Fluorinated Imidazoles as Proton Carriers for Water-Free Fuel Cell Membranes

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The quest for clean and efficient sources of electric power has intensified the research on proton-exchange membrane fuel cells (PEMFC) in the past decade. The high conductivity of hydrated Nafion membranes, along with their chemical and mechanical stability, makes them favorites in applications with temperature of operations up to 80 °C. At higher temperatures, this membrane steadily releases water, with a concomitant decrease in proton conductivity.[1] Higher temperatures of operation are desirable, however, to enhance the rate of the reaction at the Pt electrodes and more critical to avoid the poisoning of Pt by adsorption of CO, present as an impurity in the feeding gases for the fuel cell. CO poisoning can be avoided if the electrode operates at $T > 120$ °C.[2] Therefore, the development of membranes with good proton conductivity and that can operate above 120 °C with Pt electrodes has become a principal goal of fuel cell research. Alternative water-free materials, such as organic−inorganic composite membranes[3] and blends of different polymers with phosphoric acid,[4] had been tried for PEMFC in that intermediate temperature range. However, none can satisfy the high proton conductivity and chemical stability requirements for fuel cell applications.

Imidazole (Im) is a heterocyclic molecule containing two N atoms, allowing it to pick a proton on one N and deliver the H from the other N site. Its high boiling point (257 °C[5]) makes it a good candidate to replace water as proton carrier in intermediate-temperature PEMFC.[6−8] The conductivity of recast Nafion membrane with ~10 wt % imidazole at 160−180 °C was found to be ~0.1 S/cm, as high as that of 100% humidity Nafion at 80 °C.[1] Notwithstanding the excellent proton conductivity of the recast Nafion−imidazole membrane, it was discarded for fuel cell applications because imidazole poisons the Pt electrode.[8]

In this Communication, we propose using 2,4,5-trifluoroimidazole (ImF3) as the proton carrier for water-free Nafion membranes operating above 120 °C. We have carried out quantum mechanics (QM) and molecular dynamics (MD) simulations indicating (i) that the ImF3 does not adsorb significantly on Pt and (ii) that the proton conductivity of ImF3/Nafion membranes is comparable to that of Im/Nafion.

Using DFT QM methods (GGA PW91), we find that the strong adsorption of Im to the Pt(111) surface is responsible for poisoning of the electrode ($D_e = 21.1$ kcal/mol binding energy). However, for ImF3 we find $D_e = 1.3$ kcal/mol. [Details of the calculations are in the Supporting Information (SI).] Similar calculations for CO/Pt(111) lead to $D_e = 38.5$ kcal/mol (expt 42.3 ± 6.7 kcal/mol[9]), and for H_2O/Pt(111) lead to 11.0 kcal/mol (expt 12.5 kcal/mol[10]), indicating that this level of calculation is adequate. Figure 1 shows the lowest energy configuration of ImF3 on the Pt surface; the adsorbate heterocyclic ring is perpendicular to the surface. In this configuration, the sp^2 lone pair of the N binds to a surface Pt atom. The effect of fluorination is to reduce the electronic density in the sp^2 lone pair orbital of the N, decreasing the binding energy to just
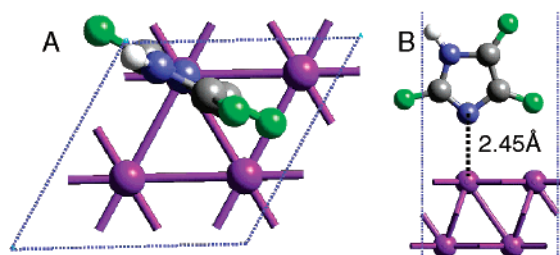
Figure 1. QM optimized structure of 2,4,5-trifluoroimidazole on Pt. (A) Top view of the periodic cell. The lower layer of Pt is hidden. (B) Side view. ImF3 binds through N to a top position in the Pt surface.

1.3 kcal/mol for ImF3. The Pt−N bond length illustrates the same trend, increasing from 2.10 Å for Im to 2.45 Å for ImF3. This result shows that perfluorination of the imidazole ring would prevent the poisoning of the Pt electrode by weakening the Pt−N bonds.

Now the question is whether the fluorination of imidazole will slow the proton transport in the Nafion matrix. In water, protons are transported through two different mechanisms: the diffusion of protonated water molecules (vehicular diffusion) and the hopping of the proton along sequences of water molecules (Grothuss diffusion). Accurate MD methodologies, such as ab initio MD[11] and the classical multistate empirical valence bond model,[12] have been used to compute proton diffusion. To provide a comparison of the total mobility in these two similar systems, we employ a simple and fast method to estimate both the vehicular mobility and the nonvehicular mobility respectively by analyzing the trajectory from classical MD simulations on a realistic model of the Nafion membrane.[13] We do this considering both (a) imidazole (Im) and (b) trifluoroimidazole (ImF3) as the proton carrier, in a proportion of three heterocyclic molecules per sulfonate. Details of the systems and simulations can be found in the SI. The temperature (177 °C) and concentration of imidazole in Nafion (15 wt %) were selected to be close to the experimental values for the recast membrane.[8] We estimate the proton diffusion D in the carrier/Nafion system as the sum of two contributions: a vehicular diffusion coefficient D_V, and a hopping diffusion coefficient D_H. The vehicular contribution was computed from the slope of the mean-square displacement of the proton carrier (ImH^+ or $ImF3H^+$) with time in the equilibrated MD trajectories, $D_V = \langle r^2(t) \rangle / 6t$.

