# A Lithium Battery Electrolyte Based on a Room-temperature Phosphonium Ionic Liquid

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The electrolytic properties of a lithium battery electrolyte based on triethyl(2-methoxyethyl)phosphonium bis(trifluoromethylsulfonyl)imide are described. Testing charge–discharge performance of the cell containing the lithium-binary phosphonium ionic liquid electrolyte showed excellent capacity and rechargeability, compared to the cell containing a comparative ammonium ionic liquid electrolyte.

Room-temperature ionic liquids (RTILs) have been regarded as promising candidates for lithium battery electrolytes due to their unique physicochemical properties.[1] Low viscosity of RTILs is a major requirement for the electrolyte use since viscosity essentially influences mobility of ions in IL systems. From this point of view, several attractive researches on imidazolium- and ammonium-based RTILs together with a bis(fluorosulfonyl)imide anion have been made directly toward the lithium battery applications.[2] On the other hand, interests in quaternary phosphonium based RTILs for their potential applications have been increasing.[3] However, there has been no report on lithium battery applications, because the known phosphonium ILs tend to be highly viscous and low-conductive owing to their large cation sizes. In order to improve such a transport property, we have synthesized RTILs based on relatively small phosphonium cations.[4] For example, triethyl(2-methoxyethyl)phosphonium ($\mathrm{P_{222(2O1)}}$) cation gave a low-viscous RTIL in combination with a bis(trifluoromethylsulfonyl)imide (TFSI) anion.[4a]

Here, we report the electrolytic properties of a binary IL system consisting of $\mathrm{P_{222(2O1)}}$–TFSI (shown in Figure 1) and the lithium salt (Li–TFSI). The effect of the transport property on the lithium redox system was investigated by evaluating the charge–discharge performance of the lithium secondary battery containing the binary IL electrolyte. As a comparative examination, we employed *N*,*N*-diethyl-*N*-methyl-*N*-(2-methoxyethyl)ammonium TFSI (DEME–TFSI, shown in Figure 1) which is an excellent quaternary ammonium IL often used as a high-performance lithium battery electrolyte.[5]

The preparation and purification of $\mathrm{P_{222(2O1)}}$–TFSI (halogen: <50 ppm, alkali metals: <5 ppm) was carried out according to the procedure described in our paper.[4a] DEME–TFSI (Kanto Chemical Co., Inc., halogen: <50 ppm, alkali metals: <10 ppm) was used without further purifications. The electrolytes were prepared by adding Li–TFSI (Kishida Chemical Co., Ltd.) into each IL to make the lithium content a 1.0 mol dm$^{-3}$, and then were dried under high vacuum for 12 h at 100 °C. The residual water contents measured by a Karl–Fischer titrator were less than 50 ppm. The measurements of viscosity and conductivity were carried out using a vibration-type viscometer (CBC Materials Co., Ltd.) and an ac impedance analyzer (Ivium Technologies, CompactStat), respectively. The thermal decomposition temperature was analyzed by using a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA 6300) at a heating rate of 10 °C min$^{-1}$ under nitrogen atmosphere.

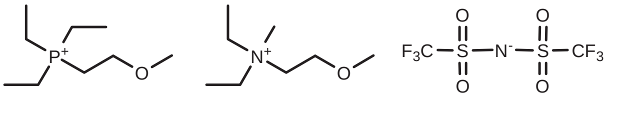
$\mathrm{P_{222(2O1)}}^+$ DEME$^+$ TFSI$^-$

