

1H-1,2,4-Triazole: An Effective Solvent for Proton-Conducting Electrolytes

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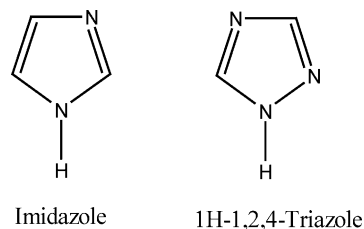
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Novel electrolyte membranes with high proton conductivity but with little or no dependence on humidity at temperatures above 100 °C can minimize or eliminate some of the key difficulties facing PEM fuel cells: CO poisoning, water management, and thermal management.^{1–4} The introduction of imidazole has generated much excitement in recent years with the hope that the imidazole-based electrolytes may meet the requirements for a new generation of PEM fuel cells.^{5–8} Imidazole is an aromatic heterocycle with two N atoms on the ring. It is believed that imidazole conducts protons through intermolecular proton transfer (structure diffusion) and thus may be used to replace water as a proton carrier in proton-conducting materials at temperatures above 100 °C.^{5–8} While the high proton mobility has been observed in imidazole-based materials, including ionic liquids, oligomers and polymers, the electrochemical stability of imidazole appears to be inadequate for fuel cell applications because of the high electronic density of imidazole ring.^{8–10}

1H-1,2,4-Triazole has a similar molecular structure as that of imidazole and therefore may conduct protons via a similar mechanism as imidazole (see Scheme 1). Compared with imidazole ($T_{\text{mp}} = 89$ °C, $T_{\text{bp}} = 257$ °C), 1H-1,2,4-triazole has a higher melting point (120 °C) and a similar boiling point (256 °C) owing to its strong hydrogen bonds. The $\text{p}K_{\text{a}}$ values of 1H-1,2,4-triazole ($\text{p}K_{\text{a}1} = 2.39$, $\text{p}K_{\text{a}2} = 9.97$) are much lower than those of imidazole ($\text{p}K_{\text{a}1} = 7.18$, $\text{p}K_{\text{a}2} =$

Scheme 1. Molecule Structures of Heterocycles



14.52),^{11–13} implying that 1H-1,2,4-triazole may have lower electron density. In this communication, we report the electrochemical stability of 1H-1,2,4-triazole and the proton conductivities of 1H-1,2,4-triazole and the derivatives. 1H-1,2,4-triazole is an ideal solvent (to replace water) to promote proton conductivity of materials at temperatures above 100 °C.

The mixtures of 1H-1,2,4-triazole and 4-dodecylbenzene-sulfonic acid ($\text{C}_{12}\text{PhSO}_3\text{H}$) were made by co-dissolving them in ethanol and then evaporating the solvents in a vacuum at 80 °C. Sulfonated polysulfone (sPSU) was prepared and purified as described elsewhere.¹⁴ To incorporate 1H-1,2,4-triazole into sPSU to form sPSU-triazole membranes, sPSU (IEC of 1.40 mequiv/g) polymers were mixed with 1H-1,2,4-triazole and kept at 120 °C in a sealed glass bottle for 24 hours. The hybrid inorganic–organic polymers with grafted heterocycles were derived from the mixtures of alkoxysilanes with grafted heterocycles (SiHc), bis(3-methyldimethoxy-silyl)polypropylene oxide (MDSPPPO), and tetraethoxysilane (TEOS) in a sol–gel process. The precursors SiHc were synthesized using a simple nucleophilic substitute reaction. The self-diffusion coefficient was measured using a ¹H PFG NMR technique.¹⁵

The proton conductivity of pure 1H-1,2,4-triazole is 1.5×10^{-4} S/cm at 115 °C and 1.2×10^{-3} S/cm at melting point 120 °C (see Figure 1). This indicates that self-dissociation of 1H-1,2,4-triazole produces proton charge carriers and the mobility of the proton charge carriers is very high, similar to that in imidazole. To increase the concentration of proton charge carriers and to suppress the motion of the acid group, the large molecule acid $\text{C}_{12}\text{PhSO}_3\text{H}$ was added to 1H-1,2,4-triazole. As shown in Figure 1, the proton conductivities of the mixtures increased with acid concentration, reaching a maximum at ~9 mol %. Similar phenomena were reported in imidazole–acid systems, reflecting the change of the proton charge carrier concentration and the geometric constrains introduced by the addition of acids.⁵ The conductivity value is 0.02 S/cm at 120 °C for the sample with 9 mol % acid. The self-diffusion coefficient of the

