

New polymeric proton conductors for water-free and high temperature fuel cells

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Due to the considerable interest in PEM fuel cells for transportation purposes there has arisen a need to examine the feasibility of proton conducting membranes that do not depend on the presence of water for their performance. The most attractive option would involve a true solid-state material that contains no free solvent, can tolerate the presence of water, is conductive at low temperatures as well as high temperatures and can be tailored to provide desired gas permeabilities for both the separator and the membrane-electrode assembly. To accomplish this, a somewhat complicated polyelectrolyte structure is necessary but an example of a candidate structure is shown in Figure 1 that illustrates some of the principles involved in proton transport in a solid polymer electrolyte.

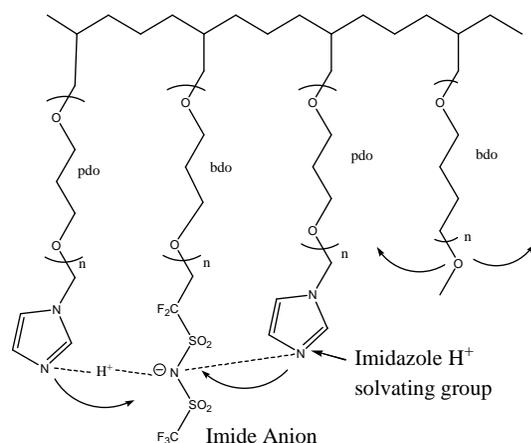


Figure 1. Schematic structure of polyether polyelectrolyte with attached imidazole groups showing mode of proton solvation.

Figure 1 shows the attachment of proton-solvating groups (imidazole) and acid groups (fluoroalkylsulfonimide) to a backbone by means of flexible side chains. The imidazoles are shown attached via an N-alkyl tether but they can easily be attached via one of the carbons (e.g. C2) so that both nitrogens would be available for proton solvation and to participate in a Grotthuss-type mechanism of proton transfer¹. The structure that is shown is completely dependent on polymer side chain segmental motion which is dependent upon the flexibility of the side chains. Modifications of the side-chain structure that can be easily made to achieve this and has already been reported for lithium ion transport in polymer electrolytes for lithium batteries. The backbone can be modified to provide a flexible structure (low T_g) with high gas permeability or a rigid chain with a high T_g (e.g. polystyrene) with low gas permeability. The structural changes that are possible in such a structure are virtually infinite if one considers side chain length, backbone flexibility, concentration of proton solvation groups and acid groups, the nature of the acid groups and the role of cross-linking to modify mechanical properties.

The object of this work is to devise an easily modified polymer structure that will allow rapid elucidation of the role of these structural features in the determination of the properties of the membrane, bearing in mind that the needs are different in the separator and the MEA. We have chosen to study imidazole as the proton solvating group due to the successful development of the Polybenzimidazole-phosphoric acid system², the recent advances reported by Kreuer et al.^{3,4} and reports of remarkable stability of imidazole-containing polymer membranes that have been used for oxygen separation^{5,6}. The base polymer structure has been under development for use in lithium polymer batteries and uses a grafting chemistry that allows easy modification of the nature and length of the side chains, the nature of the backbone, the nature and concentration of the anions and the nature and density of cross-links. This chemistry has been recently reported^{7,8} and the strategy is extended to include proton conducting units in this work. The concentration of imidazole groups relative to that of the acid groups is critical not only for the possible operation of a Grotthuss-type mechanism but also to control possible poisoning interactions with the platinum electrocatalysts. Our experimental plan is to dope various acid polyelectrolytes such as Nafion® and the polyether polyelectrolytes with imidazoles at different concentrations to determine the proton mobility and catalyst interactions and use the results as a guide to prepare the fully tethered polyelectrolyte proton conductors.

Conductivities of imidazole-containing polyelectrolyte membranes are sufficiently high to be of interest for fuel cell operation. The conductivity of membranes swollen with unsubstituted imidazole is higher than that of the N-methyl imidazole which may provide support for

the participation of a Grotthuss mechanism of proton transport. Tethering of the imidazoles to the polymer matrix results in a solid state membrane with no mobile solvent that has lower conductivity than the solvent swollen systems. The polyelectrolyte structures are presently under construction and their conductivities will be reported on. The preliminary indications are that the stronger imide acid will provide higher conductivities and that optimization of the imidazole:acid ratio will provide conductivities that are of interest to fuel cell engineers.

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