Physical and Electrochemical Properties of Room Temperature Ionic Liquids Based on Quaternary Phosphonium Cations

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Room temperature ionic liquids based on tri-$n$-butylalkylphosphonium cations were physically and electrochemically characterized. Bis(trifluoromethylsulfonyl)imide-based phosphonium ionic liquids exhibited relatively low viscosities. Tri-$n$-butyloctylphosphonium cation gave low melting salts together with a wide variety of anions. Most phosphonium ionic liquids were thermally stable up to nearly 400 °C. Linear sweep voltammetry showed that potential windows of bis(trifluoromethylsulfonyl)imide-based phosphonium ionic liquids were at least 5.7 V when a glassy carbon electrode was used. In cyclic voltammetric measurement, the redox response of Li in a phosphonium ionic liquid was observed.

Key Words: Ionic Liquids, Quaternary Phosphonium Compounds, Potential Window, Li Redox

1 Introduction

In recent years, room temperature ionic liquids (RTILs) have been intensively studied as new electrolytes for various electrochemical applications on the basis of their unique physicochemical properties. 1-3 Although most researches on RTILs have been associated with nitrogen-based RTILs, considerable interests in phosphonium-based RTILs have been also increasing since an advantage of using phosphonium ILs is suggested to provide chemical and thermal stabilities in various applications. 4,5 Several researches on phosphonium ILs have been made directly toward the electrolytes for electrochemical systems such as voltammetric measurements for various redox couples, 6 anodic polymerization of pyrrole, 7 supercapacitors, 8 dye-sensitized solar cells. 9 In most cases, the phosphonium ILs reported therein are based on relatively large cations derived from tri-$n$-hexylphosphine (C$_6$H$_{13}$)$_3$P, so that the phosphonium ILs tend to have high viscosities and low conductivities due to the large molecular weights. However, relatively low-viscous phosphonium ILs have been very rarely investigated.

In order to obtain phosphonium ILs suitable for electrochemical applications, we have paid much attention to the cation size of quaternary phosphonium compounds. Our first approach was made by preparing RTILs based on quaternary phosphonium cations derived from tri-$n$-butylphosphine (C$_4$H$_{12}$)$_3$P (TBP) together with a wide variety of anions. 10 In the report, it was found that the phosphonium ILs effectively formed their silica-based nanocomposites possessing excellent thermal stability; however, electrochemical properties of the phosphonium ILs have not been sufficiently investigated. We report herein physical and electrochemical characterizations of the phosphonium ILs derived from TBP (Fig. 1), showing the possibility to be used as electrolytes for electrochemical applications.

2 Experimental

2.1 Preparation of ILs

Phosphonium ILs were prepared according to the reference. 11 Tri-$n$-butylalkylphosphonium halides (bromides or iodides) were synthesized by nucleophilic addition of TBP to the corresponding haloalkanes under a nitrogen atmosphere, and then ion exchange reactions were carried out by metathesis of the phosphonium halides and the corresponding alkaline metal salts [lithium bis(trifluoro- methylsulfonyl)imide LiN(SO$_2$CF$_2$)$_2$ (Li-TFSI), sodium tetrafluoroborate NaBF$_4$, potassium hexafluorophosphate KPF$_6$, sodium triflate NaSO$_2$CF$_3$, sodium trifluoroacetate NaOCOCF$_3$, sodium thiocyanate NaSCN, sodium tosylate Na$_2$SO$_2$C$_6$H$_{11}$] as anion sources in pure water. The resulting crude ILs were purified by washing with pure water several times until no residual halides were detected with the use of AgNO$_3$. All the ILs were dried under high vacuum for at least 5 h at 100 °C and were stored in
a glove box of argon atmosphere. The products obtained were confirmed by $^{1}H$, $^{13}C$, $^{31}P$ and $^{31}P$ NMRs. The residual contents of alkaline metals (< 5 ppm) were checked by an inductively-coupled plasma spectrometer (Varian, ICP-AES Liberty LR Sequential). In most cases, water contents measured by a Karl Fischer method were < 400 ppm (BF$_3$ and PF$_5$ salts; < 1000 ppm). The preparation of a comparative ammonium IL, N$_{444}$-TFSI, was basically followed by the reference.\(^2\) All the reagents were used as purchased, except TBP which was internally supplied by Nippon Chemical Industrial Co., Ltd (the trade name: Hishicolin P-4).

