Fabrication of protic ionic liquid/sulfonated polyimide composite membranes for non-humidified fuel cells

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ABSTRACT

We have demonstrated that a protic ionic liquid, diethylmethylammonium trifluoromethanesulfonate ([dema][TfO]) functions as a proton conductor and is suitable for use as an electrolyte in H_2/O_2 fuel cells, which can be operated at temperatures higher than $100\,^{\circ}C$ under non-humidified conditions. In this study, in order to fabricate a polymer electrolyte fuel cell, matrix polymers for [dema][TfO] are explored and sulfonated polyimides (SPI), in which the sulfonic acid groups are in diethylmethylammonium form, are found to be highly compatible with [dema][TfO]. Polymer electrolyte membranes for non-humidified fuel cells are prepared by the solvent casting method using SPI and [dema][TfO]. The SPI, with an ion exchange capacity of $2.27\,meq\,g^{-1}$, can retain four times its own weight of [dema][TfO] and produces uniform, tough, and transparent composite membranes. The composite membranes have good thermal stability ($>300\,^{\circ}C$) and ionic conductivity ($>10^{-2}\,S\,cm^{-1}$ at $120\,^{\circ}C$ when the [dema][TfO] content is higher than 67 wt%) under anhydrous conditions. In the H_2/O_2 fuel cell operation using a composite membrane without humidification, a current density higher than $240\,mA\,cm^{-2}$ is achieved with a maximum power density of $100\,mW\,cm^{-2}$ at $80\,^{\circ}C$.

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1. Introduction

Polymer electrolyte fuel cells (PEFCs) are recognized as one of the most promising sources of clean energy power because of their high energy conversion efficiency, high energy density, and wide range of applicability, which includes applications to stationary, transport, and portable uses [1–3]. However, their application to vehicles and portable devices has not been fully realized owing to its high cost and because the simplicity and compactness required for such applications have not yet been achieved. The most commonly used polymer electrolyte membranes are perfluoro-sulfonated polymers such as Nafion®. They have excellent chemical stability and high proton conductivity, but their high cost is a serious drawback [4–8]. As alternatives, sulfonated hydrocarbon polymers such as poly(ether ketone) [9,10], poly(ether ether ketone) [11–15], polybenzimidazole (PBI) [16–18], and polyimide [19–21], which are cheaper than the perfluorinated ionomers and can be employed over a wide temperature range, have been extensively studied as polymer electrolytes for PEFCs. However, these polymers, including Nafion®, require humidification to maintain their high proton conductivity, since water molecules play the role of proton carriers in the proton conduction of such polymer electrolytes [22–24]. Additionally, such PEFC systems should be operated at temperatures lower than the boiling point of water (preferably <80 °C), at which the poisoning of the anode Pt catalyst by CO becomes inevitable [25,26].

Fuel cell operation above 100 °C under non-humidified conditions has been demonstrated using an anhydrous proton conducting electrolyte such as PBI/H_3PO_4 or $CsHSO_4$ to overcome the drawbacks of PEFCs [27–32]. However, such proton conductors still have many problems such as poor processability and mechanical properties and a narrow operational temperature range. Recently, our group reported that certain protic ionic liquids (PILs), which are synthesized by neutralization reactions of Brønsted acids and bases, undergo facile fuel cell electrode reactions (i.e., hydrogen oxidation and oxygen reduction) under anhydrous conditions. This indicates that PILs can be employed as an electrolyte in non-humidified fuel cell systems [33–36]. Further, it was found that [dema][TfO] (Fig. 1) exhibits high thermal stability ($T_d = 360\,^{\circ}C$), a low melting point ($T_m = -6\,^{\circ}C$), high ionic conductivity ($\sigma = 4.3 \times 10^{-2}\,S\,cm^{-1}$ at $120\,^{\circ}C$ under an anhydrous condition), and small overpotentials for both electrode reactions at Pt electrodes (open circuit potential at 150 °C of 1.03 V) [37].

In this study, in order to apply [dema][TfO] to PEFCs, we fabricated composite membranes using sulfonated polyimide (SPI) as a matrix polymer and investigated their thermal and electrochemical properties. Polyimides were selected owing to their good film-forming property and high thermal stability. However, simple

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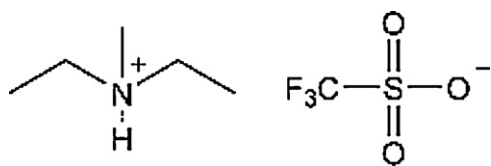E-mail address: mwatanab@ynu.ac.jp (M. Watanabe).

