

Short communication

High rate performance of a lithium polymer battery using a novel ionic liquid polymer composite

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Abstract

We present a new design of a lithium gel-polymer battery, fabricated with a (LILP) composite consisting of a lithium salt dissolved in an ionic liquid (binary Li-IL) and an ultra high molecular weight ionic liquid polymer (ILP). This polymer, with a Mw of over a million, was prepared by the bulk radical polymerization of a novel ionic liquid monomer, *N,N*-diethyl-*N*-(2-methacryloyloethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEMM-TFSI). The polymer could form a binary Li-IL solid at a concentration of only 5 wt%. We selected high power-active electrode materials, and combined them with the LILP system. The demonstration vapor-free cell had a higher discharge performance than a conventional lithium polymer battery: at 40 °C, it retained 83% of its discharge capacity at a 3 C current, and relatively good cycle performance. This is the first report of to knowledge that a lithium ion cell with a LILP system performed, in terms of cell performance and cycle durability, at a level of practical utility. © 2006 Elsevier B.V. All rights reserved.

Keywords: Lithium polymer battery; Polymerizable ionic liquids; Ultra high molecular weight polymer; Gel; Rate performance

1. Introduction

Commercialized lithium ion batteries, consisting of graphite-based anodes, LiCoO₂-based cathodes, and organic solvent electrolytes, have several advantages, such as a high operating voltage, a high energy density and a relatively good cycle durability [1]. However, the use of a flammable and easily leaking liquid electrolyte is unavoidable in the present lithium ion cells. In the last decade, many researchers and battery companies have been developing the “gel-polymer battery” to reduce the volume of inflammable liquid and protect from liquid leakage. The basic concept of the gel-polymer cell is solidifying the electrolyte by mixing into it the smallest possible amount of polymer materials. Because, recently developed polymer materials have a relatively high ionic conductivity and good mechanical properties, researchers have achieved a leakage-free, thin-prismatic cell design [2–8]. However, the applications of these lithium ion gel-polymer cells presently include only those for which a small capacity cell suffices, since the flammable electrolyte in such

polymers still raises safety concerns. To develop a truly safe, large size lithium ion cell suitable for electric or hybrid vehicles, a new kind of non-flammable, leakage-free electrolyte is necessary.

Ionic liquids are known to be non-volatile, non-flammable, and highly conductive. Recently, therefore, interest has increased in the possible use of this type of liquid in energy storage devices, for example, a lithium rechargeable battery [9–16] and an electric double layer capacitor [17–21]. In an attempt to use ionic liquids such as 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI-BF₄), that have a relatively narrow potential window, for a lithium ion cell, Nakagawa chose Li[Li_{1/3}Ti_{5/3}]O₄ as the anode active material, to avoid the cathodic decomposition of the liquid during the charge–discharge cycles [13].

In our previous study, we found that, although an aliphatic quaternary ammonium-based ionic liquid, such as *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI), had an obviously higher cathodic stability than the aromatic type ionic liquids, the limiting reduction potentials of the DEME cation was merely somewhat positive against the potential for the deposition and dissolution of lithium metal. Thus, we added carbonate solvent as an additive to provide a protective solid electrolyte interface (SEI) on the

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negative electrode materials, and were the first to achieve a reasonable cycle performance of over 350 in the graphite/binary Li-IL (specifically, a lithium salt dissolved in an ionic liquid having the same counter-ion)/LiCoO₂ cell system [16]. However, since the binary Li-IL have a considerably high viscosity, the cell containing such liquids has a poor charge/discharge performance at a relatively large current, namely a lower power density, compared to conventional cells using the flammable organic solvent. In our case, the discharge performance of the Li ion cell containing binary Li-DEME-TFSI was 75% capacity at 1 C current at 45 °C, on the basis of the discharge capacity at the 0.1 C rate at 25 °C [16]. Matsumoto and coworkers recently reported what is, to our knowledge, the best discharging performance of a Li metal half-cell. Using very low viscosity EMI-type ionic liquids containing the bis(trifluorosulfonyl)-imide (FSI⁻) anion, that cell operated at 70% of its discharge capacity at a 4 C current [22].

In parallel with these efforts, other investigators have attempted to develop a non-flammable polymer electrolyte system; they have developed various types of binary Li-IL/polymer (LILP) composites with conductivities over 10⁻³ S cm⁻¹ at room temperature [23–25]. However, there have been few reports of the performance of Li ion cells incorporating a LILP system. In this paper, aiming to develop a truly safe Li ion polymer cell with a good charge and discharge performance at a large current, we discovered that the choices of LiMn₂O₄ and Li₄Ti₅O₁₂ [26] as, respectively, the cathode and anode active material, produced a faster charge/discharge reaction than conventional LiCoO₂ and graphite systems. In addition, we prepared a novel polymer material: an ionic liquid polymer (ILP), very compatible with ionic liquids, synthesized by radical polymerization of an ionic liquid monomer that has a polymerizable functional group on its cation. Our novel Li polymer cell has the following structure: negative electrode: Li₄Ti₅O₁₂/LILP-including ultra high molecular weight ionic liquid polymer/positive electrode: LiMn₂O₄. In this paper, we will discuss the performance of this cell.

