Li/LiFePO₄ battery performance with a guanidinium-based ionic liquid as the electrolyte

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A new guanidinium-based ionic liquid (IL) was investigated as a novel electrolyte for a lithium rechargeable battery. The viscosity, conductivity, lithium redox behavior, and charge-discharge characteristics of the lithium rechargeable batteries were investigated for the IL electrolyte with 0.3 mol kg⁻¹ lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) salt. Li/LiFePO₄ cells incorporating the IL electrolyte without additives showed good cycle properties at a charge-discharge current rate of 0.1 C, and exhibited good rate capabilities in the presence of a mass fraction of 10% vinylene carbonate or gamma-butyrolactone.

lithium battery, lithium iron phosphate, ionic liquid, guanidinium

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The popularity of lithium rechargeable batteries has increased over the last two decades because of the demand for portable energy storage devices. Conventional organic electrolytes used in lithium rechargeable batteries are composed of organic solvents and inorganic salts. These batteries have a working temperature range from –20–50°C, which restricts the applications for lithium rechargeable batteries. There are also safety concerns over the organic solvents, which are volatile and flammable with flash points mostly below 30°C [1,2]. To overcome these, new and safe electrolytes need to be developed.

Room temperature ionic liquids (RTILs) that consist of only cations and anions are non-volatile, non-flammable, and have high thermal stability, which makes them promising for application as electrolytes [3,4]. These new electrolytes can be combined electrodes such as lithium iron phosphate (LiFePO₄), which has a high theoretical capacity, low cost, and low environmental impact [5–7].

Li/LiFePO₄ cells with RTILs-based electrolytes (flash point is >300°C) show good efficiency [8]. Unfortunately,

RTILs-based electrolytes exhibit higher viscosity, lower conductivity and reduced compatibility with electrodes compared to conventional organic electrolytes, and this leads to relatively poor cell performance [9,10]. To resolve these problems, some organic additives such as ethylene carbonate and vinylene carbonate (VC) have been added to obtain a stable solid electrolyte interface (SEI) on the electrode [11–15].

Recently, our group [16] synthesized a series of hydrophobic RTILs based on small guanidinium cations and the bis(trifluoromethanesulfonyl)imide (TFSI) anion. Both 1g13-TFSI (*N*-methyl-*N*-propyl-*N*',*N*',*N*'',*N*''-tetramethylguanidinium-TFSI) and 1g22TFSI (*N,N*-diethyl-*N*',*N*',*N*'',*N*''-tetramethylguanidinium-TFSI) could be used as electrolytes for Li/LiCoO₂ lithium rechargeable batteries [17]. Although the cells with guanidinium-based electrolytes had good capacities, they exhibited unfavorable cycle properties. In this study, a new guanidinium RTIL, 1g14TFSI (Figure 1), was investigated as a novel electrolyte for Li/LiFePO₄ lithium rechargeable batteries. Both VC and gamma-butyrolactone (GBL) were investigated as additives to the 1g14TFSI-based electrolyte, and their influence on electrochemical performance was studied using charge-discharge tests.

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Figure 1 Structures of cation and anion of 1g14TFSI RTIL.

1 Experimental

The guanidinium RTIL (Figure 1) was synthesized according to our reported method [16]. The RTIL was dried under high vacuum for more than 24 h at 100°C before use. The water content of the dried RTIL was measured at <50 ppm using a moisture titrator (73 KF coulometer, Metrohm, Herisau, Switzerland) based on the Karl-Fischer method. LiTFSI (0.3 mol kg⁻¹, Morita Chemical Industries Co., Ltd, Osaka, Japan) was added to the dried RTIL in an argon-filled glove box.

VC and GBL were used as additives, and their structures are shown in Figure 2.

The viscosity of the 1g14TFSI IL-based electrolyte was measured with a viscometer (DV-IIIULTRA, Brookfield Engineering Laboratories, Inc, Middleboro, MA), and the ionic conductivity was measured using a DDS-11A conductivity meter (Shanghai Yoke Instrument Co., Ltd., Shanghai, China).

