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

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Introduction.

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.

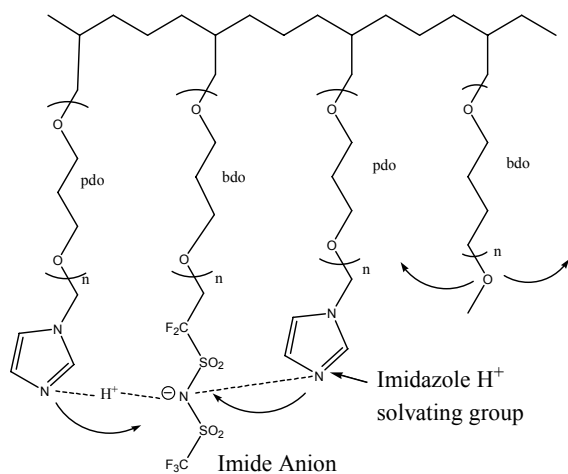


Figure 1. Schematic structure of polyether polyelectrolyte with attached imidazole groups showing mode of proton solvation.

Figure 1 shows the attachment of proton-solvating groups (imidazole) and acid groups (fluoroalkylsulfonylimide) 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 in Figure 1 is completely dependent on polymer side chain segmental motion which is dependent upon the flexibility of the side chains. The figure shows some 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 nature of 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

solavion groups and acid groups, the nature of the acid groups and the role of cross-linking to provide improved 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 separation⁵. The base polymer structure has been under development for use in lithium polymer batteries and uses a grafting chemistry that is shown in Figure 2 for lithium conductors. The grafting chemistry 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^{6,7} 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 shown in Figure 2 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

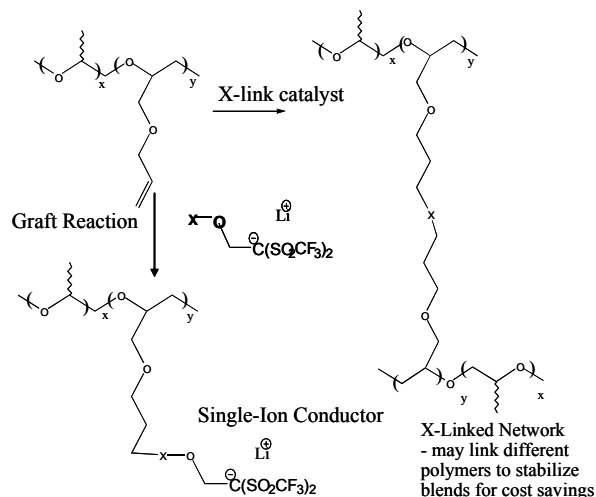


Figure 2. Grafting chemistry used to attach different acid groups (alkyl SO_3H , $-\text{CF}_2\text{SO}_3\text{H}$ and imide $-\text{CF}_2\text{SO}_2\text{NHSO}_2\text{CF}_3$) and imidazole groups to the polymer matrix.

Experimental.

The basic prepolymer synthesis and grafting chemistry for the lithium forms of polyether polyelectrolytes has been described previously and is also described in other articles in this issue. The acid forms were obtained by treatment with DOWEX^R HCR-W₂ ion exchange resin. Anion groups were prepared from tetramethyldisilyl ethane (Gelest, Inc), $\text{CH}_2=\text{CHCH}_2\text{OC}_2\text{H}_4\text{OC}_2\text{H}_4\text{SO}_3\text{Li}$ and $\text{CH}_2=\text{CHCH}_2\text{C}_2\text{F}_4\text{OC}_2\text{F}_4\text{SO}_3\text{Li}$ to give a nonfluorinated and a fluorinated acid group. The equivalent weights (EW) were about 1600-2000. Nafion (EW 1100) in the acid form was obtained from

Aldrich as a dispersion in alcohols. The polyelectrolytes were prepared as solutions in alcohol with varying amounts of imidazole added to the solution. The polymer solutions were then cast of Teflon sheets and dried over P_2O_5 dessicant to provide membranes suitable for conductivity and mechanical measurements. Conductivity measurements were carried out using ac impedance with membranes sandwiched between two stainless steel electrodes. The temperature was controlled by means of convection ovens and ambient humidity conditions were used. Mechanical measurements were carried out on a Rheometrics RSAII solids analyzer and DSC was performed using a Perkin-Elmer DSC7. The thermal and mechanical analysis showed that the presence of imidazole in the membrane leads to an increase in the main glass transition temperature.