Fig. 1. Chemical structure of protic ionic liquid, [dema][TfO].

polyimides without chemical modification were not compatible with [dema][TfO]. It was found that SPIs having diethylmethyl-lammonium as the counter cations of the sulfonate groups were highly compatible with [dema][TfO] and that the resulting composite membranes had favorable thermal and mechanical properties. Furthermore, the operation of a H_2/O_2 fuel cell using the composite membranes under non-humidified conditions could be demonstrated.

2. Experiment

2.1. Materials

Triethylamine (99%, Aldrich), *N,N*-diethylmethylamine (DEMA) (97%, Aldrich), benzoic acid (99.5%, Junsei Chem.), and trifluoromethanesulfonic acid (99%, Aldrich) were used as received. 2,2′-Benzidinesulfonic acid (BDSA) (70%, Tokyo Kasei) was washed with water and dissolved in water by adding triethylamine. Acidification with 1 M H_2SO_4(aq) afforded precipitation of pure BDSA. Bis[4-(3-aminophenoxy)-phenyl]sulfone (3BAPPS) (95%, Wako Chem.) was recrystallized from ethanol. BDSA, 3BAPPS, and pyromellitic dianhydride (PMDA) (97%, Kanto Chem.) were dried in a vacuum oven at 80 °C prior to use. *m*-Cresol (98%, Wako Chem.) was dried over molecular sieves 4A (Wako Chem.) prior to use. [dema][TfO] was prepared by direct neutralization between the Brønsted acid and base according to a previously reported method [37] and dried in a vacuum oven at 80 °C for 24 h.

2.2. Synthesis of SPI

The synthesis of SPIs is shown in Scheme 1. SPIs with different ion exchange capacities (IECs) were prepared by changing the molar ratios in the feed of the diamine comonomers. Typical synthesis is as follows. BDSA (2.9 mmol, 1.00 g), 3BAPPS (2.9 mmol, 1.26 g), DEMA (7.2 mmol, 0.73 g), and 10 ml of *m*-cresol were added to a 100 ml three-necked flask equipped with a magnetic stirring bar. Triethylamine is conventionally added to the polymerization mixture to dissolve the sulfonated diamine monomer (BDSA) in the solvent, consequently, SPIs are obtained in triethylammonium form. In this study, DEMA was employed instead of triethylamine to obtain SPIs in diethylmethylammonium form. The mixture was stirred for several minutes under nitrogen atmosphere at 100 °C until the mixture completely dissolved. After PMDA (5.8 mmol, 1.27 g) was added to the flask, the mixture was heated to 175 °C and then stirred for 15 h. Benzoic acid (14.5 mmol, 1.77 g) was added, and the mixture was stirred at 195 °C for another 3 h. After the reaction, the mixture was cooled to 100 °C and then another 50 ml of *m*-cresol was added to dilute the highly viscous solution. The solution was slowly poured into 500 ml of acetone. The resulting yellow fibrous precipitate was washed for 5 h with acetone to remove *m*-cresol completely and dried in a vacuum oven at 80 °C.

The composite membranes were fabricated using a solution casting method. Appropriate amounts of [dema][TfO], SPI powder, and *m*-cresol were added to a sample bottle equipped with a magnetic stirring bar. The mixture was stirred overnight at room temperature so that it dissolved completely, and it was then cast on a Petri dish. Evaporation of *m*-cresol at 60 °C gave a uniform composite membrane. The composite membranes were peeled from the Petri dish, dried in a vacuum oven at 80 °C for 24 h, and then stored in an argon atmosphere glovebox (VAC, $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm).

