



Short communication

## Guanidinium-based ionic liquids as new electrolytes for lithium battery

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### ABSTRACT

Two ionic liquids based on guanidinium cations and TFSA<sup>-</sup> anion were prepared, and their electrochemical stabilities were investigated. The cathodic limiting potentials of the two ILs were 0.7 V versus Li/Li<sup>+</sup>, and their electrochemical windows were 4.2 V. However, the lithium plating and stripping on Ni electrode could be observed in the two IL electrolytes containing 0.3 mol kg<sup>-1</sup> of LiTFSA without additive. And Li/LiCoO<sub>2</sub> cells using the two IL electrolytes without additive showed good capacity and cycle property at the current rate of 0.2 C.

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### 1. Introduction

Ionic liquids (ILs) are molten salts with melting points at or below ambient temperature, and they have suitable properties to be used as safe electrolytes in lithium battery due to non-volatility and nonflammability [1–7].

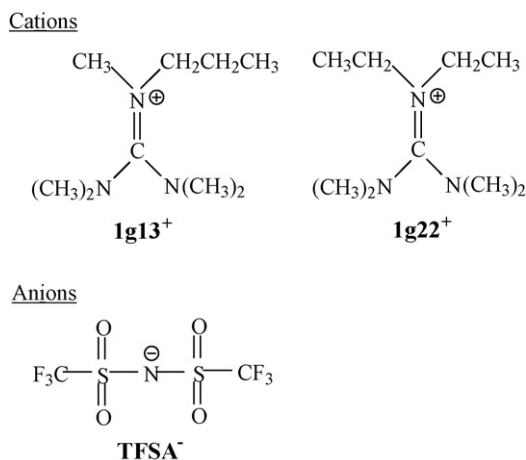
The ILs based on quaternary ammonium cations and quaternary phosphonium cations, have better electrochemical stability compared with the other kinds of ILs, and possess sufficiently lower cathodic limiting potentials to allow the deposition of lithium without additive [8–10]. Among these ILs, N-methyl-N-propylpiperidinium bis(trifluoromethanesulfonyl)amide (PP13-TFSA) and N-methyl-N-propylpyrrolidinium bis(fluorosulfonyl)amide (P13-FSA), have been reported to own good cycle performance when they are used in lithium batteries at low current rate without additive [1–4]. But the lithium batteries using the electrolyte based on trimethylpropylammonium bis(trifluoromethanesulfonyl)amide (N1113-TFSA) and P13-TFSA show nonideal performance [1], and it means that good cathodic stability is not the only decisive factor for using IL electrolyte in lithium battery.

ILs based on 1-ethyl-3-methyl imidazolium (EMI) cation has been the most widely studied due to their low viscosity and high conductivity. 1-Ethyl-3-methyl imidazolium bis(trifluoro-

methanesulfonyl)amide (EMI-TFSA) electrolyte without additive cannot be directly used in lithium battery, because the cathodic stability of EMI-TFSA is not sufficient for the reversible charge–discharge of negative electrode [11,12]. Whereas the electrolyte without additive based on EMI-FSA have been proved to allow the deposition of lithium, and it is presumed that solid electrolyte interphase (SEI) film has been formed, although the capacity of the cell (Li/LiCoO<sub>2</sub>) with EMI-FSA electrolyte at the current rate of 0.1 C has still degraded obviously after 50 cycles [3]. Interestingly, it has been found that cyano-containing imidazolium-based ILs can also allow the deposition of lithium without additive due to the forming of SEI film, but the viscosities of these functionalized ILs are very high [7,13]. Furthermore, a novel Lewis-base IL based on the 1,4-diazabicyclo[2.2.2]octane derivative has been reported to allow the deposition of lithium at 80 °C without additive, though its electrochemical stability at 80 °C is similar to EMI-TFSA [14]. So the ILs with low cathodic stability still have chances to be used in lithium battery successfully, if their electrolytes can form good SEI films.

Recently, our group have synthesized sixteen new hydrophobic ILs based on small guanidinium cations and TFSA<sup>-</sup> anion, and found that twelve products were liquids at room temperature, and some of them had low viscosity [15]. In the present study, two low-viscosity guanidinium-based ILs were chosen from these ILs and used as new electrolytes for Li/LiCoO<sub>2</sub> cells without additive. And we found that the cells had good capacity and cycle property at the current rate of 0.2 C, though the cathodic limiting potentials of the two ILs were obviously higher than 0 V versus Li/Li<sup>+</sup>.

