Brønsted acid–base ionic liquids for fuel cell electrolytes†‡

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A simple protic ionic liquid obtained from the combination of diethylmethylamine and trifluoromethanesulfonic acid exhibits the remarkable results as a medium temperature fuel cell electrolyte under non-humidifying conditions, affording a higher and stable open-circuit potential, wide liquid temperature range, and high thermal stability.

Fuel cells (FCs), especially polymer electrolyte fuel cells (PEFCs), are promising for the realization of thermoelectric co-generation systems, electric vehicles, and so forth.[1] PEFCs usually employ water-swollen ion-exchange polymer membranes as H^+-conducting electrolytes.[2,3] Conventional PEFCs require operation at temperatures at which water condenses, because the membranes exhibit high H^+-conductivity only when they are highly water-swollen.[2,3] The so-called medium temperature operation of FCs is desirable, and several reports have already appeared,[4–6] because it would make more efficient power generation possible, as well as higher tolerance to catalyst poisoning, for example, from CO. The one classical option is to use thermally stable proton carriers such as H_3PO_4, which is the electrolyte of phosphoric acid fuel cells, instead of water.[6–8] The complexation of H_3PO_4 with polymers presents an example of possible PEFCs under medium temperature operation.[9,10] However, the development of novel proton-conducting materials with little or no dependence on humidity at temperatures above 100 °C still remains an important challenge to the realization of practical FCs.

Protic ionic liquids,[11–16] consisting of combinations of Brønsted acids and bases, are a sub-class of ionic liquids (ILs),[17,18] and several of these retain characteristics that are typical of ILs, such as thermal stability, low volatility, electrochemical stability, and high ionic conductivity. In the protic ILs, the Brønsted bases function as acceptors of the protons of the Brønsted acids and thus act as proton-carriers in the liquids. Recently, we have shown that certain protic ILs support high H_2 oxidation and O_2 reduction currents at Pt electrodes under entirely non-humidifying conditions at temperatures higher than 100 °C,[14–16] which opens up the possibility of their use as fuel cell electrolytes at medium temperature.[19–21] However, sluggish O_2 reduction for poor activity and high melting temperatures of the protic ILs have placed a stumbling block in the way of further development.[14–16] Here, we report the remarkable result that a simple protic IL obtained from the combination of diethylmethylamine (dema) and trifluoromethanesulfonic acid (T_fOH) exhibits facile, stable O_2 reduction, leading to a high, stable open-circuit potential (OCP); in addition, there is a wide liquid temperature range, and high thermal stability.

Almost 70 different protic salts were prepared from aliphatic amines with either oxoacids (T_fOH, H_2SO_4, CH_3SO_3H, H_3PO_4 and H_2PHO_3) or an imide-acid ($HN(T_f)_2$), and their thermal properties and ionic conductivity were evaluated. The experimental details are provided in ESI.† Briefly, each aliphatic amine and each acid were mixed in a 1 : 1 molar ratio in Ar atmosphere with cooling, and then the mixture was heated under vacuum to eliminate excess amine or acid, if any. Handling of the protic salts was entirely carried out in an Ar-filled glove box. The thermal properties were measured with differential scanning calorimetry (DSC) and thermogravimetry (TG), and the ionic conductivity was measured by use of the complex impedance method. For typical salts, the potential window and the activity for H_2 oxidation and O_2 reduction were evaluated by use of cyclic voltammetry (CV) at a bright Pt-wire electrode (WE) *vs.* a reversible hydrogen electrode (RHE) with a two-compartment glass cell sparged with dry N_2, H_2 or O_2 gases. The counter electrode (CE) was a platinized Pt wire; the RHE was a Pt wire in a H_2-sparged solution, placed close to the WE through a Luggin capillary. The surface area of the WE was estimated from the hydrogen desorption peak of the cyclic voltammetry measured in a 1 M H_2SO_4 aqueous solution at 30 °C. For the fuel cell polarization experiments, a protic IL (or a typical H^+-conducting electrolyte for comparison) was placed in a U-shaped glass tube; from each end, Pt wire electrodes were inserted, where the distance between the two electrodes is 2.5 cm, and either O_2 or H_2 gas was sparged around each electrode at a flow rate of 2 mL/min. The current density of the cells was calculated based on the surface area of the cathode (O_2 electrode), which was also determined from the hydrogen desorption peak, as mentioned above.