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- (1) Paddison, S. J. *Annu. Rev. Mater. Res.* **2003**, *33*, 289.
- (2) Wainright, J. S.; Wang, J. T.; Weng, D.; Savinell, R. F.; Litt, M. H. *J. Electrochem. Soc.* **1995**, *142*, L121.
- (3) Casciola, M.; Alberti, G. *Solid State Ion* **1997**, *97*, 177.
- (4) Haile, S. M.; Boysen, D. A.; Chisholm, C. R. I.; Merle, R. B. *Nature* **2001**, *410*, 910.
- (5) Kreuer, K. D.; Fuchs, A.; Ise, M.; Spaeth, M.; Maier, J. *Electrochim. Acta* **1998**, *43*, 1281.
- (6) Münch, W.; Kreuer, K. D.; Silvestri, W.; Maier, J.; Seifert, G. *Solid State Ion* **2001**, *145*, 437.
- (7) Schuster, M. F. H.; Meyer, W. H.; Schuster, M.; Kreuer, K. D. *Chem. Mater.* **2004**, *16*, 329.
- (8) Noda, A.; Susan, Md.; Abu Bin, H.; Kudo, K.; Mitsushima, S.; Hayamizu, K.; Watanabe, M. *J. Phys. Chem. B* **2003**, *107*, 4024.
- (9) Yang, C.; Costamagna, P.; Srinivasan, S.; Benziger, J.; Bocarsly, A. B. *J. Power Sources* **2001**, *103*, 1–9.
- (10) Deng, W.; Molinero, V.; Goddard, W. A., III. *J. Am. Chem. Soc.* **2004**, *126*, 15644.

- (11) Catalán, J.; Abbound, J.-L. M.; Elguero, J. *Adv. Heterocycl. Chem.* **1987**, *41*, 187.
- (12) Gagliano, R. A., Jr.; Knowlton, R. C.; Byers, L. D. *J. Org. Chem.* **1989**, *54*, 5247.
- (13) Walba, H.; Isensee, R. W. *J. Org. Chem.* **1956**, *21*, 702–704.
- (14) Johnson, B. C.; Yilgor, I.; Tranc, C.; Iqbal, M.; Wightman, J. P.; Floyd, D. R.; MacGrath, J. E. *J. Polym. Sci., Polym. Chem. Ed.* **1984**, *22*, 721–737.
- (15) Dippel, Th.; Kreuer, K. D.; Lassegues, J. C.; Rodriguez, D. *Solid State Ion* **1993**, *61*, 41.

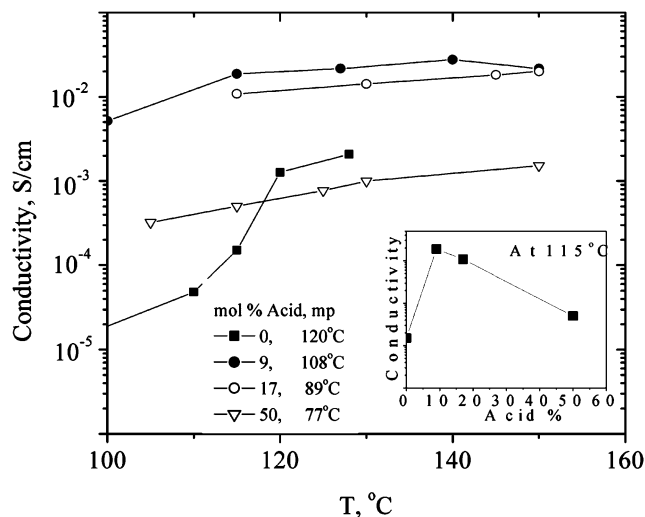


Figure 1. Proton conductivity of 1H-1,2,4-triazole mixed with $C_{12}PhSO_3H$ in anhydrous state. The inserted figure presents the conductivity dependence of the mixtures on acid concentrations.

