

A novel and shortcut method to prepare ionic liquid gel polymer electrolyte membranes for lithium-ion battery

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Received: 23 May 2017 / Accepted: 9 August 2017 / Published online: 19 August 2017
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Abstract The ionic liquid polymer electrolyte (IL-PE) membrane is prepared by ultraviolet (UV) cross-linking technology with polyurethane acrylate (PUA), methyl methacrylate (MMA), ionic liquid (Py₁₃TFSI), lithium salt (LiTFSI), ethylene glycol dimethacrylate (EGDMA), and benzoyl peroxide (BPO). *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (Py₁₃TFSI) ionic liquid is synthesized by mixing *N*-methyl-*N*-propyl pyrrolidinium bromide (Py₁₃Br) and lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The addition of Py₁₃TFSI to polymer electrolyte membranes leads to network structures by the chain cross-linking. The resultant electrolyte membranes display the room temperature ionic conductivity of $1.37 \times 10^{-3} \text{ S cm}^{-1}$ and the lithium ions transference number of 0.22. The electrochemical stability window of IL-PE is about 4.8 V (vs. Li⁺/Li), indicating sufficient electrochemical stability. The interfacial resistances between the IL-PE and the electrodes have the less change after 10 cycles than before 10 cycles. IL-PE has better compatibility with the LiFePO₄ electrode and the Li electrode after 10 cycles. The first discharge performance of Li/IL-PE/LiFePO₄ half-cell shows a capacity of 151.9 mAh g⁻¹ and coulombic efficiency of 87.9%. The discharge capacity is 131.9 mAh g⁻¹ with 95.5% coulombic efficiency after 80 cycles. Therefore, the battery using the IL-PE exhibits a good cycle and rate performance.

Keywords Lithium-ion battery · Ionic conductivities · Polymer electrolytes · Thin films

Introduction

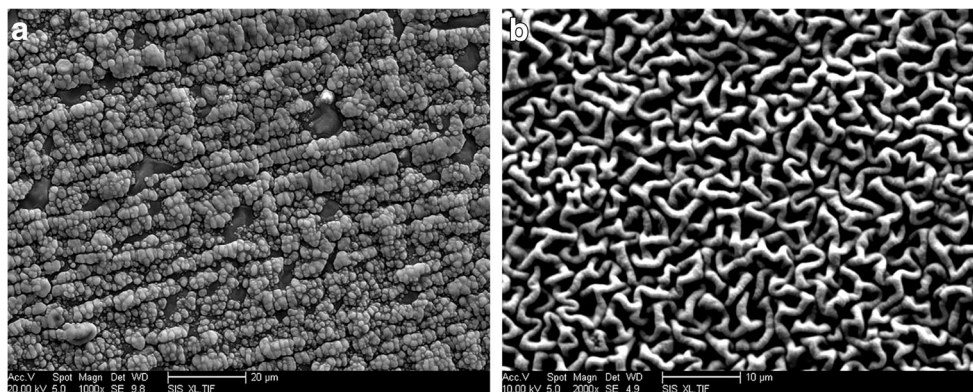
The establishment of a sustainable energy and low-carbon society is a worldwide topic [1–6]. In recent years, lithium-ion batteries with high energy density have been proved to be one of the sustainable power sources and extensively studied because of their specific energy, long cycle life, and no memory effect [7–10]. However, the new lithium batteries of a high-energy and power density are necessary with increasing safety and low cost in order to meet the market of hybrid electric vehicles, portable devices, and so on [11].