The electrochemical window of 1g14TFSI was measured by linear sweep voltammetry in the glove box. The working electrode was a glassy carbon disk (ϕ 3 mm), the counter electrode was platinum wire, and the reference electrode was silver wire. The plating and stripping behaviors of lithium in the 1g14TFSI IL-based electrolyte were examined using cyclic voltammetry in the glove box. A nickel disk (ϕ 2 mm) was used as the working electrode, and lithium metal was used as both the counter and reference electrodes. The Ni electrode was polished with alumina paste (particle ϕ 0.1 μ m). The polished electrode was washed with deionized water and dried under vacuum. Both linear sweep and cyclic voltammetry were performed using a CHI 604b electrochemistry workstation (Shanghai ChenHua Instrument Co., Ltd., Shanghai, China) at room temperature (25°C).

Li/LiFePO₄ coin cells were used to evaluate the perfor-

Figure 2 Structures of vinylene carbonate and gamma-butyrolactone.

mance of the 1g14TFSI RTIL-based electrolyte with or without additives in lithium rechargeable battery applications. The cathode was prepared by spreading a mixture of LiFePO₄ (Tianjin STL Energy Technology Co., Ltd., Tianjin, China), acetylene black (Denka, Tokyo, Japan) and polyvinylidene fluoride (Shanghai 3F New Material Co., Ltd., Shanghai, China) with a mass ratio of 8:1:1 onto battery Al foil (ShenZhen GuoXing Newpower Technology Ltd., Shenzhen, China). polyvinylidene fluoride was dissolved in *N*-methyl-2-pyrrolidone before mixing with the other cathode components. The active material mass loading was about 1–1.5 mg cm⁻². Lithium foil (battery grade) was used as the anode. The separator was a glass filter made of borosilicate glass (GF/A, Whatman, Maidstone, UK). All the components of the cell were dried under vacuum, and then cell construction was carried out in the glove box. The cells were sealed and then kept at room temperature for 4 h. The cell performance was examined by a galvanostatic charge-discharge cycling test using a CT2001A cell test instrument (Starconn, Taipei, Taiwan, China) at room temperature. Charging included the following two processes: (1) constant current with a cut-off voltage of 4.0 V; and (2) constant voltage (4.0 V) with a cutoff current of 0.01 mA. The discharge was at a constant current with a cutoff voltage of 2.5 V.

2 Results and discussion

2.1 Physicochemical properties

Van der Waals interactions and hydrogen bonding are mainly responsible for viscosity. The temperature viscosity relationship usually follows the Arrhenius equation, except for at temperatures near the melting point [18].

The temperature dependence of the viscosity was studied for 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte from 25–80°C. The Vogel-Tammann-Fulcher (VTF) plot (Figure 3, open triangles) of the viscosity was obtained using eq. (1).

Figure 3 Change in the viscosity and conductivity with temperature for the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte.

$$\eta = \eta_0 \exp\left(\frac{B}{T - T_0}\right). \quad (1)$$

The constants η_0 (mPa s), B (K) and T_0 (K), and the VTF fitting parameter R^2 are summarized in Table 1. The percentage standard errors for η_0 , B and T_0 are included in Table 1. The viscosity of the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte was 122 mPa s at room temperature, and this increased as the temperature decreased.

The temperature dependence of the conductivity was also investigated for the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte from 25–80°C and the VTF plot (Figure 3, solid circles) of conductivity was obtained using eq. (2).

$$\sigma = \sigma_0 \exp\left(\frac{-B}{T - T_0}\right), \quad (2)$$

The constants σ_0 (mS cm⁻¹), B (K) and T_0 (K), and the VTF fitting parameter R^2 are summarized in Table 2. The percentage standard errors for σ_0 , B and T_0 are included in Table 2. The conductivity of the 1g14TFSI with 0.3 mol kg⁻¹ LiTFSI electrolyte was 1.06 mS cm⁻¹ at room temperature, and this increased as the temperature increased.

The viscosity of the binary electrolyte is 42 mPa s higher than that of the neat 1g14TFSI IL (80 mPa s) at room temperature, and the conductivity of the binary electrolyte is 0.85 mS cm⁻¹ lower than that of the neat 1g14TFSI IL [16]. Addition of LiTFSI increases the viscosity of the ionic liquid and decreases its conductivity.

