

Preparation and Properties of Ionic-Liquid Mixed Solutions as a Safety Electrolyte for Lithium Ion Batteries

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The safety of lithium ion batteries becomes an obstacle technique for application of Electric vehicles (EVs), ionic liquids (ILs) are thought as one of the most promising means to solve this problem. In this paper, the mixed ILs is prepared from *N*-propyl-*N*-methyl pyrrolidinium bis (trifluoromethanesulfonyl) imide (PYR13TFSI), *N*-ethyl-*N*-methyl imidazolium bis (trifluoromethanesulfonyl) imide (EMITFSI) (9:1, 7:3, 1:1, v/v). Impedance spectroscopy and linear sweep voltammogram studies show the well stability of mixed ILs to lithium. The cells using 0.2M LiTFSI / EMITFSI-PYR13TFSI (1:1, v/v) electrolyte show good performances and higher coulomb efficiencies (the reversible capacities were 132 mAhg⁻¹ for LiFePO₄, 134mAhg⁻¹ for Li₄Ti₅O₁₂ and 275 mAhg⁻¹ for carbon material). The ionic conductivity and lithium transference number of 0.2M LiTFSI / EMITFSI-PYR13TFSI (1:1, v/v) at room temperature are 4×10⁻³ S cm⁻¹ and 0.3, respectively. Thermal stability of all ILs is higher than 350°C, all ILs show non-flammability by the burning tests.

Keywords: Lithium ion battery, ionic liquid, electrolyte, safety, thermal stability

1. INTRODUCTION

Lithium ion batteries have been widely used on personal computers and mobile phones for their high-voltage, high-energy-density characteristics [1-4]. Especially, the rapidly need for cleanly resource and crisis of energy, lithium ion batteries attract more attention as the power source of electric and hybrid electric vehicles. However, Lithium ion batteries have not been large-scale applied to electric vehicles for the safety issues, the volatile and flammable organic solvent organic solvents is the main components of electrolytes in lithium ion batteries, the cases of flaming, smoking or thermal runaway caused by electrolytes are the main reason for the safety problem. Therefore, electrolyte system, which has more stable features, is necessary to be found.

ILs have many excellent characters which made them appropriate application in energy field ,such as fuel cells, electrodeposition, capacitors and water electrolysis for hydrogen generation[5-7]. In recent years, ILs have received more interest as a new electrolyte media for lithium ion batteries, compared with traditional organic electrolytes, they exhibit excellent characteristics such as negligible volatility, non-flammability and high thermal stability [8-11], they have been thought as the most promising instrumentality for improving the safety of lithium ion battery . The widely studied IL is synthesized by the combination of imidazolium-based cation and TFSI anion. For example, 1-ethyl-3-methyl imidazolium bis (trifluoromethanesulfonyl) imide (EMITFSI), which has a conductivity of $1.06 \times 10^{-2} \text{ S cm}^{-1}$ and low viscosity at room temperature [12, 13], but the reductive potential of the cation is too positive towards lithium electrode , this limits its application in lithium ion battery. Lithium ion batteries composing of LiCoO_2 and $\text{Li}_4\text{Ti}_5\text{O}_{12}$ show good cycling behavior with this kind electrolyte [14, 15], however, if the lithium ion batteries using IL electrolytes want to get the higher energy density, low reductive potential materials must be used in the cell (e.g. carbon materials).

H.Sakaebe et al [16-18] found that Pyrrolidine (PY) -based ILs have well stable electrochemistry window, and the reductive potential is about -0.3V vs. Li/Li+, but the conductivity of this kind IL is only $1.4 \times 10^{-3} \text{ S cm}^{-1}$ at room temperature, which is too low compared with traditional organic electrolytes.

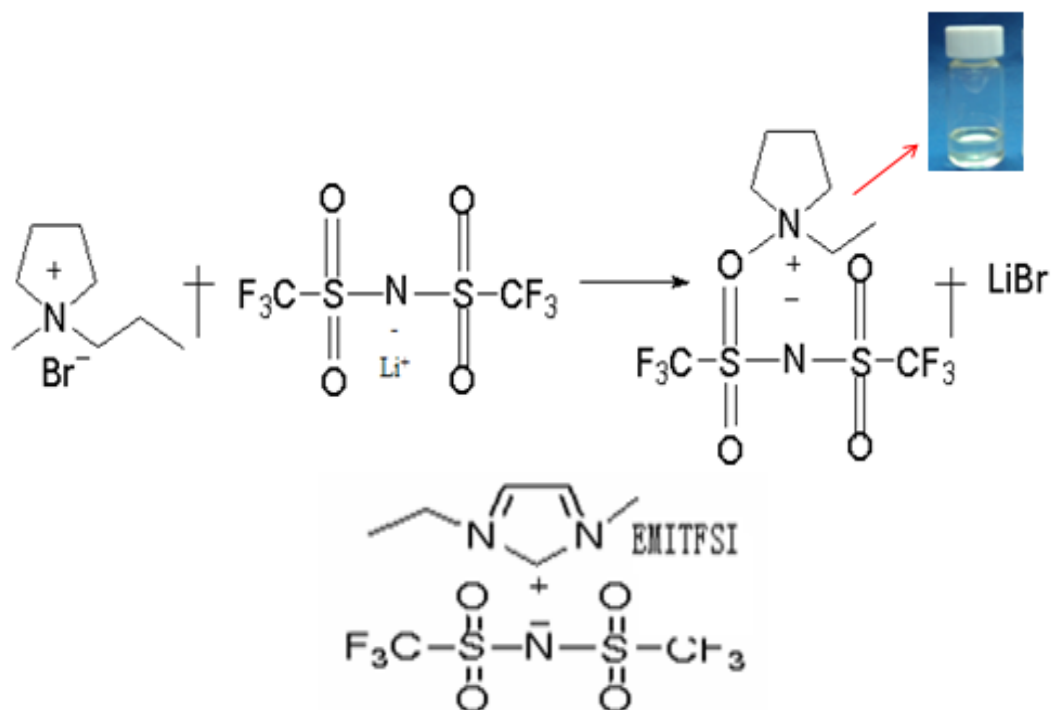
To increase the ion conductivity of IL-PYR13TFSI, thus improve the performance of the cell, we prepared the IL mixed electrolytes. Although the ILs “co-solvents” have been reported in previous work [19, 20], the mixture based on PYR13TFSI and EMITFSI is seldom reported. In this work, the mixed electrolytes are composed of PYR13TFSI and EMITFSI (9:1, 7:3, 1:1, v/v) solutions with 0.2M LiTFSI. The electrochemical character, thermal stability and flammability of mixed electrolytes were investigated.

