Short communication

Application of nonflammable electrolyte with room temperature ionic liquids (RTILs) for lithium-ion cells

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Abstract

A mixture of flammable organic solvent and nonflammable room temperature ionic liquid (RTIL) has been investigated as a new concept electrolyte to improve the safety of lithium-ion cells. This study focused on the use of *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI) as the RTIL for the flame-retardant additive. It was found that a carbon negative electrode, both graphite and hard carbon, could be used with the mixed electrolyte. A 383562-size lithium-ion trial cell made with the mixed electrolyte showed good discharge capacity, which was equivalent to a cell with conventional organic electrolyte up to a discharge current rate of complete discharge in 1 h. Moreover, the mixed electrolyte was observed to be nonflammable at ionic liquid contents of 40 mass% or more. Thus the mixed electrolyte was found to realize both nonflammability and the good discharge performance of lithium-ion cells with carbon negative electrodes. These results indicate that RTILs have potential as a flame-retardant additive for the organic electrolytes used in lithium-ion cells.
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1. Introduction

Lithium-ion cells have contributed greatly to reductions in the size of various electrical instruments, especially small electric devices. Present small-size lithium-ion cells must use a flammable organic solvent for the electrolyte, and significant efforts have been made to ensure safety in the development of larger-size lithium-ion cells.

On the other hand, room temperature ionic liquids (RTILs) have attracted growing interest for application to electrochemical devices, especially lithium cells, due to their nonflammability, thermal stability, and nonvolatility. The practical use of RTILs was suggested after the discovery of stable compounds such as 1-ethyl-3-methyl-imidazolium tetrafluoroborate (EMIBF$_4$) [1]. Nonflammable liquid electrolytes using RTILs have been developed, and the performance of cells using RTIL has been investigated [2–7]. In the latter studies, RTILs worked as the "nonflammable solvents" of the electrolyte without any conventional organic solvents. Among the various series of RTILs, combinations of 6-membered cyclic aliphatic and asymmetric quaternary ammonium cations and imide anions have been found to work as an electrolyte solvent in Li/LiCoO$_2$ system cells, performing as well as the conventional organic solvents [2]. The electrochemical stability of the RTIL was found to be sufficient for lithium cells. However, some limitations still remain for application to cells for high-power use, for example hybrid electric vehicles (HEVs) and fuel cell electric vehicles (FCEVs), due to the high viscosity and low ionic conductivity of the electrolyte [3,4].

Recently, the use of mixed electrolytes of organic solvents and RTILs has been investigated in order to improve the safety of lithium-ion cells that incorporate flammable organic solvents [8–10]. The present authors have also investigated a mixture of organic solvent and RTIL for the electrolyte in lithium-ion cells, and found that the RTIL can function as a flame-retardant additive [11]. The present study, based on the previous work, investigated the application of a typical carbon material for the negative electrode.

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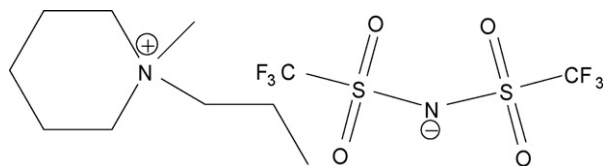*E-mail address:* hiroe.nakagawa@jp.gs-yuasa.com (H. Nakagawa).

Fig. 1. Structural formula of *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI).

2. Experimental

2.1. Preparation of the electrolyte

The compound *N*-methyl-*N*-propylpiperidinium bis (trifluoromethanesulfonyl) imide (PP13-TFSI) was used as the RTIL in this study. Fig. 1 shows a structural formula of PP13-TFSI. Details of PP13-TFSI synthesis and electrochemical/physical properties have been reported elsewhere [2,4]. The mixed electrolyte was prepared by adding predetermined amounts of PP13-TFSI to the organic solvent mixture (ethylenecarbonate (EC): dimethylcarbonate (DMC): ethylmethylcarbonate (EMC) = 1:1:1 (vol.%)) and 1.0 mol dm^{-3} of LiPF$_6$ was then dissolved into the mixture of the solvent and the RTIL. The mixed electrolyte was a homogeneous liquid over the entire composition.

