



## Li/LiFePO<sub>4</sub> batteries with room temperature ionic liquid as electrolyte

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### ABSTRACT

Room temperature ionic liquid (RTIL) was prepared on basis of *N*-methyl-*N*-butylpiperidinium bis(trifluoromethanesulfonyl)imide (PP<sub>14</sub>TFSI), which showed a wide electrochemical window (−0.1–5.2 V vs. Li<sup>+</sup>/Li) and is theoretically feasible as an electrolyte for batteries with metallic Li as anodes. The addition of vinylene carbonate (VC) improved the compatibility of PP<sub>14</sub>TFSI-based electrolyte towards lithium anodes and enhanced the formation of solid electrolyte interphase film to protect lithium anodes from corrosion. Accordingly, Li/LiFePO<sub>4</sub> cells initially delivered a discharge capacity of about 127 mAh g<sup>−1</sup> at a current density of 17 mA g<sup>−1</sup> in the ionic liquid with the addition of VC and showed better cyclability than in the neat ionic liquid. Electrochemical impedance spectroscopy disclosed that the addition of VC enhanced Li-ion diffusion and depressed interfacial resistance significantly.

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### 1. Introduction

Metallic lithium is an ideal battery material for the concern of energy density since its theoretical capacity is as high as 3860 mAh g<sup>−1</sup> [1]. However, one limitation for its practical use is the growth of dendrites during cycling, which causes non-reversibility and even safety hazard [2]. Another safety concern is the high flammability and high vapor pressure of conventional organic solvents (such as ethylene carbonate and ethyl methyl carbonate) commonly used in lithium ion batteries nowadays. Under such background, room temperature ionic liquids (RTILs) [3,4] have aroused much attention because of its excellent thermal stability, small volatility and flammability, and wide electrochemical window [5].

As the electrolytes in lithium batteries, imidazolium-based RTILs have been exploited recently; however, the stability limited up to the redox potential of lithium metal restricts its further use [6,7]. Matsumoto et al. [8] reported that *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (Py<sub>14</sub>TFSI)-based electrolyte exhibited sufficiently wide electrochemical window to allow the electrochemical deposition of lithium. Sakaebe and Matsumoto [9] designed a new RTIL based on *N*-methyl-*N*-propylpiperidinium bis(trifluoromethanesulfonyl)imide (PP<sub>13</sub>TFSI), which exhibited a wider electrochemical window and higher cathodic stability against lithium metal. Therefore, we can develop metallic lithium as active materials in lithium secondary batteries.

However, the disadvantages of RTILs, higher viscosity and lower ionic conductivity than conventional organic solvents, lead to poor electrochemical performances of the cells with RTILs as electrolytes. Molecular additives, such as zwitterionic compounds [10], tetra(ethylene glycol) dimethyl ether (TEGDME) [11], poly(ethylene glycol) dimethyl ether (PEGDME) [12], ethylene carbonate (EC), vinylene carbonate (VC), ethylene sulphite, and vinylene acetate [13,14], have been proposed as electrolyte additives to enhance the solid electrolyte interphase (SEI) film on the Li electrodes [15]. Molecular dynamics simulation also showed that the addition of neutral molecules effectively relaxed the RTIL structure and enhanced the homogeneity [16].

In this work, we selected VC as an additive to PP<sub>14</sub>TFSI-LiTFSI-based electrolyte and examined the performance of this modified electrolyte in Li/LiFePO<sub>4</sub> batteries.