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**Fig. 1.** Structures of cations and anions of two guanidinium-based ILs used in this study.

## 2. Experimental

The structures of two guanidinium-based ILs used in this study were shown in Fig. 1, and the ILs were prepared according to our reported method [15]. The ILs were dried under high vacuum for more than 24 h at 100 °C before using. The water content of the dried ILs was detected by a moisture titrator (Metrohm 73 KF coulometer) basing on Karl-Fischer method, and the value was less than 50 ppm. Then 0.3 mol kg<sup>-1</sup> of LiTFSA (kindly provided by Morita Chemical Industries Co., Ltd.), were added to the dried ILs. And this procedure was carried out in an argon-filled glove box ([O<sub>2</sub>] < 1 ppm, [H<sub>2</sub>O] < 1 ppm).

The viscosities of the ILs and IL electrolytes were measured with viscometer (DV-III ULTRA, Brookfield Engineering Laboratories, Inc.), and the conductivities were got by using DDS-11A conductivity meter.

Electrochemical windows of the ILs were measured by linear sweep voltammogram in the glove box. The working electrode was glassy carbon disk (3 mm diameter), and lithium metal was used as both counter and reference electrodes.

The plating and stripping behaviors of lithium in the IL electrolytes were examined by using cyclic voltammogram method in the glove box. The nickel disk (2 mm diameter) was used as the working electrode, and lithium metal was used as both counter and reference electrodes. The Ni electrode was polished with alumina paste ( $d=0.1\ \mu\text{m}$ ). And the polished electrode was washed with deionized water and dried under vacuum.

Li/LiCoO<sub>2</sub> coin cell was used to evaluate the performance of the ILs electrolytes in lithium battery applications. In order to compare conveniently with the performances of cells using other IL electrolytes, which have been reported by other researchers [1–4], the similar components of cell (including negative electrode, positive electrode and separator) were used. Lithium foil (battery grade) was used as a negative electrode. And positive electrode was fabricated by spreading the mixture of LiCoO<sub>2</sub>, acetylene black and PVDF (initially dissolved in N-methyl-2-pyrrolidone) with a weight ratio of 8:1:1 onto Al current collector (battery use). Loading of active material was about, ca. 1.0–1.5 mg cm<sup>-2</sup> and this thinner electrode was directly used without pressing. The separator was glass filter made of borosilicate glass (GF/A from Whatman). Cell construction was carried out in the glove box, and all the components of cell were dried under vacuum before placed into the glove box. Cell performance was examined by the galvanostatic charge–discharge (C–D) cycling test using a CT2001A cell test instrument (LAND Electronic Co., Ltd.) at room temperature. The cells were sealed and

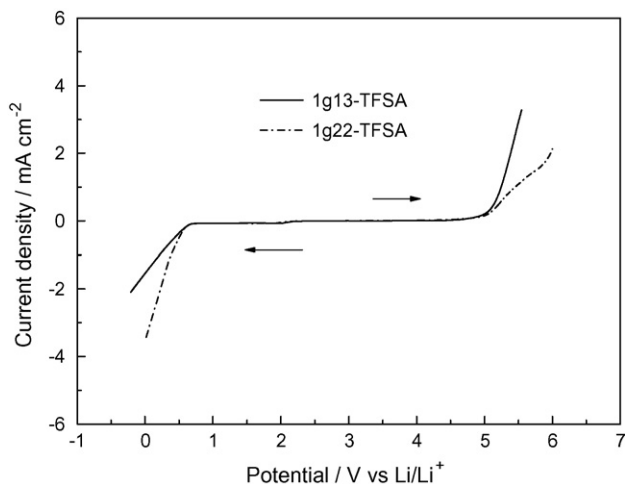
then stayed at room temperature for 4 h before the performance test. Current rate was determined by using the nominal capacity of 150 mAh g<sup>-1</sup> for Li/LiCoO<sub>2</sub> cell. Charge included two processes: (1) constant current at a rate, cut-off voltage of 4.2 V and (2) constant voltage at 4.2 V, cut-off current of 0.01 mA, and discharge had one process: constant current at the same rate, cut-off voltage of 3.2 V.