2.2. Application of carbon negative electrode for the electrolyte containing RTIL

Graphite and hard carbon negative electrodes were investigated and their properties were compared using the half cell. Graphite or hard carbon was used as the carbon material in the working electrode. The electrode binder consisted of styrene-butadiene rubber (SBR) for the graphite electrode and polyvinylidene fluoride (PVdF) for the hard carbon electrode. The ratio of carbon was 97 mass% in the graphite electrode and 94 mass% in the hard carbon electrode. Metallic lithium was used for the counter and reference electrodes. The area of the working electrode was 900 mm^2. Initial charge and discharge performance of the half cells was investigated at the current rate of complete discharge in 10 h (i.e. the current rate of 0.1 CmA) at 20 °C. Cycling properties of the half cells were also investigated by performing charging–discharging cycles 10 times at 0.1 CmA at 20 °C. Lithium ion was doped using a constant current to 0.01 V versus Li/Li$^+$ followed by a constant potential for 15 h, in order to achieve sufficient doping of the lithium ion into the carbon materials, especially graphite. The lithium-ion undoping was conducted by constant current up to 1.0 V versus Li/Li$^+$. The cell potential was measured between the working and reference electrode.

2.3. Fabrication and characterization of the lithium-ion trial cells

Two kinds of 383562-size laminate type lithium-ion trial cells were constructed using the mixed electrolyte containing 0, 25, and 50 mass% PP13-TFSI. Table 1 presents their specifications.

Table 1
Specification of the 383562-size lithium-ion trial cells

	[A] type	[B] type
Nominal voltage (V)	3.7	3.6
Rated capacity (mAh)	550	340
Dimensions (mm)	35(W), 62(L), 3.8(T)	35(W), 62(L), 3.8(T)
Mass (g)	16	16
Positive active material	LiCoO$_2$	LiCoO$_2$
Negative active material	Graphite	Hard carbon
Separator	Polyolefine porous film	Polyolefine porous film

[A] type cells used graphite for the negative electrode, while [B] type cells used hard carbon. The composition of the negative electrode was the same as that of the electrode using the half cell. The positive electrode was prepared using LiCoO$_2$ as an active material, acetylene black as an electro-conductive material, and PVdF as a binder. The ratio of LiCoO$_2$ in the positive electrode was 94 mass%.

Discharge performance of the trial cells at various current was investigated at current rates of 0.2, 1.0, and 2.0 CmA at 25 °C. Discharge performance at various temperatures was also investigated with a constant current at a current rate of 0.2 CmA at 25, 0, −10, and −20 °C. Charge/discharge cycling performance was investigated by repeating 50 times at a charging and discharging current rate of 1.0 CmA at 25 °C. The limiting voltage of discharging was 3.0 V in the [A] type cell and 2.7 V in the [B] type. The charging condition was fixed at a current rate of 1.0 CmA to 4.2 V followed by constant voltage for 2.5 h at 25 °C. Current rate of 1.0 CmA were 550 mA in [A] type cell and 340 mA in [B] type cell, respectively.

2.4. Flammability of the electrolyte

In order to confirm the safety of the mixed electrolyte, the flammability of the mixture was examined. A glass filter was soaked with the electrolyte, and the flame of an alcohol lamp was then brought close to the filter. The interval between the glass filter and the wick of alcohol lamp was kept at 100 mm. After 10 s, the alcohol lamp was removed from under the glass filter. The electrolyte was judged to be nonflammable if the electrolyte never ignited during the testing, or if the ignition of electrolyte ceased when the flame was removed. Each electrolyte was tested three times.

