

## An experimental investigation in to the use of the heteropolyacids in PEM fuel cell applications as either a membrane component or as an electro-catalyst.

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The widespread application of the PEM fuel cell is limited by the high cost of the technology. Raising the temperature of operation of a PEM cell from 80°C to >165°C would reduce cost by allowing lower loadings of precious metal catalyst, higher tolerances for CO in reformed hydrogen fuel feeds and the cogeneration of steam for heating applications.

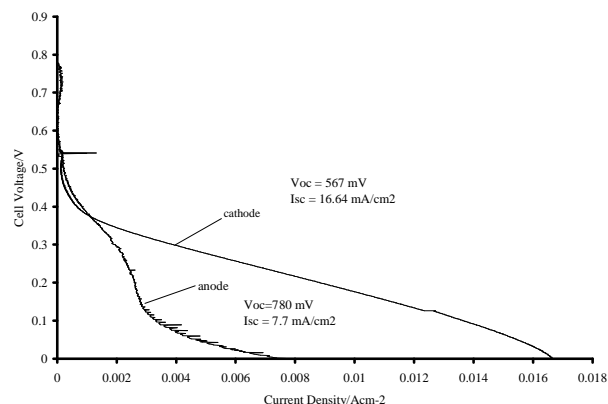
The heteropolyacids, HPA, are a class of inorganic materials that could potentially have high protonic conduction at elevated temperatures. Most studies to date have focused on the commercially available 12-phosphotungstic acid which exhibits a room temperature proton conduction of 0.3 Scm<sup>-1</sup>.<sup>1</sup> There are many other HPA of different charge and shape that may be easily synthesized by straightforward wet chemistry. We have prepared a series of HPA varying in charge from -3 to -21 and in shape from 12-phosphotungstic acid, having the Keggin structure, to the more elaborate HPA such as H<sub>21</sub>[B<sub>3</sub>W<sub>39</sub>O<sub>132</sub>]. The hydration state and protonic configurations of these materials from ambient conditions to 300°C were characterized by TGA, DRIFTS, XRD and <sup>1</sup>H MAS NMR (as well as REDOR NMR experiments for appropriate systems). Many of these HPA contain structural water molecules to temperatures well in excess of 150°C. These structures were correlated with diffusion measurements made by pulsed field gradient spin echo NMR at various temperatures between ambient and 300°C.

Whilst efforts are underway in our laboratories to fabricate practical membrane materials based on the HPA, we have run a number of fuel cells using pellets of pure HPA hot pressed to standard E-TEK electrodes. It should be pointed out that the pure HPA are not membrane ready components and loose up to 10% of their volume on the loss of their non-structural water molecules on heating to 100°C. Even so, these cells whilst only showing modest current densities, <0.35 mAcm<sup>-2</sup>, above 100°C do show an increase in performance as the temperature is raised to 200°C.

The periphery of an HPA may be functionalized with almost any transition metal. This allows us to design materials that might be useful electro-catalysts for fuel cell applications. Whilst the more stable heteropolytungstates are being studied for membrane applications, we are studying the heteropolymolybdates for electro-catalyst applications as these HPA are readily reduced and could be tailored to conduct electrons as well as being good proton conducting catalysts. Whilst we do not expect an HPA to outperform the current platinum based catalysts, such a material might have sufficiently good catalyst and transport properties as to perform well enough, especially at higher temperatures, to achieve

sufficient current densities in PEM fuel cells applications for buildings without the need for expensive precious metal catalysts.

We have prepared a series of vanadium substituted molybdo-Keggin HPA with 1, 2 or 3 adjacent vanadium atoms. These materials were supported on carbon cloth electrodes and hot pressed onto Nafion with an E-TEK electrode used as a standard on the opposite side. The MEA's were run at temperatures <100°C with the HPA electrode as either the anode or the cathode. Stable polarization curves are obtained for an HPA based cathode with reasonable current densities at 80°C (humidifiers 80°C, H<sub>2</sub>/O<sub>2</sub> 30psi) as shown in the figure. However, the reduced HPA on the anode side may be unstable especially for the tri-vanadium substituted HPA.



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### References

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