2. Experimental

2.1. Chemical materials

The chemical reagents methyl iodide, 2-(diethylamino)ethyl-methacrylate, 2,2'-azobisisobutyronitrile (AIBN), and the ionic liquid *N,N*-diethyl-*N*-(2-methoxyethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEME-TFSI) were purchased from Kanto Chemical Company Inc., and used without further purification. Electrochemical device grade propylene carbonate (PC), vinylene carbonate (VC) and lithium bis(trifluoromethylsulfonyl)imide (LiTFSI) were purchased from Kishida Chemical Co., and used without further purification.

2.2. Preparation of polymerizable ionic liquid monomer

Preparation of *N,N*-diethyl-*N*-(2-methacryloylethyl)-*N*-methylammonium bis(trifluoromethylsulfonyl)imide (DEMM-

TFSI): 2-(diethylamino)ethyl-methacrylate was treated with 1.2 equiv. of methyl iodide in tetrahydrofuran at 0 °C and stirred overnight. The precipitate was filtered off and recrystallized in tetrahydrofuran-ethanol solvent. The recrystallized *N,N*-diethyl-*N*-(2-methacryloylethyl)-*N*-methylammonium iodide was treated with exactly 1.0 equiv. of lithium bis(trifluoromethylsulfonyl)imide in deionized water for 5 h. After the reaction, the mixture was separated into two phases, the bottom phase being *N,N*-diethyl-*N*-(2-methacryloylethyl)-*N*-methylammonium bis(trifluoromethyl-sulfonyl)imide.

The infrared (IR) spectrum ionic liquid monomer was recorded on a Varian 2000 FT-IR spectrometer. The ¹H-NMR spectrum was obtained with a JEOL GX-400 spectrometer, with acetonitrile-*d*₃ as a solvent. Chemical shift values are reported in ppm with respect to a tetramethylsilane (TMS) internal reference for ¹H.

¹H-NMR(acetonitrile) δ = 1.33 (t, 6H), 1.99 (s, 3H), 3.00 (s, 3H), 3.41 (q, 4H), 3.60 (t, 2H), 4.51 (t, 2H), 5.75 (s, 1H), 6.14 (s, 1H), infrared spectra, methacryl group (1680 and 1720 cm⁻¹).

2.3. Polymerization of ionic liquid monomer

The ionic liquid polymer (ILP) was synthesized by the bulk polymerization method. First, the monomer was dissolved in acetonitrile, and the solution was treated with activated carbon; the resultant acetonitrile solution was evaporated and the purified monomer was dried in vacuum at 25 °C. The ionic liquid monomer and AIBN, at a ratio of 1.0 mol% to the amount of methacryl groups present in the monomer, were mixed until they became homogeneous. The mixture was degassed in vacuum at 50 °C, and kept standing at 70 °C for 15 h. After polymerization, the product polymer was dissolved in acetonitrile and precipitated into ethanol and water, before a final drying in vacuum at 70 °C.

Gel permeation chromatographic (GPC) analyses were performed at 40 °C, with a Shodex GPC-101 equipped with two, series-connected OHpak SB-806M HQ columns with a solution of 0.5 M acetic acid and 0.2 M sodium nitrate in acetonitrile and water (1/1 v/v) as the eluent. The weight- and number-average molecular weight were estimated on the basis of the calibration curve established with standard poly(ethylene oxide)s with the Shodex 480-II data station.

2.4. Fabrication of Li-polymer cell

All of the electrodes used for the lithium ion cell were commercial products of Enerstruct Inc. The negative Li₄Ti₅O₁₂ electrodes (AKO-6), had a charge capacity of 0.42 mAh cm⁻², an area density of 3.00 mg cm⁻², and had an active electrode layer 25 μ m thick on a 13 μ m thickness of copper foil. The other negative electrode used was a hard carbon electrode (AKT-2) with a charge capacity of 1.29 mAh cm⁻², an area density of 2.96 mg cm⁻², and a 33 μ m in thick electrode active layer on a 13 μ m thickness of copper foil.