2.2 Lithium redox in the 1g14TFSI-based electrolyte

The linear sweep voltammetry for 1g14TFSI cycled on a glassy carbon working electrode at 25°C is shown in Figure 4. The electrochemical window of the neat 1g14TFSI was 4.2 V. The anodic limiting current observed at 2.2 V (vs. Ag/Ag⁺) corresponds to oxidation of the TFSI⁻ anions, while the cathodic limiting current at -2.0 V (vs. Ag/Ag⁺) corresponds to decomposition of the 1g14⁺ cations.

Figure 5 shows the cyclic voltammetry of the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte on a Ni working electrode

Figure 4 Linear sweep voltammetry of 1g14TFSI at 25°C. Working electrode, glassy carbon; counter electrode, platinum wire; reference electrode, silver wire; scan rate, 10 mV s⁻¹.

Figure 5 Cyclic voltammetry for the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte at 25°C (-0.5 to 2.5 V vs. Li/Li⁺). Working electrode, Ni; counter electrode, Li; reference electrode, Li; scan rate, 10 mV s⁻¹.

from 2.5 to -0.5 V at a scan rate of 10 mV s⁻¹. Plating of lithium on the Ni electrode could be clearly observed. In the first cycle, lithium metal was deposited at about -0.2 V versus Li/Li⁺. The anodic peak at about 0.4 V in the return scan corresponds to stripping of lithium. The lithium redox in this electrolyte is thought to be caused by the generation of a SEI on the Ni electrode. The plating/stripping peaks decreased gradually with the cycle number, which suggests that the SEI generated in the first cycle blocks the reduction of lithium. Another cathodic peak at about 0.34 V was observed in the first cycle, and could be assigned to the electrochemical reduction of the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte. This peak decreased with increasing cycle number, which indicates that the SEI generated in the first cycle also blocks reduction of the electrolyte.

2.3 Battery performance

The discharge performance of the Li/LiFePO₄ cells

Table 1 VTF equation parameters for viscosity of the 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte

IL	η_0 (mPa s)	B (K)	T_0 (K)	R^2
1g14TFSI	0.14 (±7%)	787 (±2%)	182 (±1%)	0.999

Table 2 VTF equation parameters of conductivity for 0.3 mol kg⁻¹ LiTFSI/1g14TFSI electrolyte

IL	σ_0 (mS cm ⁻¹)	B (K)	T_0 (K)	R^2
1g14TFSI	178 (±3%)	518 (±2%)	197 (±1%)	0.999

incorporating the 0.3 mol kg^{-1} LiTFSI/1g14TFSI electrolyte were examined. The initial discharge capacity of the cell was 76.5 mAh g^{-1} , and at the 50th cycle it was 115 mAh g^{-1} (Figure 6). This demonstrates good reversibility in the battery system using the 1g14TFSI-based electrolyte. The discharge capacity increased gradually with the cycle number, which could be attributed to the poor compatibility of the 1g14TFSI-based RTIL with the LiFePO_4 cathode. The coulombic efficiency of the cell during the first cycle was 83.7%, which was a result of electrolyte decomposition and SEI formation, and in subsequent cycles it remained close to 100%.

Guerfi et al. [19] used *N*-methyl-*N*-propylpyrrolidinium-bis(fluorsulfonyl)imide (Py13-FSI) as a safe electrolyte with a LiFePO_4 cathode in lithium rechargeable cells. To improve the compatibility of the RTIL towards the cathode, LiFePO_4 was pre-treated by immersion in the Py13FSI/LiFSI RTIL, and then placed under vacuum at 60°C for 8 h. The pre-treated cell showed enhanced compatibility and better cycle properties [19]. In the present study, two methods were used to improve the poor compatibility of guanidinium-based RTIL electrolyte towards the LiFePO_4 cathode. The first method involved addition of the 1g14TFSI-based RTIL to a cathode material slurry with stirring. The second method involved dropping the 1g14TFSI-based RTIL onto the cathode plate and then drying this under vacuum for 8 h at 80°C . Treatment with method one gave an initial discharge capacity of 82.9 mAh g^{-1} , which was 6.4 mAh g^{-1} higher than that without treatment, while treatment with method two gave a discharge capacity that was 24.3 mAh g^{-1} higher than that without treatment (Figure 7). Both methods improved the discharge capacity during cycling of the Li/LiFePO₄ cells. These results demonstrate better compatibility towards the LiFePO_4 cathode with treatment, and the cell that was treated by method two showed superior performance to that treated by method one.

