Pyridine as a Brønsted Base for Anhydrous Proton Conductors

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A super-strong acid, bis(trifluoromethanesulfon) imide, was combined with pyridine and 4,4' trimethylenedipyridine at various molar ratios to prepare novel series of ionic liquids. Direct current polarization experiments show that proton conduction in these protic ionic liquid systems occurs under entirely non-humidifying conditions and at elevated temperatures. A comparison of the physicochemical behavior of both of the systems have been made to prognosticate a polymeric model of solid-state anhydrous proton conductors based on pyridine as a Brønsted base.
Key words: pyridine, 4,4'-trimethylenedipyridine, bis(trifluoromethanesulfon) imide, anhydrous proton conductors

1. INTRODUCTION

The efficacy of proton exchange membrane fuel cells (PEMFCs) as a power source for vehicles as well as stationary and portable applications has resulted in an upsurge of interest on polymer electrolytes for such devices. However, water management, "flooding", catalyst poisoning by CO in the reform gas etc are frequently cited constraints associated with the most significant PEMFCs, which employ perfluoro sulfonate ionomer typically Nafion® as their electrolytes under humidifying conditions. The fact that the drawbacks are primarily related to their limited temperature range for the use of water, has pointed eyes on the innovation of alternate efficient, highly proton conducting polymer electrolytes with high operational temperature. Quite reasonably, ionic liquids with the potential of maintaining high ionic conductivity over a wide temperature range have attracted significant attention as fuel cell electrolytes[1]. However, positive fuel cell tests using ionic liquids have for the first time been reported by our group, wherein imidazole-bis(trifluoromethanesulfon) imide system could serve as fuel cell electrolytes at elevated temperatures under non-humidifying conditions[2,3]. Recently, we have also communicated[4] our results on a protic ionic liquid based on 4, 4'-trimethylene dipyridine and revealed that to be proton conducting, organic amines in the Brønsted acid-base systems do not essentially need to have the molecular structures of typical heterocycles like imidazole, benzimidazole and pyrazole.

In this study, we prepared series of ionic liquids by simple combination of pyridine (Py) and 4, 4'-trimethylene dipyridine (TMDP) with a super strong acid bis(trifluoromethanesulfon) imide (HTFSI) (Scheme 1). The thermal property, ionic conductivity and the proton conduction behavior of
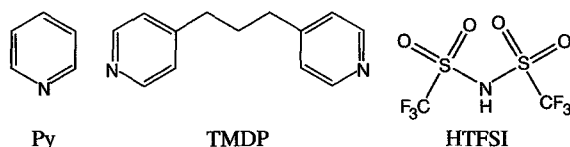
the systems have been discussed to envisage a polymeric model of anhydrous proton conductors based on pyridine as a Brønsted base.

2. EXPERIMENTAL

2.1 Materials

Bis(trifluoromethanesulfon) imide (Morita Chemical Industries, 99.8%), dehydrated pyridine (Wako) and 4,4'-trimethylene dipyridine (Aldrich, 98%) were used as received. Appropriate amounts of HTFSI and Py or 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).

2.2 Thermal Properties

Differential scanning calorimetry (DSC) was carried out with a Seiko Instruments differential scanning calorimeter (DSC 220C) under a N_2 atmosphere. Thermograms of the samples tightly sealed in Al pans were recorded during cooling (30 to –150°C) scans, followed by heating (-150 to a temperature below the decomposition temperature, T_d) at a cooling and heating rate of 10°Cmin⁻¹. High-temperature stabilities for the samples were measured on a Seiko Instruments thermo-gravimetry/differential thermal analyzer (TG/DTA 6200) from 30 to 550°C at a heating rate of 10°Cmin⁻¹ under N_2 atmosphere with open Al pans.

2.3 Ionic Conductivity

The ionic conductivity (σ) was determined using the ac impedance method in the temperature range of 60 to 130°C in a constant temperature chamber (Yashima BX-10). The samples were thermally equilibrated at each temperature for at least 1 h prior to the measurements. The electrolytes were filled in a homemade glass cell with two coil-shaped Pt wires fixed at a constant electrode distance in the glove box. The cell constant was determined by 0.1 M KCl standard solution (Kanto Kagaku) at 30°C. The experiments were carried out with a computer-interfaced Hewlett-Packard 4192A LF impedance analyzer over the frequency range from 5 Hz to 13 MHz.