Results and Discussion

The conductivities of the Nafion® membranes doped with imidazole and N-methylimidazole as a function of temperature are shown in Figures 3 and 4. These are all carried out in the absence of water and the conductivity of undoped Nafion® is shown for comparison. It is clear that the best conductivities occur at imidazole:acid ratios of 6-7 and that there is an apparent change in dependence once the imidazole is in excess over the acid group. The N-methylimidazole doped membranes, however, show a lower conductivity and the temperature dependence is similar to that of the low imidazole concentration system.

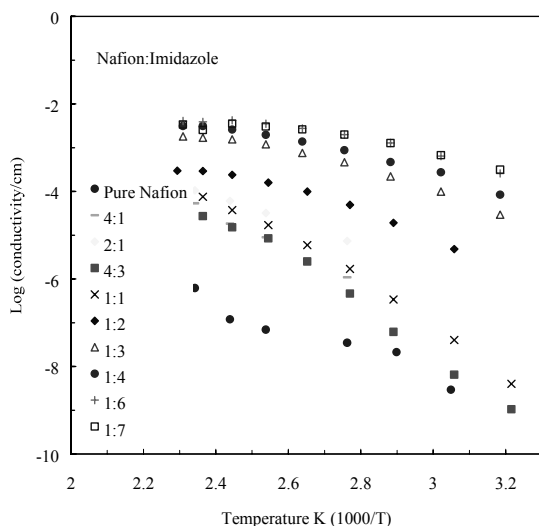


Figure 3. The conductivity of Nafion® doped with imidazole at different concentrations relative to the concentration of acid groups.

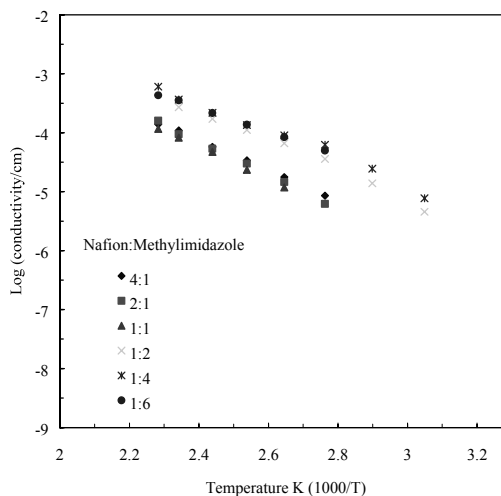


Figure 4. The conductivity of Nafion® doped with N-methyl imidazole at different concentrations relative to the concentration of acid groups.

Conductivities of the two polyether polyelectrolytes doped with imidazole are shown in Figure 5. These results illustrate the effect of the acid group. The alkyl sulfonate polymer has distinctly lower conductivities than the fluorinated alkylsulfonate, illustrating the effect of acid strength. At this time no data is available on the effect of EW. Cyclic voltammetry experiments carried out on a platinum electrode in sulfuric acid in the presence of imidazole shows no poisoning of the platinum activity until the imidazole is present in excess indicating that the imidazole base strongly interacts with platinum but the protonated form does not. This indicates that the polymer in the MEA must be completely protonated to avoid problems with catalytic activity.

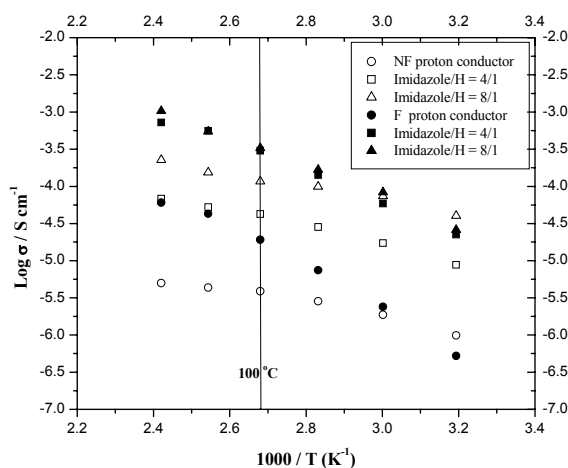


Figure 5. Proton conductivities of the proton conductors based on both non-fluorinated and fluorinated sulfonic acid with different amounts of imidazole.

Conclusions

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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