2. EXPERIMENTAL PART

2.1. Preparation of IL mixed electrolytes

The synthesis of PYR13TFSI has been carried out as followed: PYR13Br(99%, Meisibei Shanghai) and EMIBr (99%, Chemer Hangzhou) were dried at 50°C for 48h under vacuum, LiTFSI (99%, TCI) was also dried at 150°C for 48h. LiTFSI and PYR13Br (1:1 mole ratio) were dissolved in deionized H_2O , separately, the pure ionic liquid PYR13TFSI was formed by ion exchange according to Scheme.1, and PYR13TFSI was phase-separated from the aqueous layer (LiBr dissolved in aqueous layer).

The content of Br^- in PYR13TFSI was checked by 5% AgNO_3 solution, the PYR13TFSI was washed several times with deionized H_2O until the aqueous layer was no AgBr deposit. The final PYR13TFSI was purified by activated carbon (Cabot). A colorless PYR13TFSI was obtained at room temperature after drying under vacuum at 120°C for 24 h and then, it was stored in a glove box. EMITFSI was also prepared by the same method, the mixed ILs were prepared from PYR13TFSI and EMITFSI at rate (9:1, 7:3, 1:1, v/v), finally the 0.2M LiTFSI salt was added.



Scheme 1. Synthesis process of ionic liquid PYR13TFSI, and structure of EMITFSI

2.2. Thermal and burning tests

The thermal stability of ILs was measured by thermal gravimetry (TG, PerkinElmer Diamond) from 25 to 500 °C at the rate of 5 °C min⁻¹.

The flammability of the electrolytes was examined by directly observing the flame on the surface of the electrolytes for 10 seconds [21, 22].

2.3. Electrochemical measurements and cell preparation

Linear sweep voltammograms of EMITFSI, PYR13TFSI and mixed ILs were measured on Pt / IL electrolyte / Li cell and Pt / IL electrolyte / Cu cell by electrochemical analyzer (CHI604B) respectively.

The ionic conductivity of IL with 0.2M LiTFSI solutions was measured by impedance spectroscopy, performed with electrochemical analyzer CHI604B on a two stainless steel-electrode cell.

Interface stability was tested on Li / IL electrolyte / Li cell by impedance spectroscopy on electrochemical analyzer (CHI604B).

The electrodes of cathode were prepared by casting slurry containing 80wt% LiFePO₄ (LiKai, Taiwan), 10wt% acetylene black (AB) and 10wt% poly vinylidene fluoride on aluminum foil and dried at 120 °C for 10h under vacuum, the electrodes were punched into disks (Ø= 14mm, ~3mg cm⁻² active materials) and pressed as the research electrodes by hydraulic press at the pressure of 10MPa,

then they were assembled to Li/LiFePO₄ half cells. The electrodes of Li₄Ti₅O₁₂ were also prepared in the same manner as LiFePO₄ electrode. Hard carbon as anode material has many merits, especially, hard carbon is stable during charge-discharge cycling in PC and ILs-based electrolytes, but hard carbon suffers from a high irreversible capacity compared with graphite for 1st cycle. In this paper, we used carbon coating-hard carbon and graphite composite materials as anode, hard carbon was used as received (Kureha Corp, Japan), the hard carbon-coating process was performed by mechanically mixing the hard carbon with 30wt% coal-tar pitch in a planetary ball mill machine and then pyrolyzing the mixture at 1000 °C for 1 h under argon, the obtained hard carbon was evidenced to be coated with pitch-pyrolyzed carbon, then the carbon-coated hard carbon was mixed with graphite (MAGD,BTR) at the mass ratio of 1:2. The anode sheet was consisted of active materials 97wt%, poly vinylidene fluoride 3wt%, the electrodes of anode were prepared as the above mentioned method.

Cells were subjected to battery test system (NewwareTC51), the Li/LiFePO₄ cell cycled between 2.7-4.0V, the Li/Li₄Ti₅O₁₂ cell cycled between 1-3V and the Li/hard carbon-graphite composition cell cycled between 0.02–1.5V.