### 2. Experimental

#### 2.1. Preparation of RTIL electrolytes

The room temperature ionic liquid, PP<sub>14</sub>TFSI, was prepared through a usual route [17,18]. First, *N*-methylpiperidine (Aldrich, 98.0%) and iodobutane (Aldrich, 99%) with equivalent moles were mixed in ethyl acetate and the resulting solution was stirred at 50 °C for 5 h. A white crystalline precipitate of *N*-methyl-*N*-butylpiperidinium bromide (PP<sub>14</sub>Br) was obtained with vacuum filtration. Impurities were removed by repeatedly rinsing the precipitate. Second, PP<sub>14</sub>TFSI was obtained by mixing PP<sub>14</sub>Br and LiTFSI (3 M, 99%) with equivalent molar amounts at room temperature in deionized water for 1 h. The resulting organic phase

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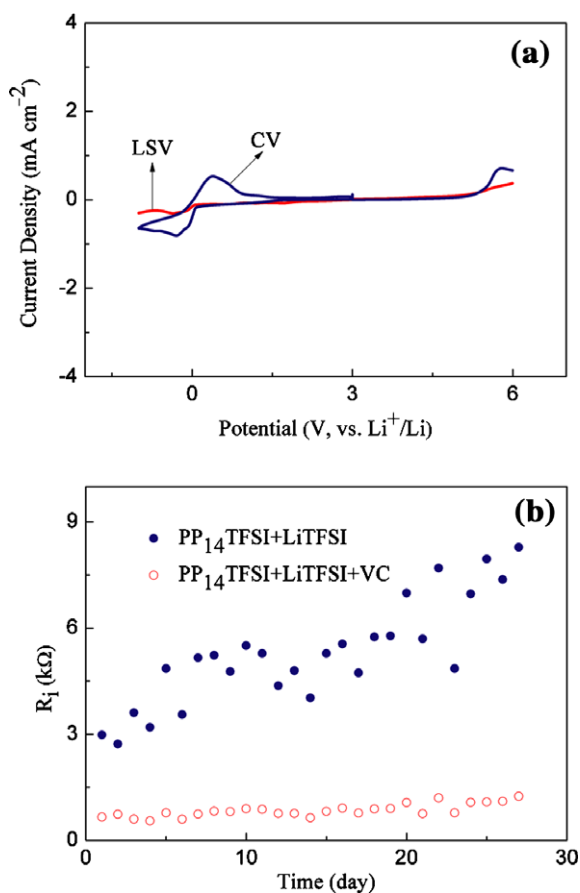
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was extracted with dichloromethane, washed with water, and then purified with activated carbon and acid alumina. The final product  $\text{PP}_{14}\text{TFSI}$  was a clear colorless liquid at room temperature. The ionic liquid was dried in vacuum at 80 °C for 12 h and at 120 °C for 24 h to remove residual solvent and water. The binary electrolyte (0.32 mol  $\text{kg}^{-1}$  solution of LiTFSI in  $\text{PP}_{14}\text{TFSI}$ ) was prepared by dissolving dried LiTFSI in  $\text{PP}_{14}\text{TFSI}$  in an argon-filled glove box and stirring the solution at room temperature for 48 h. The ternary electrolyte was obtained through the addition of 10 wt% VC to the above binary electrolyte. The chemical structure of  $\text{PP}_{14}\text{TFSI}$  was checked by  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ) (AVANCE 300, Bruker).

## 2.2. Tests of stability of Li electrodes in RTIL electrolytes

Evaluation of the electrochemical window of RTILs was carried out by linear sweep voltammetry (LSV, scan rate of 10  $\text{mV s}^{-1}$ ) as reported previously [19] and cyclic voltammetry (CV) in two-electrode cells with copper as the working electrode (surface area 0.95  $\text{cm}^2$ ), and lithium as both counter and reference electrode.

The time-evolution dependence of the Li/electrolyte interfacial resistance ( $R_i$ ) was measured in Li/electrolyte/Li symmetric cells through the ac impedance on a Zahner-Elektrik IM6e electrochemical workstation with the frequency ranging from 200 kHz to 10 MHz and an AC signal of 5 mV in amplitude as the perturbation at room temperature. The measurement was performed with 1 day interval.



**Fig. 1.** LSV of copper electrode in  $\text{PP}_{14}\text{TFSI}$  and CV of copper electrode in LiTFSI- $\text{PP}_{14}\text{TFSI}$  binary electrolyte (a) and interfacial resistance for Li/electrolyte/Li symmetric cells at open circuit condition at room temperature (b).