The first positive electrode, a LiMn₂O₄ electrode (CKT-22) that was paired with the AKO-6 negative electrode, had

Table 1
Electrode specifications

Code	Active material	Polarity	Charge capacity (mAh cm ⁻²)	Area density (mg cm ⁻²)	Active layer thickness (μm)	Current collector/(μm)
AKO-6	Li ₄ Ti ₅ O ₁₂	Negative	0.42	3.00	25	Copper/13
CKT-22	LiMn ₂ O ₄	Positive	0.49	6.60	36–37	Aluminum/20
AKT-2	Hard carbon	Negative	1.29	2.96	33	Copper/13
CKT-9	LiMn ₂ O ₄	Positive	1.075	12.51	65	Aluminum/20

a charge capacity of 0.49 mAh cm⁻², an area density of 6.60 mg cm⁻² and an electrode active layer 36–37 μm in thickness on a 20 μm aluminum foil. The second LiMn₂O₄ electrode (CKT-9), paired with the AKT-2 had a charge capacity of 1.075 mAh cm⁻², an area density of 12.51 mg cm⁻², and a 65 μm thick electrode active layer on 20 μm of aluminum foil. The specification of the electrodes are summarized in Table 1.

The chosen electrodes were cut into a 116 mm × 35 mm rectangle for the anode with an active layer of 31.85 cm², and a 114 mm × 33 mm rectangle for the cathode which had an active layer of 29.37 cm². The electrodes were arranged with 30 μm of a non-woven type of separator consisting of a poly(aromatic amide) fiber (DuPont) sandwiched between them. The two types of lithium ion cell were assembled as follows: (1) hard carbon negative electrode/non-woven type separator/LiMn₂O₄ positive electrode and (2) Li₄Ti₅O₁₂ negative electrode/non-woven type separator/LiMn₂O₄ positive electrode. We inserted the resultant stack of electrodes into a bag made of thermoplastic film laminated to an aluminum sheet. Then, we allowed a mixed solution, composed of LiTFSI, the ionic liquid polymer poly(DEMM-TFSI), the ionic liquid DEME-TFSI, propylene carbonate and vinylene carbonate (40:8:100:128:15; weight ratio) to penetrate the electrode assembly in the bag by keeping the whole under reduced pressure at 25 °C. At that point, we kept the cell standing at 70 °C in vacuum for 12 h to evaporate the organic solvent, until the cell weight became constant. In a measurement from two similar cells, the weight percentage of stabilized solvent (PC + VC) in the binary Li-IL/polymer (LILP) composite was 1.6–1.7 wt%. Afterward, the cell bag was sealed by hot pressing under reduced pressure, and we confirmed that there was no liquid leakage, even if the open part of the cell bag faced down for 1 h. We performed all of this fabrication process in a dry atmosphere (dew point of air < -80 °C). The other details of the preparation method have been described in our previous paper [16].

2.5. The charge–discharge operation and other measurements

We charged the hard carbon negative cell at a small constant current, $I = 1.25$ mA (current corresponds to about 0.05 C) to 4.2 V, and discharged the cell to 2.5 V at 40 °C. Then, we repeated the charge–discharge cycles three times. We calculated the specific capacity of the cell from the result of the 0.1 C charge–discharge process in the fourth cycle. The design capacity, calculated from the material weight of the cell, was 25 mAh,

so that the charge–discharge current of 2.5 mA corresponded to approximately, 0.1 C. The nominal operating voltage of the cells ranged from 2.5 V to 4.2 V.

The Li₄Ti₅O₁₂ negative cell was initially charged at a small constant current, $I = 0.65$ mA (current corresponds to about 0.05 C) to 3.0 V, at which point we discharged the cell to 1.5 V at 40 °C. Then, we operated this cell in the same manner as the hard carbon cell. The design capacity of the Li₄Ti₅O₁₂ negative cell was 13 mAh. The nominal operating voltage of the cells ranged from 1.5 V to 3.0 V. For these operations, we used a charge–discharging system HJ1010SM8 (Hokuto Denko Co. Ltd.).

To carry out the voltammetry of the ionic liquid and polymer materials, and the thermal analysis – differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) – of the materials, we employed the methods described in our previous papers [16,21].