3. RESULTS AND DISCUSSION

Fig.1 shows the TG response of PYR13TFSI, EMITFSI and their mixture. The figure demonstrates the high thermal stability of the IL. The decompose temperature of all samples is higher than 350°C. The values of decompose temperature are as [show](#) below: PYR13TFSI (403°C), PYR13TFSI+EMITFSI (1:1, v/v) (379°C), EMITFSI (358°C), thermal stability of PYR13TFSI shows no significant reduction by addition of EMITFSI.

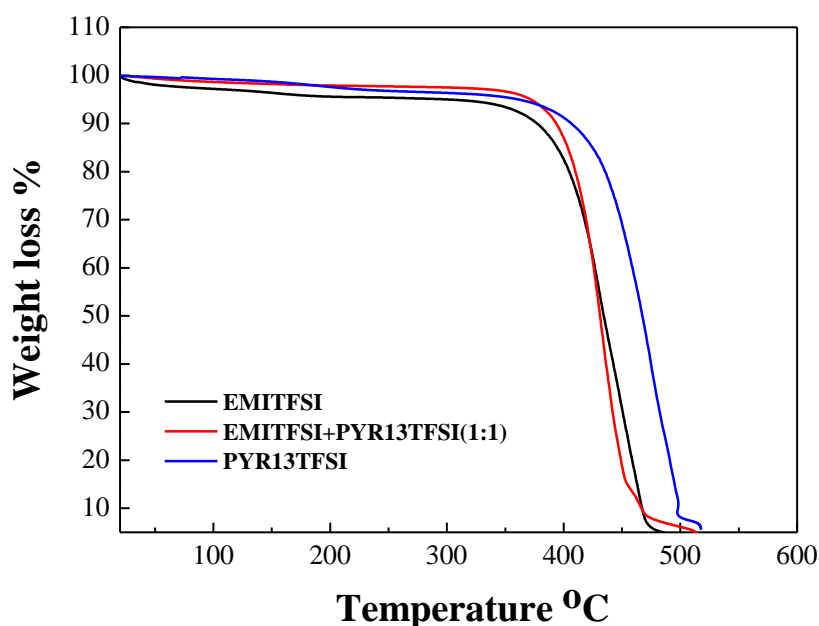


Figure 1. Thermal gravimetric analysis of ILs.

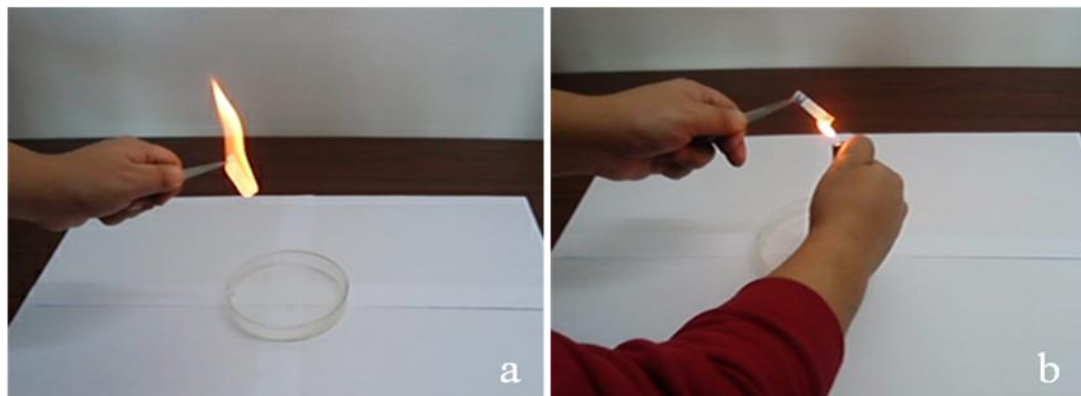


Figure 2. Burning tests on electrolytes. (a) 1M LiPF₆ in EC: DEC (1:1), (b) ionic liquid mixed electrolytes.