Table 1 highlights the properties of typical protic salts (See ESI† for details). Weight loss temperatures (T_d) of the protic salts based on H_3PO_4 and H_2PHO_3 were low due to condensation reactions of the phosphates and phosphites. The T_d values of the salts tended to increase with increasing acidity of the acids: $H_3PO_4 < H_2PHO_3 < CH_3SO_3H < H_2SO_4 < T_fOH < HN(T_f)_2$; the basicities of the amines did not differ to a large degree. Since the proton transfer reactions to form the salts are exothermic reactions, and logarithms of the equilibrium constants are equal to the difference in the pK_a values of the acids and bases,[22] the thermal stability appears to be explained in terms of the changes in the equilibrium constants with temperature (Le Chatelier's principle). With increased temperature, the back proton-transfer generates the acid and base, which are less thermally stable than the salt. Most of the protic salts in Table 1, with some exceptions, become liquids below

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‡ The HTML version of this article has been enhanced with colour images.

Table 1 Thermal properties, ionic conductivities and open circuit potential (OCP) of O_2 reduction (V *vs.* RHE at 150 °C) for the protic ionic liquids

Ionic liquid [base]/[acid] = 1/1	$T_g{}^a$/°C	$T_m{}^b$/°C	$T_d{}^c$/°C	σ^d	OCP
[dmea]/[$HN(T_f)_2$]	−42	66	377	4.6	—^{e}
[dema]/[$HN(T_f)_2$]	−67	24	375	4.1	0.77
[Im]/[$HN(T_f)_2$]	—^{f}	73^f	379^f	2.4^f	0.57
[BIm]/[$HN(T_f)_2$]^f	—	117	390	1.0	0.87
[ea]/[T_fOH]	—	179	372	—^{e}	—^{e}
[dea]/[T_fOH]	—	125	362	—^{e}	—^{e}
[tea]/[T_fOH]	—	34.3	358	2.76	0.94
[tba]/[T_fOH]	—	128	353	—^{e}	—^{e}
[tha]/[T_fOH]	−83	−1.0	361	0.209	—^{e}
[dmea]/[T_fOH]	−117	41.6	360	5.6	1.01
[dema]/[T_fOH]	—	−13.1	360	4.33	1.03
[EPp]/[T_fOH]	−76.2	52	372	2.58	1.08
[ea]/[H_2SO_4]	−64.1	39.7	262	3.41	—^{e}
[dea]/[H_2SO_4]	−67.1	60.5	262	1.97	0.63
[tea]/[H_2SO_4]	—	74.7	270	1.31	0.55
[tba]/[H_2SO_4]	−56	73	254	0.0922	—^{e}
[tha]/[H_2SO_4]	−62.1	28.8	247	0.0236	—^{e}
[dmea]/[H_2SO_4]	−75.9	—	271	3.83	—^{e}
[dema]/[H_2SO_4]	−82.1	—	268	1.97	0.60
[EPp]/[H_2SO_4]	−53.7	—	246	0.88	0.79
[dea]/[CH_3SO_3H]	−67.8	31.4	185	—	0.81
[tea]/[CH_3SO_3H]	−62.1	17.4	225	1.63	0.80
[ea]/[CH_3SO_3H]	—	137	230	—^{e}	—^{e}
[tba]/[CH_3SO_3H]	−69.4	41	254	0.752	—^{e}
[tha]/[CH_3SO_3H]	—	—	266	—^{e}	—^{e}
[dema]/[CH_3SO_3H]	−72.2	10.6	180	2.22	—^{e}
[EPp]/[CH_3SO_3H]	−73.3	67.6	201	1.27	—^{e}
[dea]/[H_2PHO_3]	—	—	161	—^{e}	—^{e}
[tea]/[H_2PHO_3]	−78.4	—	135	—^{e}	—^{e}
[tba]/[H_2PHO_3]	−60	—	150	0.126	—^{e}
[tha]/[H_2PHO_3]	−59.8	—	158	—^{e}	—^{e}
[dema]/[H_2PHO_3]	−84.6	—	137	—^{e}	—^{e}
[EPp]/[H_2PHO_3]	−71.3	—	136	—^{e}	—^{e}
[dea]/[H_3PO_4]	—	—	140	—^{e}	—^{e}
[tea]/[H_3PO_4]	−27.8	—	175	—	—^{e}
[tba]/[H_3PO_4]	−6.5	—	150	—^{e}	—^{e}
[tha]/[H_3PO_4]	−24.3	—	167	—^{e}	—^{e}
[dema]/[H_3PO_4]	−37.9	—	175	0.651	—^{e}
[EPp]/[H_3PO_4]	−11.7	—	144	—	—^{e}

[a] Glass transition temperature. [b] Melting point. [c] Onset temperature of decreasing weight. [d] Ionic conductivity at 120 °C (10^{-2} S cm^{-1}). [e] Not measured. [f] The data for [Im]/[$HN(T_f)_2$] = 1/1 and [BIm]/[$HN(T_f)_2$] = 1/1 are cited from ref. 15 and 16, respectively. [g] ea: ethylamine, dea, diethylamine, tea: triethylamine, tba: tributylamine, tha: trihexylamine, dmea: dimethylethylamine, dema: diethylmethylamine, EPp: *N*-ethylpiperidine, Im: imidazole, BIm: benzimidazole, $HN(T_f)_2$: bis(trifluoromethanesulfonyl) imide, T_fOH: trifluoromethanesulfonic acid.