2.2 Measurements of physical and thermal properties

The melting point of each IL was obtained by using a differential scanning calorimeter (Seiko Instruments Inc., DSC6200) with a cooling and heating rate of 3°C min$^{-1}$. The density of each IL was determined by gravimetric analysis using a calibrated pipette. The measurements of viscosity (CBC Materials Co., Ltd., VM-10A Laboratory Viscometer calibrated with the Brookfield Viscosity Standard) and conductivity (Ivium Technologies. CompactStat, using impedance mode) were carried out under an argon atmosphere. The thermal decomposition temperature of each IL was measured by using a thermogravimetric analyzer (Seiko Instruments Inc., TG/DTA6300) at a heating rate of 10°C min$^{-1}$ under a nitrogen atmosphere.

2.3 Voltammetric measurements

Linear sweep and cyclic voltammograms were carried out using a three-electrode potentiostatic mode (Hokuto Denko Co. Ltd., HZ-5000) under an argon atmosphere at 25°C. A glassy carbon disk electrode (surface area: 0.008 cm$^2$) and a Ni disk electrode (surface area: 0.018 cm$^2$) were used as the working electrodes. The glassy carbon and Ni electrodes were polished with diamond paste ($d = 1$ μm) and alumina paste ($d = 0.05$ μm), respectively. An Ag wire immersed in 0.1 mol dm$^{-3}$ Ag$_2$SO$_4$/CF$_3$/ -ethyl-3-methylimidazolium-TFSI solution with a Vycor$^\text{®}$ glass separator was employed as an Ag/Ag$^+$ reference electrode.\(^1\) The potential was referenced to the ferrocene (Fc)/ferrocenium (Fc$^+$) redox couple in each measurement.

3 Results and Discussion

3.1 Physical and thermal properties of phosphonium ILs

The physical and thermal properties of phosphonium ILs are summarized in Table 1. As in the case of typical RTILs, TFSI was an appropriate anion to give low melting point and low viscosity. P$_{444}$-TFSI exhibited the lowest melting point in the TFSI-based ILs, which seems to be attributed to the asymmetrical structure of the cation. The viscosities of P$_{444}$-TFSI, P$_{444}$-OTf and P$_{444}$-Tosyl-TFSI were 207, 250 and 303 mPa s at 25°C, respectively, depending on the cation size. It should be noted that these viscosities were much lower than that of the known phosphonium IL (P$_{444}$-TFSI: 450 mPa s at 20°C).\(^1\) In contrast, the density and conductivity were decreased with increasing the cation size.

In addition, P$_{444}$-based RTILs together with typical anions, e.g., tetrafluoroborate (BF$_4$), hexafluorophosphate (PF$_6$), triflate (OTf), trifluoroacetate (OCOCF$_3$), thiocyanate (SCN) and tosylate (Tosyl), were also obtained. However, such P$_{444}$-based RTILs tended to show high viscosities and low conductivities, compared to those of TFSI-based phosphonium ILs.

The physical properties of N$_{444}$-based RTILs have been reported by Sun et al.\(^1\) The viscosities of P$_{444}$-TFSI and N$_{444}$-OTF reported therein are 574 and 2030 mPa s at 25°C, respectively, which are higher than those of the corresponding P$_{444}$-based ILs (250 and 778 mPa s at 25°C, respectively). This allows us to infer that phosphonium cations can form relatively low-viscous ILs in comparison with the corresponding ammonium cations.

The thermal decomposition temperature data (T$_{dec}$) for the phosphonium ILs are listed in Table 1. It was found that the thermal stability greatly depended on the variety of anions. For example, phosphonium ILs based on TFSI, BF$_4$ and OTf anions were thermally stable up to nearly 400°C, whereas the OCOCF$_3$ anion drastically reduced the thermal stability. Similar tendency has been displayed in the reference describing the thermal stability of conventional imidazolium ILs with various anions.\(^1\)