2.3. Characterization of materials

^{1}H NMR spectra were recorded by a spectrometer (JEOL AL-400, 400 MHz), using DMSO-d_6 as a solvent and tetramethylsilane as an internal reference. Gel permeation chromatography (GPC) was carried out using an HPLC system (Shimadzu) equipped with two columns (Shodex KD-803 and KD-804). A 0.01 M LiBr dimethyl-formamide solution was used as the eluent at a flow rate of 1 ml min^{-1}. The analyte solutions were filtered through a polyte-trafluoroethylene filter (pore size of 0.2 μm) before being injected into the columns. The molecular weights of the obtained polymers were calculated using a calibration curve based on polystyrene standards.
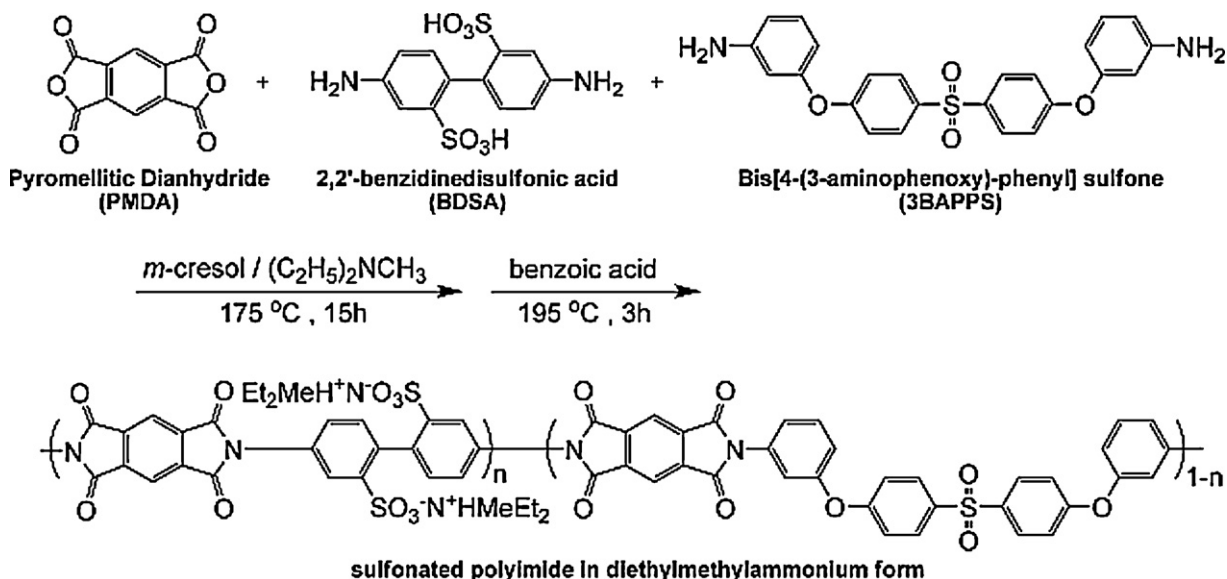
Scheme 1. Synthetic procedure of sulfonated polyimides in diethylmethylammonium form.

Differential scanning calorimetry (DSC) was carried out on a Seiko Instruments DSC 220C under a nitrogen atmosphere. The samples were tightly sealed in aluminum pans in the dry glovebox. The samples were heated to 150 °C, then cooled to −150 °C, and finally heated again to 150 °C at cooling and heating rates of 10 °C min^{-1}. The DSC traces were recorded during the reheating scans. Thermogravimetric analysis was performed using a Seiko Instruments TG-DTA 6200C under a nitrogen atmosphere. The samples were weighed and placed in aluminum pans and then heated from room temperature to 550 °C at a heating rate of 10 °C min^{-1}.

Ionic conductivities of the pure ionic liquid ([dema][TfO]) and the composite membranes were determined by means of the complex impedance method in the temperature range of 40–160 °C. The pure ionic liquid was poured into a dip-type glass cell with two Pt rods fixed at a constant electrode distance in the glovebox. The cell constant was determined using a 0.1 M KCl standard aqueous solution at 30 °C [34]. The composite membranes were placed between the two Pt electrodes (12 mm electrode diameter) and sealed in cylindrical cells in the glovebox. These measurement cells were placed in a thermostat oven and thermally equilibrated at each temperature for 1.5 h before measurements. The measurements were carried out with a potentiostat (Autolab, PGSTAT30) in the frequency range of 1–10 MHz.

2.4. Fabrication of membrane electrode assembly (MEA) and a single-cell test

A membrane electrode assembly (MEA) was fabricated by sandwiching a composite membrane between two gas diffusion electrodes (E-TEK GDL, LT140EW; 30% Pt on Vulcan XC-72, 0.5 mg cm^{-2}, and ionomer free) and hot-pressed by applying a pressure of 20 kgf cm^{-2} at 120 °C for 3 min. The MEA was tested in a single-cell with a serpentine-shaped gas flow field and an active area of 4 cm^2 at ambient pressure. The H_2/O_2 fuel cell polarization curves were determined at 30 °C and 80 °C by using an Eiwa Corp. FC test station. Anhydrous H_2 (99.99%) and O_2 (99.6%) gases were supplied to the test station at gas utilization ratios of 30% and 15%, respectively, without any humidification.