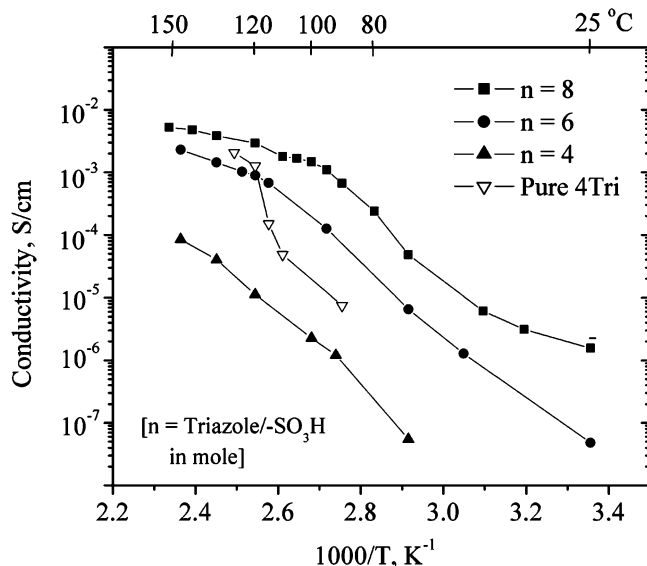


Figure 2. Ionic conductivities of 1H-1,2,4-triazole (4Tri) and that intercalated into sulfonated polysulfone polymers ($n = \text{triazole-ring}/-\text{SO}_3\text{H}$ in mol).

sample with 9 mol % acid at 120 °C is $2.0 \times 10^{-10} \text{ m}^2/\text{s}$, which is about one-fourth (1/4) of the diffusion coefficient calculated from conductivity data ($7.2 \times 10^{-10} \text{ m}^2/\text{s}$), suggesting that proton transfer between the triazole rings makes a major contribution to the observed ionic conduction.

To study proton conductivity of 1H-1,2,4-triazole in a solid polymeric membrane, 1H-1,2,4-triazole was intercalated into a sulfonated polysulfone (sPSU) membrane. As shown in Figure 2, the conductivity increased with the concentration of 1H-1,2,4-triazole. For a membrane with $n = 8$ (n is defined as the ratio of [1H-1,2,4-triazole] to $[-\text{SO}_3\text{H}]$), the conductivity reached $1.5 \times 10^{-3} \text{ S/cm}$ at 100 °C and $5.0 \times 10^{-3} \text{ S/cm}$ at 140 °C. Since the sPSU polymer itself has very low ion conductivity under anhydrous (or low humidity) conditions, it is believed that the 1H-1,2,4-triazole is responsible for the observed ionic conductivity of sPSU-1H-1,2,4-triazole membranes. Furthermore, 1H-1,2,4-triazole grafted onto the

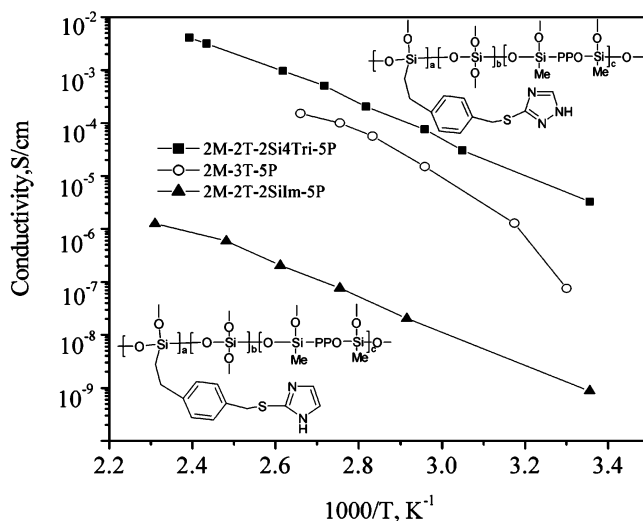


Figure 3. Proton conductivity of the membranes with compositions of 2MDSPP0-2TEOS-2SiHc-5H₃PO₄ (Hc = 4Tri and Im) and 2MDSPPO-3TEOS-5H₃PO₄ in anhydrous state. The inserts are the schemes of the hybrid inorganic-organic polymers with grafted 1H-1,2,4-triazole and imidazole, respectively.

hybrid inorganic-organic polymer network enhanced the proton conductivity of the membranes doped with H₃PO₄. This may be attributed to the low-barrier hydrogen bonds formed between 1,2,4-triazole and H₃PO₄ molecules because the pK_a values of protonated 1,2,4-triazole and H₃PO₄ are about the same.¹⁶ As shown in Figure 3, the proton conductivity of the membrane with grafted 1H-1,2,4-triazole is higher than that without grafted heterocycles, but the grafted-imidazole (Im) reduced the proton conductivity under similar conditions. One possible explanation is that imidazole rings may trap the acid and thus reduces the concentration of protons.²