At present, ionic liquid electrolyte has developed into gel polymer electrolyte and whole solid polymer electrolyte [12, 13]. Gel polymer electrolyte with higher conductivity and better security has attracted more attention [14–16]. Ionic liquids realize the cleaner produce, environment protection, and cycle economics due to its advantages including non-flammable and non-toxic property, low vapor pressure, high conductivity, high ion transference number, wide electrochemistry window, and good stability performance [17–19]. Therefore, ionic liquids are one of most important components in the ionic liquid polymer electrolyte (IL-PE) membrane since it is one of main conduct mediums. *N*-methyl-*N*-alkyl (alkyl(a)=methyl, ethyl, propyl and butyl) pyrrolidinium bis(trifluoromethanesulfonyl)imide (Py_{1a}TFSI) ionic liquid has good electrochemistry, especially propyl and butyl as side chain [20]. Jae-Kwang Kim prepares the gel polymer electrolyte with *N*-methyl-*N*-butyl pyrrolidinium bis(trifluoromethanesulfonyl)imide (Py₁₄TFSI) based on poly(vinylidene fluoride-co-hexafluoropropylene)

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Fig. 1 SEM of $\text{Py}_{13}\text{TFSI}/\text{LiTFSI}/\text{PUA}$ (a) and $\text{Py}_{13}\text{TFSI}/\text{LiTFSI}/\text{PUA}/\text{PMMA}$ (b) ionic liquid polymer electrolyte membrane



(P(VdF-HFP)) by the electrostatic spinning method which shows the conductivity of $1.1 \times 10^{-4} \text{ S cm}^{-1}$ at 0°C [21]. Mumin Rao uses electrostatic spinning technique to prepare $\text{PYR}_{14}\text{TFSI}/\text{poly}(\text{acrylonitrile-co-methyl methacrylate})$ (PAN/PMMA) electrolyte film with the conductivity of $3.6 \times 10^{-3} \text{ S cm}^{-1}$ [22].

Polymer matrix is one of the indispensable materials as supporting framework of gel polymer electrolytes [23]. So far, there are mainly four systems as polymer matrix for polymer lithium-ion battery, including polyvinylidene fluoride (PVDF) system [24], polyether (PEO) system [25–27], polymethyl methacrylate (PMMA) [28], and polyacrylonitrile (PAN) system [29]. Wei Zhai prepares [BMIM] $\text{BF}_4/\text{PVDF-HFP}/\text{PMMA}$ gel polymer electrolyte by the phase inversion method which has the conductivity of $1.4 \times 10^{-3} \text{ S cm}^{-1}$ and the electrochemistry stability window of 4.5 V.

In this work, ultraviolet cross-linking technique is adapted to create a photochemical reaction for the bonds

linking one polymer chain to another as a speed curing process. The IL-PE membrane contains the polymethyl methacrylate (PMMA) and light-sensitive urethane acrylate (PUA) as the electrolyte matrix, the lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) as the lithium salt and the *N*-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{Py}_{13}\text{TFSI}$) ionic liquid as improving agent of the conductivity. Meanwhile, the performances of the IL-PE membrane are measured.

Experimental

Preparation of ionic liquid

N-methyl-*N*-propyl pyrrolidinium bis(trifluoromethanesulfonyl)imide ($\text{Py}_{13}\text{TFSI}$) was obtained by the substitution reaction between Py_{13}Br and LiTFSI. The anion substitution reaction

Fig. 2 Molecular structure diagram of $\text{Py}_{13}\text{TFSI}$ (a), photograph (b), and (c) AFM images of the ionic liquid polymer electrolyte membrane

