A Novel Brønsted Acid–base System as Anhydrous Proton Conductors for Fuel Cell Electrolytes

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A super-strong acid, bis(trifluoromethanesulfonyl)amide, was combined with 4,4′-trimethylenedipyridine at various molar ratios to prepare a novel series of Brønsted acid–base ionic liquids. The protic neutral salt was electroactive for H_2 oxidation and O_2 reduction at a platinum electrode under non-humidifying condition, which shows the potential of pyridinal systems as new fuel cell electrolytes for elevated temperature operation and foretells the polymeric model of solid-state anhydrous proton conductors.

The need for an efficient, highly proton conducting polymer electrolyte with high operational temperature for proton exchange membrane fuel cells has resulted in increased attention to the use of ionic liquids as fuel cell electrolytes.[1] However, there had been no report on the positive fuel cell tests using these potential electrolytes. Recently, we have reported a very expedient way to prepare Brønsted acid–base ionic liquids and demonstrated positive fuel cell tests for the imidazole (Im)–bis(trifluoromethanesulfonyl)amide (HTFSI) system under non-humidifying conditions.[2,3] In this study, with a view to envisaging a polymeric model for solid-state anhydrous proton conductors, we have derived a new series of proton conducting ionic liquids based on a Brønsted base with a molecular structure different from typical heterocycles,[2] like imidazole, benzimidazole and pyrazole, and electrochemically provide insight into the proton conduction.

We simply combined a super strong monoprotonic acid, HTFSI with 4,4′-trimethylenedipyridine (TMDP) (Figure 1) under solvent-free conditions. Appropriate amounts of HTFSI and TMDP maintaining defined molar ratios were mixed and heated above the respective melting points. All the samples were handled and stored in an argon atmosphere glove box (VAC, $[O_2] < 1$ ppm, $[H_2O] < 1$ ppm).

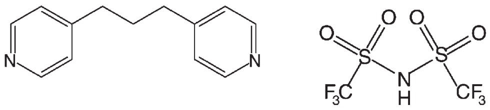
TMDP HTFSI

Figure 1. Molecular structures of the components of the Brønsted acid–base system.

Table 1. Thermal properties, ionic conductivities, and activation energies for TMDP/HTFSI compositions

Molar Ratio [TMDP]/[HTFSI]	T_m/°C[a]	T_d/°C[b]	σ at 130 °C/ 10^{-2} S cm^{-1}[c]	E_a/ kJ mol^{-1}[d]
10/0	63.0	216	0.01	45.3
95/5	59.0	219	0.43	21.9
9/1	57.3	220	0.49	23.3
85/15	57.1	—[e]	1.13	27.1
8/2	112.5	222	1.25	—[e]
75/25	125.1	224	1.38	—[e]
7/3	137.0	228	—[e]	—[e]
6/4	143.1	251	—[e]	—[e]
55/45	152.2	267	—[e]	—[e]
1/1	160.0	301	—[e]	—[e]
45/55	157.0	319	—[e]	—[e]
4/6	154.0	353	—[e]	—[e]
36/64	142.0	370	—[e]	—[e]
1/2	62.0	386	1.05	39.8

[a] Onset temperature of an endotherm peak (melting temperature, T_m) during heating scans from −150 °C by using differential scanning calorimetry. [b] Temperature of 10% weight loss during heating scans from room temperature by using thermo-gravimetry. [c] Ionic conductivity, σ was determined by complex impedance method in the frequency range of 5 Hz to 13 MHz at AC amplitude of 10 mV. [d] Activation energy, E_a was determined from the temperature dependence of ionic conductivity using Arrhenius equation. [e] Not measured or determined.

The thermal properties of various compositions for TMDP–HTFSI system have been summarized in Table 1. The melting point, T_m of the [TMDP]/[HTFSI] = 1/2 composition is 62.0 °C, while the [TMDP]/[HTFSI] = 1/1 composition melts at 160.0 °C. The T_m varied with the composition change. There is a eutectic at ca. 57 °C for the compositions between a salt with the composition of [TMDP]/[HTFSI] = 1/1 and pure TMDP, showing the typical behavior of a binary mixture. The fact that the T_m of the compositions increases from the corresponding value of the [TMDP]/[HTFSI] = 1/2 composition until the composition reaches [TMDP]/[HTFSI] = 1/1, may be ascribed to the strong interaction between the pyridine moiety in TMDP and the protonated counterparts by intermolecular hydrogen bonding. It is worthwhile to mention that the compositions of [TMDP]/[HTFSI] = 85/15, 9/1, and 95/5 easily form super cooled liquids at ambient temperature. The thermogravimetric (TG) curve of the [TMDP]/[HTFSI] = 1/2 composition shows a single-step weight loss process indicating the formation of a neutral salt, which possesses excellent thermal stability as an ionic liquid (Table 1). On the contrary, the TMDP-rich compositions show two-step weight loss processes.

The TMDP–HTFSI system exhibited high ionic conductivity (Table 1). The activation energies, E_a of different compositions as calculated from temperature dependence of ionic conductivity (60–130 °C) in the liquid state of the system using Arrhenius equation, have been tabulated in Table 1. For the compositions studied, the E_a decreases with increasing mole fraction of TMDP for TMDP rich compositions from the corresponding value for [TMDP]/[HTFSI] = 1/2 composition, with a maximum value for neat TMDP.