**Figure 1.** Structural illustration of ionic components of RTILs.

The lithium secondary batteries used for the charge–discharge tests were fabricated using CR2032-type coin cells in an argon atmosphere glove box ([$H_2O$] < 1 ppm, [$O_2$] < 1 ppm). A mixture paste containing $LiCoO_2$ (Nippon Chemical Industrial Co., Ltd., Cellseed® C-5), conductive carbon black and poly(vinylidene fluoride) with a weight ratio of 95:2.5:2.5 was prepared using *N*-methylpyrrolidone as a dispersant. Preparation of the cathode sheets was carried out by spreading the mixture paste onto an Al current collector (battery use, 99.5%). The content of the active material in the cathode sheet was ca. 8.5 mg cm$^{-2}$. Li foils (1 cm$^2$) were used as anodes. The catholyte and anolyte were separated with polyethylene sheets (Celgard Co., 45 µm). Charge–discharge tests on the cells were operated by using a charge–discharge system (Hokuto Denko Co., Ltd, HJR-110mSM6) at 4.2–3.4 V of cut-off voltage with 0.07 mA cm$^{-2}$ of a current density (0.05 C) at 25 °C. The cells were fully charged and discharged by constant current/constant voltage (CCCV, 25 h) and constant current (CC) modes, respectively.

Table 1 summarizes the transport and thermal properties of neat and the corresponding lithium-binary ILs. $\mathrm{P_{222(2O1)}}$–TFSI exhibited relatively low viscosity (44 mPa s) and high ionic conductivity (3.6 mS cm$^{-1}$) compared to those of DEME–TFSI. Even when Li–TFSI was added with a high concentration (1.0 mol dm$^{-3}$), $\mathrm{P_{222(2O1)}}$–TFSI showed much lower viscosity (189 mPa s) and higher conductivity (0.81 mS cm$^{-1}$) than those of the corresponding DEME–TFSI electrolyte. This transport property suggests that $\mathrm{P_{222(2O1)}}$–TFSI enables relatively high lithium-concentrations for lithium battery applications.

Thermal stability of lithium battery electrolytes is of practical importance. The thermogravimetric analysis data listed in Table 1 reveal high thermal stability of the lithium-

**Table 1.** Transport and thermal properties of neat and lithium-binary ILs

| Ionic liquid | $\eta^a$ /mPa s | $\sigma^b$ /mS cm$^{-1}$ | $T_{dec}{}^c$ /°C | Reference |
|---|---|---|---|---|
| $\mathrm{P_{222(2O1)}}$–TFSI | 44 | 3.6 | 404 | 4a |
| Li-binary $\mathrm{P_{222(2O1)}}$–TFSI$^d$ | 189 | 0.81 | 402 | This work |
| DEME–TFSI | 69 | 2.6 | 390 | 6 |
| Li-binary DEME–TFSI$^d$ | 281 | 0.61 | 395 | This work |

$^a$Viscosity at 25 °C. $^b$Conductivity at 25 °C. $^c$Thermal decomposition temperature of 10% weight loss. $^d$[$Li^+$] = 1.0 mol dm$^{-3}$.

