Hydrophobic Protic Ionic Liquid for Nonhumidified Intermediate-temperature Fuel Cells

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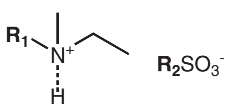
A novel protic ionic liquid ethylmethylpropylammonium nonafluorobutanesulfonate ([empa][NfO]) was found to exhibit hydrophobicity, high ionic conductivity, and facile electroactivity toward hydrogen oxidation and oxygen reduction reactions; these properties make it a suitable electrolyte for nonhumidified intermediate-temperature fuel cells.

Polymer electrolyte fuel cells (PEFCs) have attracted considerable attention as next-generation power sources[1] because of their environment-friendly nature and high maximum energy utilization efficiency, which is close to 80%; this efficiency is obtained when both electrical and thermal energy are utilized. One of the key materials used in PEFCs is polymer electrolyte membranes (PEM) made from perfluoroalkyl ionomers[1] and hydrocarbon ionomers.[2–6] It has been demonstrated that the suitable use of either perfluorinated cation-exchange membrane or sulfonated hydrocarbon membranes[5] enables the long-term operation of PEFCs; further, by morphology control of the PEMs, which consist of an ionic hydrophilic domain and a nonionic hydrophobic domain, the membranes can become highly proton conductive even under low humidity, which in turn enables low-humidity operation of the PEFCs.[7] These reports suggest that the performance of PEFCs nearly reaches a level suitable for their practical application; however, fuel cells have not been as widely commercialized as lithium-ion batteries.[8] One of the most crucial drawbacks of PEFCs is their high cost. Conventional PEMs need water for proton conduction, since water molecules serve as proton carrier.[9] Consequently, such PEFC systems cannot be operated at temperatures higher than 100 °C; this can lead to a low catalytic activity of the electrocatalyst (Pt) and the low utilization of exhaust heat.[10,11] Moreover, water management of the PEFC systems is necessary for their practical use, and this increases the volume and cost of PEFCs. Therefore, the development of novel proton-conducting materials with little or no dependence on humidity, which can function at temperatures above 100 °C, remains an important challenge in the realization of practical fuel cells.[12–14]

Recently, we found that certain protic ionic liquids, which are prepared by the neutralization of Brønsted bases with Brønsted acids, function as electrolytes in nonhumidified fuel cells.[15] Moreover, after screening more than 80-different protic ionic liquids, diethylmethylammonium trifluoromethanesulfonate ([dema][TfO], Figure 1) was found to exhibit properties that were most favorable for electrolytes (melting temperature: $T_m = -6\,°C$, decomposition temperature: $T_d = 360\,°C$, and ionic conductivity: $\sigma = 53\,mS\,cm^{-1}$ at 150 °C under anhydrous conditions); in addition, it showed a high electroactivity for hydrogen oxidation reaction (HOR) and oxygen reduction reaction (ORR), which resulted in a high open-circuit potential (OCP) of 1.03 V at 150 °C under anhydrous conditions.[16] It is also important for the protic ionic liquids to be hydrophobic, since hydrophilic protic ionic liquids may leak out of the membrane electrode assembly along with water that is continuously generated during fuel cell operation. However, most of the protic ionic liquids suitable for fuel cell applications are soluble in water. In this study, we report the preparation of hydrophobic protic ionic liquids and their electrolyte properties.



	R1 -	R2 -
[dema][TfO]	CH_3CH_2-	CF_3-
[dema][NfO]	CH_3CH_2-	$CF_3(CF_2)_2CF_2$-
[empa][NfO]	$CH_3CH_2CH_2$-	$CF_3(CF_2)_2CF_2$-

Figure 1. Chemical structures of protic ionic liquids.

Hydrophobic protic ionic liquids are easily prepared from bis(trifluoromethanesulfonyl)amide acid. We have demonstrated that diethylmethylammounium bis(trifluoromethanesulfonyl)amide ([dema][NTf_2]) exhibits bulk electrolyte properties ($T_m = 24\,°C$, $T_d = 375\,°C$, and $\sigma = 41\,mS\,cm^{-1}$ at 120 °C under anhydrous conditions),[16] which are comparable to those of [dema][TfO]. However, the electroactivity of [dema][NTf_2] toward HOR and ORR is completely different from that of [dema][TfO]; in the case of [dema][NTf_2], the overpotentials for both reactions are quite large, and thus, its OCP is only 0.77 V at 150 °C under anhydrous conditions. After investigating more than 80-different protic ionic liquids, we attribute the large difference in their activities toward electrode reactions to the nature of the anion. Protic ionic liquids based on oxoacid anions tend to exhibit low overpotentials for electrode reactions, while those based on amide-acid anions tend to exhibit high overpotentials. Therefore, oxoacid anions are considered preferable for designing protic ionic liquids for fuel cells. The use of fluorinated cations or anions is a well-known and convenient way of enhancing the hydrophobicity of ionic liquids. However, an increase in the molecular weight of the ions may lead to an increase in the T_m and viscosity, which in turn decreases ionic conductivity. Moreover, the asymmetric structure of the cation causes the T_m of ionic liquids to decrease; this is because with an asymmetric structure, the number of possible conformers increases, and hence, the change in entropy at T_m, when the phase transforms from liquid to solid, increases. The lowering of T_m can lead to an increasing choice of the anion.