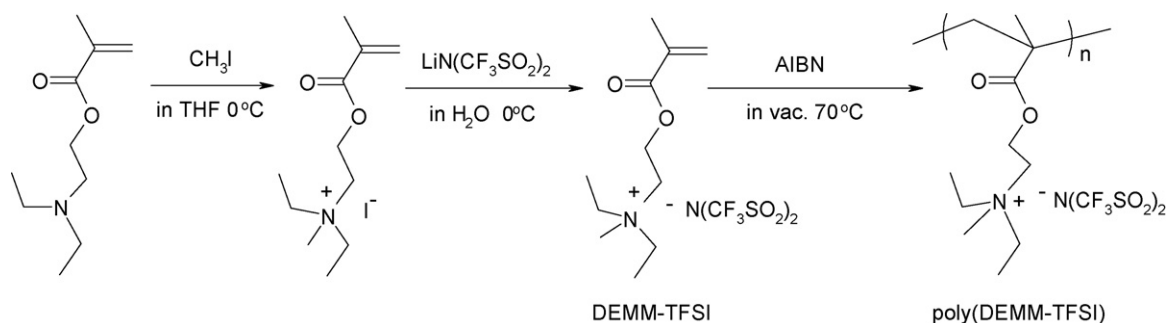
3. Results and discussion

The syntheses of the novel ionic liquid monomer, DEMM-TFSI, and the ionic liquid polymer (ILP), poly(DEMM-TFSI), are shown in Scheme 1.

The DEMM-TFSI monomer did not exhibit a clear melting or freezing temperature in a typical DSC measurement; however, the glass transition temperature T_g was observed at -68 °C. The decomposition temperature corresponding to a 10% weight loss according to TGA measurements occurred at 328 °C. DEMM-TFSI exists as an ionic liquid over a very wide temperature range, approximately 400 °C.

It has been reported that poly(methyl methacrylate) (PMMA) reactions are much more rapid in an ionic liquid than in a non-polar solvent such as benzene, and that a PMMA prepared in an ionic liquid has a molecular weight approximately five times higher than in benzene [27]. The ionic liquid monomer DEMM-TFSI also gives the ultra high molecular weight poly(DEMM-TFSI) by bulk polymerization with an AIBN initiator. Fig. 1 illustrates the GPC trace of the poly(DEMM-TFSI) product polymerized using a mol ratio of [monomer]/[AIBN] = 1:0.01. The resulting polymer was a rubbery solid, with a weight-average molecular weight (Mw) of 1,084,000 and a polydispersity index by GPC analysis of 2.95 [PID = Mw/number-average molecular weight (Mn)].

Poly(DEMM-TFSI) has the capability to dissolve a lithium salt independent of the presence of a liquid electrolyte. In a polarizing microscope analysis of Poly(DEMM-TFSI) which contained 1 M concentration of dissolved lithium salt LiClO₄,



Scheme 1. Synthesis of ionic liquid monomer (DEMM-TFSI) and poly(DEMM-TFSI).

we did not observe the birefringence indicating the existence of crystals. Thus, there must have been a complete dissociation of the lithium salt in the polymer matrix as the polymer itself has a non-crystalline nature. DSC measurements indicate that prepared poly(DEMM-TFSI) has a glass transition temperature (T_g) of approximately 50 °C. Thus, a poly(DEMM-TFSI)/lithium salt composite could potentially serve as an all-polymer electrolyte at temperatures over 50 °C. The physicochemical and electrochemical properties of this polymer and the electrolyte containing this polymer will be described elsewhere.

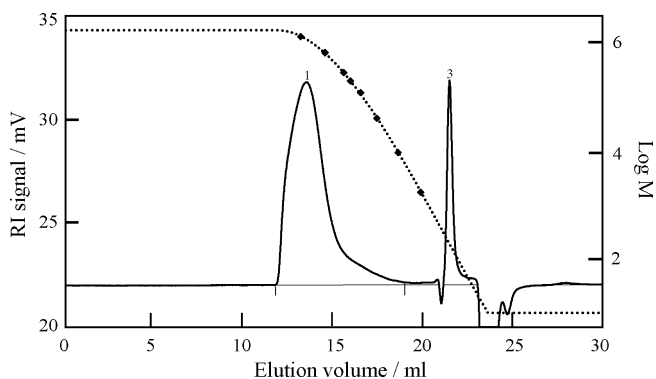
Moreover, poly(DEMM-TFSI) dissolves in a variety of quaternary ammonium ionic liquids to make a gel. For example, the ionic liquid DEME-TFSI containing only 5% of the ultra high molecular weight poly(DEMM-TFSI) lost its liquid characteristics and became a gel. It seems that the strong cohesiveness and loss of liquidity appear because of the entanglement effect of long polymer chains. When we adjusted the solution to a suitable viscosity by adding a supplementary solvent, in our case a PC and VC mixture, it filled the pore space in the electrode and the separator.

