Increased Stability of PFSA Proton Exchange Membranes Under Fuel Cell Operation by the Decomposition of Peroxide Catalyzed by Heteropoly Acids.

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Abstract

Proton exchange membranes were cast from mixtures of the 3M perfluorinated sulfonic acid ionomer, with side chain $-O-(CF_2)_4-SO_3H$, and various heteropoly acids (HPAs) at a 10 or 20 wt% doping level. The membrane electrode assemblies (MEAs) prepared from these membranes were subjected to a fuel cell testing protocol involving incubation to steady state, temperature challenge, accelerated testing, and post mortem analysis. The cell temperature was varied from 70 - 100 ºC under relatively dry conditions, 70 ºC dewpoint, to avoid leaching of the HPA. The most important finding from this study was that the more stable HPAs, $H_4SiW_{12}O_{40}$, $\alpha-H_3P_2W_{18}O_{62}$, and $H_6P_2W_{21}O_{71}$ reduce the rate of F^- release threefold and improve the performance of the MEA dramatically under these conditions. For HPAs that possibly rearrange in peroxide or at elevated temperatures, $H_3PW_{12}O_{40}$, $H_6CoW_{12}O_{40}$, $H_5SiAlW_{11}O_{39}$, $H_6As_2W_{21}O_{69}$, and $H_{21}B_3W_{39}O_{162}$, the results were mixed as fragments of these molecules possibly interfere with the fuel cell electrochemistry.

Introduction

Even with the use of perfluorosulfonated (PFSA) ionomers, insufficient durability of the proton exchange membrane (PEM) in the oxidizing, acidic environment of an operating PEM fuel cell continues to be a major impediment to the commercialization of these devices. One cause of the insufficient lifetime of the PEM is thought to be oxidative degradation by hydroxyl and peroxyl radicals originating from hydrogen peroxide (1). These reactive species are present throughout the MEA as they are liberated from either the anode (using crossover oxygen) or the cathode after a 2e⁻ reduction of oxygen. The degradation efficiency of the peroxide is known to be dramatically enhanced by the presence of trace amounts of certain transition metal cations such as iron, which efficiently produces hydroxyl radical from peroxide in Fenton reagents. It has been suggested that PEM lifetimes and functionality for operation in hotter and drier conditions may be enhanced by the addition of catalytic additives such as Pt or heteropoly acids (HPAs) that convert any H_2 or O_2 permeating the PEM into water.

It is also implied that any peroxide is also decomposed to water (2, 3). Whereas hotter and drier operation of a PEM fuel cell has been demonstrated, little data exists to support the assumption that these same additives will enhance MEA lifetime in a fuel cell.
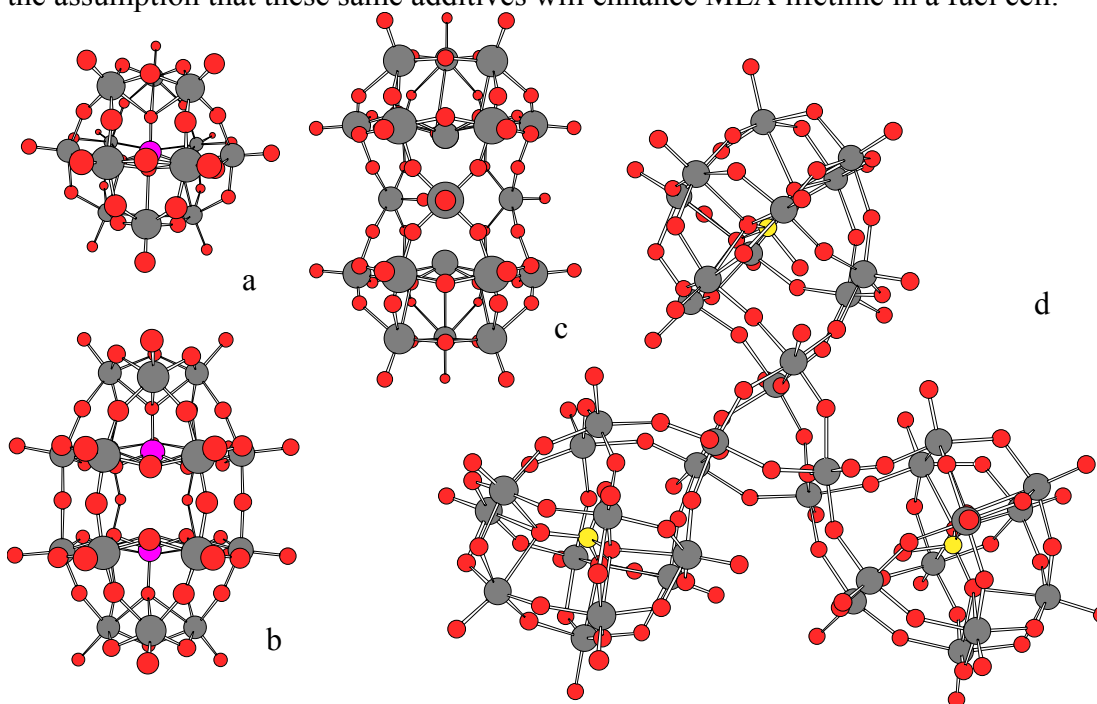