3. Results and discussion

3.1. Synthesis and fabrication of the composite membrane

SPIs with different IECs, 1.51 and 2.27 meq g^{-1}, were synthesized. It is confirmed that the experimental IECs estimated from the ^{1}H NMR spectra agree well with those calculated from the feed molar ratios (Table 1). Table 1 also shows the number-average molecular weight (M_n), the weight-average molecular weight (M_w), and the polymer dispersion (M_w/M_n) of the SPIs determined by GPC, which indicate that polyimides of molecular weight sufficiently high for thin-film fabrication are obtained. These results demonstrate that quantitative polycondensation proceeds in this system, and that the reactivity difference between the diamines, BDSA, and 3BAPPS is negligible.
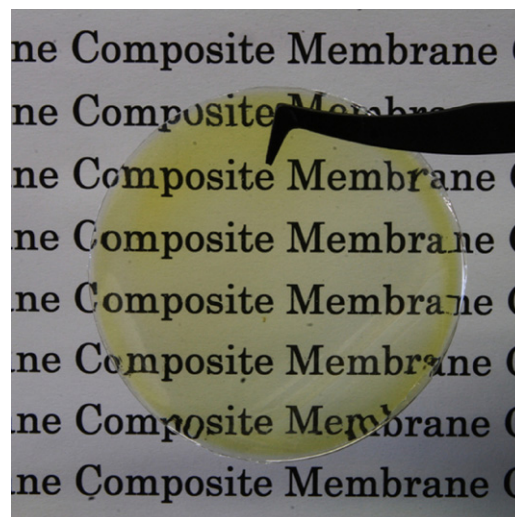

Fig. 2. A photograph of SPI-2.27(67) composite membrane.

Compatibility between these matrix polyimides and the PIL, [dema][TfO], is important in applying the resulting composite membranes as the electrolyte membranes of PEFCs. The SPIs in the composite membranes were employed in diethylmethylammonium form, since the polyimides with a diethylmethylammonium sulfonate group have good compatibility with [dema][TfO]. The structural similarity appears to contribute to the good compatibility. The composite membranes can be fabricated using the solution casting method and *m*-cresol as the casting solvent. Note that the SPI in diethylmethylammonium form with an IEC of 2.27 meq g^{-1} can retain four times its own weight in [dema][TfO] without crosslinking (*vide infra*). The composite membranes have a thin-film-forming property (thickness of 50–100 μm), flexibility, and transparency (bright yellow), as shown in Fig. 2. Scanning electron microscope observations (data not shown) revealed that these composite membranes are not porous but pinhole-free and dense. The membranes are abbreviated as SPI-*X*(*Y*), where *X* and *Y* are the IEC values (meq g^{-1}) of the SPI matrix and the contents of [dema][TfO] (wt%).

3.2. Thermal properties

It is important to study the thermal stability of polymer electrolyte membranes because a medium temperature operation at higher than 100 °C is eventually being aimed for the PEFCs using these membranes. Fig. 3 shows thermogravimetric curves of the SPI/[dema][TfO] composite membranes recorded from room temperature to 550 °C together with the data for pure [dema][TfO]. For [dema][TfO], T_d is 360 °C, as reported previously [37]. It is interesting to note that the first-step weight loss for the SPIs also occurs at ca. 360 °C, which corresponds to the weight loss of diethylmethylammonium sulfonate groups on the polyimides. For the composite membranes, as the content of [dema][TfO] in the
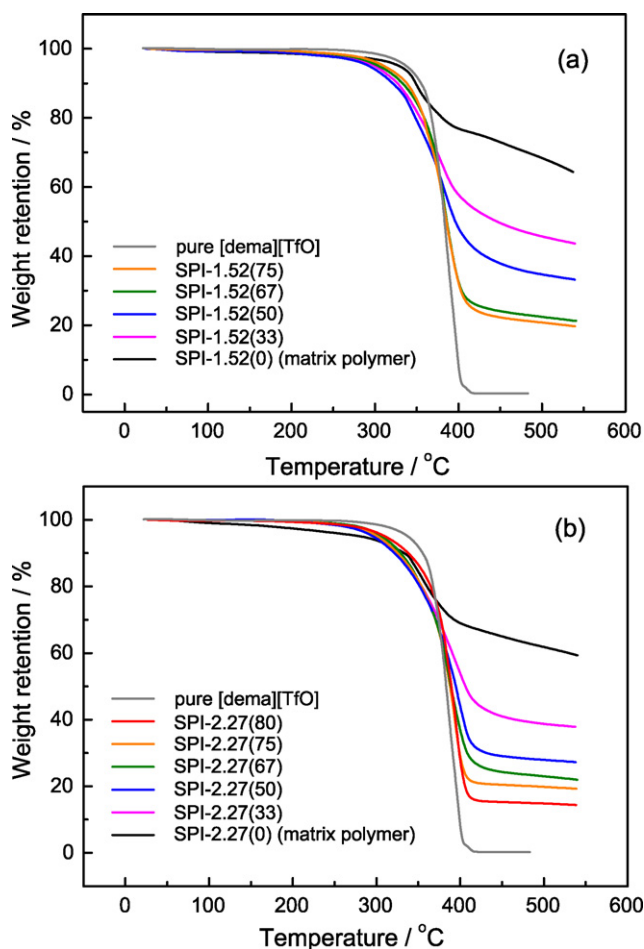
Table 1
IEC and GPC data of the SPIs.

