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4,5-Dicyano-1*H*-[1,2,3]-Triazole as a Proton Transport Facilitator for Polymer Electrolyte Membrane Fuel Cells

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High-temperature operation of proton exchange membrane (PEM) fuel cells is highly desirable due to many expected advantages, such as higher CO tolerance and enhanced performance. In order to maintain their high proton conductivity at temperatures in excess of 100 °C, most proton conducting polymer membranes have to be kept under high humidity conditions. System considerations then dictate that the fuel cell operating temperature is kept below the boiling point of water. Many sulfonated aromatic polymers,[1,2] membranes doped with high boiling point liquids, such as phosphoric acid,[3] and organic/inorganic composites[4] have been investigated to overcome this drawback by providing adequate conductivity with minimal or no water. However, with the exception of poly(benzimidazole)/H_3PO_4, the requirements for high performance are not met; none of these membranes have shown reasonable conductivity and stability at high temperature (>100 °C) and low humidity. Other recent studies have focused on using high boiling nitrogenous bases such as imidazole[5] and triazole[6] as water replacements to facilitate proton transfer. These azoles can improve the conductivity of the doped membranes under anhydrous conditions. However, the conductivity drops significantly when these molecules are attached as a pendent chain to a polymer matrix due to a decrease in the mobility which proton conductivity predominantly relies on in the types of systems studied.

The amphoteric nature of water makes it a viable medium for proton conduction in proton exchange membranes. The proton affinity of water in forming hydronium ions plays a significant role in the ease of proton exchange between different water molecules. The main purpose of this paper is to focus on this attribute for alternative proton transport facilitators. While the mobility of excess and deficient protons, that is, the rate of the transport, is critical for proton conduction, the importance of the proton affinity cannot be neglected. Proton affinity is a measure of the ability of the protonated molecule to give up its excess proton and is comparable to pK_a1 values reported in literature for various molecules such as imidazole and triazole.[5,6] This parameter defines the thermodynamics of proton conduction.

Gas phase proton affinity calculations for a number of substituted triazole molecules show that electron-donating groups have little or no effect on the proton affinity of the triazole, while the effect of electron-withdrawing groups is very significant (Figure 1). These calculations were performed using Gaussian 03 with the CBS-4M method.[7] The proton affinity is calculated from the difference in free energy between the neutral and the protonated molecules. This value for triazole is 200.07 and 213.62 kcal/mol depending on the site of protonation, compared to the value of 165.7 kcal/mol for water. These values for 4,5-dicyano-1*H*-[1,2,3]-triazole (DCTz) are 173.22 and 185.4 kcal/mol for protonation of the 2-N and 3-N positions, respectively, which makes it an interesting compound for further study. DCTz is a solid crystalline compound (mp = 147−150 °C) which forms an acidic aqueous solution (1 wt %, pH ∼2).

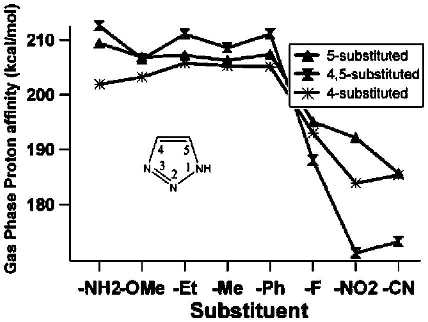

Figure 1. Effect of substituents on proton affinity of the triazole.

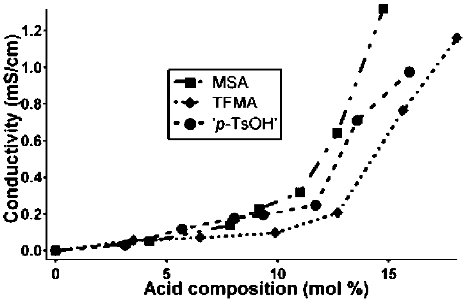

Figure 2. Conductivity of DCTz pellets as a function of acid loading.

To investigate the proton conductivity of DCTz under various conditions, two types of samples were prepared. Samples were made by pelletizing DCTz doped with varying amounts of an acid and by preparing composites from DCTz mixed with a polymeric binder. Pellets were prepared by pressing DCTz powder in the dry state with a pressure of 15 000 psi to ensure maximum compression. For the doped pellets, a selected acid was first added to the DCTz powder and ground thoroughly before pressing. A triazolium salt was expected to form upon mixing of an acid with DCTz. Trifluoromethanesulfonic acid (TFMA), methanesulfonic acid (MSA), and *p*-toluenesulfonic acid (*p*-TsOH) were used to separate the effect of acidity and size of the anion in the triazolium compound. MSA and *p*-TsOH are of comparable acidity, and TFMA and MSA have similar structures but very different acidity. Figure 2 shows the proton conductivity of pellets as a function of acid content at 20 °C. The conductivity depends on the strength of the acid and apparently exhibits a percolation threshold. The threshold is approximately 13.5−14 mol % for both *p*-TsOH and MSA ($pK_a \sim -2$) and around 16 mol % for TFMA ($pK_a \sim -14$). The effect of anion size on proton conductivity seems insignificant for the acidified DCTz pellets.

