition of the ionic liquid electrolyte and kinetically extends the cathodic stability to 0 V *vs.* Li/Li$^+$. The small reductive peak around 0.8 V *vs.* Li/Li$^+$ is probably due to LiTFSI impurities and water contamination, as previously reported.[19,20] Both reductive peaks observed at 1.7 and 0.8 V decrease with content of cross-linking agent, which indicates the reductive stability is improved by curing the ionic liquid electrolyte by PEGDMA. Beyond that, the large reductive current observed around 0 V *vs.* Li/Li$^+$ corresponds to the deposition of lithium onto the electrode. A slight decrease of reduction potential for lithium deposition with increasing content of cross-linking agent is associated with an increase of ionic resistance of gel polymer electrolyte. In the anodic scan shown in Figure 3(b), the oxidative current corresponding to the anodic decomposition starts at around 5.3 V *vs.* Li/Li$^+$ for the ionic liquid electrolyte. On the other hand, the curing of the ionic liquid electrolyte by PEGDMA decreased the anodic stability of the cross-linked gel polymer electrolyte, which may originate from the anodic decomposition of the PEGDMA itself. Nevertheless, they show a broad electrochemical stability window higher than 4.6 V.

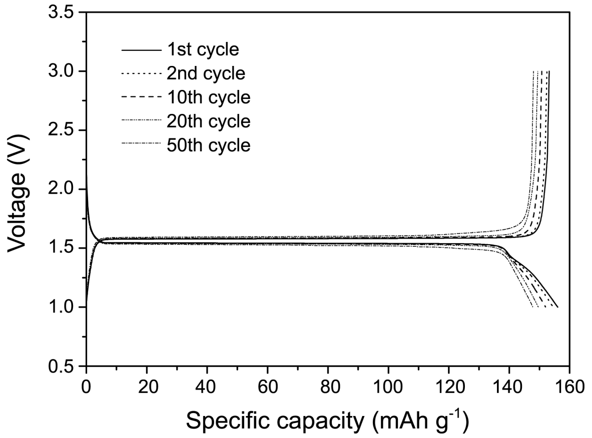

Figure 4. Charge and discharge curves of the $Li_4Ti_5O_{12}$ electrode in ionic liquid-based gel polymer electrolyte cured by 8 wt % of cross-linking agent (0.1 C rate, cut-off voltage range of 1.0-3.0 V, 55 °C).

Cycling performance of the $Li_4Ti_5O_{12}$ electrode in the ionic liquid-based gel polymer electrolytes was evaluated at 55 °C. Figure 4 shows the typical charge-discharge curves of the Li/$Li_4Ti_5O_{12}$ cell assembled with ionic liquid-based gel polymer electrolyte cured with 8 wt % of cross-linking agent. The voltage profiles are flat and the capacity is relatively high, although a highly cross-linked gel polymer electrolyte is used in the cell. The cell delivers an initial discharge capacity of 153.3 mAh g^{-1} based on the $Li_4Ti_5O_{12}$ active material. Its low coulombic efficiency in the first cycle may be related with reductive electrolyte decomposition on the electrode surface at the end of charging cycle. (i.e., at low potential below 1.5 V) The first coulombic efficiency of the cell is found to increase with content of cross-linking agent, which is attributable to improvement of reductive stability of the cross-linked gel polymer electrolyte at low potential, as shown in Figure 3(a). The coulombic efficiency increases with cycling and remains greater than 99.0% throughout cycles after the initial few cycles.

The discharge capacities of the $Li_4Ti_5O_{12}$ electrodes in the

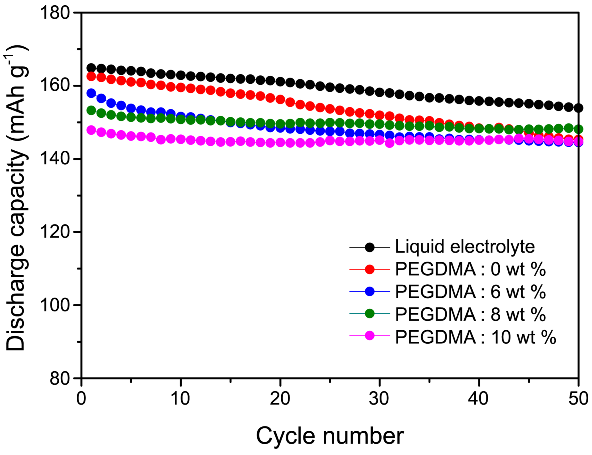

Figure 5. Discharge capacities as a function of the cycle number for the $Li_4Ti_5O_{12}$ electrode in different electrolyte systems (0.1 C rate, cut-off voltage range of 1.0-3.0 V, 55 °C).