2.4 Electrochemical polarization

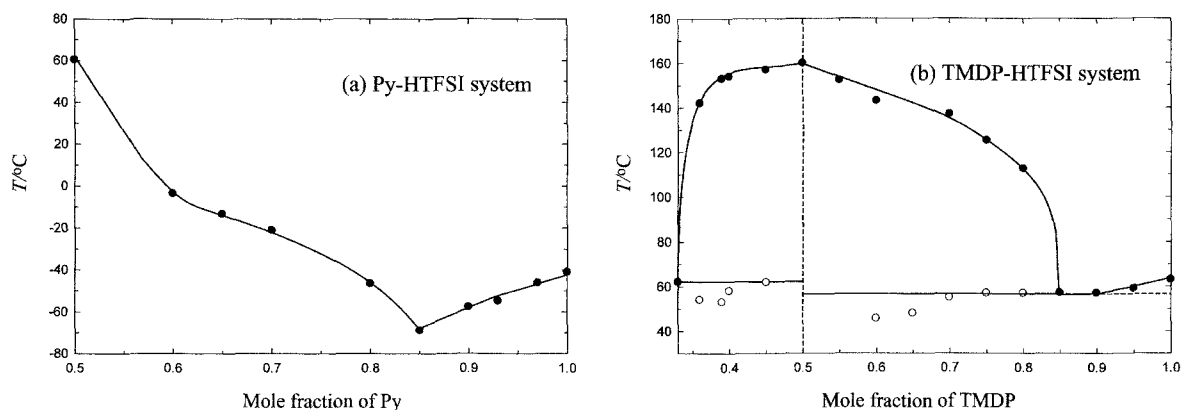Direct current polarization was performed at 130°C using a U-shaped glass tube with two Pt-wire

Scheme 1. Molecular structures of the components of the Brønsted acid-base systems.

Py   TMDP   HTFSI

Figure 1. Phase diagrams of the systems (a) Py-HTFSI and (b) TMDP-HTFSI. The melting temperatures (T_m or T_e) have been determined from DSC measurements.

electrodes (proton pump cell). H_2 or N_2 gas was introduced at the vicinity of the anode by means of a Teflon® tube. The electrodes and gas tubes were mounted in the glass cell using a Swagelok® tube connector. The electrodes were treated by repetitious cathodic and anodic polarization in 2 M H_2SO_4 solution before every experiment. The electrochemical control was accomplished using a Solartron electrochemical interface (model 1287). The temperature was regulated by using a constant temperature chamber (Yashima, BX-10).

3. RESULTS AND DISCUSSIONS

3.1. Thermal behavior

The thermal properties for the Py/HTFSI and TMDP/HTFSI compositions were studied using DSC. The single endotherm peak in the DSC thermogram corresponds to the melting point, T_m while in the cases of two endothermic peaks; the peak at lower temperature corresponds to the melting temperature of the eutectic mixtures (T_e) with that of the high temperature to the T_m. Figure 1 depicts the phase diagrams of Py-HTFSI and TMDP-HTFSI systems. Py is liquid, while HTFSI and TMDP are solid. The 1:1 composition of Py/HTFSI and 1:2 composition of TMDP/HTFSI are both solid at room temperature and have the T_m as 60.3, 62.0 °C, respectively. It is worthwhile to mention that TMDP has two pyridine groups in the structure and therefore, the complete neutralization requires two HTFSI molecules per TMDP molecule. Resembling the thermal behavior of typical Lewis acid-base ionic liquids[5] and Im-HTFSI system[3], the T_m varied with change in composition. There is a eutectic at ca. -69°C for the compositions between a salt with the composition of [Py]/[HTFSI] = 1/1 and pure Py (Figure 1a), showing the typical behavior of a binary mixture (salt and Py). Similar behavior could be observed for TMDP-HTFSI system with a eutectic at ca. 57°C for the compositions between a salt with the composition of [TMDP]/[HTFSI] = 1/1 and pure TMDP (Figure 1b). It is interesting to note the increase in the T_m from the corresponding value of the [TMDP]/[HTFSI] = 1/2 composition until the composition reaches [TMDP]/[HTFSI] = 1/1. For [TMDP]/[HTFSI] = 1/1, where the protonation of a single pyridine moiety is feasible with the other