3. Results and discussion

3.1. Application of carbon negative electrode for the electrolyte containing RTIL

Initial charge and discharge curves of the carbon negative electrode half cells with mixed electrolyte containing PP13-TFSI and organic solvent are shown in Fig. 2. Because electricity is consumed for solid-state electrolyte interface (SEI) formation on the surface of the carbon material, irreversible capacity is always observed at first charging. The specific capacity of the graphite in the conventional electrolyte was 330 mAh g^{-1} and
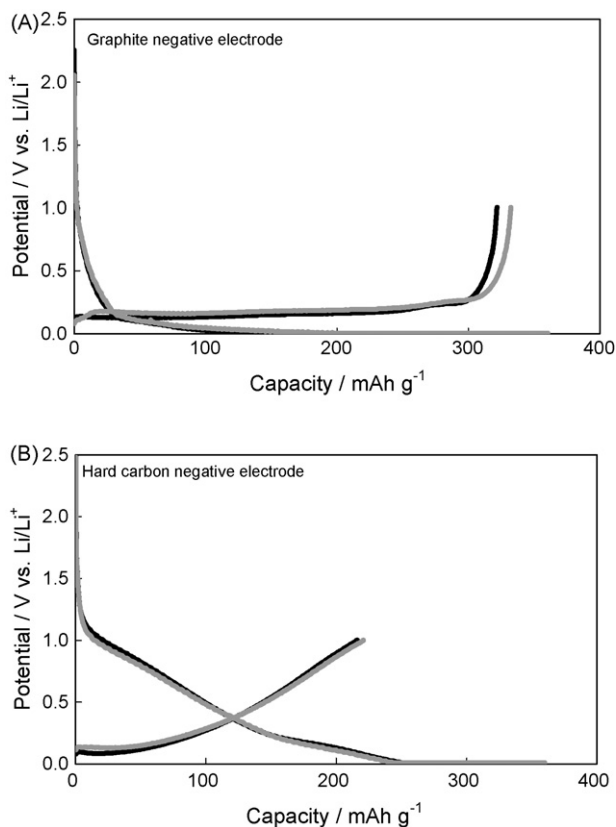
Fig. 2. Initial charge and discharge curves of the carbon negative electrode half cells with mixed electrolyte containing PP13-TFSI and organic solvent at 20 °C. The concentration of PP13-TFSI was 0 (black line), and 50 (gray line) mass%. Working electrode was (A) graphite or (B) hard carbon. Counter and reference electrode was metallic lithium. Charging condition: 0.1 CmA to 0.01 V followed by constant potential; discharging condition: 0.1 CmA to 1.0 V.
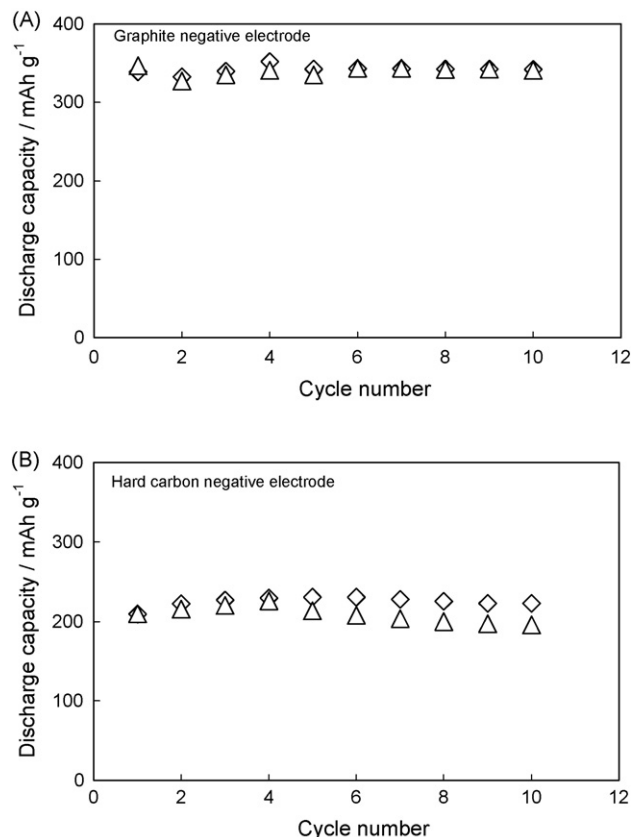
Fig. 3. Cycle-ability of the carbon negative electrode half cells with mixed electrolyte containing PP13-TFSI and organic solvent at 20 °C. The concentration of PP13-TFSI was 0 (◊), and 50 (△) mass%. Working electrode was (A) graphite or (B) hard carbon. Counter and reference electrode was metallic lithium. Charging condition: 0.1 CmA to 0.01 V followed by constant potential; discharging condition: 0.1 CmA to 1.0 V.

