

## Performance of Nonhumidified Intermediate-temperature Fuel Cells Based on Protic Ionic Liquids Prepared from Oxo and Amide Acids

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A distinct difference between the use of protic ionic liquids (PILs) prepared from oxo and amide acids as an electrolyte of nonhumidified intermediate-temperature fuel cells has been demonstrated in terms of the fuel cell performance by using composite membranes made of a sulfonated polyimide and the PILs.

Polymer electrolyte fuel cells (PEFCs) have attracted considerable attention as next-generation power sources<sup>1,2</sup> for stationary and vehicular applications because of their environmental friendliness and high maximum energy utilization efficiency of close to 80% when both the electrical and thermal energies are utilized. Although a PEFC system for stationary applications used at home is now commercially available in Japan, a PEFC system for vehicular application is still a long way from commercialization. The high cost of PEFC systems is one of the serious issues responsible for the postponement of the widespread use of the PEFC technology. This high cost is attributed to the Pt catalyst, proton-conducting electrolyte membrane, and the complicated subsystems required for the PEFC systems. PEFC systems that can be operated at intermediate temperatures (>100 °C) under nonhumidified conditions are believed to be a solution to these problems because of the following reasons. (a) The activity of the Pt catalyst can be improved at high temperatures. (b) The Pt catalyst poisoning by carbon monoxide can be suppressed. (c) The amount of Pt catalyst required can be reduced. (d) A water management system becomes unnecessary. (e) The temperature control of the system using a radiator becomes easy. (f) A simpler system can be designed. (g) High-quality heat can be utilized. Thus far, certain proton conductors such as phosphoric-acid-doped polybenzimidazole (PPA/PBI)<sup>3</sup> and solid acid proton conductors (CsHSO<sub>4</sub><sup>4</sup> and CsH<sub>2</sub>PO<sub>4</sub><sup>5</sup>) have been proposed for use in such PEFC systems.

Ionic liquids (ILs) are salts that have melting points ( $T_m$ ) at ambient temperatures. They are composed entirely of ions, and therefore, typical ILs exhibit unique properties such as unmeasurable vapor pressure, high decomposition temperature ( $T_d$ ), and high ionic conductivity ( $\sigma$ ).<sup>6</sup> We have reported that protic ionic liquids (PILs), which are prepared by the neutralization reactions of Brønsted acids and bases, and their base-rich melts, can be employed as proton conductors in nonhumidified fuel cell systems.<sup>7</sup> In other words, protons can be transported by the cations via the vehicle and Grotthuss mechanisms; further, the fuel cell electrode reactions, i.e., hydrogen oxidation reduction (HOR) and oxygen reduction reaction (ORR), can be facilitated at the interface of a Pt electrode and the PILs. Furthermore, we have found that diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) exhibits the most preferable electrolyte

properties ( $T_m = -6$  °C,  $T_d = 360$  °C,  $\sigma = 55$  mS cm<sup>-1</sup> at 150 °C, and open circuit voltage of a H<sub>2</sub>/O<sub>2</sub> liquid fuel cell (OCV) = 1.03 V at 150 °C).<sup>8</sup> More recently, we reported that a sulfonated polyimide (SPI) in the ammonium form exhibits a good compatibility with [dema][TfO] to form flexible and mechanically strong composite membranes. We also reported that a nonhumidified fuel cell using such a composite membrane can be successfully operated at 80 °C.<sup>9</sup>

In order to realize membrane PIL fuel cells, the hydrophobic nature of PILs is preferable because the concomitant evolution of water at the cathode during fuel cell operation may result in the leakage of the PILs from the membrane. Therefore, we have proposed a method to prepare hydrophobic PILs by using hydrophobic acids. It was found that ethylmethylpropylammonium nonafluorobutanesulfonate ([empa][NfO])<sup>10</sup> has favorable electrolyte properties with a high activity of the electrode reactions compared to [dema][TfO] and is not miscible with water. An amide acid, bis(trifluoromethanesulfonyl)amide, easily forms hydrophobic water-immiscible PILs. However, PILs based on an amide acid such as [dema][NTf<sub>2</sub>] exhibit poor activity toward the fuel cell electrode reactions in spite of their favorable bulk properties. Although such differences in the activity of the fuel cell reactions depending on PIL structures have been demonstrated by using cyclic voltammetry at a Pt electrode under H<sub>2</sub> and O<sub>2</sub> bubbling atmosphere<sup>8,10</sup> (see Supporting Information Figure S1),<sup>11</sup> the effects of these differences on the fuel cell performances are unknown. In this study, we confirm the effect of the differences in the electrochemical activity of PILs on the performance of membrane fuel cells.

Figure 1 shows the chemical structures of the SPI and PILs used in this study. The PILs have different affinities toward water (hydrophilic or hydrophobic) and different anionic structures (the conjugate acid is oxo or amide acid). The PILs were prepared by the direct neutralization of the Brønsted acid and base according to a previously reported method<sup>8</sup> and dried in a vacuum oven at 80 °C for 24 h. Their fundamental properties are listed in Table 1. [dema][TfO] exhibits the most preferable

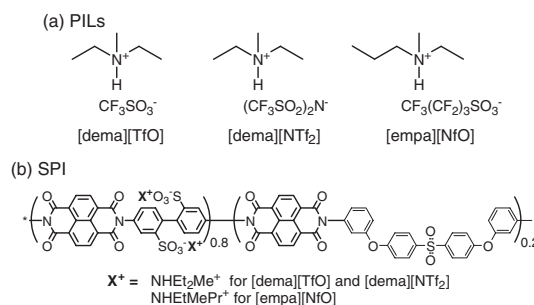


Figure 1. Chemical structures of (a) PILs and (b) SPI.