Polymer	Mole fraction in feed			IEC[a] (meq g^{-1})	IEC[b] (meq g^{-1})	M_n (×10^5)	M_w (×10^5)	M_w/M_n
	PMDA	BDSA	3BAPPS					
SPI-1.51	0.5	0.25	0.25	1.52	1.51	1.21	1.73	1.43
SPI-2.27	0.5	0.40	0.10	2.34	2.27	1.05	1.43	1.36

[a] Calculated from feed monomer ratio.
[b] Observed by ^{1}H NMR.

Fig. 3. Thermogravimetric curves for [dema][TfO] and composite membranes based on (a) SPI-1.51 and (b) SPI-2.27.

Fig. 4. DSC traces for [dema][TfO] and SPI/[dema][TfO] composite membranes based on (a) SPI-1.51 and (b) SPI-2.27.

SPIs increases, the weight loss at this temperature becomes more dominant. For all membranes, the decomposition temperatures are determined as >300 °C, indicating good thermal stability. This result suggests that the composite membranes can be employed as electrolyte membranes for intermediate-temperature fuel cell systems.

Fig. 4a shows the DSC thermograms of the pure ionic liquid and SPI-1.51 composite membranes containing different amounts of PIL (wt% in parentheses). For the pure PIL, the single endothermic peak corresponds to the T_m of [dema][TfO]. The peak is observed when the [dema][TfO] content is higher than 67 wt%. On the other hand, when the PIL content is lower than 50 wt%, significant phase transitions are not detected, indicating that the [dema][TfO] incorporated in the SPI cannot be crystallized at this cooling rate (10 °C min^{-1}) and is compatible with the SPI. In the case of the composite membranes based on the SPI with an IEC of 2.27 meq g^{-1} (Fig. 4b), endothermic peaks are not observed for [dema][TfO] contents up to 80 wt%. This clearly indicates that diethylmethyl-lammonium sulfonate groups in the SPIs play an important role in [dema][TfO] being compatible with the polyimides, and that [dema][TfO] strongly interacts with the ammonium sulfonate groups in the polymers.

3.3. Ionic conductivity under non-humid conditions

The ionic conductivities of the pure PIL and the composite membranes were measured in the temperature range of 40–160 °C