100 °C (protic ILs), since either the melting (T_m) or glass transition (T_g) temperatures are lower than this temperature. The protic ILs prepared from H_3PO_4 and H_2PHO_3 are apt to form super-cooled liquids without crystallization because of the high viscosities. Notably, [dema]/[T_fOH] = 1/1 has a particularly low T_m. The ionic conductivity (σ) at 120 °C also varies depending on the structures (Table 1). With decreasing alkyl chain length, decreasing symmetry of the amines, and decreasing valency of the acids, the ionic conductivity increased due to a decrease in the viscosity. The salt [dema]/[T_fOH] = 1/1 had the most favorable properties of the protic ILs in this study in terms of the thermal stability (360 °C), liquid temperature range (T_m = −13 °C), and ionic conductivity (4.3×10^{-2} S cm^{-1} at 120 °C). The pulsed field gradient NMR measurements for ^1H and ^{19}F revealed that in [dema]/[T_fOH] = 1/1 the dissociated active proton from T_fOH mainly diffuses with dema (vehicle mechanism) and that the proton transference number is 0.57 at 30 °C and reaches 0.50 at 130 °C, slightly decreasing with increased temperature.

Fig. 1 shows the CVs at 150 °C under entirely non-humidifying conditions for [dema]/[T_fOH] = 1/1, together with those for [BIm]/[$HN(T_f)_2$] = 1/1 for comparison.[16,23] The CV under N_2 atmosphere represents the electrochemical stability range of the protic ILs. Thus, the electrochemically stable windows for both ILs were wide: *ca.* 0 to +1.3 V *vs.* RHE. In the H_2-sparged solution, steady state oxidation current was observed at potentials higher than 0 V *vs.* RHE for both ILs, clearly demonstrating that they both support active H_2 oxidation. A striking difference was seen for O_2 reduction in the O_2-sparged solution: the reduction for [dema]/[T_fOH] = 1/1 starts to occur at 1.03 V, whereas that for [BIm]/[$HN(T_f)_2$] = 1/1 only begins to occur at 0.87 V with very low current. The sluggishness of the reduction was commonly observed for the protic ILs based on $HN(T_f)_2$ in our previous study.[14–16] It should be noted here that the O_2 reduction rates of the protic ILs based on T_fOH in this study are generally greater than those of the imide-acid salts (Table 1, ESI†), which can been seen in the higher OCP values. [dema]/[T_fOH] = 1/1 gave the best results for the facile O_2 reduction.

The facile O_2 reduction for [dema]/[T_fOH] = 1/1 was also reflected in the H_2/O_2 fuel cell polarization results. Fig. 2 shows the fuel cell polarization results for [dema]/[T_fOH] = 1/1, [BIm]/[$HN(T_f)_2$] = 1/1, and H_3PO_4 at 150 °C under non-humidifying conditions and for a 1 M H_2SO_4 aqueous solution at 30 °C for comparison, where the electrochemical cell, electrodes and flow rates for H_2 and O_2 gas-sparging were the same. It is clearly seen that the cells with the electrolytes using oxoacids ([dema]/[T_fOH] = 1/1, H_3PO_4, and the H_2SO_4 aqueous solution) exhibit OCPs higher

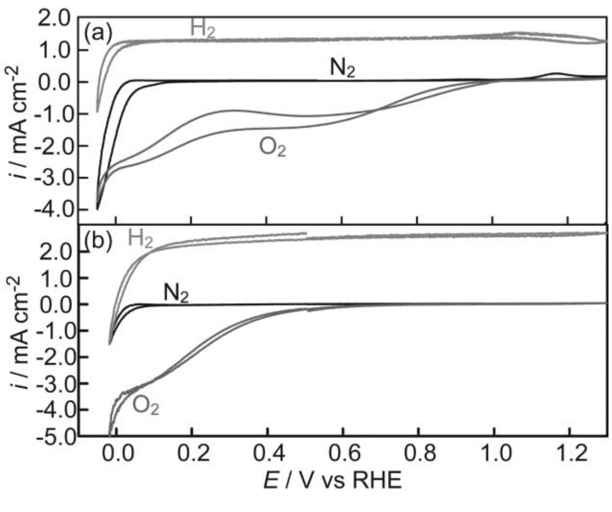

Fig. 1 Cyclic voltammograms for [dema]/[T_fOH] = 1/1 (a) and [BIm]/[$HN(T_f)_2$] = 1/1 (b)[16] at 150 °C. The scan rate is 10 mV s^{-1}. The gas flow rates of (b) are more than that of (a).