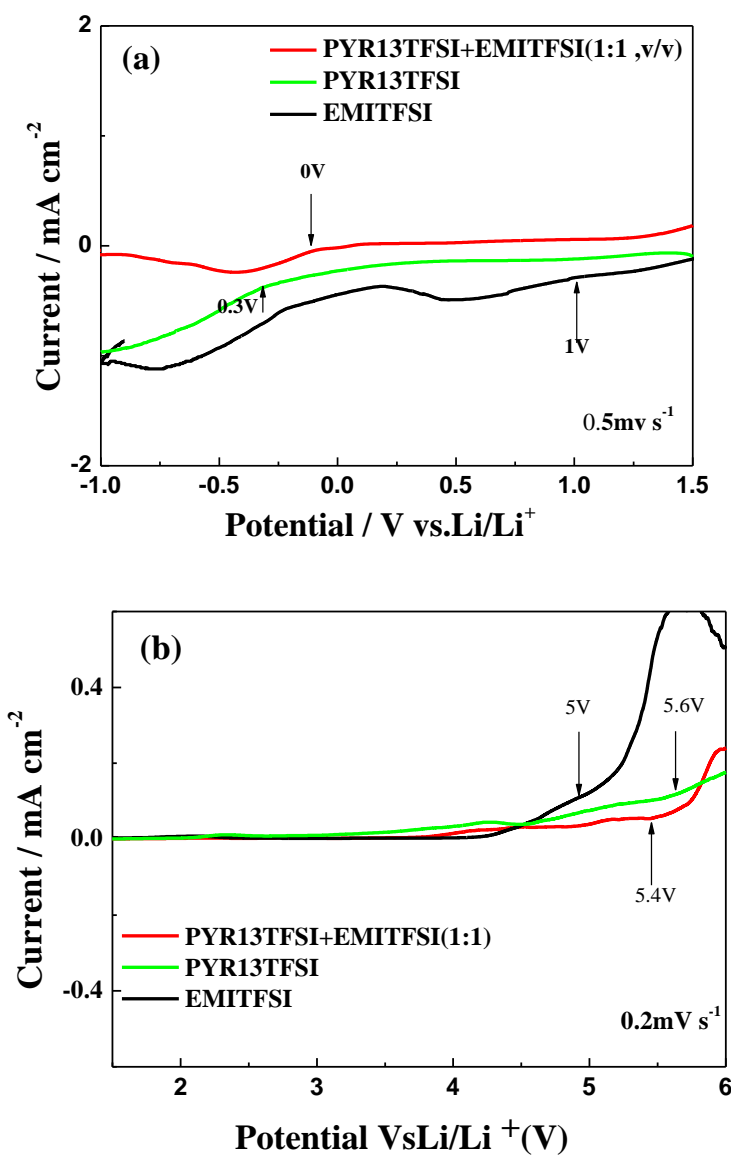


Figure 3. Linear sweep voltammograms of platinum electrode in different ionic liquid at room temperature. Counter electrode: copper foil (a) and lithium foil (b).

To clarify the safety of mixed electrolytes, burning tests of traditional organic electrolytes (1M LiPF₆ in EC: DEC) and 0.2MLiTFSI / EMITFSI+PYR13TFSI (1:1, v/v) were carried out. Fig.2 shows the photographs of a direct flame on the organic electrolyte and mixed electrolytes. The flammability occurred with organic electrolyte in the first second of ignition (Fig.2 a); in contrast to this behavior, mixed electrolytes did not show any combustion even after more than 10 s of flame exposure, this result indicates that safety of electrolyte can be improved by using IL mixture.

Electrochemical stability of the electrolytes within the operation voltage of the battery is important for application in lithium ion battery. The electrochemical window of ILs is shown in Fig.3, as can be seen, oxidative potential of all samples is higher than 4V vs. Li/Li⁺ (PYR13TFSI 5.6V, EMITFSI 5V, EMITFSI-PYR13TFSI mixed ILs 5.4V), but the reductive potential of ILs is different, the PYR13TFSI has the well reductive potential (about -0.3 V vs. Li/Li⁺), while the reductive potential of EMITFSI is only 1V vs. Li/Li⁺, this is in accord with the previous reports, EMITFSI can't be solely used as electrolyte in symmetrical lithium cell. But the excited result we found in PYR13TFSI-EMITFSI mixed electrolytes, the PYR13TFSI-EMITFSI mixed ILs have the well reductive potential, the value close to 0V vs. Li/Li⁺. From this result, it could be expected that the mixed ILs can work as an electrolyte base in lithium ion batteries.

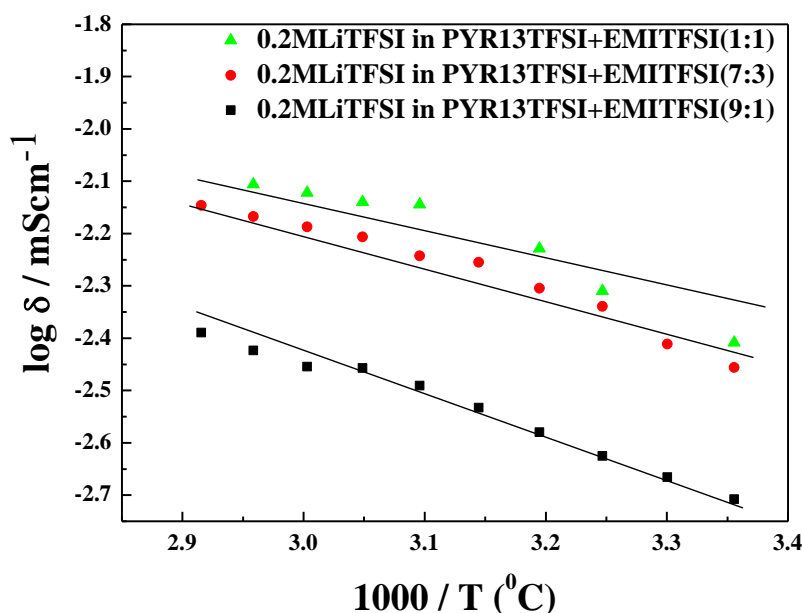


Figure 4. Temperature dependence of ionic conductivity for IL mixed electrolytes.

Fig.4 shows the ion conductivity of IL solutions with 0.2M LiTFSI at different temperature. The ion conductivity values of neat PYR13TFSI and EMITFSI are 1.4 mS cm⁻¹ and 8.7 mS cm⁻¹ at room temperature (not mentioned in the figure), by adding 0.2M LiTFSI salt to the IL, the viscosity obviously increases and thus, as expected, the value of the conductivity clearly decreases as previously reported [9]. However, the ion conductivity of all 0.2M LiTFSI / IL solutions is higher than 10⁻³ Scm⁻¹ (PYR13TFSI-1.21mScm⁻¹, EMITFSI-7.83mScm⁻¹), it also can be seen that ion conductivity of

mixed electrolytes is also increasing with increasing volume rate of EMITFSI, the conductivity values of PYR13TFSI+EMITFSI mixed electrolytes (9:1, 7:3, 5:5, v/v) at room temperature are 2.46 mS cm^{-1} , 4.33 mS cm^{-1} , 4.92 mS cm^{-1} respectively, the values are near to the traditional organic electrolytes (1M LiPF_6 in EC-DEC-DMC, ranges about 10^{-2} to $10^{-3} \text{ S cm}^{-1}$).