that of hard carbon was 220 mAh g^{-1}. According to Fig. 2, the potential change exhibited by the half cells with 50% PP13-TFSI was nearly the same as that of the pure organic solvent electrolyte. That is, lithium ions could be completely doped and undoped into the carbon material, both graphite and hard carbon, in the electrolyte containing 50 mass% of PP13-TFSI. Fig. 3 shows the cycling properties of the cells. In this result, no capacity decline was observed at least during the initial 10 cycles, and both the graphite and the hard carbon negative electrodes showed good cycle performance in the electrolyte containing 50 mass% PP13-TFSI.

As already reported, metallic lithium [2,4] or Li[Li$_{1/3}$Ti$_{5/3}$]O$_4$ [5] can work as the negative electrode material in neat RTIL; however, a carbon negative electrode does not offer sufficient capacity [12]. In previous studies, organic solvents have been used as additives to improve the performance of carbon electrodes in RTIL electrolytes [13,14]. These studies reported that a small amount of EC or vinylene carbonate (VC) could dramatically improve the properties of the graphite in neat RTIL. However, the literature also contains reports that an electrolyte which mixed organic solvents and imidazolium-type RTILs was difficult to apply to carbon material [8]. On this matter, the authors found that a good SEI, which was favorable for electrochemical doping and undoping of lithium ions, could form on

the surface of carbon material if the mixed electrolyte was used. As shown in Fig. 2, the initial charge and discharge curves of the half cells were almost the same even if the electrolyte contained PP13-TFSI. That is, in the electrolyte containing PP13-TFSI, the surface of the carbon material could be covered by a good SEI easily before beginning the first lithium doping reaction in the mixed electrolyte, because of the coexistence of the organic solvent, such as EC. Furthermore, the SEI should help to prevent any side reaction, such as reduction or co-insertion into the graphite layer of the PP13 cation. The result in Fig. 3 also implies that the SEI still existed and acted to protect active sites of the carbon material from the electrolyte even after 10 cycles. The very small amount of VC was also found to form a stable SEI on the graphite even in neat PP13-TFSI [15]. This result suggests that certain types of organic solvent are able to form a stable SEI in an electrolyte containing PP13-TFSI.