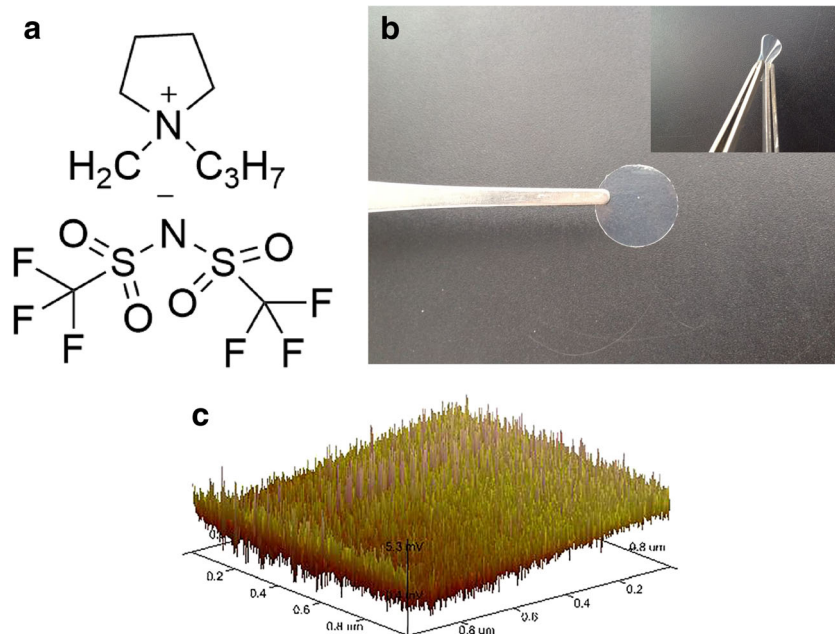
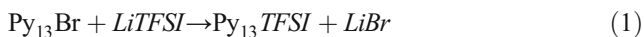


Table 1 Conductivity of Py₁₃TFSI/LiTFSI/PUA/PMMA electrolyte membrane at room temperature

No.	(PUA) /g	(MMA) /g	(Py ₁₃ TFSI) /g	(LiTFSI) /g	σ $\times 10^{-4}$ S cm ⁻¹
1	0.2	1.6	0.5	0.2	1.72
2	0.4	1.6	0.5	0.2	13.7
3	0.6	1.6	0.5	0.2	3.03
4	0.8	1.6	0.5	0.2	8.92
5	1.0	1.6	0.5	0.2	1.14
6	0.4	1.6	0.3	0.2	0.68
7	0.4	1.6	0.4	0.2	1.64
8	0.4	1.6	0.5	0.2	13.7
9	0.4	1.6	0.6	0.2	4.12
10	0.4	1.6	0.7	0.2	2.32
11	0.4	1.6	0.5	0.05	1.76
12	0.4	1.6	0.5	0.1	3.02
13	0.4	1.6	0.5	0.2	13.7
14	0.4	1.6	0.5	0.3	7.12
15	0.4	1.6	0.5	0.4	1.91

from bis(trifluoromethane sulfonyl)imide (TFSI⁻) to bromide ion (Br⁻) was performed as following chemical formula Eq. (1).



The proper Py₁₃Br and LiTFSI (molar ratio of 1:1) was dissolved in deionized water and drastically mixed for 24 h. The solution was divided into two layers after 2-h standing, including the upper hydrophilic layer and the bottom hydrophobic layer of the ionic liquid. The bottom layer was repeatedly washed with deionized water to completely remove the Br⁻ until the precipitate did not appear as adding of Ag⁺. Then, the bottom layer solution was heated for 12 h at 80 °C in vacuum for the evaporation of water. At last, the ionic liquid was quickly moved to an argon-filled glove box.

Preparation of the ionic liquid polymer electrolyte membrane

Py₁₃TFSI ionic liquid, LiTFSI, PUA, and 5 wt% ethylene glycol dimethacrylate (EGDMA) as cross-linking agent to promote the formation of covalent bonds during polymer chains were mixed with a certain mass ratio according to the each experiment. Then, the solution A was formed by heating for 1 h at 60–70 °C. Another solution B was prepared by mixing proper MMA and 0.6 wt% benzoyl peroxide (BPO) for 20 min. The prodromic solution was obtained by mixing the above A and B solutions for 20-min stirring in the DMF solvent. Finally, IL-PE membranes were achieved by UV 6-min cross-linking of the curable solution on the glass template.

Characterization of electrolyte membranes

The scanning electron microscope (SEM, FEI Sirion, Philips) and the atomic force microscope (AFM, Dimension Icon, Bruker) were used to characterize the surface morphology of the ionic liquid polymer electrolyte membrane.