3.2 Electrochemical property of phosphonium ILs

The TFSI-based phosphonium ILs that show relatively low viscosities and high conductivities are of particular interest from electrochemical aspects. Figure 2 illust-

\begin{table} [h]
\centering
\caption{Physical and thermal properties of RTILs based on tri-$n$-butylalkylphosphonium cations.}
\begin{tabular}{lccccccc}
\hline
Ionic liquid & MW$^{a}$ & T$_{m}$$^{b}$/°C & d$^{c}$/g cm$^{-3}$ & ν$^{o}$/mPa s & σ$^{o}$/10$^{-4}$ S cm$^{-1}$ & A$^{0}$/10$^{-2}$ S cm$^{-2}$ mol$^{-1}$ & T$_{dec}$$^{a}$/°C \\
\hline
P$_{444}$-TFSI & 497.50 & 16 & 1.28 & 207 & 41.6 & 16.1 & 379 \\
P$_{444}$-TFSI & 505.68 & <50 & 1.18 & 250 & 26.8 & 13.4 & 373 \\
P$_{444}$-BF$_4$ & 402.34 & <50 & 1.02 & 1240 & 6.90 & 2.71 & 399 \\
P$_{444}$-PF$_6$ & 460.50 & 20 & 1.12 & 1720 & 4.65 & 1.91 & 363 \\
P$_{444}$-OTf & 464.68 & <50 & 1.08 & 778 & 8.73 & 3.75 & 408 \\
P$_{444}$-OCOCF$_3$ & 428.55 & <50 & 1.03 & 453 & 13.1 & 5.48 & 194 \\
P$_{444}$-SCN & 373.62 & <50 & 0.95 & 450 & 17.7 & 6.94 & 378 \\
P$_{444}$-Tosyl & 486.73 & <50 & 1.02 & 2435 & 2.12 & 1.01 & 344 \\
P$_{444}$-TFSI & 651.79 & 16 & 1.13 & 303 & 17.7 & 10.1 & 383 \\
P$_{444}$-TFSI & 485.48 & 25 & 0.97 & 1310 & 4.68 & 2.21 & 391 \\
\hline
\end{tabular}
\footnotesize{$^{a}$ Molecular weight. $^{b}$ Melting point. $^{c}$ Density at 25°C. $^{d}$ Viscosity at 25°C. $^{e}$ Ionic conductivity at 25°C. $^{f}$ Molar conductivity at 25°C. $^{g}$ Thermal decomposition temperature of 10% weight loss.}
\end{table}
Electrochemistry

Fig. 2 Linear sweep voltammograms (the first cycle) for neat TFSI-based phosphonium ILs at a glassy carbon electrode with a 5 mV s⁻¹ potential sweep rate.

Fig. 3 Cyclic voltammograms (the first cycle) for 0.8 M LiTFSI in (a) P₄₄₄ificación-based phosphonium ILs at a glassy carbon electrode. The potential window lies between approximately −3.2 and at least +2.5 V vs. Fe/Fe⁺ for each IL, revealing the high electrochemical stability. It is also found that relatively large cations, i.e., P₄₄₄ificación and [P₄₄₄ificación][TFSI] seem to increase both anodic and cathodic stabilities. The potential windows thus observed closely resemble those of the quaternary ammonium ILs reported by Matsumoto et al.²³

As an example to show the electrochemical property of phosphonium ILs, Fig. 3 exhibits the cyclic voltammograms representing the redox behavior of Li in P₄₄₄ificación-TFSI and the corresponding ammonium IL, N₃₃₃ificación-TFSI. As shown in Fig. 3 (a), Li redox peaks appearing around −3.2 V vs. Fe/Fe⁺ with a current loop were observed in P₄₄₄ificación-TFSI. Similar voltammetric patterns measured in various quaternary ammonium ILs have been reported by Matsumoto et al.²³ However, as shown in Fig. 3 (b), small redox response of Li was observed in N₃₃₃ificación-TFSI due to the relatively high viscosity (631 mPa s at 25°C). The coulombic efficiency of the Li redox in P₄₄₄ificación-TFSI was 74%, which is higher than that in N₃₃₃ificación-TFSI (54%). These results reveal that the cathodic deposition and anodic dissolution of Li effectively take place in the phosphonium IL. Further research concerning the electrochemical behavior of Li in phosphonium ILs is in progress and will be reported.

4 Conclusion

The RTILs based on tri-n-butylalkyphosphonium cations together with a wide variety of anions were physically, thermally and electrochemically characterized. The phosphonium ILs, particularly TFSI-based ILs, significantly showed relatively low viscosity, high thermal and electrochemical stabilities. The redox response of Li in a TFSI-based phosphonium IL was observed, which also indicates the electrochemical availability.

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References