different gel polymer electrolytes, as a function of the cycle number, are shown in Figure 5. For the purpose of comparison, the cycling result of the cell assembled with liquid electrolyte (1.0 M LiTFSI in ethylene carbonate/diethylene carbonate, 1:1 by volume) is also given in the figure. The cycling characteristics of the cells are found to depend on the content of the cross-linking agent. As can be seen in the figure, the initial discharge capacity of the cell gradually decreases with increasing content of cross-linking agent, which arises from the increased resistance for ion migration in both the electrolyte and the electrodes. Accordingly, the initial discharge capacity is the lowest in the cell prepared with the cross-linked gel polymer electrolyte cured by 10 wt.% of cross-linking agent. On the other hand, capacity retention was improved with an increasing degree of cross-linking. Upon gelling by thermal curing with cross-linking agents, the liquid electrolyte becomes a chemically cross-linked gel polymer electrolyte and serves as a strong adhesive to bond the electrolyte and electrodes together, which results in good capacity retention. An improvement of reductive stability of cross-linked gel polymer electrolyte cured by high content of cross-linking agent may also contribute the enhanced capacity retention. After 50 cycles, the discharge capacity of the cell prepared with cross-linked gel polymer electrolyte cured by 8 wt % of cross-linking agent is higher than that of the cell assembled with an ionic liquid electrolyte. Thus, the optimum content of cross-linking agent to ensure both acceptable initial discharge capacity and good capacity retention is thought to be about 8 wt %.

Rate capability of the $Li_4Ti_5O_{12}$ electrode in ionic liquid-based gel polymer electrolytes was evaluated, as shown in Figure 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 cross-linking of the ionic liquid electrolyte decreases the discharge capacity at high current rate. This result is due to the fact that a reduction in the ionic mobility in both the electrolyte and the electrode may occur as a result of the chemical cross-linking, even though the chemical cross-linking improves the interfacial adhesion.

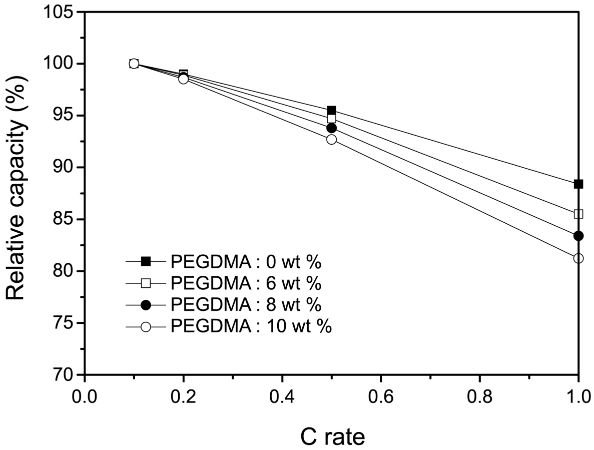

Figure 6. Relative capacities, as a function of C rate, of the Li/$Li_4Ti_5O_{12}$ cells assembled with ionic liquid electrolyte and cross-linked gel polymer electrolytes cured by different amounts of cross-linking agent.

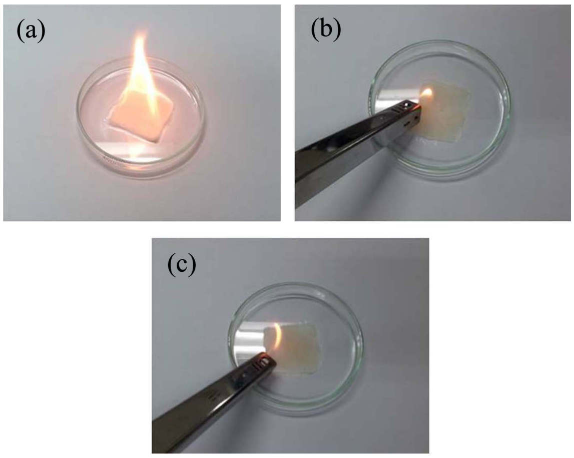

Figure 7. Photographic images showing the flammable behavior of different electrolyte systems during flammability test: (a) liquid electrolyte, (b) ionic liquid electrolyte and (c) ionic liquid-based gel polymer electrolyte.

Flammability of the ionic liquid-based electrolyte is investigated. Figure 7 shows photographic images showing the flammable behavior of different electrolyte systems during flammability test. As can be seen in the Figure 7(a), the liquid electrolyte is very flammable, and its SET value is measured to be about 33 s g^{-1}. By contrast, both ionic liquid electrolyte and ionic liquid-based gel polymer electrolyte do not show any combustion, even during ignition with the flame source, which indicates their non-flammable behavior.

Conclusion

Cross-linked ionic liquid-based gel polymer electrolytes composed of BMP-TFSI and VC were prepared and their electrochemical properties were investigated. When the content of the cross-linking agent was higher than 6 wt % in the ionic liquid, quasi-solid-state gel polymer electrolytes could be obtained by thermal chemical cross-linking reactions. The optimum content of cross-linking agent to ensure both high initial discharge capacity and good capacity retention of the $Li_4Ti_5O_{12}$ electrodes in the ionic liquid-based gel polymer electrolytes was about 8 wt %. The $Li_4Ti_5O_{12}$ electrode in the ionic liquid-based gel polymer electrolyte cured by 8 wt % cross-linking agent delivered an initial discharge capacity of 153.3 mAh g^{-1} and exhibited good capacity retention (97% after 50 cycles).

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