The experimental data can be fitted with the Vogel–Tamman–Fulcher (VTF) equation in the form:

$$\sigma = AT^{1/2} \exp \left[\frac{-B}{T-T_0} \right] \quad (1)$$

Here, A and B are the parameters related to the number of charge carriers and the activation energy for conduction, T_0 is the reference temperature and usually near to the glass transition temperature T_g . The analysis of the experimental conductivity data in terms of the VTF relationship leads to the determination of three empirical parameters: A , B and T_0 .

Table1. The conductivity and E_a values of IL mixed electrolytes at room temperature

	Conductivity(mS cm^{-1})	$E_a(\text{KJ mol}^{-1})$
PYR13TFSI+EMITFSI(9:1)	2.46	3.67
PYR13TFSI+EMITFSI(7:3)	4.33	2.69
PYR13TFSI+EMITFSI(1:1)	4.92	2.20

Calculated B values for chosen mixed electrolytes are summarized in Table 1. The B values are strongly affected by the conductivity, the conductivity values of IL mixed electrolytes are mainly depended on the volume rate of EMITFSI.

Fig.5a shows the stability of interface between the Li / IL at longer times of storage at open-circuit, the symmetrical Li / PYR13TFSI+EMITFSI (1:1, v/v) mixed electrolytes / Li cell was measured by impedance spectroscopy. In accordance with the circuit analysis (Fig.5a insets), the impedance evolves with the expected semicircle trend, where, the intercept of the high-frequency semicircle with the real axis gives the value of the bulk electrolyte resistance (R), while its amplitude provides the resistance of the interface. Clearly, the interfacial resistance, including film resistance (R_1) and charge transfer resistance (R_2), increases consistently by time, reaching values about several thousand ohms after a few days storage. The main contribution to the cell impedance is from the interface resistance, while the bulk resistance is very low, the date of interfacial resistance got from two intercepts with the real axis, impedance of IL mixed electrolytes decreases in first hours, then slowly increases in 8 days deposited, it may be reaction between the lithium metal and the PYR13TFSI for SEI formation, then value of the interface resistance decreases to 3800Ω after 9 days. The similar experiment on symmetrical Li / EMITFSI / Li cell is done (Fig.5b), a greatly faster increasing of the interfacial impedance is found, from an initial value of about 1700Ω to 12000Ω within 9 days of storage.

Compared the EIS results in different electrolytes, the mixed ILs effectively reduces the reaction between EMITFSI and lithium.

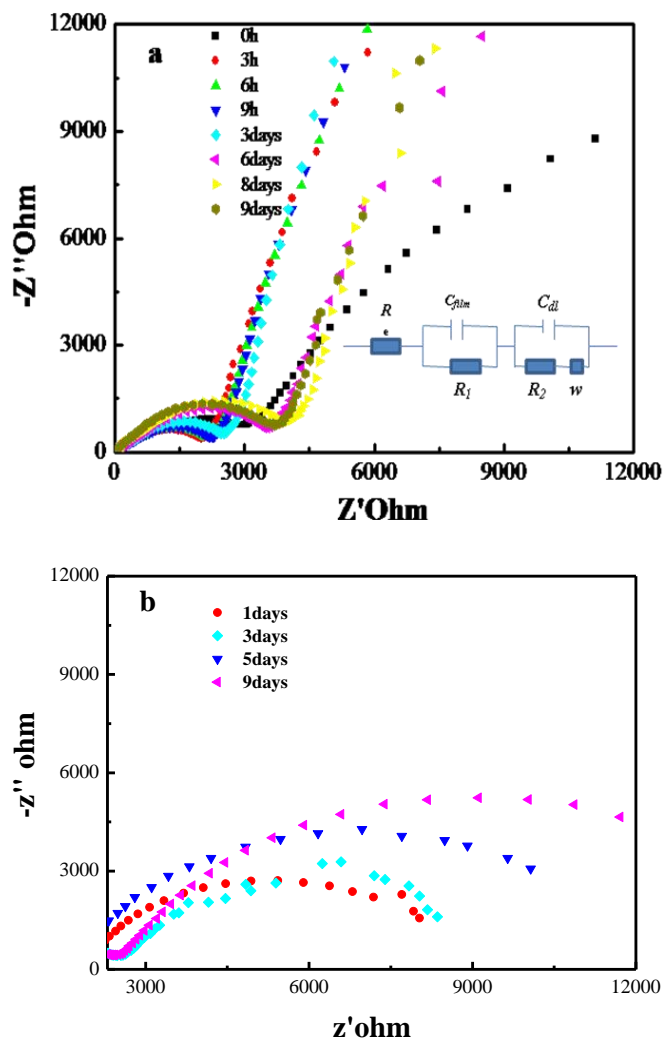


Figure 5. Time evolution of the impedance response and interfacial resistance response of a symmetrical Li / ionic liquid electrolytes / Li cell.(a) 0.2M LiTFSI in PYR13TFSI+EMITFSI(1:1,v/v) electrolyte system,(b) 0.2M LiTFSI in EMITFSI electrolyte system.