The stainless steel/electrolyte/stainless steel system (The electrodes area was 0.785 cm² of SS/IL-PE/SS.) was assembled to test the conductivity of the electrolytes by electrochemical impedance spectroscopy (EIS) using CHI760E electrochemical workstation with a frequency range of 0.01 Hz–100 kHz between 20 and 80 °C. The conductivity was evaluated by using the following equation.

$$\sigma = d / (R_b \cdot S) \quad (2)$$

Where σ is the conductivity of electrolytes, R_b is the bulk resistance, and S and d are the area and thickness of the electrolyte films, respectively.

In order to examine the ionic conductivities of the electrolytes, the Li/electrolyte membrane/Li was assembled and tested by electrochemical impedance spectroscopy and chronoamperometry using CHI760E electrochemical workstation for electrochemical cells. Li transference number (t_{Li^+}) of the electrolytes was estimated according to a Bruce-Vincent-Evans method [7]. The t_{Li^+} was evaluated by using the following equation.

$$t_{\text{Li}^+} = I_{\text{ss}}(\Delta V - R_0 I_0) / [I_0(\Delta V - R_{\text{ss}} I_{\text{ss}})] \quad (3)$$

Where I_0 is the initial current, I_{ss} is the steady-state current, ΔV is the polarization voltage (10 mV), and R_0 and R_{ss} are the electrode/electrolyte interfacial resistances measured before and after the direct current polarization, respectively.

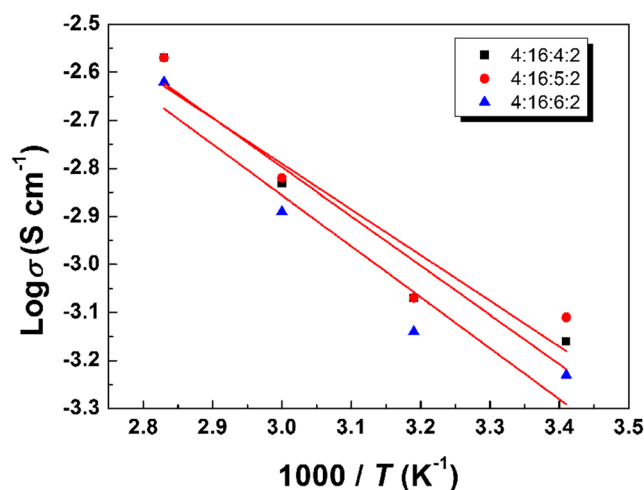
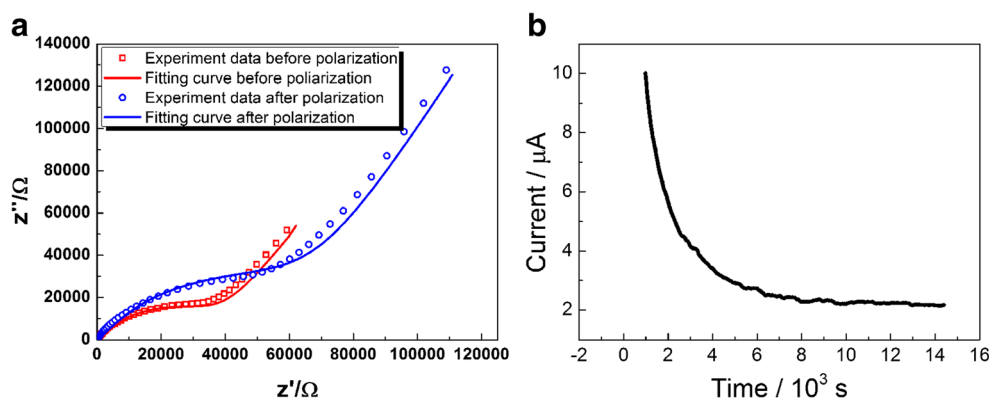


Fig. 3 Temperature dependence of the ionic conductivity for ionic liquid polymer electrolyte (IL-PE) during 20–80 °C

Fig. 4 EIS (a) and $I-t$ curve (b) of the ionic liquid polymer electrolyte membrane



Linear sweep voltammetry (LSV) was used to test the electrochemical stability window of the ionic liquid polymer electrolytes. SS/electrolyte/Li cell was assembled and tested using CHI760E electrochemical workstation at 20 °C and a scan rate of 2 mV s⁻¹ with the range of -1~7 V.

