Communication

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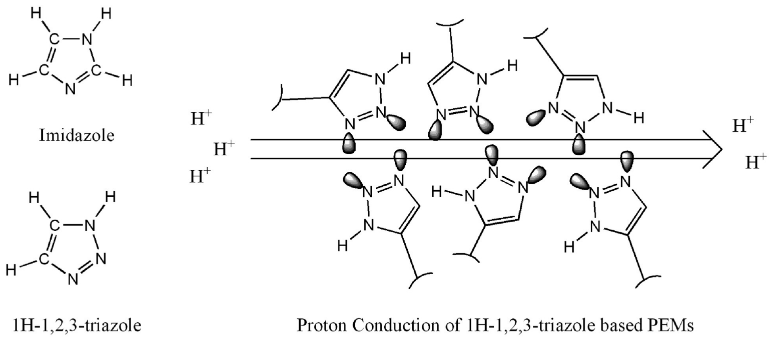

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Promotion of Proton Conduction in Polymer Electrolyte Membranes by 1*H*-1,2,3-Triazole

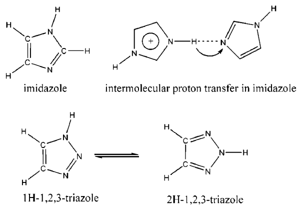
Zhen Zhou,[†,‡] Siwen Li,[†] Yuelan Zhang,[†] Meilin Liu,*[,†] and Wen Li[§]

School of Materials Science and Engineering, and School of Chemistry and Biochemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332-0245, and Materials Engineering Department,
Toyota Technical Center, USA, Inc.

Received April 8, 2005; E-mail: meilin.liu@mse.gatech.edu

The development of novel polymer electrolyte membranes (PEMs) with dense structure, good mechanical flexibility, and high proton conductivity, but with little or no dependence on humidity at temperatures above 100 °C, remains an important challenge to the realization of practical PEM fuel cells. Compared with the extensively studied perfluorosulfonic polymer membranes,[1] in which the proton conductivity depends critically on humidity, PEMs based on H_3PO_4, imidazole, and other functional groups[2] may allow fuel cell operation above 100 °C without the need of humidification, which could minimize or eliminate some of the key difficulties facing PEM fuel cells, including CO poisoning and the management of water, heat, and pressure. To date, however, the application of these membranes in fuel cells is still problematic because of their low proton conductivity or inadequate stability under practical fuel cell operating conditions.

Heterocycles, such as imidazole, were studied by Kreuer et al.[2b] as proton solvent in PEMs for fuel cells. The conductivity of liquid imidazole was reported[3] as high as 10^{-3} S/cm at the melting point of 90 °C. It was proposed[4] that imidazole conducts the proton through intermolecular proton transfer. The introduction of imidazole has generated much excitement in recent years with the hope that the investigations of imidazole-based polymer electrolytes may lead to PEMs with high proton conductivity, good mechanical properties, and long-term stabilities.[5] Unfortunately, the electrochemical stability of the imidazole group appears to be inadequate for fuel cell applications.[6] To date, functional fuel cells based on imidazole-containing PEMs are yet to be demonstrated.



1*H*-1,2,3-Triazole has a molecular structure similar to that of imidazole and, thus, may conduct a proton via a similar mechanism as in imidazole. Unlike imidazole (mp 90 °C, bp 257 °C), 1*H*-1,2,3-triazole (mp 23 °C, bp 203 °C/752 Torr) is a liquid at room temperature. Also, 1*H*-1,2,3-triazole has a tautomer, 2*H*-1,2,3-triazole, and the tautomerism may happen through intra- or intermolecular proton transfer.[7] Although 2*H*-1,2,3-triazole is more stable in the gas phase, 1*H*-1,2,3-triazole becomes more stable in solution[8] because of its larger dipole moment. Also, 1*H*-1,2,3-triazole ($pK_a1 = 1.17$, $pK_a2 = 9.26$) is much more acidic than imidazole ($pK_a1 = 7.18$, $pK_a2 = 14.52$),[9] which may significantly influence proton conduction of 1*H*-1,2,3-triazole-based solid electrolytes.