By taking the above-mentioned facts into consideration, we prepared a protic ionic liquid using *N*,*N*-ethylmethylpropyl-

Table 1. Fundamental properties of protic ionic liquids[a]

Protic ionic liquids	T_m/°C	T_d/°C	η^b/mPa s	σ^b/mS cm^{-1}
[dema][TfO]	−6	360	10.9	21.5
[dema][NfO]	67	363	27.5	10.4
[empa][NfO]	9	334	21.9	4.6

[a] T_m, T_d, η, and σ are melting point, decomposition temperature, viscosity, and ionic conductivity, respectively. [b] Measured at 70 °C.

amine and *n*-nonafluorobutanesulfonic acid. *N*,*N*-ethylmethylpropylamine consists of three different alkyl groups, and its protonated form has a chiral nitrogen. *n*-Nonafluorobutanesulfonic acid is a commercially available superstrong perfluoroalkyl acid. *N*,*N*-ethylmethylpropylamine was synthesized from *N*-ethylmethylamine and 1-iodopropane.[17] The corresponding protic ionic liquids could be easily prepared according to a procedure reported previously;[16] the liquids thus obtained were stored in an Ar-filled glove box after drying in vacuo at 100 °C for 24 h.

The chemical structures of [dema][TfO], diethylmethylammounium nonafluoromethanesulfonate ([dema][NfO]), and ethylmethylpropylammonium nonafluoromethanesulfonate ([empa][NfO])[18] are shown in Figure 1; their fundamental properties are listed in Table 1. [empa][NfO] shows slightly higher viscosity and lower ionic conductivity than [dema][TfO]; nonetheless, these values are still acceptable for fuel cell electrolytes. T_m of [dema][NfO] is 67 °C, while that of [empa][NfO] is 9 °C. This difference is attributed to the cationic structural effect; the structure of the [empa] moiety is more asymmetric than that of the [dema] moiety. T_d of all the protic ionic liquids is ca. 350 °C, as shown in Table 1. In order to confirm their hydrophobicity, [empa][NfO] and [dema][TfO] were mixed with water. Figure 2a shows a photograph of the mixtures. [dema][TfO] was miscible in water, while [empa][NfO] (lower phase in Figure 2a) showed a clear phase separation from water (upper phase in Figure 2a); this implies that nonafluorobutyl group of [NfO] enhances the hydrophobicity of the protic ionic liquid.

Finally, we examined the activity of the protic ionic liquids toward electrode reactions. A Pt-wire working electrode, a Pt-black counter electrode, and a reversible hydrogen electrode (RHE: a Pt-black electrode in an ionic liquid with hydrogen bubbling) were completely immersed in the protic ionic liquid filled in a three-electrode glass cell. Cyclic voltammetry was performed at 150 °C after the reaction gas was bubbled into the ionic liquid for 30 min (2 mL min^{-1}; H_2 for HOR and O_2 for ORR). Figure 2b shows the cyclic voltammograms of [empa][NfO] for HOR and ORR with those of [dema][TfO] shown as reference. It should be noted that the overpotentials of [empa][NfO] for both HOR and ORR are rather low and comparable with those of [dema][TfO]. The limiting current density of [empa][NfO] for HOR is much higher than that of [dema][TfO], although the viscosity of [empa][NfO] is higher than that of [dema][TfO]. This behavior can be attributed to the considerably higher solubility of H_2 in [empa][NfO] than in [dema][TfO].

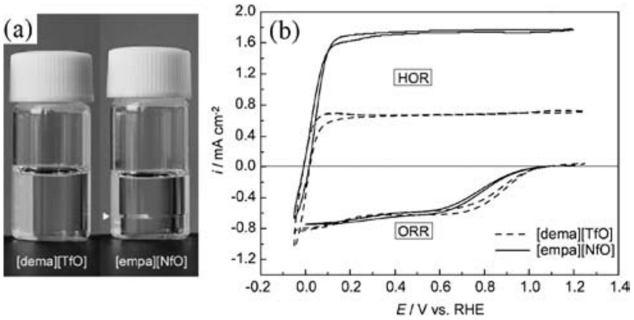


Figure 2. (a) A photograph of water/[dema][TfO] (left) and water/[empa][NfO] mixtures (right). White triangle indicates the interface of water-rich upper phase and [empa][NfO]-rich lower phase. (b) Cyclic voltammograms of HOR and ORR for [dema][TfO] and [empa][NfO] at 150 °C under anhydrous conditions. Scan rate was set at 10 mV s^{-1}.

The results of this study suggest that [empa][NfO] is suitable as an electrolyte for nonhumidified intermediate-temperature fuel cells.

This study was supported in part by a Grant-in-Aid for Scientific Research (#452/17073009) from the MEXT of Japan and by a NEDO Research Grant.

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17 ^{1}H NMR (DMSO-d_6, 400 MHz; δ): 2.32 (q, $J = 7.2$ Hz, 2H), 2.20 (t, $J = 7.2$ Hz, 2H), 2.09 (s, 3H), 1.39 (m, 2H), 0.95 (t, $J = 7.2$ Hz, 3H), 0.83 (t, $J = 7.2$ Hz, 3H).
18 ^{1}H NMR (DMSO-d_6, 400 MHz; δ): 7.91 (m, 1H), 3.25–3.00 (m, 4H), 2.79 (d, $J = 4.4$ Hz, 3H), 1.69 (m, 2H), 1.25 (t, $J = 6.8$ Hz, 3H), 0.88 (t, $J = 7.2$ Hz, 3H).

Published on the web (Advance View) June 6, 2009; doi:10.1246/cl.2009.692