Battery test

The LiFePO₄/electrolyte/Li cells were assembled in an Ar-filled dry glove box. For preparing LiFePO₄ electrode, LiFePO₄ as active material, acetylene black (AB) as conductive agent, and polyvinylidene fluoride (PVDF) as binding agent with a weight ratio of 85:10:5 were mixed in *N*-methyl-2-pyrrolidone (NMP) as the organic solvent. The homogeneous solution after stirring 24 h was cast on an aluminum foil and heated for 12 h at 120 °C in a vacuum drying oven.

The cyclic voltammetry (CV) tests were performed by using CHI760E electrochemical workstation at 20 °C and the scanning rate of 0.1 mV s⁻¹ of voltage range of 2.5~4.2 V. The charge-discharge cycling performances of the cells were measured on a Land battery test system (CT20001A) at room temperature.

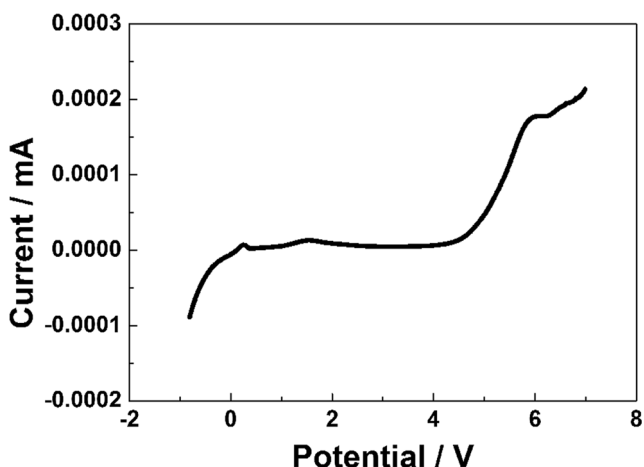


Fig. 5 Linear sweep voltammetry curves of ionic liquid polymer electrolyte membrane

Results and discussion

Morphology of electrolyte films

Figure 1 shows two SEM images of different samples for the microstructures. Figure 1a is the structure of the Py₁₃TFSI/LiTFSI/PUA ionic liquid polymer electrolyte membrane. It can be observed in Fig. 1a that the Py₁₃TFSI/LiTFSI/PUA ionic liquid polymer electrolyte membrane is aligned to be dense and tight chains without the hole, so the Py₁₃TFSI/LiTFSI/PUA ionic liquid polymer electrolyte membrane is not conducive to the intercalation/deintercalation behavior of Li ion. As shown in Fig. 1b, the structure of the membrane changes obviously after MMA is added. The segments of PMMA, PUA, and Py₁₃TFSI are mutual cross-linking and finally present a plicated state. The path of Li⁺ is a circulation process of complexation and complex dissociation on the amorphous fraction of polymer. It is good for the intercalation/deintercalation behavior of Li ion. The mechanical properties of membranes are promoted because of PMMA supporting. Therefore, Py₁₃TFSI/PUA/PMMA ionic liquid polymer electrolyte is better for the membrane.