The ionic liquid/ILP composite from which the solvent is removed by vacuum evaporation at a relatively high temperature has no components that leak out of the electrode. However, the high-polarity LILP matrix interacted with the supplementary solvent (PC + VC) and probably obstructed perfect evaporation of added solvents. The weight percentage of remained solvent in the composite was 1.7 wt%. We reported that the vinylene carbonate (10 wt%) in the electrolyte Li-DEME-TFSI, composed of an ionic liquid, DEME-TFSI and Li-TFSI was effective as

solid electrolyte interface (SEI) forming additives on the carbon materials such as graphite used as an active material in the anode of a lithium ion cell [16]. Holzapfel and co-workers reported that 2% VC to ionic liquid, EMI-TFSI, contributed to the SEI formation, although the effect was not perfect [28]. Also in this case, there will be a possibility that the remained VC in composite contributes to the SEI formation. However, we realized that the effective SEI to prevent capacitance deterioration with charge/discharge cycles was not formed by the too small amounts (1.7 wt%) of carbonate solvents in LILP composite from the cycling behavior of the cell.

A highly reliable polymer battery is not easily obtained when the polymerization is carried out in the battery bag. In such an “in-situ radical polymerization”, some initiator and unreacted monomer may remain in the polymer matrix. However, our process makes possible the preparation of an electrolyte with few impurities through the use of the purified polymer combined with the binary Li-IL.

Fig. 2 shows both the limiting reduction potentials (E_{red}) on platinum of the ionic liquid monomer as measured by cyclic voltammetry at room temperature, and a voltammogram of an ordinary organic electrolyte LiTFSI in PC. The sharp peaks around -3.0 V are probably due to the deposition and dissolution of Li metal, since a color change of the working electrode by the metal deposition appears with a current loop at that potential. A similar result has been reported by two or more research groups [13,16,22]. The E_{red} and the limiting oxidation potentials (E_{oxd}) were defined as the potential where the limiting current density reached 1 mA cm^{-2} . The E_{red} of the DEMM-TFSI ionic liquid monomer was positioned about 0.7 V positive against the Li/Li^+ . We confidently expected this result, because the monomer molecule had an easily reduced double bond. However, the E_{red} of the poly(DEMM-TFSI) can definitely be seen at around 2.0–2.5 V positive relative to Li/Li^+ . However, its presence is not clear, and the current density is small because, we carried out the measurement in rather dilute conditions to avoid turbulence caused by an increased viscosity in the more concentrated polymer solution. In addition, the E_{red} of the DEME based ionic liquids was merely somewhat positive against the Li/Li^+ [16]. Thus, we realized the need either to select an electrode that would avoid cathodic decomposition during the charge–discharge cycling, or to form a more effective protective layer, such as a solid electrolyte interface (SEI), on the negative electrode material.

Fig. 1. GPC trace of poly(DEMM-TFSI). $M_n = 368,000$; $M_w = 1,084,000$; $M_w/M_n = 2.95$.

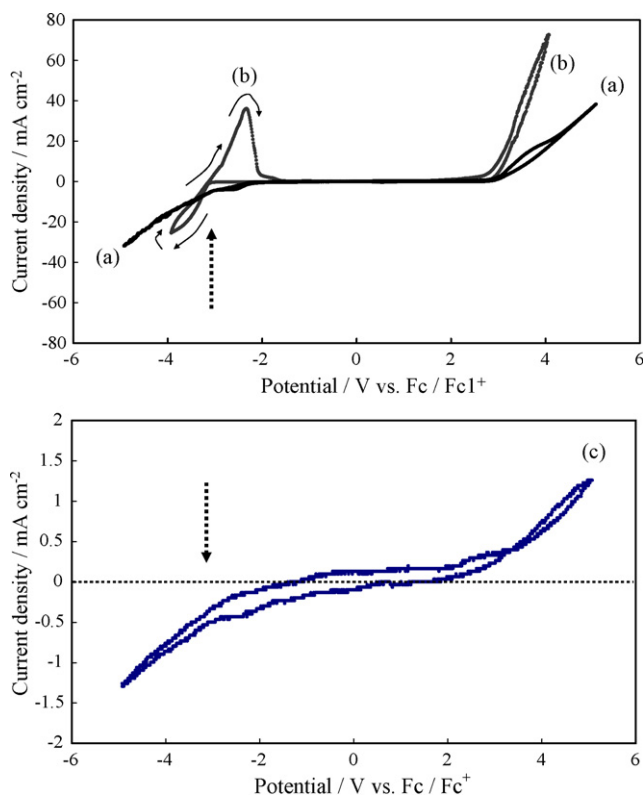


Fig. 2. Cyclic voltammogram of an ionic liquid monomer, an organic electrolyte and an ionic liquid polymer at 25 °C. Scan rate: 10 mV s⁻¹; platinum working and counter electrodes; Ag/Ag⁺ reference electrode. The potential value (V) was referenced to the ferrocene (Fc)/ferrocenium (Fc⁺) redox couple in each salt. (a) 0.1 mol kg⁻¹ of DEMM-TFSI monomer in propylene carbonate (PC) solution, (b) 0.1 mol kg⁻¹ of LiTFSI in PC solution, and (c) 0.002 mol kg⁻¹ poly(DEMM-TFSI) in PC solution. The concentration is defined in terms of molality = (mol solute/kg solvent). The dashed line arrow indicates the potential of the Li/Li⁺ couple.