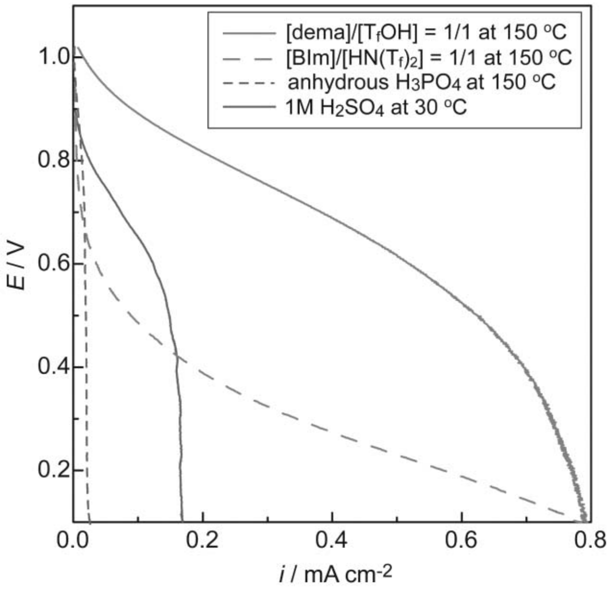

Fig. 2 H_2/O_2 fuel cell polarization curve scanned at 10 mV s^{-1} using [dema]/[T_fOH] = 1/1 as electrolyte under non-humidifying conditions at 150 °C. The polarization curves at 150 °C using [BIm]/[HN(T_f)$_2$] = 1/1 and anhydrous H_3PO_4 under non-humidifying conditions and that at 30 °C using 1 M H_2SO_4 are shown for comparison.

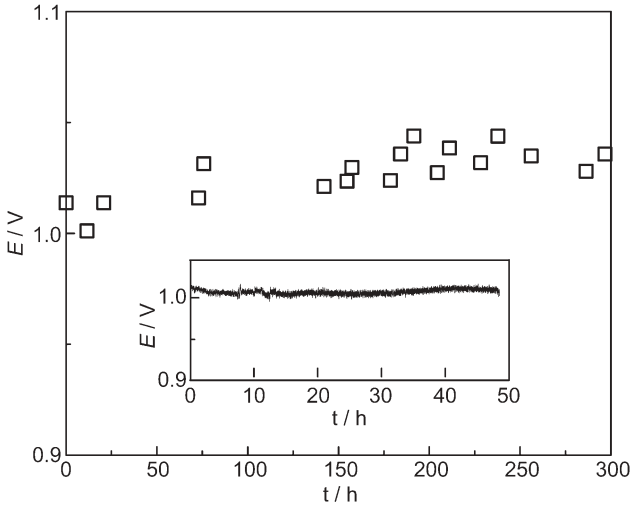

Fig. 3 Time dependence of OCP for a H_2/O_2 fuel cell using [dema]/[T_fOH] = 1/1 as electrolyte under non-humidifying conditions at 150 °C. Inset: Continuously monitored OCP as a function of time. The gas (H_2 and O_2) flow rates are 2 mL min^{-1}.

than 1.0 V, whereas the OCP of the cell with the imide-acid based IL ([BIm]/[HN(T_f)$_2$] = 1/1, as well as others in Table 1 and ESI) was lower. In addition to this high OCP, the cell based on [dema]/[T_fOH] = 1/1 supported higher currents. It is remarkable that the cell performance using [dema]/[T_fOH] = 1/1 was significantly better than those using H_3PO_4 or aqueous H_2SO_4 solution. The higher proton activities and less adsorption onto the electrode surface for [dema]/[T_fOH] = 1/1, compared with H_3PO_4 and [BIm]/[HN(T_f)$_2$] = 1/1, appear to be responsible for the better performances.[24,25] The thermal and electrochemical stability of [dema]/[T_fOH] = 1/1 at 150 °C under continuous H_2 and O_2 gas-sparging conditions was explored (Fig. 3). The OCP remained higher than 1 V for at least 300 h.

The protic ILs based on T_fOH, typically [dema]/[T_fOH] = 1/1, have well-balanced properties as a fuel cell electrolyte at medium temperature, and to the best of our knowledge, this is the first report of the experimental observation of a new electrolyte in which the fuel cell exhibits much better performance than that obtained using H_3PO_4 under the same conditions. For practically applying these electrolytes to FCs, the protic ILs need to be processed into thin membranes that ensure O_2/H_2 gas separation, which is our future study.

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