remaining unprotonated, the melting point rose up to as high as 160°C. As it is evident for Im-HTFSI[3] or other related systems[6], intermolecular hydrogen bonding between the pyridine moiety and their protonated counterparts is also very likely for such pyridine systems. However, it is the strong interaction originated from the intramolecular hydrogen bonding between the protonated pyridine moiety with that of pyridine in TMDP-HTFSI system, which results in the increase in T_m until the interacting species becomes stoichiometrically equal. Unlike the Im-HTFSI[3] or TMDP-HTFSI systems, the T_e could not be observed for compositions between the neutral salt and Py. Most of the compositions with certain molar ratios of Py and HTFSI were liquid at room temperature, while the compositions of [TMDP]/[HTFSI] = 85/15, and 95/5 easily form super cooled liquids at ambient temperature.

The thermogravimetric (TG) curve of the [Py]/[HTFSI] = 1/1 composition shows a single-step weight loss process with the detection of changes only above ca. 250°C indicating the formation of a neutral salt, which possesses excellent thermal stability as an ionic liquid. On the contrary, the Py-rich compositions show two-step weight loss processes, the initial losses corresponding to the excess amount of Py in the system. Similar behavior could also be observed for TMDP-HTFSI system. Figure 2 shows the T_d i.e. temperature corresponding
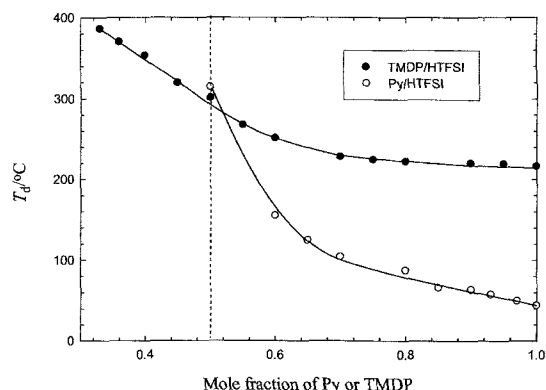

Figure 2. Composition dependence of the temperature of 10% weight loss during heating scans for Py-HTFSI and TMDP-HTFSI systems.

to 10% weight loss for both of the Py-HTFSI and TMDP-HTFSI systems plotted against mole fraction of Py or TMDP. TMDP has much higher thermal stability than that of Py. The thermal stability of the [TMDP]/[HTFSI] = 1/2 is also higher than that of [Py]/[HTFSI] = 1/1. The thermal stability in both of the systems decreases with increasing Py or TMDP content.

3.2 Ionic conductivity behavior and proposition of proton transport phenomenon

The compositions of Py and TMDP with HTFSI exhibited high ionic conductivity. Figure 3 shows the Arrhenius plots of ionic conductivity of neutral salts of Py and TMDP with HTFSI along with some base rich TMDP/HTFSI compositions. As can be seen in Figure 3, [Py]/[HTFSI] = 1:1 has much higher ionic conductivity compared to that of [TMDP]/[HTFSI] = 1:2. This is due to the higher ionic mobility of small pyridinium cation, HPy^+ compared to the larger trimethylene dipyridinium cation, H_2TMDP^{2+}.
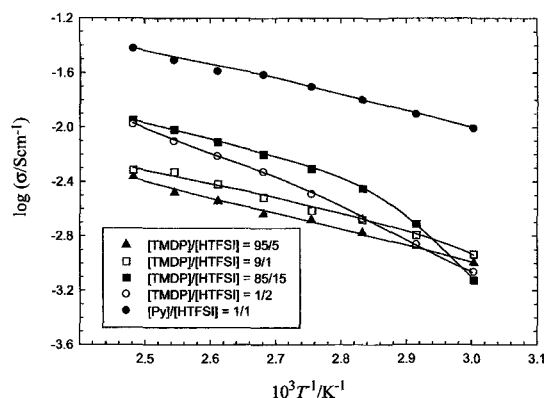

Figure 3. Arrhenius plots of ionic conductivity for Py-HTFSI and TMDP-HTFSI systems.