Composite membranes were prepared by solution casting of polyacrylonitrile (PAN) in dimethylformamide (DMF) containing various amounts of DCTz. PAN was chosen for this preliminary study because of the expected affinity of the polymer for DCTz. The films were mechanically stable until the concentration of DCTz

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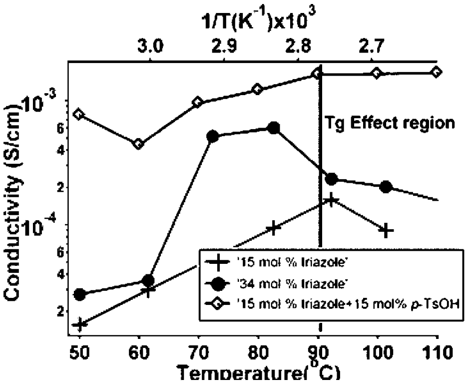

Figure 3. Conductivity of DCTz in PAN.

exceeded 100 mol % with respect to the PAN repeat units. Figure 3 shows the proton conductivity of PAN−DCTz membranes at various temperatures. The conductivity increases as a function of temperature and becomes steady around the glass transition temperature (T_g) of PAN. This could be due to an irreversible rearrangement of the polymer−DCTz network to a less ordered structure. Dipole−dipole interaction between nitrile groups in DCTz and PAN could lead to the arrangement of the triazole rings through the polymer matrix to form an ordered structure suitable for proton conductivity via a hopping mechanism through the network of triazole molecules. The lack of this type of network structure could be the reason for low proton conductivity ($<10^{-7}$ S/cm) of undoped DCTz pellets compared with PAN−DCTz membranes. Addition of an acid to the PAN−DCTz composite suppresses the T_g of PAN while increasing the proton conductivity. For example, the conductivity of the samples doped with *p*-TsOH (1:1 molar ratio of *p*-TsOH to DCTz) was almost an order of magnitude higher than that of the undoped samples (Figure 3).

The proton diffusion coefficient in the PAN−DCTz composite (48 mol %) was measured using pulse field gradient (PFG) NMR spectroscopy. The measured proton diffusion coefficient at room temperature was 1.03×10^{-7} cm^2/s, close to the value ($\sim 8 \times 10^{-8}$ cm^2/s) calculated from the proton conductivity. Translational diffusion of DCTz in the composite is likely to have negligible contribution in this process. Molecular diffusion of similar crystalline organic molecules characterized by diffusion coefficients is on the order of 10^{-9} to 10^{-11} cm^2/s.[9] This result suggests that the triazole is not acting as a “carrier”. Since there is no species present in the system, other than DCTz, which is solid during the course of experiment (under dry conditions), the only possible explanation is the existence of a proton conducting network which translates into small distances for proton movement. On this basis, we suggest that the formation of local structure for proton “hopping” between triazoles is a determining factor in proton conduction. This, in turn, suggests the persistence over a substantial length scale of the hydrogen-bonded percolation network formed by triazole rings. These systems require further study to support the existence of the hydrogen-bonded network.

Electrochemical properties of DCTz were studied in both nonaqueous electrolyte and acidic electrolyte systems. The electrochemical stability is verified by looking for oxidation/reduction peaks in nonaqueous media. DCTz was found to be stable in the electrochemical window of interest (see Supporting Information). Adsorption of DCTz on platinum was further studied under acidic conditions. One possible pathway for adsorption of DCTz on the platinum surface is through the π-electrons or nitrogen lone-pair electrons. As Figure 4 shows, the platinum activity decreases with the initial introduction of DCTz. However, increasing concentration has little effect on the platinum activity (see inset). This is in contradiction with the results reported for imidazole,[10] where the decrease in platinum activity is a strong function of the imidazole concentration. Further investigation on the adsorption of DCTz on platinum surfaces is necessary to understand this behavior.

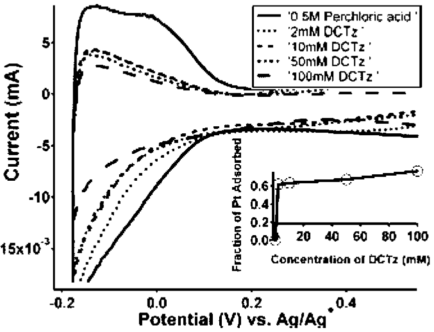

Figure 4. Cyclic voltammograms of DCTz in 0.5 M aqueous $HClO_4$.

In conclusion, 4,5-dicyano-1*H*-[1,2,3]-triazole is a viable proton transport facilitator. The fact that DCTz is a crystalline compound suggests that the mechanism of proton conduction is different than the rotationally coupled intermolecular proton transfer. Conductivity and NMR diffusion coefficients of the DCTz composites and pellets under dry conditions provide evidence of formation of a network that facilitates proton transfer. DCTz is found to be electrochemically stable in the potential window for fuel cell operation, and the adsorption behavior of this compound has no drastic poisoning effect on platinum. While these conductivity levels are not yet to the level needed for fuel cell applications, the data represent a promising starting point for creating more highly conducting systems. Further development of these electrolytes will focus on fixing DCTz in polymer matrices in such a way that we preserve or even improve the randomly formed proton conducting network created here.

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

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