To compute the hopping diffusion in the membrane, we first parametrized the rate constant for the transfer of a proton from the protonated to the neutral carrier as a function of the intermolecular donor and acceptor N−N distance, using transition state theory,[14]

$$k_{ij}(r) = \kappa(T,r)\frac{k_B T}{h}\exp\left(-\frac{E_{ij}(r) - 1/2h\omega(r)}{RT}\right) \quad (1)$$

where the tunneling factor κ is given in ref 14 and $E(r)$ is the energy barrier for the proton to be transferred from donor to acceptor in a
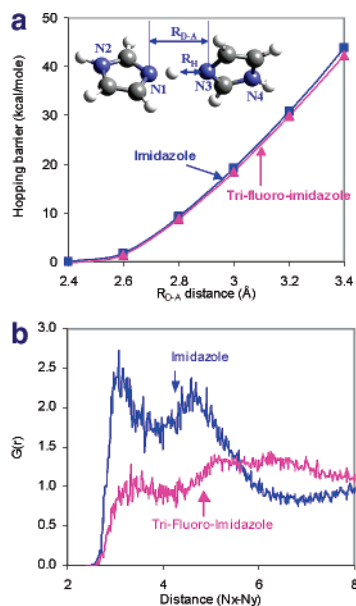
Figure 2. (a) Barriers for the proton transfer between Im/ImH$^+$ (blue) and ImF3/ ImF3H$^+$ (magenta) in a dielectric with $\epsilon = 23$ at representative donor/ acceptor N−N distances. The hopping barriers differ by less than 0.9 kcal/ mol. (b). Radial distribution function $g(r)$ between donor and acceptor N sites of Im (blue) and ImF3 (magenta) Nafion membranes. The perfluori- nation decreases the number of close donor/acceptor neighbors.

Table 1. Computed Proton Diffusion Coefficients

	T (K)	D_V (10^{-5} cm^2/s)	D_H (10^{-5} cm^2/s)	D (10^{-5} cm^2/s)
Im/Nafion	450	0.15	0.30	0.45
ImF3/Nafion	450	0.12	0.13	0.25
water^a	300	1.52	1.63	3.15^b

^{a} See SI for details. ^{b} Experimental $D = 9.3 \times 10^{-5}$ cm^2/s, from ref 15.

medium that we assume has the dielectric constant of imidazole ($\epsilon = 23$), while they are at a distance r. We used QM to calculate the proton hopping barriers for imidazole and trifluoroimidazole. The hopping barriers depend strongly on the distance r between the proton donors and acceptor, as can be seen in Figure 2a, but not significantly on the fluorination of the carrier.

We computed the probability P_{ij} for the proton to jump from each protonated carrier i to any the neutral one j, and averaged over all protonated carriers along the MD trajectories to obtain D_H:

$$D_H = \frac{1}{6Nt}\int_0^{t\rightarrow\infty}\sum_i^N\sum_j^M k_{ij}r_{ij}^2 P_{ij}\,dt \qquad (2)$$

Table 1 lists the estimated proton diffusion coefficients $D = D_H + D_V$ in the (fluorinated) imidazole−Nafion membranes at 177 °C, and their contributions D_H and D_V. We also computed D_H and D_V for proton in water (see SI for details) to validate the methodology. The results for water (Table 1) show that our method gives the right order of magnitude for proton diffusion.

For the ImF3/Nafion membrane, we obtain a proton diffusion coefficient that is ∼56% of that for the Im/Nafion one. Since the specific conductivity of Im/Nafion is $S = 0.1$ S/cm at 177 °C,[8] we expect trifluoroimidazole/Nafion to have $S \approx 0.06$ S/cm, making it a good candidate for fuel cell applications. The vehicular contributions are comparable for the two membranes. The 44% decrease in the hopping contribution to the transport for ImF3 arises mainly from the decrease in the probability of close donor/acceptor distances (see Figure 2b). This decrease arises because replacement of H by bulkier F atoms decreases the number of pairs at the close distances where the proton hopping mechanism is more effective.

It has also been argued[11] that the proton transfer in imidazole is limited by the reorientation of the molecule. We computed the characteristic reorientational times τ_R for ImH$^+$ and ImF3H$^+$ in the Nafion membrane from the decay of the first-order autocorre- lation function $C_1(t)$ for the intramolecular NN vector. We find that the characteristic rotational time for ImF3 is 20% smaller than for Im (89 versus 113 ps; see SI). Thus, if this were the limiting factor, the decrease in mobility would be just 20%, rather than the 44% we calculated considering proton transfer as the limiting step. In summary, we have demonstrated using QM and MD simulation methods that the perfluorination of the proton carrier in imidazole− Nafion membranes would solve the problem of electrode poisoning, while still providing a high proton conductivity.

Supporting Information Available: Computational methods and detailed results. This material is available free of charge via the Internet at htttp://pubs.acs.org.

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