In Fig. 3, we show the first and second charge–discharge potential curves at 40 °C of the demonstration cells, consisting of hard carbon/LILP (1.3 mol of LiTFSI dissolved in poly(DEMM-TFSI)/DEME-TFSI composite, giving a polymer concentration

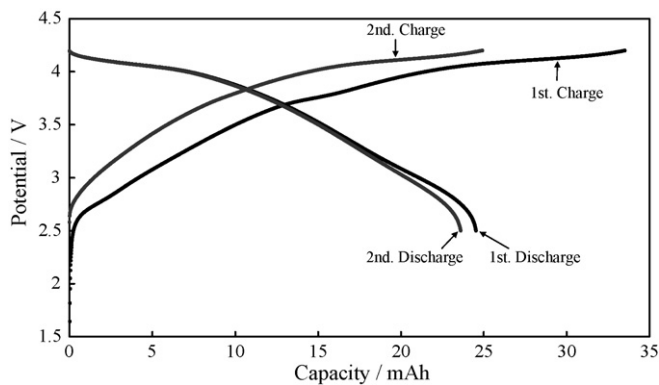


Fig. 3. First and second charge/discharge curves of lithium polymer cell at 0.05 C current at 40 °C. Positive electrode = LiMn₂O₄; negative electrode = hard carbon; electrolyte = 1.30 mol kg⁻¹ of LiTFSI in a DEME-TFSI and poly(DEMM-TFSI) composite. The concentration is defined in terms of molality = (mol solute/kg polymer-ionic liquid composite). The polymer concentration for the composite electrolyte was 5.4 wt%.

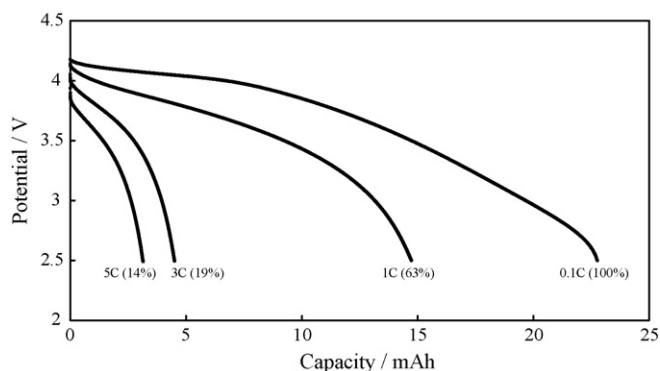


Fig. 4. Discharge curves of the lithium polymer cell at various current densities at 40 °C. The positive electrode = LiMn₂O₄; negative electrode = hard carbon; electrolyte = 1.30 mol kg⁻¹ of LiTFSI in DEME-TFSI and poly(DEMM-TFSI) composite. The concentration is defined in terms of molality = (mol solute/kg polymer-ionic liquid composite). The polymer concentration for the composite electrolyte was 5.4 wt%.

of 5.4 wt%)/LiMn₂O₄. About 26% of the charge capacity was lost in the first cycle; however, from that point on, the cell exhibited an efficiency of 96% or more. The rate capability of this cell at 40 °C appears in Fig. 4. As the discharge current increased, the discharge capacity of this cell decreased significantly faster than that of a cell using conventional materials. The capacity at 1 C discharge was approximately 63% of that at 0.1 C discharge. Most likely, the greater decrease at large discharge currents in the capacity of the cell using the LILP electrolyte resulted from a large internal resistance in the cell. The cycling behavior of this cell, plotted in Fig. 5, was not suitable for practical use. When we set the upper limit voltage at 4.2 V, the cell deteriorated sooner than with a voltage of 4.0 V. The CV measurements suggested that degradation of the polymer or ionic liquid was occurring during the charge–discharge cycles. It is necessary to establish a method of forming an effective SEI if a practicable cycle performance is to be achieved.

