Role of Inorganic Additives in Determining Polymer Morphology and Transport Properties in Polymer Proton Exchange Membranes

> M. Hickner and J.E. McGrath Virginia Tech Department of Chemistry Materials Research Institute Blacksburg, VA 24060

Inorganic acid hydrates such as zirconium hydrogen phosphate and phosphotungstic acid have been proposed as additives to increase the high temperature performance of sulfonated proton conducting polymers. These additives may primarily reside in the hydrophilic domains of the polymer and possibly influence the transport of species across the membrane. The particular transport processes of interest in this study are electroosmotic drag, methanol permeation, and limiting crossover current convective velocity. By understanding the effects of these additives on mass transport, it will be possible to elucidate the mechanisms by which they improve high temperature properties of ion conducting polymers.

The ¹H NMR T1 and T2 relaxation times of hydrated membranes are a key indicator of the transport characteristics of the membrane. In initial studies, zirconium hydrogen phosphate and phosphotungstic acid have shown different methanol transport characteristics when incorporated into polymeric proton conducting polymers. Zirconium hydrogen phosphate has been shown to decrease the ionic conductivity, methanol permeation, and limiting crossover current convective velocity of the membrane, where the opposite trends are observed for phosphotungstic acid composites. Since the state of water is closely tied to the membrane transport properties, the additives' main effect may be to change the state of imbibed water in the membrane. These changes in the water motion can be monitored by ¹H NMR of hydrated membranes.