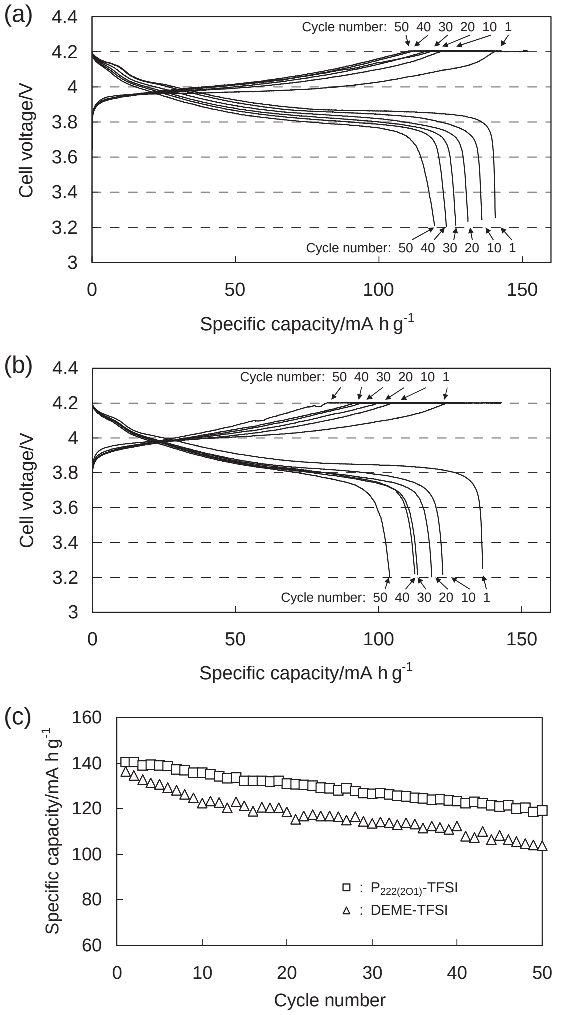

**Figure 2.** The charge–discharge properties of Li/1.0 mol dm$^{-3}$ Li–TFSI in ILs/$LiCoO_2$ cells; (a) the charge–discharge curves of the cell containing $P_{222(2O1)}$–TFSI; (b) the charge–discharge curves of the cell containing DEME–TFSI; (c) the dependence of cycle number on the discharge capacities of the cell containing $P_{222(2O1)}$–TFSI in comparison with that of DEME–TFSI.

binary $P_{222(2O1)}$–TFSI electrolyte.

The charge–discharge curves and the dependence of the cycle number on the discharge capacity of the lithium battery cells containing lithium-binary ILs are exhibited in Figure 2. It was found that the cell containing lithium-binary $P_{222(2O1)}$–TFSI electrolyte showed sufficient capacities for the charge and discharge at the first cycle (152 and 141 mA h g$^{-1}$, respectively) which were close to a theoretical capacity of $Li_xCoO_2$ ($0.5 < x < 1$, voltage range: 4.2–3.4 V). Compared to the DEME–TFSI electrolyte, the discharge capacity of the cell containing the $P_{222(2O1)}$–TFSI electrolyte was highly maintained even after 50 cycles (the discharge capacity: 119 mA h g$^{-1}$, the capacity retention ratio: 85%).

In general, charge–discharge processes involve the decomposition of electrolytes at the electrode (anode and/or cathode) interface, so that the capacity is gradually decreased. As shown in Figure 2c, the cycle number dependence on the discharge capacity of the cell containing the $P_{222(2O1)}$–TFSI electrolyte indicates the typical decreasing behavior. It is well known that the decomposition of electrolytes often gives a lithium-conductive passivation film, the so-called solid electrolyte interface (SEI) film. The charge–discharge processes might be associated with a formation of the SEI-like film.

The transport property is one of the major factors in charge–discharge processes. The mobility of lithium cation seems to be significantly influenced by the electrostatic interactions between cations and anions. We have found that quaternary phosphonium cations tended to weaken the electrostatic interactions when compared to the corresponding ammonium cations, thereby giving relatively low viscosities to the phosphonium IL systems.[4a] A similar tendency was also seen in the result of Table 1. Therefore, it seems likely that $P_{222(2O1)}$–TFSI provides an electrolytic medium favorable for the motion of lithium cation, resulting in the relatively high charge–discharge performance.

In addition, lower lithium concentrations than 1.0 mol dm$^{-3}$ might be favorable because the transport property should be improved by reducing the concentration. At 0.8 mol dm$^{-3}$ of the concentration, somewhat high discharge capacity of the cell containing lithium-binary $P_{222(2O1)}$–TFSI electrolyte was observed (155 mA h g$^{-1}$ at the first cycle); however, an optimization of the lithium concentrations is required.

In conclusion, we have shown that lithium-binary $P_{222(2O1)}$–TFSI exhibited favorable transport property and high thermal stability as an electrolyte for lithium secondary batteries. It was found that a lithium battery cell containing the $P_{222(2O1)}$–TFSI electrolyte showed higher charge–discharge performance than that containing the DEME–TFSI electrolyte, due to the low viscosity and high conductivity of $P_{222(2O1)}$–TFSI. Further investigations for lithium battery applications using phosphonium ILs are in progress.

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