

The Use Of Heteropoly Acids In Composite Membranes For Elevated Temperature PEM Fuel Cell Operation; Lessons Learnt From Three Different Approaches.

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There is increasing interest in using the heteropoly acids, HPA, as proton conducting components in PEM fuel cells for elevated temperature operation, 120 – 200 °C.¹⁻⁵ The HPA are a large and structurally diverse class of inorganic proton conducting materials with extremely high room temperature proton conductivities, as high as 0.2 S cm⁻¹ for 12-phosphotungstic acid, 12-HPW. Importantly, for elevated temperature PEM fuel cell operation, the HPA are structurally stable to temperatures in excess of 600 °C and incorporate water molecules and protons to temperatures in excess of 300 °C depending on the system. Most studies to date have only considered the commercially available Keggin structures. Many other structures of increasing complexity are possible.

Because of their structural diversity these materials are particularly suitable for incorporation into a wide variety of membranes materials for which they can be specifically tailored. We have studied HPA in three systems: HPA cast in inert matrices such as polyvinylidenedifluoride, PVDF, HPA infused into perfluorinated sulfonic acid, PFSA, polymers such as Nafion[®] and in polymer/silicate nanocomposites. All of these membranes were characterized by solid state NMR, IR, XRD and SAXS. Membrane electrode assemblies, MEAs, were constructed using standard E-tek electrodes, so that electrochemical measurements could be made, but the MEAs were not optimized for fuel cell operation.

The most convenient method of studying the HPA in inert supports in fuel cell environments is to cast composite films of HPA in PVDF- HFP from acetone solution. These HPA/PVDF membranes can show very high current densities at ambient temperatures, a limiting current over 1 A cm⁻², with no external humidification has been achieved with 12-HPW. The open circuit value in these materials is poor, 0.7 V, as these membranes are quite porous and exhibit excessive cross-over. Attempts to achieve high current densities at elevated temperatures with a very limited set of HPA have so far failed. At 120 °C, similar membranes only exhibit a limiting current of 2 mA cm⁻², but as the lattice has shrunk on dehydration cross-over is expected to deteriorate at these higher temperatures. Excess hydrogen applied to these porous membranes results in the reduction of the HPA and short circuiting of the cell as the reduced HPA in the dry unsupported state is electronically conducting in this system.

In contrast the addition of small amounts of HPA to PFSA polymers such as Duponts Nafion[®] by infusion

from aqueous solution dramatically increases the performance of the membranes at temperatures up to 150 °C depending on the HPA. The polarization for Nafion[®] doped with four different HPA at 120 °C with ca. 25% RH are shown in the Figure. All doped samples show improved performance relative to the control, membrane, the best performance is seen with 21-disrenotungstic acid, 21-HAsW21, but it is currently unclear what the exact moiety involved in this system is as this HPA equilibrates in to an number of HPA species. These membranes have been studied in terms of understanding the interaction of the HPA with the polymer to enable a full understanding of this beneficial interaction. The HPA do not appear to be chemically reduced by hydrogen in these systems but are not immobilized and so may be leached from the membrane over time.

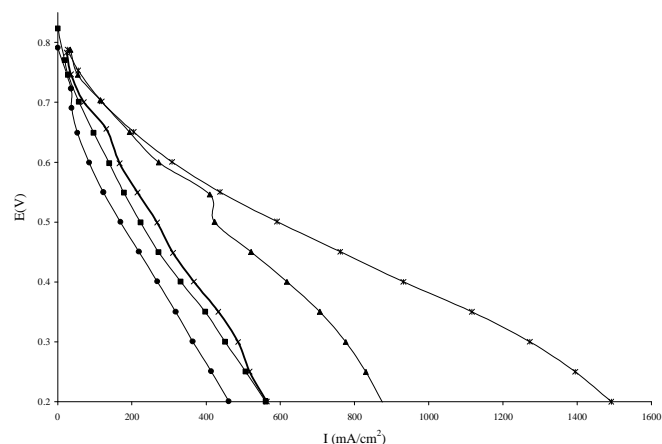


Figure. Polarization curves for HPA doped Nafion[®] at 120 °C using H₂ and O₂ humidified at 80 °C. ● - control, ■ - 12-HPW, ▲ - 12-HSiW, x - 18-HP2W, * - 21-HAs2W21.

One approach to the leaching problem is to immobilize the HPA in a nanocomposite membrane using silicate sol-gel chemistry.^{1,2} A number of polymer backbones has been investigated by us and ion exchange capacities, higher than 3 moleq g⁻¹, and diffusion coefficients as high as 1.2 × 10⁻⁶ cm² s⁻¹ have been achieved with these materials with excellent *ex situ* mechanical and thermal properties. The HPA are stable in these systems to leaching in boiling water. TEM analysis indicates that there is no ordering of proton conducting channels in these systems. In addition, preliminary data from MEA testing of these materials indicates that significant optimization of the membrane/electrode interface will be required for these membranes to exhibit their full potential.

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