## 3. Results and discussion

The viscosity of IL is regarded as an important factor for the lithium battery system using IL electrolyte, because the C–D rate property can be affected by the diffusion of Li<sup>+</sup> in IL electrolyte [2,3]. For example, cyano-containing imidazolium-based ILs have high viscosities, which result in nonideal C–D rate property [7,13]. As shown in Table 1, the viscosities of the two guanidinium-based ILs in this study (1g13-TFSA and 1g22-TFSA) were 73 and 56 mPa s at 25 °C. When compared with the ILs, which had been proved to be used in lithium battery without additive, the viscosities of the two ILs were slightly higher than EMI-FSA and P13-FSA, and they were obviously lower than PP13-TFSA and several other quaternary ammonium-based ILs [1,3,10]. Usually, the viscosity of ILs increases and conductivity of ILs decreases after dissolving Lithium salts. Table 1 shows that the two guanidinium-based ILs also accord with this rule.

Fig. 2 shows the electrochemical windows of the two guanidinium-based ILs at 25 °C, which are measured with linear sweep voltammogram (LSV) using lithium metal as reference electrode. The electrochemical stabilities of the two ILs were almost same. The cathodic limiting potentials of the two ILs were 0.7 V versus Li/Li<sup>+</sup>, and the anodic limiting potential were 4.9 V versus Li/Li<sup>+</sup>. So their electrochemical windows were 4.2 V. The cathodic limiting potentials of the two ILs were close to imidazolium-based ILs, and obviously higher than quaternary ammonium-based or quaternary phosphonium-based ILs, such as PP13-TFSA (about –0.3 V versus Li/Li<sup>+</sup>) [10,16].

According to the cathodic limiting potentials of the two guanidinium-based ILs, it was very possible that their IL electrolytes could not allow the deposition of lithium without additive like the EMI-TFSA electrolyte. But the cyclic voltammogram (CV) measurement gave the opposite result. The CVs of the two IL electrolytes at 25 °C are shown in Fig. 3(a) and (b), and the plating of lithium on nickel electrode can be clearly observed. In the first cycle for the 1g13-TFSA electrolyte, the plating of lithium was at about –0.17 V versus Li/Li<sup>+</sup>, and the anodic peak at about 0.38 V in the returning



**Fig. 2.** Linear sweep voltammograms of 1g13-TFSA and 1g22-TFSA at 25 °C. Working electrode: glassy carbon; counter electrode: Li; reference electrode: Li; scan rate: 10 mV s<sup>-1</sup>.

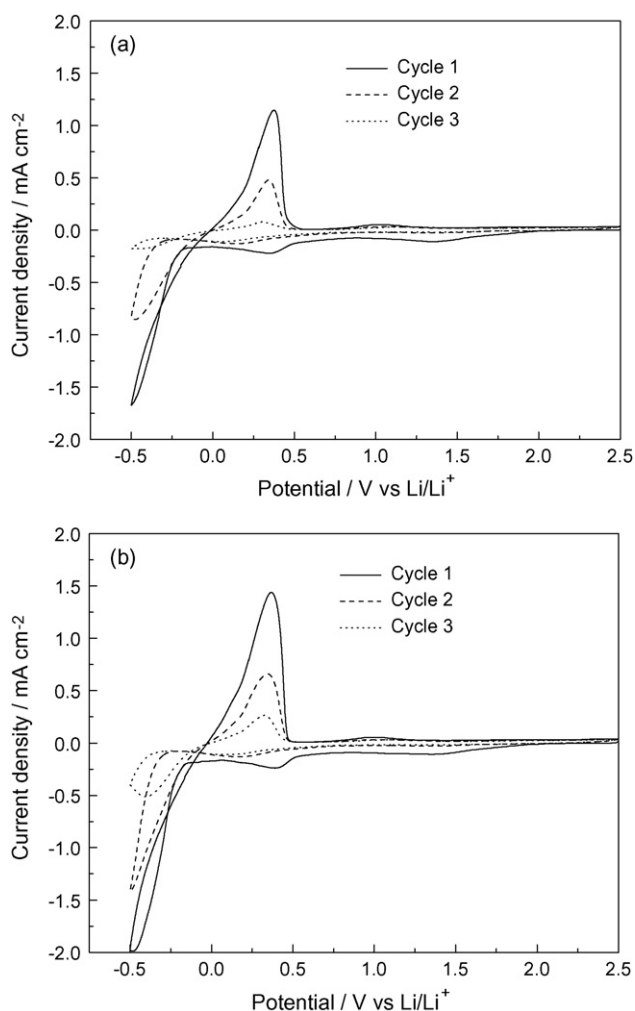
**Table 1**Viscosity and conductivity of guanidinium ILs without and with 0.3 mol kg<sup>-1</sup> of LiTfSA at 25 °C.

