Anhydrous Proton Conducting Electrolytes Based on Polymeric Amine Salts

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Hydrogen-air fuel cells based on a polymer electrolyte membrane such as Nafion currently operate at a stack temperature of 75-85°C. It would be desirable to operate at temperatures as high as 120°C for transportation applications and 180°C for stationary applications. Reduction in overall system size and higher carbon monoxide tolerance are the key benefits from operation at these higher temperatures. In order to operate at such high temperatures a membrane that can retain proton conductivity under conditions of low ambient water content is required. Several researchers are aiming at modifying Nafion with inorganic materials that would help retaining water close to 120°C under conditions of low to moderate relative humidity [1]. However at temperatures as high as 180°C, few substances can retain water and we must turn to "water-free" proton conduction concepts. The focus of the present study is on understanding the behavior of anhydrous proton conductors based on polymeric amine salts[2].

The present study investigates the properties of membranes prepared from high molecular weight poly-2-vinylpyridinium (P2VP) , poly-4-vinylpyridinium (P4VP) and polyvinylimidazolinium (PVI) salts prepared by quaternization with sulfuric and phosphoric acids. These salts had stoichiometry of 1mole of the nitrogenous base to 1 mole of acid. No excess acid was present in these materials beyond that needed to quaternize the nitrogen, differentiating them from proton conducting PBI/Phosphoric acid [3]. The proton conductivity has been measured over the temperature range of 25-180°C. Thermal stability was measured by TGA and DSC. Also, the effects of addition of hydroxylated nano-particulate silica additives on the conductivity have been investigated.

All the materials studied exhibit good thermal stability up to 200°C. Results shown in Figures 1 and 2 indicate that in the temperature range 25-70° C, phosphates exhibit lower conductivity and higher activation energy than the sulfates. In the range of 160 –180° C, the phosphates exhibit significantly higher conductivities and lower activation energy than the sulfates. Change of activation energy with temperature is more dramatic with the phosphates than the sulfates. Activation energy values vary from 0.05-.0.09 eV at 180°C and 0.14 - 0.3 eV at 60°C. The addition of silica lowers the activation energies by 0.05-.0.1 eV at temperatures below 100°C and raises the conductivity significantly. The highest conductivity values measured at 180°C are in the range of 0.5-0.7 x 10^{-2} S/cm.

Reduction of activation energy with increasing temperature suggests that at lower temperatures polymer mobility limits the concentration of defect states and reorganization processes. As a result, nano-particulate silica could help in providing additional pathways for proton conduction. However, as the temperature is raised well above the glass transition temperature of the polymer backbone, a high degree of polymer mobility is achieved, and other factors such as the dissociation of the proton could become rate determining for proton diffusion. Consequently, reducing the strength of the acid-base interactions in the polymeric amine salt can increase the high temperature conductivity.

Membranes based on these materials can be prepared by impregnating inert non-woven substrates such as polybenzoxazole with the polymeric amine salt. Performance of a hydrogen/oxygen fuel cell measured at 180°C show that the polymer amine salts conduct protons and that the membranes are quite impermeable to hydrogen. However, it is not surprising that the high ohmic resistance of the electrolyte limits the power densities realized with these materials.

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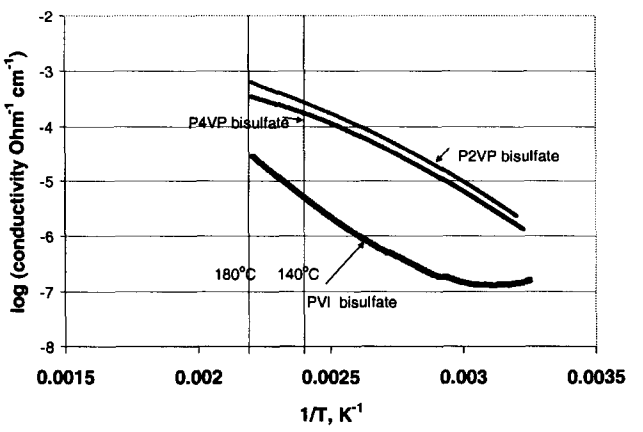

Figure 1. Conductivity of anhydrous P2VP, P4VP and PVI bisulfates as function of temperature

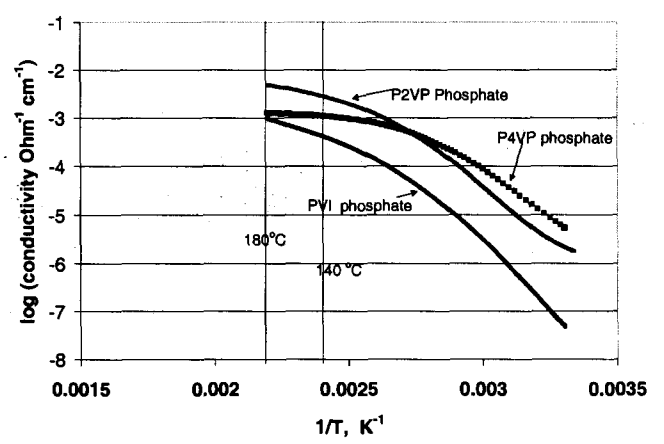

Figure 2. Conductivity of anhydrous P2VP, P4VP and PVI phosphates as function of temperature

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