Figure 1. Structures of some of the HPAs used in this study, a) Keggin $[X^{+n}M_{12}O_{40}]^{(8-n)-}$ where $X=P^V$ (HPW), Si^{IV}(HSiW), Co^{III} (HCoW) b) Dawson $[P_2M_{18}O_{62}]^{6-}$ (HP2W$_{18}$) c) $H_6As_2W_{21}O_{69}$ (HAs2W$_{21}$), d) $H_{21}B_3W_{39}O_{162}$ (HB3W).

Of the additives used the HPAs are the most intriguing as they are a subset of a large class of inorganic oxides, the polyoxometalates, and only a few members of this class of compounds have been investigated as PEM additives (4-6). The most well known, and common, structure is the Keggin structure in which 12 metal oxygen octahedral (where the metal is typically W or Mo) are arranged as four groups of three tetrahedrally around a central heteroatom, Figure 1a. More complex structures including the Dawson structure are also illustrated in Figure 1. 1, 2, or 3 metal-oxygen octahedra may be removed from the HPA to form the lacunary HPAs. The HPAs have an extensive known chemistry with peroxides owing to their use in commercial olefin epoxidation systems (7-9). HPAs are known that can efficiently activate peroxide for olefin epoxidation with little decomposition and others are known that will perform little epoxidation while efficiently decomposing the peroxide. The structure of the HPA used as the catalyst in these systems is important, the phosphotungstates are known to be less hydrolytically stable than the silicotungstates. The phosphotungstates when based on the Keggin structure are known to rearrange in peroxide solution to a four tungsten phosphorous based superoxo HPA that is an extremely efficient peroxide activation catalyst (7). The silicotungstates are also very active peroxide activation catalysts but appear to retain their structures in solution (9). It would seem, therefore, that the choice of optimum HPA for use as a peroxide mitigation catalyst in a PEM membrane would not be straightforward especially in light of the expected differences between solution phase behavior and the strong interaction between the HPA and the ionomer in the solid state (10). Because of this wide variation in activity for HPAs with peroxide and to extend the knowledge base of

this chemistry of benefit to PEM fuel cells, beyond the few HPAs available commercially, we now report the effect of a variety of easily synthesized HPAs as dopants in cast PEMs on performance and membrane stability in a working fuel cell.

The PEM chosen was the perfluorosulfonic acid polymer ionomer developed by 3M (3M PFSA). This material is related to the well known Nafion® ionomer in that the proton conducting side chain of the PFSA polymer is a shorter $-O-(CF_2)_4-SO_3H$ rather than the longer $-O-CF_2CFCF_3-O-(CF_2)_2-SO_3H$ in Nafion®. The HPAs in this study were not immobilized and so the doped PEM MEAs were run under relatively hot and dry conditions in the fuel cells to ensure that the MEA was not exposed to liquid water, therefore, minimizing the risk of the HPA washing out of the PEM. The rate of degradation was measured by the rate of F^- released from the HPA doped PEMs under identical conditions.

Experimental

MEA Preparation

The HPAs were ether obtained commercially and used as received: $H_3PW_{12}O_{40}$ (HPW); $H_4SiW_{12}O_{40}$ (HSiW)(Aldrich); or were prepared by literature methods (11, 12) (13) and purified by recrystallization followed by conversion to the free acid via the ether adduct: $H_6CoW_{12}O_{40}$ (HCoW); $H_5SiAlW_{11}O_{39}$ (HSiAlW$_{11}$); α-$H_3P_2W_{18}O_{62}$ (HP2W$_{18}$); $H_6P_2W_{21}O_{71}$ (HP2W$_{21}$); $H_6As_2W_{21}O_{69}$ (HAs2W$_{21}$); $H_{21}B_3W_{39}O_{162}$ (HB3W).

An appropriate amount (10 or 20 wt%) of the HPA was mixed with a casting solution consisting of aqueous alcohols and the 1000 EW 3M PFSA ionomer. The solution was cast on a glass plate and spread to a thickness of 38 μm, dried and then heated further above the T_g for 15 min. Membrane electrode assemblies (MEAs) were fabricated using symmetric electrodes made by hand brushing a catalyst ink onto the microlayer of a carbon paper (3M). The ink consisted of a commercially available catalyst 50% Pt on high surface area carbon mixed with 3M PFSA ionomer with an I/C weight ratio of 0.6. The catalyst loading hand brushed on the carbon paper was nominally 0.4 mg/cm^2.