**Table 1.** Fundamental properties of PILs

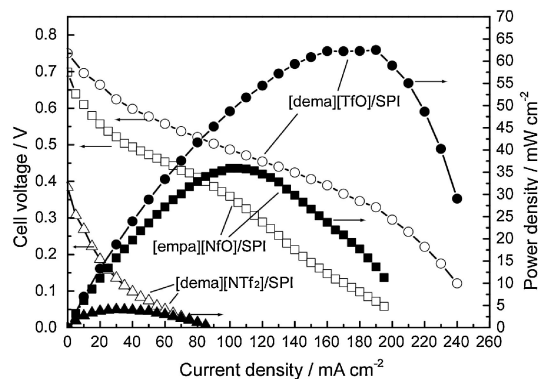
PILs	$T_m/T_d$ (°C)	$\eta^a$ /mPa s <sup>-1</sup>	$\sigma^a$ /S cm <sup>-1</sup>	Affinity to water
[dema][TfO]	-6/360	10.9	21.5	hydrophilic
[dema][NTf <sub>2</sub> ]	24/374	10.9	19.6	hydrophobic
[empa][NfO]	8.6/334	21.9	4.6	hydrophobic

<sup>a</sup>Measured at 70 °C.

bulk properties but is hydrophilic. [dema][NTf<sub>2</sub>] exhibits bulk properties similar to those of [dema][TfO] and is hydrophobic although the value of the  $T_m$  of [dema][NTf<sub>2</sub>] is considerably higher than that of [dema][TfO]. [empa][NfO] exhibits the lowest value of  $\sigma$  and the highest value of  $\eta$  among the PILs used under anhydrous conditions and is hydrophobic. This is probably because the perfluoroalkyl chain in its anionic structure is longer than that in the others.

A matrix polymer, SPI, was synthesized by using a polycondensation reaction and adding a conjugate base of the cation in each PIL. The SPI was obtained in an ammonium form as reported in a previous paper.<sup>9</sup>  $M_n$  (number-average molecular weight) =  $1.6 \times 10^5$  and ion exchange capacity = 2.15 mequiv g<sup>-1</sup>. Composite membranes were fabricated by casting a *m*-cresol solution containing SPI and a PIL on a petri dish, followed by drying the solution at 80 °C. For each PIL, flexible, uniform, and mechanically strong composite membranes that contained 75 wt % PIL could be fabricated. The composite membranes have been abbreviated as PIL/SPI (e.g., [dema][TfO]/SPI).

The  $\sigma$  values of the composite membranes, [dema][TfO]/SPI, [dema][NTf<sub>2</sub>]/SPI, and [empa][NfO]/SPI under anhydrous conditions at 120 °C were 9.3, 15.1, and 2.8 mS cm<sup>-1</sup>, respectively, which are acceptable values for fuel cell applications. In order to demonstrate the operation of a nonhumidified fuel cell by using a composite membrane, membrane electrode assemblies (MEAs) were fabricated using ionomer-free gas-diffusion electrodes (E-TEK GDE, LT-140EW; 30% Pt on Vulcan XC-72, 0.5 mg cm<sup>-2</sup>) according to the same procedure as that reported earlier.<sup>9</sup> Figure 2 shows the polarization curves of non-humidified fuel cells operated at 120 °C. It should be noted that the fuel cells can generate electric power even under non-humidified conditions at 120 °C and that the fuel cell performances strongly depend on the PILs in the membranes. In the case of the [dema][TfO]/SPI composite membrane, a current density of 250 mA cm<sup>-2</sup> with a maximum power density of 64 mW cm<sup>-2</sup> is achieved. The fuel cell using the [empa][NfO]/SPI composite membrane exhibits a slightly lower performance (the maximum current density and power density are 200 mA cm<sup>-2</sup> and 36 mW cm<sup>-2</sup>, respectively) with an OCV similar to that in the case of the [dema][TfO]/SPI composite membrane. This difference in the fuel cell performances may be explained by the difference in the bulk conductivity of the PILs (Table 1). On the other hand, the fuel cell using the [dema][NTf<sub>2</sub>]/SPI composite membrane exhibits a considerably inferior performance (OCV is ca. 0.4 V, maximum current density is 85 mA cm<sup>-2</sup>, and maximum power density is 4 mW cm<sup>-2</sup>) compared to the others. This indicates that the poor activity of [dema][NTf<sub>2</sub>] for HOR and ORR is responsible for the inferior fuel cell performance since the bulk transport properties of [dema][NTf<sub>2</sub>] and its composite membrane are similar to or superior to those of the



**Figure 2.** Polarization curves of nonhumidified fuel cells using the composite membranes at 120 °C. Flow rate of the reaction gases (H<sub>2</sub> and O<sub>2</sub>) was set at 12 mL min<sup>-1</sup> for all of the measurements.

other PILs. We recognize at present that such poor electroactivity of [dema][NTf<sub>2</sub>] is caused by the fact that it is a salt of a super-strong amide acid, HNTf<sub>2</sub>, whereas [dema][TfO] and [empa][NfO] are salts of superstrong sulfonic acids (oxo acids).

Our membrane fuel cells have not been optimized, especially in terms of the structure of the catalyst layer in the MEAs. However, the results shown in Figure 2 strongly suggest the importance of the HOR and ORR of PILs in addition to the bulk transport properties for fuel cell applications.

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