Shown in Figure 4 are some cyclic voltammograms for 1H-1,2,4-triazole and imidazole in CH₃CN solution purged with N₂. The cyclic voltammetric measurements were performed in a typical three electrode cell containing 0.1 mol·dm⁻³ CH₃CN solution of tetrabutylammonium hexafluorophosphate (TBAPF6) and $5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ of imidazole or 1H-1,2,4-triazole, using a platinum work electrode, a platinum auxiliary electrode, and an Ag/Ag⁺ reference electrode (0.1 mol·dm⁻³ AgNO₃-CH₃CN containing 0.1 mol·dm⁻³ TBAPF6). Clearly, a large irreversible oxidation peak appeared near +1.0V (vs Ag/Ag⁺) in the voltammogram for imidazole. It was found that the oxidation products of imidazole were absorbed on the surface of the platinum electrode and thus blocked the electrode surface. This may be the reason that fuel cells using imidazole-based PEMs are not yet electrochemically functional.^{8,9} In contrast, no obvious redox peaks observable for 1H-1,2,4-triazole in a wider potential range, 0 to +1.8V (vs Ag/Ag⁺), and no obvious change took place in the subsequent 50 cycles. Similar results were observed when the CH₃CN solutions were purged with O₂. These results imply that 1H-1,2,4-triazole has adequate electrochemical stability under fuel cell conditions.

(16) Garcia-Viloca, M.; Gonzalez-Lafont, A.; Lluch, J. N. M. *J. Phys. Chem. A* 1997, 101, 3880.

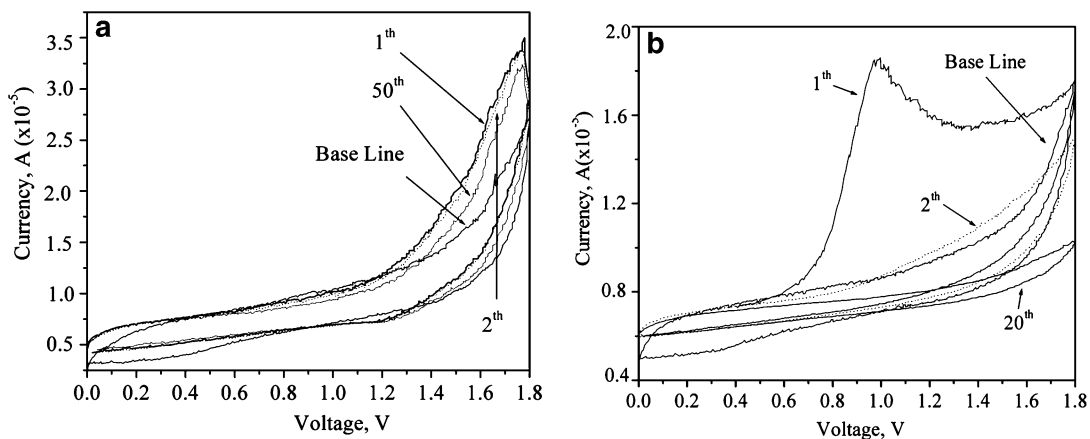


Figure 4. Typical cyclic voltammograms (CV) of 1H-1,2,4-triazole (a) and imidazole (b) with baselines, $C = 5 \times 10^{-3} \text{ mol}\cdot\text{dm}^{-3}$ in $0.1 \text{ mol}\cdot\text{dm}^{-3}$ TEAP- CH_3CN solution.

In conclusion, 1H-1,2,4-triazole is electrochemically stable for fuel cell applications and effectively promotes proton conductivity of materials under anhydrous conditions. Grafting 1H-1,2,4-triazole onto suitable polymer backbones may lead to new membranes with excellent properties for a new generation of PEM fuel cells to be operated at temperatures above $100 \text{ }^\circ\text{C}$ with much higher energy efficiencies. Further, 1H-1,2,4-triazole and the derivatives

may be used in nonaqueous proton-conducting electrolytes for other applications.

Supporting Information Available: The synthesis of precursors and hybrid inorganic-organic polymers and the characterization of samples. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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