Figure 6 Discharge capacity during cycling of Li/LiFePO₄ cells incorporating the 0.3 mol kg^{-1} LiTFSI/1g14TFSI electrolyte (solid circles), and coulombic efficiency (open squares). The charge-discharge current rate was 0.1 C.

Figure 7 Cycling behavior of the Li/LiFePO₄ cells incorporating the 0.3 mol kg^{-1} LiTFSI/1g14TFSI electrolyte, with and without treatment. The charge-discharge current rate was 0.1 C.

The rate capability of the Li/LiFePO₄ cell with 0.3 mol kg^{-1} LiTFSI/1g14TFSI was also tested. The discharge capacity was recorded at various charge-discharge current rates between 0.1 C and 1 C (Figure 8, solid squares). The discharge capacity of the Li/LiFePO₄ cell decreased as the charge-discharge current rate increased. It has been reported that the discharge capacity of a RTIL-based lithium rechargeable battery is lower than that of a conventional organic electrolyte-based lithium rechargeable battery, especially at high charge-discharge rates, which probably results from the high resistance of the SEI [20–23].

To improve the rate properties of the Li/LiFePO₄ cell using the 1g14TFSI-based electrolyte, two common additives, VC and GBL, were introduced to the 0.3 mol kg^{-1} LiTFSI/1g14TFSI electrolyte. Curves for the rate capability versus the cycle number for the cell with VC (open circles) or GBL (open triangles) containing electrolytes are shown in Figure 8. The initial discharge capacities of the cells without additives at 0.1 C, 0.2 C, 0.5 C, and 1 C were 74.9, 78.8, 67.3,

Figure 8 Rate capability of the Li/LiFePO₄ cell incorporating 0.3 mol kg^{-1} LiTFSI/1g14TFSI (solid squares), 0.3 mol kg^{-1} LiTFSI/1g14TFSI +VC (mass fraction 10%) (open circles), and 0.3 mol kg^{-1} LiTFSI/1g14TFSI+GBL (mass fraction 10%) (open triangles). The charge-discharge current rate was 0.1 C (1–5), 0.2 C (6–10), 0.5 C (11–15), and 1.0 C (16–20).

and 44.2 mAh g⁻¹, respectively. These initial discharge capacities increased to 84.2 (0.1 C), 92.2 (0.2 C), 87.6 (0.5 C), and 75.6 mAh g⁻¹ (1 C) when with a mass fraction of 10% VC, and to 114.2 (0.1 C), 103.2 (0.2 C), 91.3 (0.5 C), and 80.7 mAh g⁻¹ (1 C) with a mass fraction of 10% GBL in the electrolyte. The Li/LiFePO₄ cells with VC and GBL-modified RTIL electrolytes exhibited better charging rate capabilities than the cell without additives. The cell with the GBL-modified RTIL electrolyte performed better than that containing the VC-modified RTIL electrolyte. The above results confirmed the addition of VC or GBL could enhance the SEI formation, which gives a better charge rate capability for the cell [8,14,15].

3 Conclusions

The temperature dependence of the conductivity and viscosity of the LiTFSI/1g14TFSI IL electrolyte fit the VTF model, and the electrochemical window of 1g14TFSI was 4.2 V according to its cyclic voltammetry. The LiTFSI/1g14TFSI IL-based electrolyte was not stable at about 0.34 V, but formation of a SEI could block reduction of the electrolyte. Li/LiFePO₄ cells incorporating the LiTFSI/1g14TFSI electrolyte showed high coulombic efficiency and good capacity at a current rate of 0.1 C. Dropping the ionic liquid onto a cathode plate and then drying under vacuum for 8 h at 80°C improved the compatibility of the LiTFSI/1g14TFSI IL electrolyte towards the LiFePO₄ cathode. Li/LiFePO₄ cells using VC or GBL-modified LiTFSI/1g14TFSI IL electrolytes exhibited better rate capabilities than those without VC or GBL.

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