The activation energies, E_a of different compositions as calculated from temperature dependence of ionic conductivity in the liquid state of the systems using Arrhenius equation, have been plotted against mole fraction of TMDP in Figure 4. The E_as for [Py]/[HTFSI] = 1/1 and [TMDP]/[HTFSI] = 1/2 are 21.43 and 39.8 kJmol⁻¹, respectively. For the compositions studied, the E_a decreases with increasing TMDP content from the corresponding value for [TMDP]/[HTFSI] = 1/2 composition, with the highest value for neat TMDP.

Figure 4 also shows composition dependence of ionic conductivity of TMDP at certain temperatures. For the base-rich composition of [TMDP]/[HTFSI] = 75/25, the ionic conductivity is higher than the value of [TMDP]/[HTFSI] = 1/2 composition at 130°C. This is in good agreement with Kreuer et al. in excess Im for Im-sulfanilic acid system[6a] or our past observations for Im-HTFSI system[3]. 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
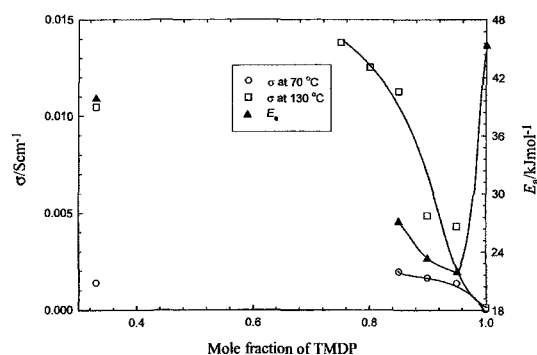

Figure 4. Composition dependence of ionic conductivity and activation energy for the system TMDP-HTFSI.

values (Figure 4). The conductivity therefore may be due not only to ionic species like H_2TMDP^{2+} or $HTMDP^+$ and TFSI⁻, but also to intermolecular or intramolecular proton transfer between the protonated Py moiety in TMDP and neat Py (the proton defect, i.e. vacant nitrogen site of TMDP). The conductivity measurements for other compositions with 7/3 ≧ [TMDP]/[HTFSI] ≧ 36/64 could not be conducted due to their high melting points with our present available resources. The conductivity is likely to pass through a maximum in that composition range. In the temperature range studied, the ionic conductivity decreases with further increase in TMDP content with significantly low values for only TMDP, which cannot undergo self-protolysis reaction.

3.3 Electrochemical polarization and decisive feature of proton transport

In order to corroborate the protonic conduction electrochemically, we conducted a simple direct current polarization experiment (proton pump). Figure 5 shows the current-voltage characteristics of the proton pump cell for the compositions of [Py]/[HTFSI] = 1/1 and [TMDP]/[HTFSI] = 1/2 at 130°C, where the anode was under a H_2 or a N_2 bubbling atmosphere. In both cases, the current detected under a N_2 atmosphere was quite low, whereas a very noticeable change could be distinguished upon the change of the atmosphere to a H_2 gas atmosphere resulting in the observation of much higher current. Furthermore, evolution of gas (H_2) was confirmed 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) imide[2], which resulted in an imperceptible change in the current in a N_2 to a H_2 atmosphere, indicating that for proton conduction in neutral ionic liquids, the species should be a protic one. The phenomenon occurring at the anode, electrolyte, and cathode for [Py][HTFSI] = 1/1 composition can be expressed as