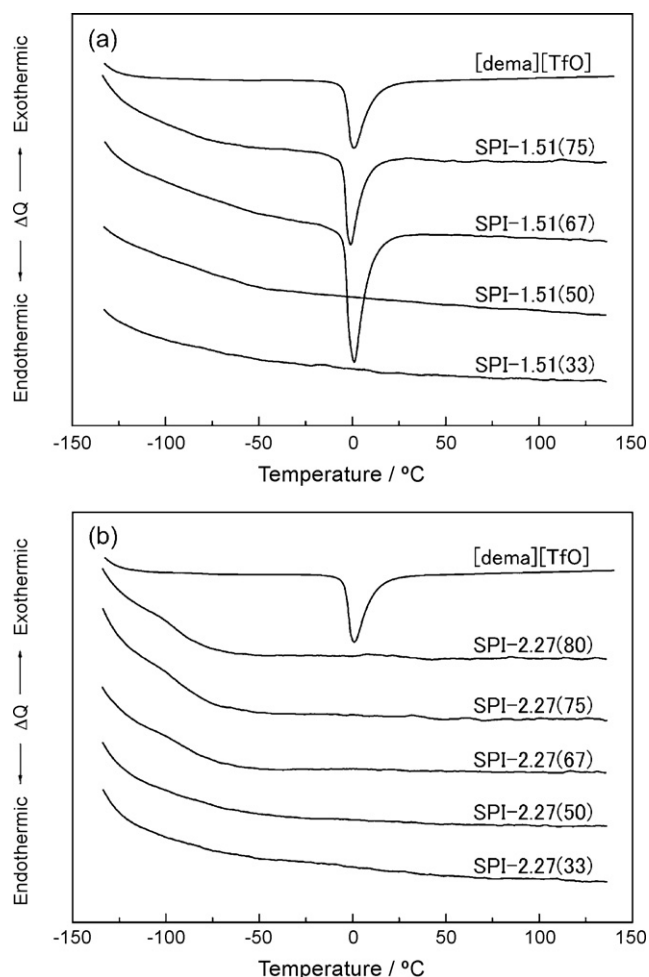under anhydrous conditions. Fig. 5 shows the Arrhenius plots of the ionic conductivities of the composite membranes based on SPI-1.51 (Fig. 5(a)) and SPI-2.27 (Fig. 5(b)). The ionic conductivities of pure [dema][TfO] are higher than 10^{-2} S cm^{-1} in the measurement temperature range and reach 54 mS cm^{-1} at 150 °C. It has been revealed that the H$^+$ (cationic) transference number of [dema][TfO] is 0.6 at 30 °C and 0.5 at 130 °C [37]. The composite membrane SPI-1.51(33) has ionic conductivity of ca. 10^{-4} S cm^{-1} at 160 °C and only ca. 10^{-8} S cm^{-1} at 40 °C. However, the ionic conductivity greatly increases with an increase in the [dema][TfO] content, and SPI-1.51(75) has ionic conductivity of 14.6 mS cm^{-1} at 160 °C. This behavior can be explained by assuming that [dema][TfO] in the composite membranes forms an ion conduction domain with diethylmethyl-lammonium sulfonated groups in the SPIs, and that the ion conduction domain is continuously connected as the [dema][TfO] content increases. The composite membranes based on SPI-2.27 have higher ionic conductivity than those based on SPI-1.51, when the [dema][TfO] contents are the same. We assume that [dema] counter cations of the sulfonate groups in the SPIs also contribute to the ionic conduction by a cation exchange reaction between the matrix polymer and [dema][TfO], which can be a reason for the conductivity difference at the same [dema][TfO] contents. The following observation supports the assumption; SPI in triethylammonium form was synthesized and a composite membrane was fabricated with [dema][TfO]. After extracting the PIL, it was confirmed for the residual SPI that triethy-
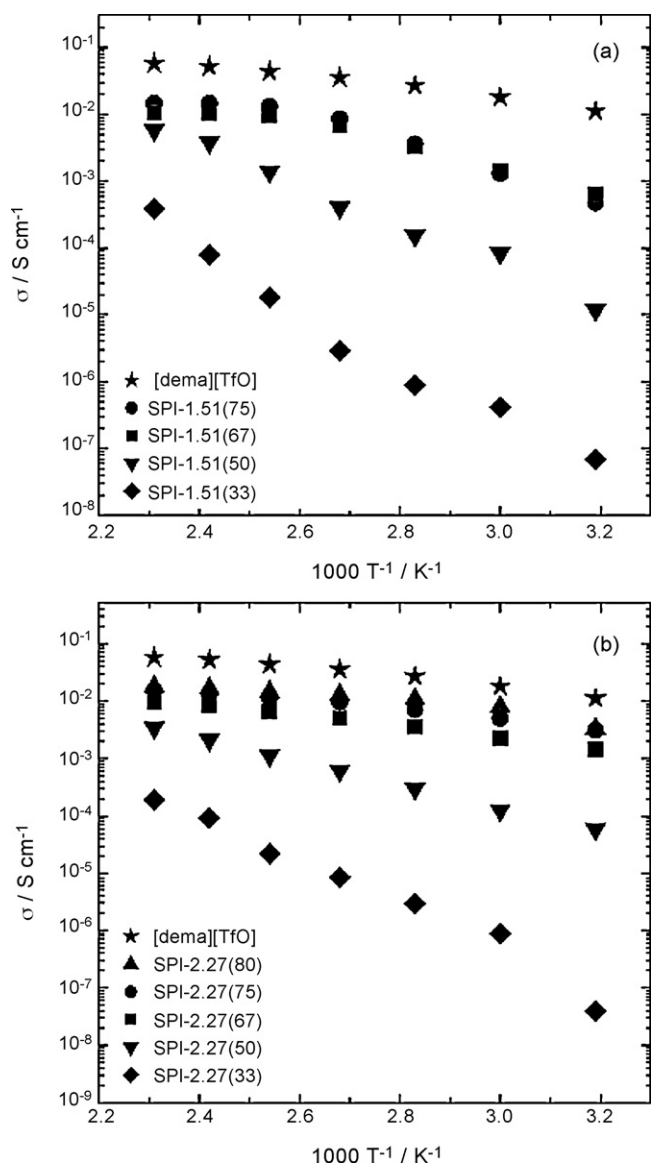
Fig. 5. Arrhenius plots of ionic conductivities for [dema][TfO] and SPI/[dema][TfO] composite membranes based on (a) SPI-1.51 and (b) SPI-2.27.