Transference numbers is determined by the method of Bruce et al [23], Fig. 6a indicates that constant potential, 10mV (ΔV), was applied across the Li / 0.2M LiTFSI in PYR13TFSI+EMITFSI (1:1, v/v) / Li cell until the current (I_{ss}) reached a steady state. The interfacial resistance (initial state R_0 and steady state R_{ss}) was measured by AC impedance, Fig.6b shows the impedance of the cell before and after polarization, there is no great difference between the R_0 and the R_{ss} , and this shows the stability of the lithium electrode in electrolytes based mixed ILs. The value of I_0 , I_{ss} , R_0 and R_{ss} insert in Eq. (2), the result of the lithium transference number is 0.3, i.e. a reasonable value for practicable application in lithium batteries.

$$t_{Li+} = I_{ss}(\Delta V - I_0 R_0) / I_0(\Delta V - I_{ss} R_{ss}) \tag{2}$$

The EMITFSI-PYR13TFSI (1:1,v/v) with 0.2M LiTFSI solution is used as the electrolyte in the battery, the electrochemical behavior of the electrode materials, i.e. $LiFePO_4$, $Li_4Ti_5O_{12}$ and hard

carbon-graphite composition is described in this section, in order to form stabilize the SEI layer, 5% Vinylene carbonate (VC) was added into the mixed electrolytes.

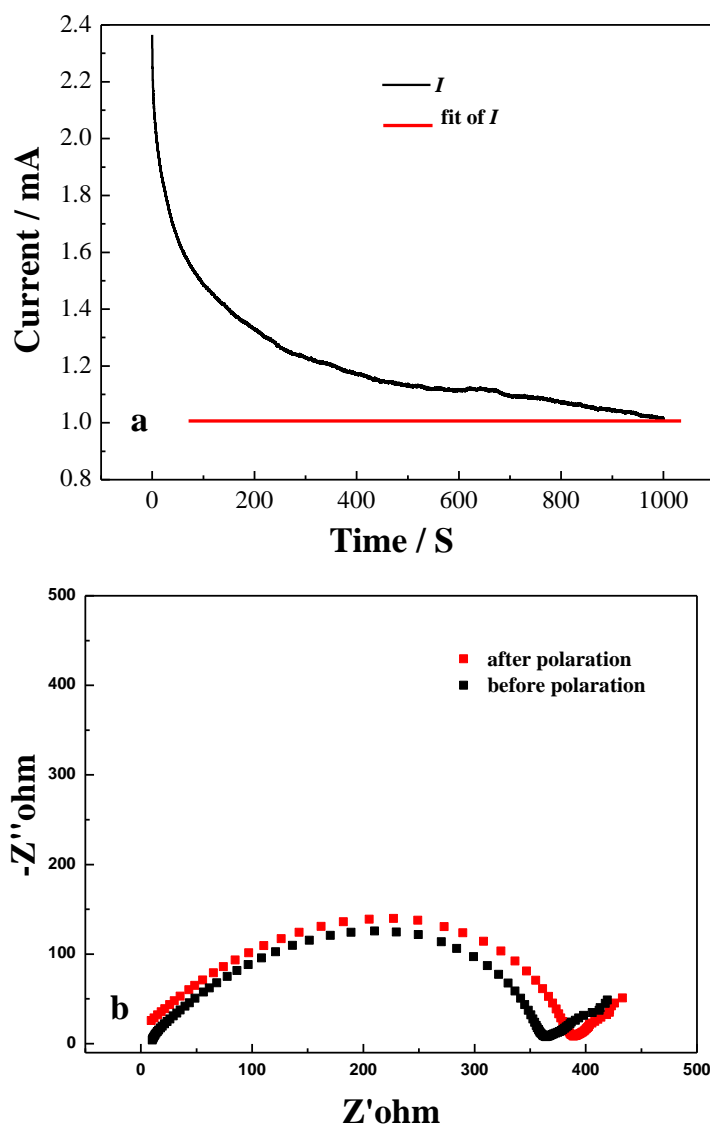


Figure 6. Chronoamperometric curve of a Li / 0.2 mol LiTFSI in PYR13TFSI+EMITFSI (1:1, v/v) / Li cell after a 10mV dc pulse (a) and impedance response of the same cell before and after the dc polarization (b).

Fig.7a shows the voltage-capacity plots of Li/LiFePO₄ cell using mixed electrolytes at 1 / 15C rate. The sufficient discharge capacities with small irreversible capacity are observed for the cycles, it can be said the properties of the cell with mixed electrolytes could be close to the half-cell using the conventional organic electrolytes. Fig.7b shows the cycle performance of Li/LiFePO₄ half cell with IL mixed electrolytes at 1 / 15C rate, the high revisable capacity and reasonable coulomb efficiency can be seen, the half battery demonstrates 132Ah g⁻¹ reversible capacity (75.4% theory capacity of LiFePO₄) for 1st cycle, although the coulomb efficiency which is affected by the reaction between the

electrolyte and electrode, the first coulomb efficiency is only 89%, from second cycle, coulomb efficiency is higher than 90%, this is account for the previous reports on IL electrolytes[16], the discharge capacity is no obviously decay even after 10 cycles .