Anode: $H_2 + 2Py \rightarrow 2HPy^+ + 2e^-$
Electrolyte: proton conduction
Cathode: $2HPy^+ + 2e^- \rightarrow 2Py + H_2$.
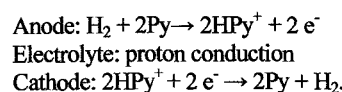
Interestingly, the neutral salts without stoichiometric excess of free Py or TMDP exhibited proton conductivity.
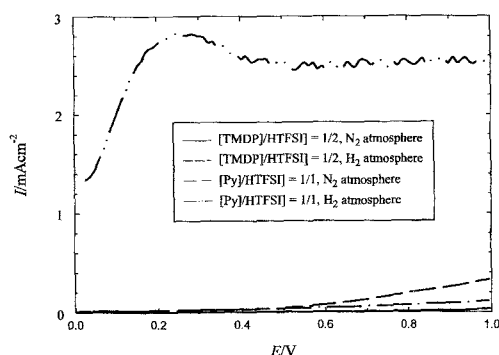
Figure 5. Relationship between cell voltage and direct current for [Py]/[HTFSI] = 1/1 and [TMDP]/[HTFSI] = 1/2 compositions at 130°C. The scan rate is 10 mVs⁻¹.

We have earlier evidenced electric power generation by a H_2/O_2 fuel cell at 130°C under non-humidifying condition using [TMDP]/[HTFSI] = 1/2 as a proton conducting non-aqueous electrolyte. The major contribution in proton conductivity should come from the translational dynamics[7] of the protonated amines in such neutral ionic liquids. The striking difference in current detected for the systems under H_2 atmosphere, as can be seen in Figure 5, therefore, corresponds to the difference in the mobility with which the protonated vehicles (HPy^+ or H_2TMDP^{2+}) move to the electrode interface.

The combination of a Brønsted acid with a Brønsted base causes proton transfer from the acid to the base under solvent-free condition. The drive to transfer proton can be measured by the difference in the aqueous solution pK_a values of the acid and the base[8]. Angell and coworkers have recently shown that when the difference in pK_a is small, the proton transfer is incomplete and such species can be classified as "poor" ionic liquids[8]. Obviously, when the acid and base both are strong with large difference in pK_a, the transferred proton locates so strongly on the base, and the reverse process does not occur with any significant probability to constitute the class of "good" ionic liquids.

HTFSI is a super strong acid, while Py and TMDP both are weak bases. The pK_a of Py and TMDP reported are 5.19[9a] and 6.29±0.2[9b], respectively. Although reliable pK_a value for HTFSI is not available in the literature, a comparison of the nature of the ionic liquids formed can be readily made. Since in both cases HTFSI has been used, with lower pK_a value of Py, the [Py]/[HTFSI] = 1/1 composition is likely to be a "poorer" ionic liquid compared to that of [TMDP]/[HTFSI] = 1/2. Therefore, hopping through free amine by Grotthuss mechanism[6] persisting in the system from the equilibrium between the salt and the starting amine and HTFSI can be more prominent in the equimolar composition of Py/HTFSI. The "structure diffusion"[6] (Grotthuss mechanism) may also be facilitated by Py for enhancement of reorientation, since in the case of TMDP, this may be hindered by restricted local mobility for the steric effect. Whether, the imide ion (TFSI⁻) can function as a proton acceptor site is not still clear and investigation is underway.

3.4 Polymeric model of anhydrous proton conductors with pyridine as a Brønsted Base

The concept of ionic liquid may be used with compatible polymers for the construction of solid-state anhydrous proton conductors[10]. To realize fast proton conductors, fast proton exchange between protonated and free amine by structure diffusion should be ensured, which can be achieved by using base-rich compositions for Brønsted acid-base ionic liquid systems. However, Py-HTFSI system suffers from the drawback of low thermal stability at Py-rich compositions. TMDP-HTFSI system also showed remarkable electrochemical instability at Pt electrodes with increasing free TMDP content in the system[4].

The TMDP molecule, with two-pyridine groups linked with a trimethylene chain in the structure can be a polymeric model for proton conductors. It is likely that Py molecule will retain reasonably high ionic conductivity, as in the case of TMDP and ability to conduct proton even in the polymeric state. However, the proton diffusion via H-bonds with local rearrangement of the system requires local mobility[6b]. Introduction of a flexible spacer is therefore, necessary. The properly designed polymers with sufficient chemical, thermal and electrochemical stability with the pyridine site affixed to the polymer backbone may then be partially neutralized by a Brønsted acid or by an acidic site affixed to the identical or a different polymer backbone, which will open up a new field of fuel cells operating under non-humidifying conditions and elevated temperatures.

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