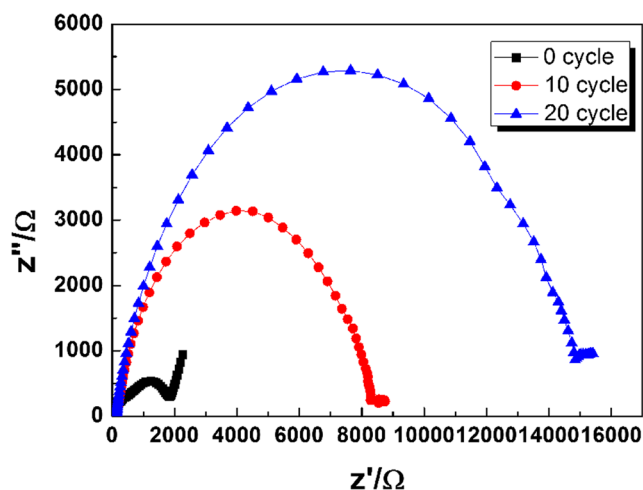


Fig. 6 EIS spectra of ionic liquid polymer cell after the different cycles

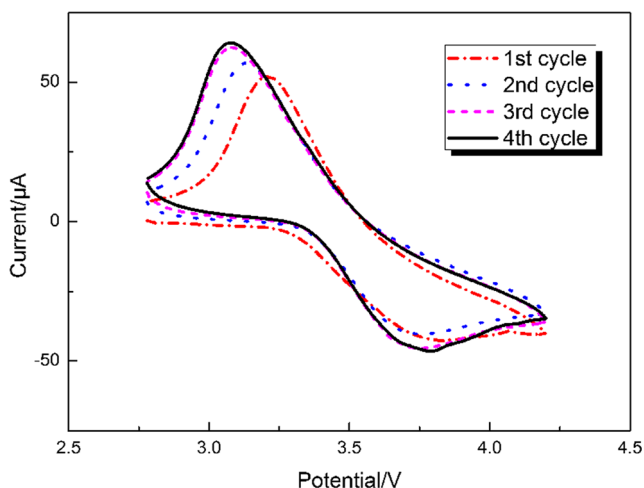


Fig. 7 Cyclic voltammety of the Li/IL-PE/LiFePO₄ cell

The chemical structure of Py₁₃TFSI ionic liquid is given in Fig. 2a. A graphic image of the Py₁₃TFSI + LiTFSI + PUA + PMMA complex ionic liquid polymer membrane is given in Fig. 2b. The IL-PE is highly transparent, uniform, and soft even when is 180° bended. As shown in Fig. 2c of AFM, a lot of pores of nanometer size homogeneously and densely emerge on the surface of the complex polymer membrane. The pores can provide excellent condition for intercalation/deintercalation behavior of Li ion in membrane.

Ionic transport properties

The conductivity of the gel polymer electrolytes is calculated according to Eq. (2), and the results are listed in Table 1. The conductivity of $1.37 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature can completely satisfy the service condition of the lithium-ion batteries. The influence of temperature on the ionic conductivity of electrolytes with different mass fraction of Py₁₃TFSI at the temperature of 20, 40, 60, and 80 °C is shown in Fig. 3. The relationship of $\log \sigma$ and $1000/T$ conforms to typical Arrhenius conductive behavior. The activation energy of the IL-PE membranes with 15, 18, and 21 wt% Py₁₃TFSI