On the other hand, positive electrode materials, for example LiCoO$_2$, exhibit good performance even in neat RTIL [2,4,5,12]. Naturally the same effect would be expected in the mixed electrolyte which was used in this study. Thus, it is suggested that a carbon/LiCoO$_2$ system lithium-ion cell should be designed with the electrolyte containing PP13-TFSI and the organic solvent, as well as for the case of the cell with the conventional organic electrolyte.
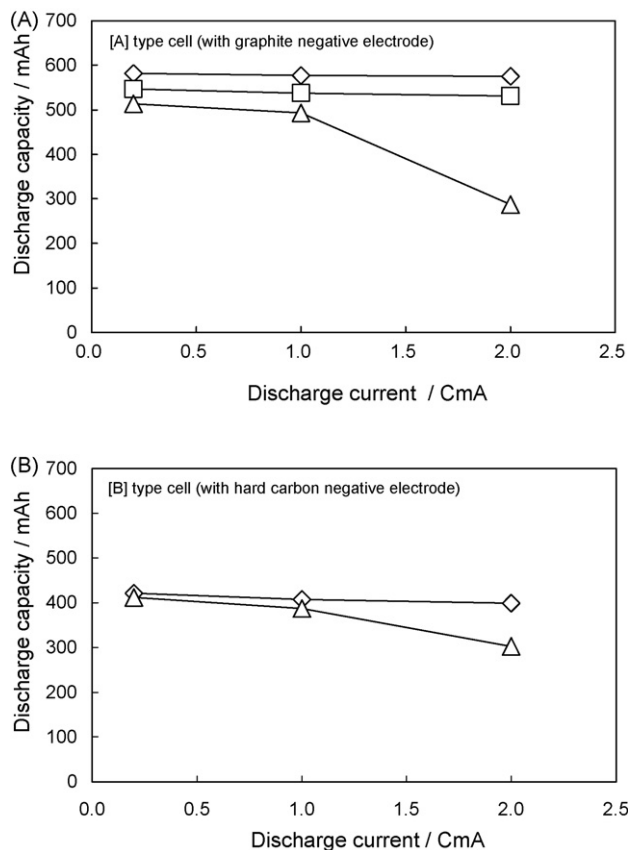
Fig. 4. Discharge performance of the 383562-size lithium-ion trial cells with mixed electrolyte containing PP13-TFSI and organic solvent at 25 °C. The concentration of PP13-TFSI was 0 (◇), 25 (□), and 50 (△) mass%. Negative active material of [A] type cell was graphite and that of [B] type cell was hard carbon. Charging condition: 1.0 CmA to 4.2 V followed by constant voltage; discharging condition: 0.2, 1.0, and 2.0 CmA to 3.0 V. 1 CmA are 550 mA ([A] type cell) or 340 mA ([B] type cell).
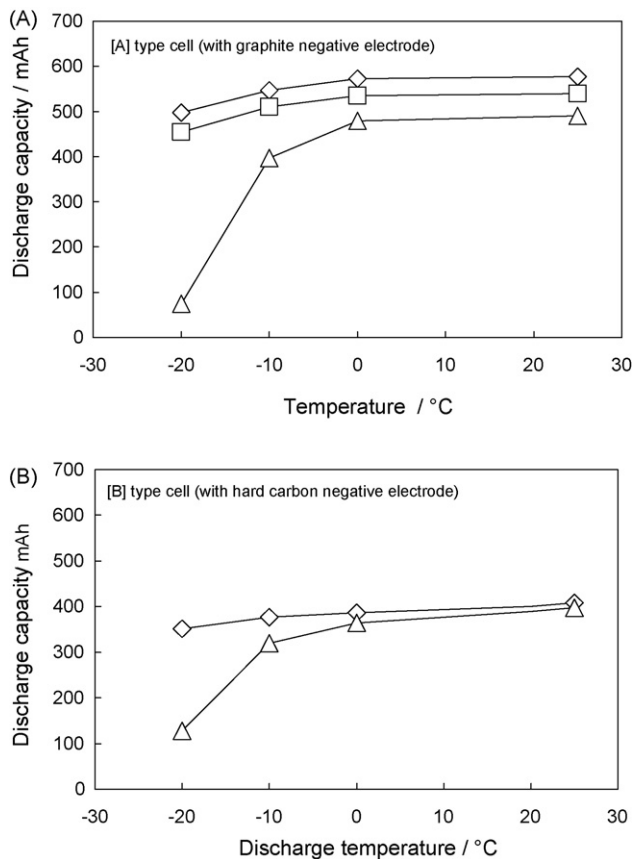

Fig. 5. Discharge performance of the 383562-size lithium-ion trial cells with mixed electrolyte containing PP13-TFSI and organic solvent at various temperatures. The concentration of PP13-TFSI was 0 (◇), 25 (□), and 50 (△) mass%. Negative active material of [A] type cell was graphite and that of [B] type cell was hard carbon. Charging condition: 1.0 CmA to 4.2 V followed by constant voltage at 25 °C; discharging condition: 0.2 CmA to 3.0 V at 25, 0, −10, and, −20 °C. 1 CmA are 550 mA ([A] type cell) or 340 mA ([B] type cell).

3.2. Performance of the 383562-size lithium-ion trial cells

Fig. 4 shows the discharge performance of the carbon/LiCoO$_2$ system 383562-size lithium-ion trial cells with the electrolyte composed of a mixture of PP13-TFSI and organic solvent. At 0.2 and 1.0 CmA discharges, almost no capacity degradation was observed from the cell containing 50 mass% PP13-TFSI. However, discharge capacity at 2.0 CmA decreased. Fig. 5 also shows the temperature dependence of the discharge capacity of the lithium-ion trial cells with all electrolytes. Large capacity retention was observed even at 0 °C, but it was not enough below −10 °C in the electrolyte containing PP13-TFSI.

