Substituted Imidazoles as Proton Transport Facilitators in Fuel Cell Membranes

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With the development of high temperature membranes that function above 100°C, water is no longer a viable solvent for facilitating proton transport through the membrane. Imidazoles are presented as an alternative due to their high boiling point, proton affinity (high pKa) and resonance structure that allows for a Grotthuss-type proton transport mechanism. Imidazole, however, adsorbs onto the surface of platinum, thus reducing the activity of the catalyst. By adding functional substituents to the imidazole ring, it is possible to alter the chemistry of the molecule in order to reduce the adsorption of imidazole onto platinum. However, these structural modifications will also have implications on the proton affinity, imidazole mobility and water solubility. This paper presents a systematic study of the effect of different functional substituents on the properties of imidazoles.

Substituents were added at the 2, 4 and 5 position, and combinations thereof (Fig 1). Proton affinities were calculated using a compound model (CBS-4M) in Gaussian 03. Cyclic voltammetry highlighted the adsorption characteristics for these substituted imidazoles. Measurements were performed in 0.5M $HClO_4$ with varying imidazole concentrations. Samples of the solutions were saved for conductivity measurements.

The proton affinity of unsubstituted imidazole is 224.2kcal/mol. Adding an ethyl group to all three sites on the imidazole ring (2, 4 and 5 positions) resulted in the greatest increase in proton affinity, 238.8kcal/mol. 2,4,5-trimethylimidazole and 2,5-ethylmethylimidazole also showed high proton affinities (235.6 and 234.6kcal/mol respectively).

The cyclic voltammetry for the unsubstituted imidazole solution showed a significant decrease in activity upon increasing the imidazole concentration. At low imidazole concentrations, it is thought that the acid protonates the imidazole ring to form the imidazolium ion. This ionic form appears to interact less with the platinum. Upon exceeding a 1:1 concentration of acid:imidazole, the imidazole adsorption is so great that the platinum loses all activity. Adding a methyl group to the 2 position on the imidazole ring showed similar cyclic voltammagrams as a function of imidazole concentration. Investigation will continue to examine the electrochemical behavior of other substituted imidazoles under similar conditions.

Figure 1. Structure of imidazole.

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