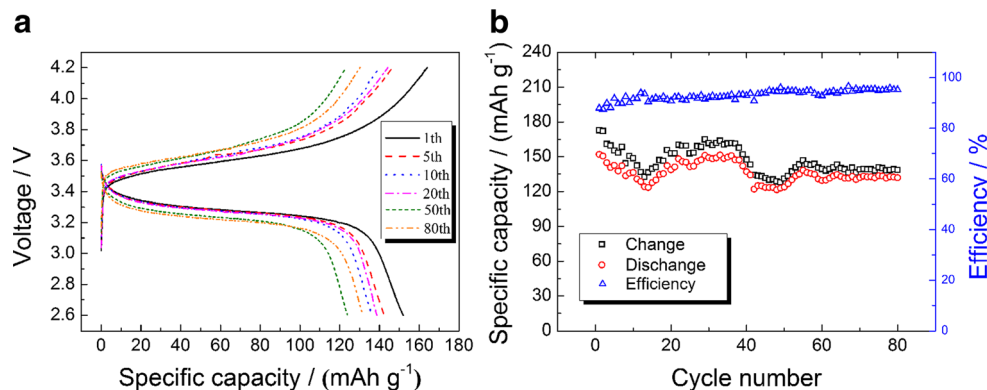
according to the Vogel-Fulcher-Tammann (VFT) are 19.647, 18.201, and 20.329 kJ mol⁻¹, respectively. The activation energy decreases with the increase of Py₁₃TFSI content presumably due to -F of the Py₁₃TFSI chains as an electron donor coupled with Li⁺ ion which benefits to transfer Li⁺. However, the activation energy decreases when the Py₁₃TFSI content is more than 18 wt%. The reason is probably the increase of the space steric hindrance due to the Py₁₃TFSI volume.

Lithium-ion transference number (t_{Li^+}) is obtained by electrochemical impedance spectroscopy and chronoamperometry method. Figure 4 shows impedance behavior of the ionic liquid and gel polymer electrolyte membrane with 18 wt% Py₁₃TFSI ionic liquid at 20 °C. The impedance spectra are composed of semi-circles at the highest frequency and a straight line of Warburg impedance at the low frequency. The bulk electrolyte resistance (R_b) as the resistance of gel polymer electrolyte membrane and electrode/electrolyte interfacial resistance (R_f) as the resistance of the passive film on the lithium make up a semi-circle [30]. The initial electrode/electrolyte interfacial resistance R_o and the electrode/electrolyte interfacial resistance R_{ss} after polarization are obtained in Fig. 4a, the initial polarization current I_o ($1.009 \times 10^{-5} \text{ A}$) and the steady-state current I_{ss} ($2.171 \times 10^{-6} \text{ A}$) are observed in Fig. 4b, and ΔV is the applied potential difference (10 mV). The ion transference number is 0.22 according to Eq. (3).

Electrochemical stability

The electrochemical stability of electrolyte is very important for the practical application of batteries, especially for the high voltage system of the lithium battery because the decomposition of the electrolyte may lead to security issues. Linear sweep voltammetry (LSV) has been used in this study in order to characterize the stability of the IL-PE membrane. The linear sweep voltammetry of Li/IL-PE/SS (the stainless steel) at ambient temperature is shown in Fig. 5. Obviously, IL-PE based on Py₁₃TFSI/PUA/PMMA manifests an anodic stability about 4.8 V (vs. Li⁺/Li) and a reduction potential about 0 V (vs. Li⁺/Li). Therefore, Py₁₃TFSI PUA/PMMA polymer electrolyte membrane has

Fig. 8 Voltage vs. specific capacity curves (a) and specific capacity vs. cycle numbers (b) of the Li/IL-PE/LiFePO₄ cells during the charge-discharge process



electrochemical stability window of about 4.8 V (vs. Li^+/Li) at room temperature. The $\text{Py}_{13}\text{TFSI}/\text{LiTFSI}/\text{PUA}/\text{PMMA}$ polymer electrolyte membrane has enough electrochemical stability as an electrolyte material in $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cells.