The ionic conductivity of pure 1*H*-1,2,3-triazole is about 1.3×10^{-4} S/cm, as measured at room temperature with impedance spectroscopy. This value implies that self-dissociation of 1*H*-1,2,3-triazole produces protonic charge carriers, and that there is considerable proton conductivity in liquid 1*H*-1,2,3-triazole.

To study this phenomenon in a solid polymeric membrane, 1*H*-1,2,3-triazole was imbibed into a sulfonated polysulfone (sPSU) polymer membrane. The conductivities of the membranes with different concentrations of 1*H*-1,2,3-triazole increased with the concentration of 1*H*-1,2,3-triazole (Figure 1). For a membrane with $n = 8.3$ (n is defined as the ratio of [1*H*-1,2,3-triazole] to [$-SO_3H$]), the conductivity reached about 0.01 S/cm at ∼110 °C under dry conditions. Because the sPSU polymer itself has very low ionic conductivity under these conditions, it is believed that 1*H*-1,2,3-triazole is an active group to promote proton conduction through the polymeric membrane. This situation is similar to that of sPEEK−imidazole and sPEEK−pyrazole membranes,[2b] in which imidazole and pyrazole are responsible for the observed proton conductivities.

As a small molecule in the polymer, however, 1*H*-1,2,3-triazole may contribute to the observed proton conduction in two ways: (i) by long-range translative motion of the triazole groups, and (ii) by intermolecular proton transfer between adjacent triazole groups. The latter is vital to membranes with immobilized triazole groups, in which long-range translative motion of triazole groups is no longer possible. Pulsed magnetic field gradient (PFG) NMR spectroscopy[2b] was used to study the self-diffusion coefficient of 1*H*-1,2,3-triazole in sPSU polymers ($n = 8.3$). Compared to the self-diffusion coefficients (1.98×10^{-7} at 60 °C, 9.87×10^{-7} at 120 °C), as determined from ^{1}H PFG NMR spectroscopy, the diffusion coefficients (9.30×10^{-7} at 60 °C, 3.67×10^{-6} at 103 °C) calculated from conductivity are about 4−5 times higher, suggesting that proton transfer between the triazole rings makes the major contribution to the observed ionic conduction.

To further confirm this finding, poly(4-vinyl-1*H*-1,2,3-triazole) was synthesized to covalently immobilize 1*H*-1,2,3-triazole on the polymer backbone. Shown in Figure 2 are the conductivities of poly(4-vinyl-1*H*-1,2,3-triazole) as measured in dry air. The conductivities of poly(4-vinylimidazole)[5c] under similar conditions are also shown for a simple and direct comparison, in that the molecular structures of the two polymers are nearly identical. The conductivities of the triazole-containing polymer are 10^5 times higher than those of the imidazole-containing polymer in the temperature range studied. For other imidazole-grafted polymers,[1b,5d] imidazole has to be spaced (by soft segments) to allow for the formation of dynamical hydrogen bonds and, therefore, similar conductance as poly(4-vinyl-1*H*-1,2,3-triazole). These results suggest that triazole groups can promote long-range proton motion in the polymer system far better than the imidazole groups.

Similar to imidazole and pyrazole, 1*H*-1,2,3-triazole as a small molecule in a PEM may leach out gradually, which would lead to

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[†] School of Materials Science and Engineering, Georgia Institute of Technology.
[‡] School of Chemistry and Biochemistry, Georgia Institute of Technology.
[§] Toyota Technical Center.

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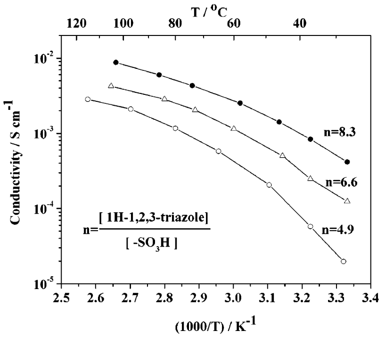

Figure 1. Ionic conductivities of 1*H*-1,2,3-triazole intercalated into sulfonated polysulfone polymer membranes with three different ratios of [1*H*-1,2,3-triazole] to [$-SO_3H$].