	ILs without LiTfSA		ILs with LiTfSA	
	Viscosity (mPa s)	Conductivity (mS cm <sup>-1</sup> )	Viscosity (mPa s)	Conductivity (mS cm <sup>-1</sup> )
1g13-TFSA	73	2.30	111	1.32
1g22-TFSA	56	2.76	78	1.72

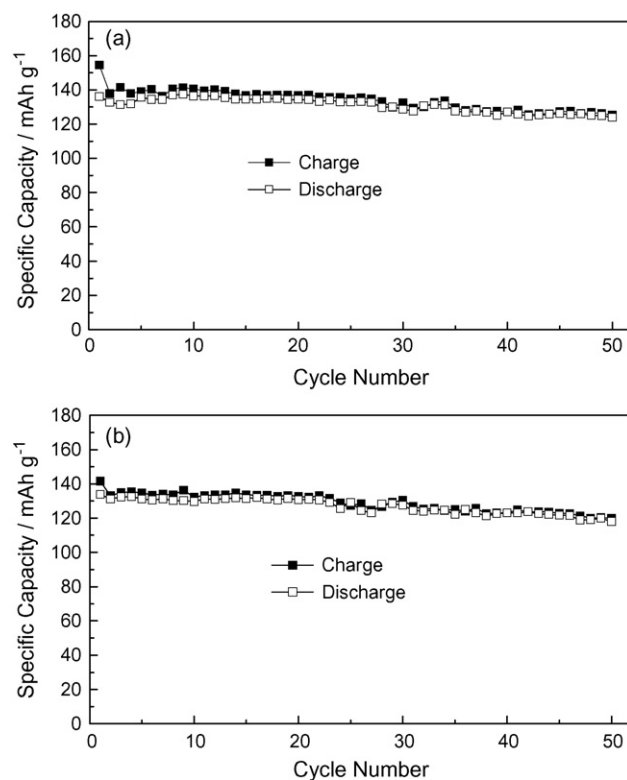
scan corresponded to the stripping of lithium. The lithium redox in the 1g13-TFSA electrolyte might be caused by the generation of a certain surface film (SEI) on the Ni electrode. The peak currents of the lithium redox decreased gradually with the cycle number, and this suggested that the SEI film turned thicker so that the lithium redox was restrained markedly. Another cathodic peak at about 0.34 V was found in the first cycle, and this cathodic peak at the approximate position was also found in CVs for some quaternary ammonium-based IL electrolyte, such as the PP13-TFSA electrolyte [10,16]. For the PP13-TFSA electrolyte, it is considered that this cathodic peak possibly results from the underpotential deposition of lithium due to the good cathodic stability of PP13-TFSA [16]. But this cathodic peak of the 1g13-TFSA electrolyte might be assigned to the electrochemical reduction of the electrolyte, and at the same time it could be presumed that this reduction might generate the SEI film on Ni electrode. Furthermore, in the sec-

ond and third cycles the position of this peak shifted negatively and the current of this peak decreased, so it could mean that SEI film generating in the first cycle also restrained the reduction of the electrolyte. For the 1g22-TFSA electrolyte, the phenomena of the lithium redox in the three cycles is similar to the 1g13-TFSA electrolyte.