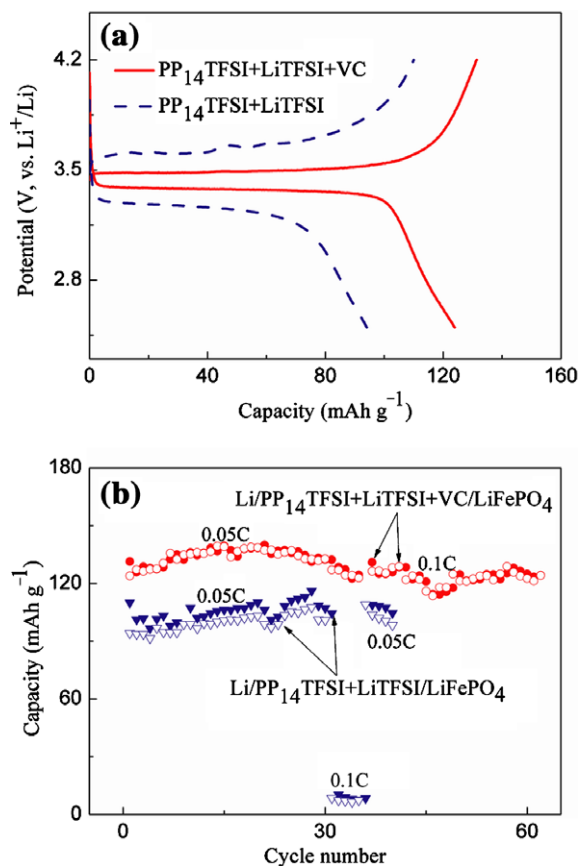
## 2.3. Cell assemblies and electrochemical measurements

Li/electrolyte/ $\text{LiFePO}_4$  cells were used for electrochemical measurements. The  $\text{LiFePO}_4$  cathode electrode was made up of  $\text{LiFePO}_4$ , acetylene black, and polytetrafluoroethylene (PTFE) binder with a weight ratio of 85:10:5. The Li anode, Celgard 7320 separator, RTIL electrolyte, and  $\text{LiFePO}_4$  cathode were assembled in sequence into cells in an argon-filled dry glove box. The mass ratio of the Li anode to the cathode material was about 20. Charge–discharge tests were performed at 2.5–4.2 V (vs.  $\text{Li}^+/\text{Li}$ ) at room temperature under the Land CT2001 battery tester. Electrochemical impedance spectroscopy (EIS) was also recorded under the same condition as in Section 2.2.

## 3. Results and discussion

### 3.1. Electrochemical window and Li/RTIL interfacial properties

Fig. 1a displays LSV and CV to clarify the anodic and cathodic electrochemical stability of  $\text{PP}_{14}\text{TFSI}$  and LiTFSI- $\text{PP}_{14}\text{TFSI}$  at room temperature. LSV shows that the electrochemical window of neat  $\text{PP}_{14}\text{TFSI}$  was ca. -0.1–5.2 V. The anodic limiting current flow observed at 5.2 V (vs.  $\text{Li}^+/\text{Li}$ ) corresponds to the oxidation of the TFSI $^-$  anions, while the cathodic limiting current at -0.1 V (vs.  $\text{Li}^+/\text{Li}$ ) indicated the decomposition of the  $\text{PP}_{14}^+$  cations. This confirms the feasibility of  $\text{PP}_{14}\text{TFSI}$  for the application to Li secondary batteries. CV exhibits a pair of redox peaks around 0 V (vs.  $\text{Li}^+/\text{Li}$ ) in the presence of LiTFSI, which corresponds to the deposition and dissolution of Li on and from the copper substrate, respectively. These evidences demonstrate that LiTFSI- $\text{PP}_{14}\text{TFSI}$  binary electrolyte



**Fig. 2.** Initial charge/discharge profiles of Li/electrolytes/ $\text{LiFePO}_4$  cells at 0.05 C rate (a) and cyclic performances (b) at room temperature.

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