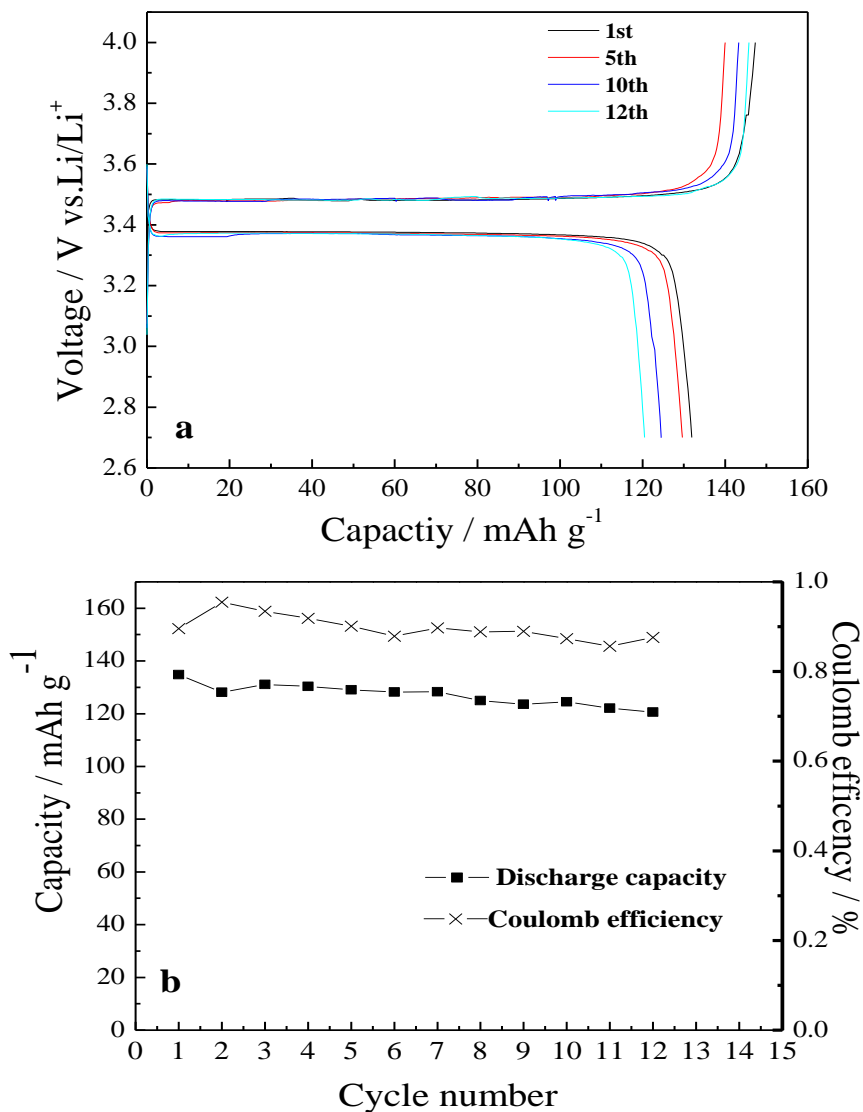


Figure 7. Voltage–capacity curves of the Li / LiFePO₄ cell (a) and capacity vs. cycle number of cell (b) using IL mixed electrolytes at 1/20 C at room temperature .

We also tested the IL mixed electrolytes at high rate (1C, 2C) charge-discharge cycle, like other IL electrolyte, the reversible capacity decreases obviously (date not shown) .

Fig.8 shows cycle performance of the Li/Li₄Ti₅O₁₂ cell using mixed electrolytes at 0.1 C charge-discharge rate. The cell presents higher reversible capacity and coulomb efficiency, the cell shows the capacity of 134mAhg⁻¹ with 99% coulomb efficiency even after 30 cycles. It is attributed to the stability of the Li₄Ti₅O₁₂ framework and the stabilization of mixed electrolytes during the course of lithium insertion and extraction.

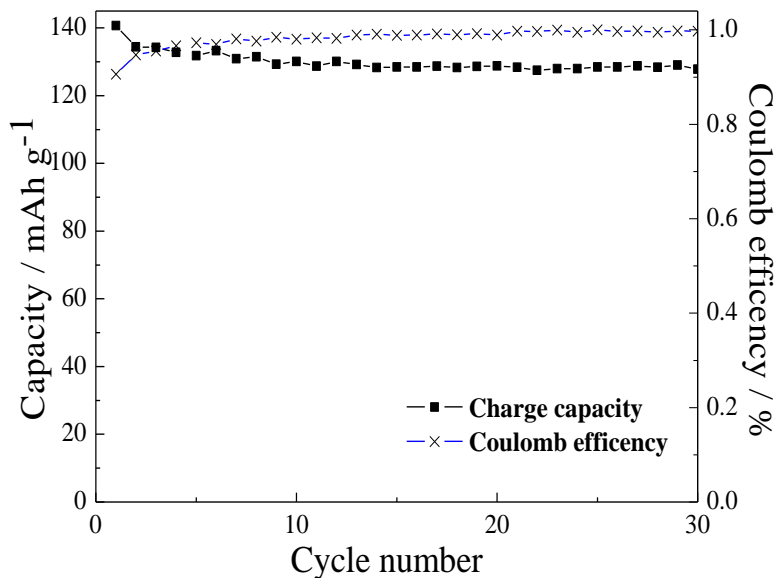


Figure 8. Cycle performance of Li / 0.2MLiTFSI in PYR13TFSI+EMITFSI (1:1) / Li₄Ti₅O₁₂ cell