We then prepared another type of lithium polymer cell, comprising Li₄Ti₅O₁₂/LILP (1.3 mol of LiTFSI dissolved in poly(DEMM-TFSI)/DEME-TFSI composite, 5.4 wt%

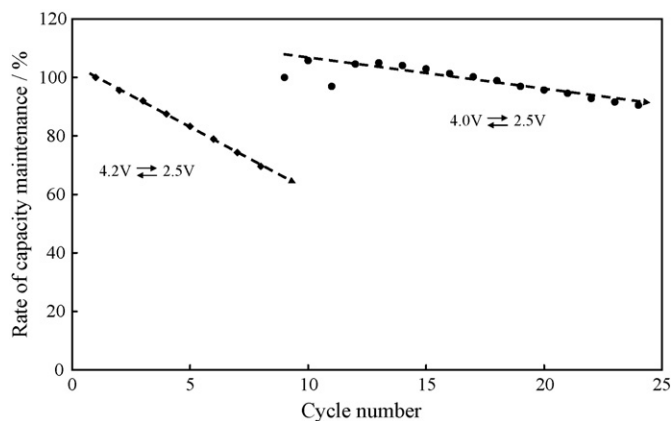
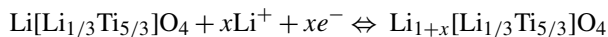


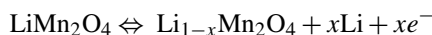
Fig. 5. Cycle life of lithium polymer cell including hard carbon as negative active material. The charge–discharge process was performed at 0.1 C at 40 °C. The cut-off voltages were 4.2 V and 2.5 V for nine cycles, and 4.0 V and 2.5 V from 10th to 24th cycle.

polymer concentration)/LiMn₂O₄. Because the intercalation–deintercalation potential of Li₄Ti₅O₁₂ is around 1.5 V versus Li/Li⁺ potential, our prepared cell had about 3.0 V of charging potential with LiMn₂O₄. The overall cell reactions can be described as follows:

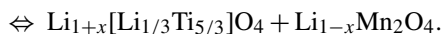
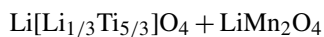
negative electrode,



positive electrode,



overall reaction,



The theoretical capacity of Li₄Ti₅O₁₂ was expected to be approximately 175 mAh g⁻¹. In our electrode, the discharge capacity was 171 mAh g⁻¹. The performances of the prepared cell are shown in Figs. 6–8.

The discharge specific capacities and Coulombic efficiency of the cell at the first was 11.8 mAh, and 82%; at the second cycle, they were 11.4 mAh, and 92%. After the 5th cycle, the Coulombic efficiency of this cell remained at approximately 97–98%. The battery in Fig. 7 that combined the Li₄Ti₅O₁₂ anode with the LiMn₂O₄ cathode showed an excellent rate discharge character as for a lithium polymer battery. Evidently, this battery retains 83% or more of the capacity maintenance rate at a 3 C high power discharge. Thus, it was possible to create a new, leak-free battery with a vapor-free, practical discharge performance, and a prismatic cell design by selecting an electrode material with a high-speed charge/discharge reaction when combined with an LILP system. The rate performances of the Li₄Ti₅O₁₂ negative cell and the hard carbon negative cells differ greatly, even though the electrolyte in each is the same LILP system. The interfacial compatibility of the active material and the electrolyte seem to have a bigger influence on the rate performance than

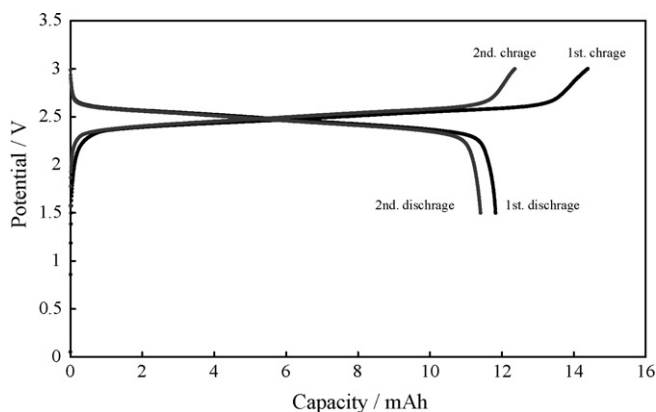


Fig. 6. First and second charge/discharge curves of lithium polymer cell at 0.05 C current at 40 °C. The positive electrode = LiMn₂O₄; negative electrode = Li₄Ti₅O₁₂; electrolyte = 1.30 mol kg⁻¹ of LiTFSI in DEME-TFSI and poly(DEMM-TFSI) composite. The concentration is defined in terms of molality = (mol solute/kg polymer-ionic liquid composite). The polymer concentration for the composite electrolyte was 5.4 wt%.