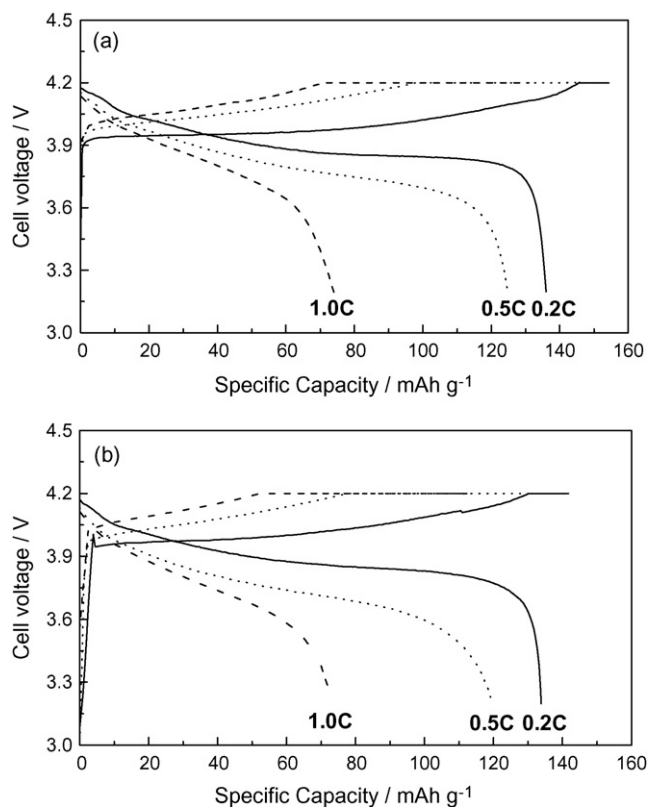
The C–D characteristics of Li/LiCoO<sub>2</sub> cells using these IL electrolytes without additive were examined at 0.2 C current rate. Fig. 4(a) and (b) shows the C–D capacity during cycling of the cells. The initial discharge capacity of the cell with the 1g13-TFSA electrolyte was 136 mAh g<sup>-1</sup>, and the discharge capacity at the 50th cycle was 124 mAh g<sup>-1</sup>, which retained 91% of its initial capacity. The initial discharge capacity of the cell with the 1g22-TFSA electrolyte was 134 mAh g<sup>-1</sup>, and the discharge capacity at the 50th cycle was 118 mAh g<sup>-1</sup>, which retained 88% of its initial capacity. In the first C–D cycle, the lower coulombic efficiency could be observed for the two IL electrolytes, and it might result from the reaction of the electrolyte and the forming of SEI film. The coulombic efficiency for the two IL electrolytes was higher than 97% after the initial several cycles. In a word, the Li/LiCoO<sub>2</sub> cells using the two IL electrolytes without additive showed the satisfactory discharge capacity and cycle property at 0.2 C current rate, which were close to the performances of Li/LiCoO<sub>2</sub> cells using the PP13-TFSA and P13-FSA electrolytes without additive at 0.1 C current rate [1,3].



**Fig. 3.** Cyclic voltammograms for ionic liquid electrolytes at 25 °C (–0.5 to 2.5 V vs. Li/Li<sup>+</sup>): (a) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g13-TFSA; (b) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g22-TFSA. Working electrode: Ni; counter electrode: Li; reference electrode: Li; scan rate: 10 mVs<sup>-1</sup>.



**Fig. 4.** Charge–discharge capacity during cycling of Li/LiCoO<sub>2</sub> cells with different ionic liquid electrolytes: (a) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g13-TFSA; (b) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g22-TFSA. Charge–discharge current rate is 0.2 C.



**Fig. 5.** Charge–discharge curves of Li/LiCoO<sub>2</sub> cells with different ionic liquid electrolytes: (a) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g13-TFSA; (b) 0.3 mol kg<sup>-1</sup> LiTfSA in 1g22-TFSA. Charge–discharge current rate is indicated in this figure.

Fig. 5(a) and (b) shows C–D curves of Li/LiCoO<sub>2</sub> cells with the two IL electrolytes without additive at different current rates. It could be easy to find that the initial discharge capacity decreased obviously with the increasing of the current rate. The initial discharge capacities of the two IL electrolytes at the three current rates were very similar, though their viscosities were different. It suggested that the rate property had been also by other factor besides the viscosity, which might be the SEI film.

#### 4. Conclusions

Two low-viscosity guanidinium-based ILs were prepared and used as new electrolytes of lithium battery. Though their cathodic limiting potentials were found to be higher than 0V versus Li/Li<sup>+</sup>, the lithium plating and stripping on Ni electrode could be observed in their electrolytes without additive due to the forming of SEI film. The Li/LiCoO<sub>2</sub> cells using the two IL electrolytes without additive showed high coulombic efficiency, good discharge capacity and stable cycle property at 0.2 C current rate.

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