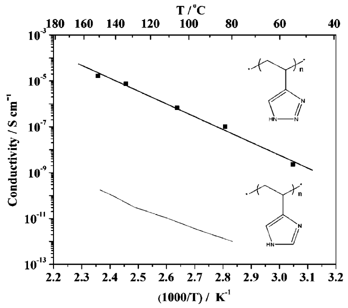

Figure 2. Ionic conductivities of poly(4-vinyl-1*H*-1,2,3-triazole) and poly(4-vinylimidazole).

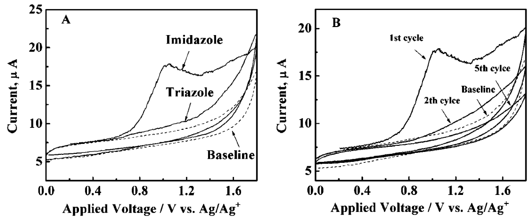

Figure 3. (A) Typical cyclic voltammograms of imidazole and triazole with baseline; $C = 5 \times 10^{-3}$ mol/dm^3 in 0.1 mol/dm^3 TBAPF6$-$CH$_3$CN solution at 25 °C. (B) Cyclic voltammograms of 5×10^{-3} mol/dm^3 imidazole in 0.1 mol/dm^3 TBAPF6$-$CH$_3$CN solution at 25 °C.

continuous decrease in proton conductivity and, hence, degradation in performance. The remarkable proton conducting ability of triazole groups immobilized on a polymer backbone may open up new avenues to rational design of PEMs with not only high proton conductivity but also long-term stability.

Shown in Figure 3 are some cyclic voltammograms (CVs) for 1*H*-1,2,3-triazole and imidazole as studied in CH$_3$CN. Clearly, a large irreversible oxidation peak appeared near +1.0 V (vs Ag/Ag$^+$) in the voltammogram for imidazole. In contrast, no obvious redox peaks were observed for 1*H*-1,2,3-triazole in a wider potential range (0 to +1.8 V), implying that 1*H*-1,2,3-triazole has adequate electrochemical stability under fuel cell operating conditions.

The CV studies of imidazole show that the current density decreased dramatically with the number of cycles. The oxidation peak, which was obvious in the very first positive going scan, dramatically diminished in the second and disappeared in the subsequent scans (Figure 3B). It seems that the oxidation products of imidazole were absorbed on the surface of the platinum electrode and, thus, blocked the active sites for further oxidation of imidazole. In fact, the oxidation peak reappeared only when the platinum electrode was polished and cleaned. In contrast, in the CV studies of 1*H*-1,2,3-triazole, the consecutive CVs were nearly identical and independent of the number of cycles. In a subsequent experiment, imidazole was added to the solution containing 1*H*-1,2,3-triazole after repeated CV scans, and the imidazole oxidation peak once again reappeared in the very first scan after the addition of imidazole. Further, identical results were obtained when the purge gas was switched from nitrogen to oxygen. These observations show that 1*H*-1,2,3-triazole is stable under the electrochemical conditions, whereas imidazole is not. We note that fuel cells using imidazole-based PEMs are not electrochemically functional because of the instability and poisoning effect of imidazole.[6]

In summary, 1*H*-1,2,3-triazole has been proven to effectively promote the proton conduction in polymer electrolyte membranes through an intermolecular proton-transfer mechanism. One possible reason is the low melting point of triazole[5a] resulted possibly from some special intermolecular interactions and aggregations. Also, on the basis of previous studies,[7,10] we thought the tautomerization or intramolecular proton transfer from N2 to N3 of 1*H*-1,2,3-triazole may play a vital role for the proton conducting procedure. Unlike 1*H*-1,2,3-triazole, imidazole does not have any tautomers, and intramolecular proton transfer within the imidazole ring is rather difficult, if not impossible. As a result, significant local motion of the imidazole branches is necessary for proton conduction in a particular direction. Further, electrochemical characterizations suggest that 1*H*-1,2,3-triazole has adequate electrochemical stability for fuel cell applications. Further investigation into 1*H*-1,2,3-triazole and its derivatives, especially copolymers with suitable acidic groups, may lead to new membranes with excellent properties for a new generation of PEM fuel cells to be operated at temperatures above 100 °C with much higher energy efficiencies.

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Supporting Information Available: Synthetic procedures and experimental data. This material is available free of charge via the Internet at http://pubs.acs.org.

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