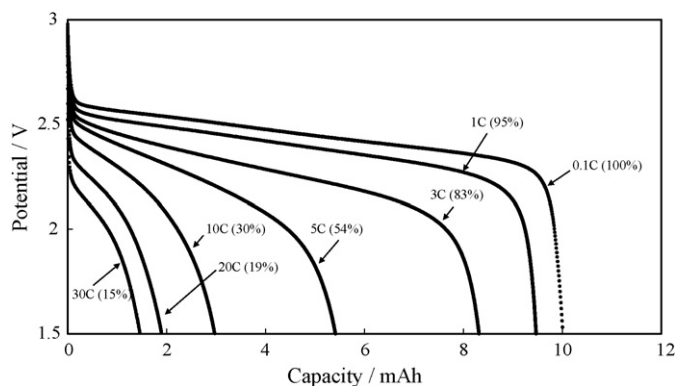


Fig. 7. Discharge curves of lithium polymer cell at various current densities at 40 °C. The positive electrode = LiMn₂O₄; negative electrode = Li₄Ti₅O₁₂; electrolyte = 1.30 mol kg⁻¹ of LiTFSI in DEME-TFSI and poly(DEMM-TFSI) composite. The concentration is defined in terms of molality = (mol solute/kg polymer-ionic liquid composite). The polymer concentration for the composite electrolyte was 5.4 wt%.

the bulk ionic conductivity of the electrolyte itself. The cycling behavior of the cell, plotted in Fig. 8, indicated a good cycle durability, almost equivalent to that of a conventional lithium ion cell.

As in the case of the hard carbon electrode, we expected that electrochemical degradation of the DEME-TFSI or poly(DEMM-TFSI) probably occurred. In our previous study, we suggested that some kinds of organic solvents, such as VC and ethylene carbonate, are effective as SEI-forming additives on the graphite used as an active material in the anode of a lithium ion cell with a binary Li-IL electrolyte. In this study, we did use a small amount of VC as a dilution solvent; however, because almost all the VC evaporates from the battery in the process of establishing the composite, it appears the small amounts of remained VC did not have large contribution to the SEI formation.

On the other hand, however, we should point out that the use of Li₄Ti₅O₁₂ as the negative electrode for the lithium-ion LILP cell avoids cathodic decomposition of the LILP composite during the charge/discharge cycling.

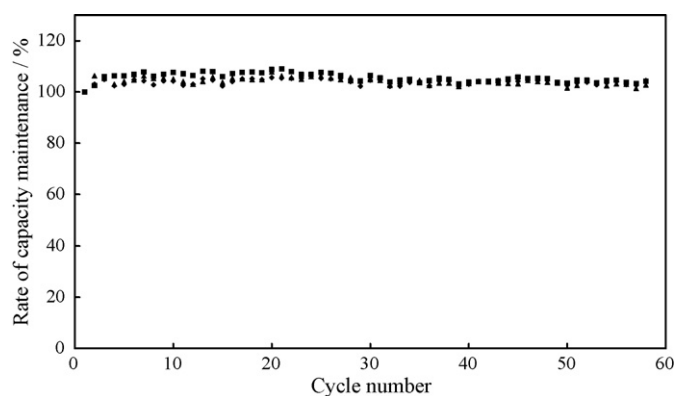


Fig. 8. Cycle life of lithium polymer cell including Li₄Ti₅O₁₂ as negative active material. The charge–discharge process was performed at 0.1 C at 40 °C. The cut off voltages were 3.0 V and 1.5 V. Three cells were tested.

4. Conclusion

We have synthesized a novel polymerizable ionic liquid monomer by attaching a methacryl functional group to the cation species in an ionic liquid molecule with relatively wide potential windows. The resulting monomer was easily radical-polymerized in bulk, and yielded an ultra high molecular weight polymer with an over Mw of one million. We obtained a polymer electrolyte by combining a small amount of the polymer and a binary Li-IL. In order to penetrate the polymer and a binary Li-IL into electrode assembly, we used the PC and VC mixture as a supplementary solvent. Small amount of carbonate solvent was remained in the polymer matrix. However, the effective SEI to prevent capacitance deterioration with charge/discharge cycles was not formed by too small amounts of remained solvents.

The system of a lithium salt dissolved in an ionic liquid polymer and ionic liquid composite (LILP) could potentially comprise an electrolyte having zero vapor pressure. The discharge performance of a cell with an LILP system might be expected to show a poor discharge performance, because the solidified ionic liquid decreases the mobility of the ionic species. However, we have conceived a method of making a polymer battery with a practicable performance by combining electrodes that can offer a high-speed charge/discharge reaction. The experimental battery that combined a $\text{Li}_4\text{Ti}_5\text{O}_{12}$ anode with a LiMn_2O_4 cathode and included an LILP electrolyte showed an excellent rate discharge character for a lithium polymer battery; at a 3 C current rate, it retained 83% of its discharge capacity, and relatively good cycle performance. This is the first report to our knowledge that a lithium ion cell with a LILP system performed, in terms of cell performance and cycle durability, at a level of practical utility. This novel lithium polymer cell, non-flammable and leak-free, is a promising candidate as a safe, large size lithium secondary battery.

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