Interface impedance

When the anode or the cathode is contacted with the electrolyte, a passive film that is the solid electrolyte interphase (SEI) film will produce in the charge-discharge process of lithium-ion batteries. SEI film is not conductive, but it can allow lithium-ion through. During intercalation/deintercalation of the lithium ion, some lithium ions remain in the SEI film to produce lithium dendrites. This will not only prevent the transferring of lithium ions to increase the interface impedance of the electrode but also lead to microshort circuit within the battery if the lithium dendrite continues to increase, and seriously, even explosion is raised from the direct contact of the positive and the negative electrodes by piercing the membrane. Therefore, interface impedance characteristic plays an important role in lithium-ion battery. EIS spectra after the different cycles of $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ cell are given in Fig. 6. The resistance of the battery after 0, 10, and 20 cycles is 1985, 8956, and 13,648 Ω , respectively, indicating the increase with the number of cycles increasing. The change in resistance corresponds to the formation of the passivation film (SEI) at the electrolyte/electrode interface. The interfacial resistance is less increased in 10–20 cycles than 0–10 cycles, suggesting that the formation and decomposition of SEI film are in tendency of dynamic equilibrium to reach a stable state. The ionic liquid polymer electrolyte membrane has better compatibility with LiFePO_4 electrode and Li electrode. Therefore, the ionic liquid polymer batteries are expected to exhibit good cycle and rate performance.

Cycle performance for the $\text{Li}/\text{LiFePO}_4$ cell

Figure 7 shows the cyclic voltammetry of $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ cells. The voltage of the first-time intercalation/deintercalation of lithium ions occurs at 3.82 and 3.21 V, respectively, while the voltages in the latter cycles are 3.75 and 3.12 V, respectively. The SEI film is being formed at the first cycle and tread to steady at the third cycle and the fourth cycle. Thus, the ionic liquid polymer electrolyte membrane has a good compatibility with the LiFePO_4 cathode and the Li anode.

Figure 8a shows voltage vs. specific capacity curves of the $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ cells during charge-discharge process at room temperature. The initial charging platform of $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cell is about 3.60 V, and the discharging platform is about 3.28 V. After the fifth cycle, the charge-discharge potential polarization gradually stabilizes with the number of cycles increasing, which leads to the steady state of the cell internal resistance. The first charge and discharge

capacity of the cell is 172.7 and 151.9 mAh g^{-1} , respectively. However, the coulombic efficiency is only 87.9%, probably because the passivation film has not been completely formed.

The charge and discharge capacities and coulombic efficiency of $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cells at 0.5 C in the range of 2.6–4.2 V are shown in Fig. 8b. The discharge capacity of the $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cell is 151.9 mAh g^{-1} , and the discharge capacity is maintained at 131.9 mAh g^{-1} after 80 cycles, illustrating better the charge and discharge stability. With the increase of the cycle number, the coulombic efficiency is also increased to 95.5% of 80 cycles although the first coulombic efficiency is only 87.9% since the SEI film may not be well formed. The good cycle performance of the battery including the ionic liquid electrolyte excellent thermal stability, electrochemical stability, and electrical conductivity is promising.

Conclusions

In this paper, a series of tests on the $\text{Py}_{13}\text{TFSI}/\text{LiTFSI}/\text{PUA}/\text{PMMA}$ ionic liquid polymer electrolyte membrane and the $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cell were carried out and analyzed. The structure and surface morphology of the membrane can be seen from the scanning electron microscopy (SEM) and atomic force microscopy (AFM), from which they can provide favorable conditions for Li^+ intercalation/deintercalation. An electrochemical stabilization window of about 4.8 V was obtained, and the electrolyte membrane had sufficient electrochemical stability to act as an electrolyte material in the $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cell. The $\text{Li}/\text{IL-PE}/\text{Li}$ cell's transference number was calculated to be 0.22 according to the electrochemical impedance spectroscopy (EIS) and the polarization current. It was found that the ionic liquid polymer electrolyte membrane had a good compatibility with LiFePO_4 electrode and Li electrode; the charge and discharge performance of Li-ion battery was studied. It was found that $\text{Li}/\text{IL-PE}/\text{LiFePO}_4$ half-cells had good electrochemical stability and cycling performance. Therefore, the $\text{Py}_{13}\text{TFSI}/\text{LiTFSI}/\text{PUA}/\text{PMMA}$ type ionic liquid polymer electrolyte membranes were promising in lithium-ion battery.

Acknowledgements This work has been supported financially by the Harbin Application Technology Research and Development Projects [grant number 2015RAQXJ030].

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