lammonium cation of the SPI was partly exchanged to [dema] cation.

3.4. Single-cell test of the composite membrane without humidification

The H_2/O_2 fuel cell was operated at 30 and 80 °C using a SPI-1.51(50) composite membrane without humidification. Because the preparation of MEA has not been optimized, an ionic conductivity difference of the SPIs depending on the IEC values did not greatly affect the fuel cell performances. Fig. 6 shows the fuel cell polarization curves. At 30 °C, a current density higher than 300 mA cm^{-2} is achieved with a maximum power density of 68 mW cm^{-2}, while at 80 °C, a current density higher than 240 mA cm^{-2} is achieved with a maximum power density of 100 mW cm^{-2}. Although the performance is much lower than that of conventional PEFCs with hydrated ion exchange membranes, it should be noted that the fuel cell operation of the present system becomes possible at room temperature and without any humidification of supplied gases (H_2 and O_2).
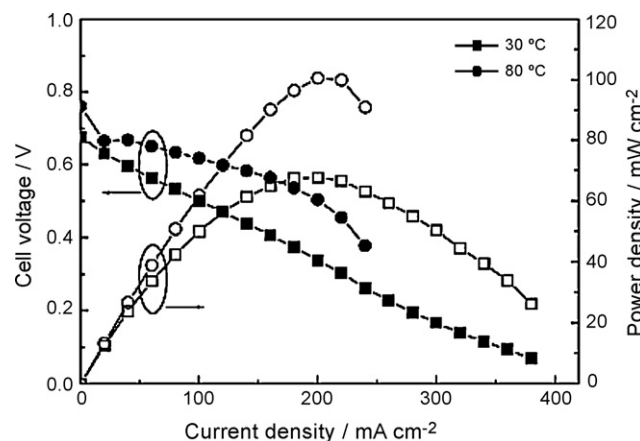

Fig. 6. Polarization curves of a H_2/O_2 fuel cell using a SPI-1.51(50) composite membrane without humidification at gas utilization ratios of 30% for H_2 and 15% for O_2: (■,□) operation at 30 °C, (●,○) operation at 80 °C.

4. Conclusions

In this study, composite membranes were fabricated from a PIL, [dema][TfO], and sulfonated polyimides having diethylmethylammonium counter cations, as electrolyte membranes for non-humidified intermediate-temperature fuel cells. The obtained composite membranes were flexible, tough, and transparent and also exhibited good thermal stability ($T_d > 300$ °C) and ionic conductivity ($\sigma > 10^{-2}$ S cm^{-1} at 160 °C when the [dema][TfO] content was higher than 67 wt%) under anhydrous conditions. In the H_2/O_2 fuel cell operation using a composite membrane, a current density higher than 240 mA cm^{-2} was achieved with a maximum power density of 100 mW cm^{-2} without humidification at 80 °C. All the results obtained in this study indicate that the PIL, [dema][TfO], is promising as an intrinsic proton conductor and that sulfonated polyimide composite membranes in which [dema][TfO] is molecularly compatible can function as fuel cell electrolyte membranes under non-humidified conditions.

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