For the base-rich composition of [TMDP]/[HTFSI] = 75/25, the ionic conductivity is higher than the value of

[TMDP]/[HTFSI] = 1/2 composition (Table 1). Since the number of ion carriers, H_2TMDP^{2+} and $TFSI^-$ are maximum at [TMDP]/[HTFSI] = 1/2 composition, the increase in ionic conductivity with increase in mole fraction of TMDP indicates enhanced ionic mobility, which is also confirmed by the lower E_a values (Table 1). The conductivity therefore may be due not only to ionic species like H_2TMDP^{2+} or $HTMDP^+$ and $TFSI^-$, but also to intermolecular proton transfer. The conductivity measurements for other compositions with $7/3 \geqq$ [TMDP]/[HTFSI] $\geqq 36/64$ could not be conducted due to their high melting points with our present available resources. The ionic conductivity of neat TMDP is significantly low in the temperature range studied.

To substantiate the protonic conduction, we conducted a simple direct current polarization experiment at 130 °C using a U-shaped glass tube with two Pt-wire electrodes (proton pump cell). The anode was under a H_2 or an Ar bubbling atmosphere. The current detected under an Ar atmosphere for [TMDP]/[HTFSI] = 1/2 composition was quite low, whereas a noticeable change could be distinguished upon change to a H_2 gas atmosphere resulting in observation of higher current. This is indicative of the following phenomenon, occurring at the anode, electrolyte, and cathode:

Anode: $H_2 + TMDP \rightarrow H_2TMDP^{2+} + 2e^-$

Electrolyte: proton conduction

Cathode: $H_2TMDP^{2+} + 2e^- \rightarrow TMDP + H_2$

In fact, evolution of H_2 gas could be observed as bubbles at the cathode for prolonged polarization experiment. This contrasts to our early results[2] on a similar experiment conducted on an aprotic ionic liquid, 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)amide, which resulted in an imperceptible change in the current in N_2 to H_2 atmosphere, indicating that for proton conduction in neutral ionic liquids, the species should be a protic one. It should be noted that the neutral salt without stoichiometric excess of free TMDP exhibited proton conductivity. The elucidation of the proton conduction mechanism in neutral ionic liquid systems is now underway. The probable mechanisms include functioning of the imide ion ($TFSI^-$) as a proton acceptor site, translational dynamics of the protonated amines[4] (vehicle mechanism), and hopping through free amines by Grotthuss mechanism[5,6] probably persisting in the system from the equilibrium between neutral salt and the starting amine and HTFSI.

The current vs potential (vs RHE) characteristics of an H_2/O_2 fuel cell under non-humidifying condition has been depicted in Figure 2. The measurements were carried out using a two-compartment glass cell (Inset of Figure 2) by a Solartron electrochemical interface at 130 °C. The working electrode (W.E.) and reference electrode (R.E.) in this experiment were coil-shaped Pt-wires and the counter electrode was a coil-shaped Pt-black wire. The W.E. was set under an O_2 gas bubbling atmosphere, while the C.E was under a H_2 gas bubbling atmosphere. The Pt wire in a H_2 atmosphere worked as a reversible hydrogen electrode (RHE).[3] Although a potential drop with increasing current density is apparent possibly due to the electrode polarization and to some extent to IR drop, this is a clear evidence of electric power generation by an H_2/O_2 fuel cell. This resembles to our positive fuel cell tests using imidazole–HTFSI system as a proton conducting non-aqueous electrolyte[2,3] and sharply contrasts to the negative result reported on a related material.[7] Despite the fact that TMDP-rich compositions are promising as proton condcting non-aqueous electrolytes for probable proton conduction by fast proton exchange between protonated and free TMDP by structure diffusion[8] (Grotthuss mechanism), as anticipated from the conductivity results, the electrochemical polarization results showed remarkable electrochemical instability at Pt electrodes with increasing free TMDP content in the system.

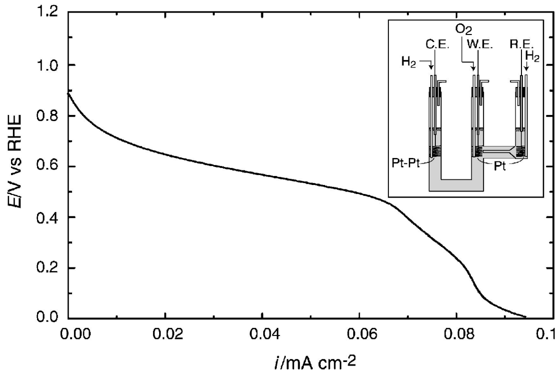

Figure 2. Fuel cell characteristics for TMDP/HTFSI = 1/2 composition at 130 °C. Scan rate is $10\,mV\,s^{-1}$. W.E. is a Pt-wire in an O_2 atmosphere, C.E. is a Pt-black wire in a H_2 atmosphere and R.E. is a Pt-wire in a H_2 atmosphere. Inset shows the schematic diagram of the two-compartment cell used.

The TMDP molecule, with two-pyridine groups linked with trimethylene chain in the structure, prognosticates a polymeric model for proton conductors. It is likely that pyridine molecule will retain reasonably high ionic conductivity and ability to conduct proton even in the polymeric state. This finding is therefore, a herald of a new field of fuel cells under non-humidifying conditions, which may be operated at temperatures above 100 °C and provide a firm underpinning for the development of solid-state anhydrous proton conductors using the concept of ionic liquid.[9]

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