The reason for the capacity decrease at higher current and lower temperature is that the viscosity of the electrolyte containing PP13-TFSI is higher than the conventional electrolyte. In addition, the temperature dependence of viscosity is large in the mixed electrolyte. These effects combined to make PP13-TFSI much more viscous than the organic solvent [2,4]. In this case, ionic conductivity and mobility of ions in the electrolyte also depends mainly upon bulk viscosity. This suggests that the supply of lithium ions from the bulk electrolyte to the surface of the LiCoO$_2$ was insufficient under severe conditions, such as large current discharging or discharging at low temperatures. This effect was clearly exhibited in the electrolyte which contained a high ratio of PP13-TFSI, because the viscosity of the electrolyte is dependent upon PP13-TFSI content [11]. However, as reported previously, a large capacity degradation was observed even at 1.0 CmA discharge for a cell that used neat PP13-TFSI [2,4]. It is evident from this study that a cell with the mixed electrolyte is able to exhibit large capacity even at 1.0 CmA. This result suggests that lithium-ion cells with the mixed PP13-TFSI/organic solvent electrolyte may be suitable for high-power applications, such as HEVs and FCEVs, through optimisation of the cell design.

Fig. 6 shows cycle life performance of the trial cells. All cells maintained more than 90% of their initial discharge capacity after 50 cycles. This suggests that the SEI of the negative electrode can prevent any side reaction during charge/discharge cycling, even in the electrolyte containing PP13-TFSI. Based on these results, the cells with the mixed electrolyte and the carbon negative electrode are considered to show good cycle life performance.
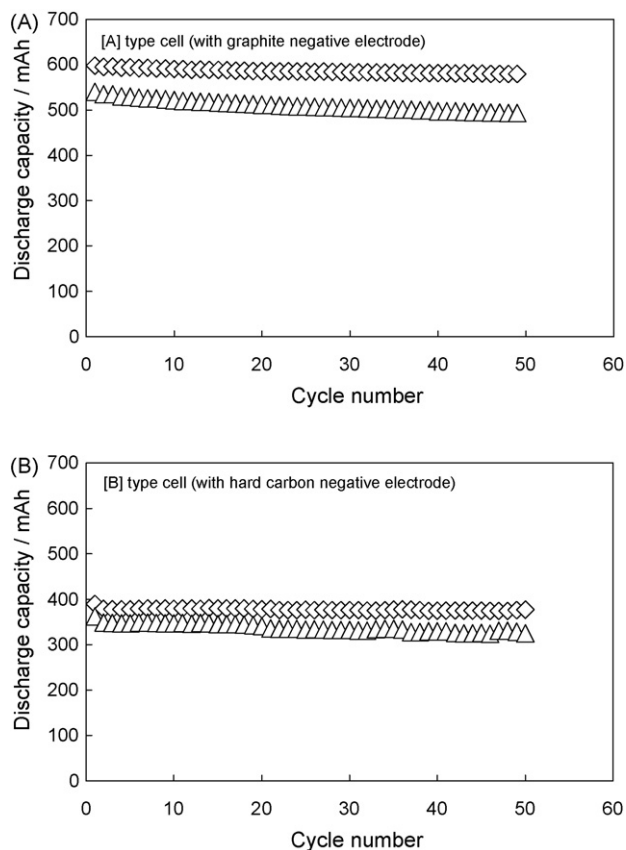
Fig. 6. Cycle life performance of the 383562-size lithium-ion trial cells with mixed electrolyte contained PP13-TFSI and organic solvent at 25 °C. The concentration of PP13-TFSI is 0 (◇), and 50 (△) mass%. Negative active material of [A] type cell is graphite and it of [B] type cell is hard carbon. Charging condition: 1.0 CmA to 4.2 V followed by constant voltage; discharging condition is 1.0 CmA to 3.0 V. 1 CmA are 550 mA ([A] type cell) or 340 mA ([B] type cell).