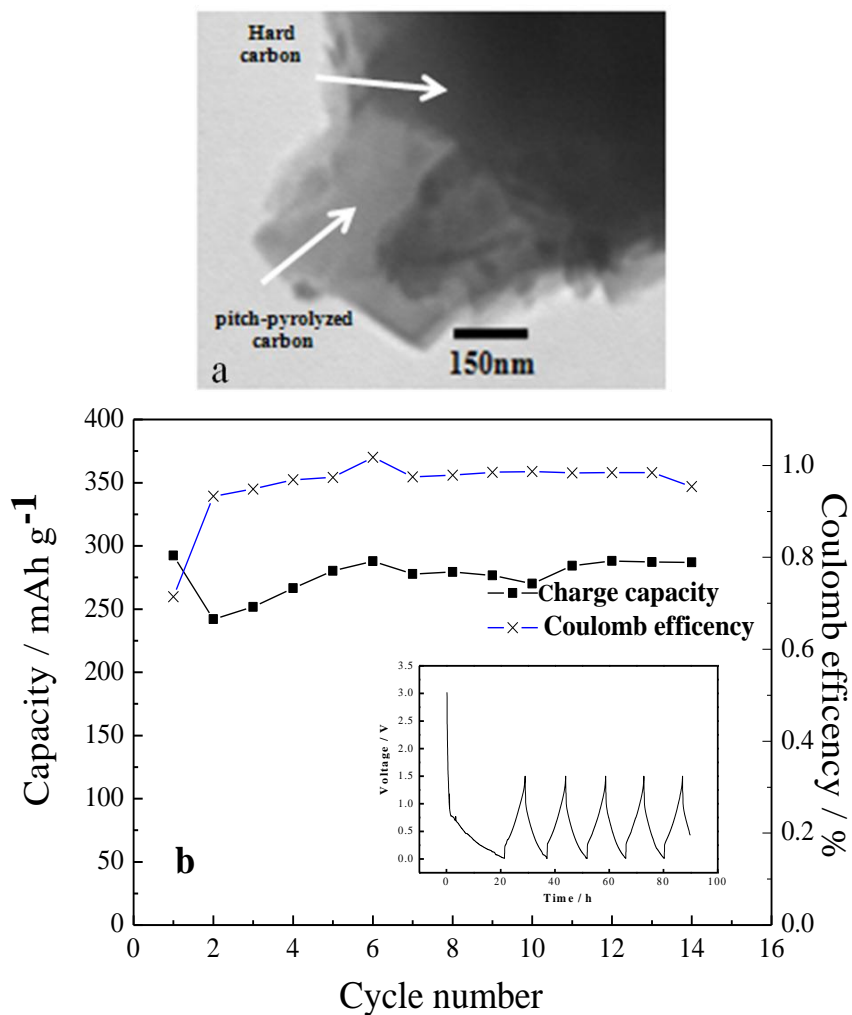


Figure 9. TEM images of carbon-coated hard carbon (a) and Li / 0.2MLiTFSI in PYR13TFSI+EMITFSI (1:1) / hard carbon-graphite composition cell (b).

It is a common problem that ionic liquid electrolyte can't steadily cycle on graphite. The decomposition reaction of cations refutes the formation stable SEI. Many methods have been done to solve this problem, such as using (EC) and VC additives in electrolytes, or using Non-carbon materials (Sn, Si-Cu). In this paper, we use carbon-coated hard carbon (Fig9.a) and graphite composition as anode. Fig9.b shows the cycle performance of Li/hard carbon-graphite composition cell using the mixed electrolytes, the range of charge-discharge voltage is between 1.5V and 0.01V. Compared with single EMITFSI electrolyte-system (the discharge capacity of the graphite is at the level of only 80–90mAh g⁻¹ after the first intercalation) [24, 25, 26], the first charge capacity and discharge capacity of Li / 0.2M LiTFSI in EMITFSI-PYR13TFSI (v/v 1:1) / hard carbon-graphite composition cell at 1 / 20C rate are 440mAhg⁻¹ and 300mAhg⁻¹ respectively, from second cycle, capacity of the electrode goes down and stabilize to 275mAh g⁻¹ (inset shows the voltage-time plots of cell in first few cycles). The loss of capacity is because of the graphite exfoliation during its continuous insertion and extraction processes, which leads to the degradation of its structure.

Although the performance of the cell using IL mixed electrolytes is still lower than traditional organic electrolytes, the results discussed in this article demonstrate the basic possibility of the mixed ILs for lithium ion batteries.

4. CONCLUSIONS

The results of this article demonstrate that, the advantage of the ILs' property of offering a wide flexibility in applying in lithium ion battery, we prepared a kind of electrolytes -the IL mixed (PYR13TFSSI+EMITFSI 9:1, 7:3, 1:1, v/v) solutions with 0.2MLiTFSI, which is a very promising electrolytes for lithium ion battery. The mixed electrolytes show the well stability to carbon material and lithium. The good cycle performance of the cells using 0.2MLiTFSI / IL is testified (the reversible capacities were 132 mAhg⁻¹ for cathode material, 134mAhg⁻¹ for Li₄Ti₅O₁₂ and 275 mAhg⁻¹ for carbon materials). The mixed electrolytes also show the characters of thermal stability and incombustibility, this is significant for improving the safety of lithium ion battery which can't be surpassed by traditional organic electrolytes. In future, how to apply the IL mixed electrolytes to EV and HEV is need further researched.

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