3.3. Comparison between graphite and hard carbon

The performance of cells using graphite and hard carbon as negative electrode material is compared in Figs. 4–6. In this study, the dimensions and the mass of each trial cell were designed to be the same for both of the two cell types. Therefore the rated capacity of the cell with graphite ([A] type cell) was higher than that with hard carbon ([B] type cell), because of a difference of the specific capacity between graphite and hard carbon. However, the capacity decline observed at large current in the [B] type cell was less than that of [A] type cell at large current or low temperature discharge. In addition, the discharge capacity of both cells at 2 CmA was almost the same with the electrolyte containing 50 mass% ratio of PP13-TFSI. By a similar phenomenon, the discharge capacity at −20 °C of the [B] type cell was larger than that of the [A] type cell.

As already described, these effects were clearly found with cells using electrolyte which contained a high ratio of PP13-TFSI. The viscosity of the electrolyte mainly depend upon content of PP13-TFSI. Thus the capacity decline may depend upon the poor mobility of lithium ion in the electrolyte. It is

also expected that the mobility of lithium ions within the interface between the carbon material and the electrolyte might have contributed to these results.

It is generally assumed that an interface of hard carbon can prevent the decomposition of electrolyte more easily than that of graphite. This leads to the conclusion that a lithium-ion cell that uses a hard carbon negative electrode will show superior performance, especially good long term cycle life performance. However, the choice of carbon material to be used for lithium-ion cells with a mixed electrolyte of RTIL and organic solvent will depend on the application. Graphite may be more suitable for some applications that need large capacity or consecutive discharging at low current, such as certain industrial uses. Hard carbon would appear to be more suitable for high-power applications, such as HEVs and FCEVs.

3.4. Flammability of the electrolyte containing RTIL

Table 2 shows the results of flammability testing on mixed electrolyte containing PP13-TFSI and organic solvent. During the testing, the conventional electrolyte (0 mass% ratio of PP13-TFSI) ignited and continued burning for 10 s every time, since the organic solvent is flammable at the ambient temperature. The flash point of linear-chained carbonates is near ambient temperature (for example, the flash point of DMC is 16 °C, and that of EMC is 24 °C), and they are easily ignited. To add PP13-TFSI in the mixed electrolyte, the content of the organic solvent is decreased. The mixed electrolyte is still flammable at 25 mass% of PP13-TFSI, but these experiments found it difficult to consistently maintain a flame in an electrolyte composed of 30 mass% of RTIL. At a 40 mass% ratio of PP13-TFSI, the mixed electrolyte appeared to be nonflammable, even though it contained 60 mass% flammable organic solvent.

This result can be explained because the partial pressure of the flammable gas (i.e. the organic solvent vapour) around the test flame was decreased by the addition of nonflammable PP13-TFSI, and was brought under the range of flammability. Therefore, it is concluded that the electrolyte containing 50 mass% ratio of PP13-TFSI shows both the good discharge performance of a lithium-ion cell with a carbon negative electrode and the enhanced safety of a nonflammable electrolyte. It is suggested that PP13-TFSI and other RTILs will be applicable as flame-retardant additives to improve the safety of cells incorporating organic electrolytes.

Table 2
Results of flammability testing of mixed electrolyte containing PP13-TFSI and organic solvent. Each sample was tested three times

Content of PP13-TFSI (mass%)	Occurrence of ignition
0	3/3
25	3/3
30	2/3
40	0/3
50	0/3
100	0/3

4. Conclusion

The mixture of flammable organic solvent and a non-flammable RTIL, PP13-TFSI, has been investigated for a new concept electrolyte for use in a lithium-ion cell. The mixed electrolyte was found to be both nonflammable and capable of the good discharge performance of a lithium-ion cell. Carbon negative electrode material, both graphite and hard carbon, was able to perform in the electrolyte containing 50 mass% ratio of PP13-TFSI. The 383562-size lithium-ion trial cell with an electrolyte containing 50 mass% ratio of PP13-TFSI showed large discharge capacity even at a large current of 1.0 CmA. The mixed electrolytes containing 40 mass% or more of PP13-TFSI were found to have nonflammable or self-extinguishing properties. Therefore, room temperature ionic liquids should have significant potential as flame-retardant additives for the organic electrolyte used in the lithium-ion cells for HEV and FCEV applications.

Acknowledgements

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