Fuel Cell Testing

All samples were tested at 3M in co-flow mode using Fuel Cell Technologies 50 cm^2 cells equipped with a quadruple serpentine flow fields. An ambient outlet pressure was used, the pressure drop across the cell being a fraction of a psi. There were four different stages to the fuel cell testing: incubation to steady state; temperature challenge, accelerated testing, and post-test analysis. To minimize HPA dissolution, at all times during the testing the inlet gasses were sub-saturated and only during the highest currents in the incubation stage could the exit gas streams reach saturation. The cell was brought to operating temperature before gasses were saturated. The test station humidification system was modified to insure complete vaporization of the inlet gas streams. This was accomplished by metering the 18MΩ DI water using an HPLC pump with the water being pumped into a pre-sparge bottle filled with 916 stainless steel wool along with the inlet gas. The bottle was heated to 10°C above the dewpoint setpoint and the humidified

gas steam exited the top of the bottle precluding any chance of liquid water leaving the bottle. For all testing the outlet gas steams were at ambient pressure.

Fuel Cell Incubation. Cell incubation was carried out at 80°C cell temperature with H_2/air flows of 800/1800sccm and with 70°C inlet gas streams. Polarization scans were taken every ten minutes with the cell sitting at 0.5 V between scans. Polarization scans were taken by changing the cell potential from 0.9 to 0.3 V and back in 50mV steps and 10 s dwell times while recording the current. The incubation period lasted for approximately 6 h, always a sufficient time to reach a steady state level of performance.

Temperature Challenge. During the temperature challenge of the test, the flows were set to 348 and 833 sccm, hydrogen and air respectfully, a stoichiometry of 2/2 at the 0.5amps/cm^2 setpoint. The cell was first heated to 85°C. For the rest of the challenge phase only the cell temperature was varied from 85 to 100°C in 3°C intervals. At each temperature the cell was held at condition and current for 20 min before the final voltage was recorded at the setpoint in another 10 min scan. In that last 10 min scan, full spectrum impedance measurements were taken three to four times during the last scan to assess cell stability. The impedance measurement was carried out under load and made use of a square wave of potential >10mV that was sent across the cell and a known shunt resistor in the circuit. Fast Fourier transforms were used to derive the impedance as a function of frequency.

Accelerated Testing. During the accelerated testing the cell temperature was held at 90°C with the hydrogen/air flows at 348/833 sccm and the inlet gas steams held at 70°C dewpoints. The cell cycle between 30 min at 500 mA/cm^2 and then a 2 min measurement was taken at OCV before returning to the constant 500 mA/cm^2 scanning. At least four pairs of effluent water collections were made unless the cell was not holding current or the OCV was dropping precipitously. Effluent water was collected from both the anode and the cathode outlet steams recording both times of collection and the mass of water collected. Water samples where later analyzed for F$^-$ concentration using a Dionex Ion Chromatography setup.

Post-Test Analysis. Most samples were later remounted in a cell and tested under a hydrogen pump script. For this testing hydrogen was used on both the anode and the cathode flows of 640 and 276sccm respectfully. The dewpoint was held at 70°C and the cell temperature was incremented from 80-85-90-85-80-75-70-76°C. Five galvanodynamic scans were taken at every temperature with the scans going from 100 to 700 mA/cm^2 and back in 50 mA/cm^2 steps and a dwell time of 20 s. In the event that the potential across the cell was greater than 0.5 volts the load would default to a setpoint of 0 A/cm^2.

Results and Discussion

The conditions of the final aging test, cell 90°C, dew point 70°C are somewhat severe for a PFSA PEM and were designed to increase membrane degradation. In Figure 2 we show the rate of F$^-$ release averaged for the entire 40 h test and the average voltage of the cell at 500 mA cm^{-2} for hours 2 – 7 during the aging test for the control MEA and each of the HPA doped MEAs. The control undoped MEA has an average voltage at 500 mA cm^{-2} of 0.5 V and a F$^-$ release rate of 1.6 µg F$^-$/day/cm^2. This represents a total loss of F$^-$

for the 40 h test of 3.5 µMols which represents the minimum amount of peroxide seen by the membrane if we assume that 2 mol of F^- is released for every mol of peroxide and the process is 100% efficient. The latter assumption is very unlikely and so the actual amount of peroxide experienced by the membrane would most likely be very much higher. It is immediately apparent from Figure 2 that not only do some HPA loadings, 10 wt% $HP2W_{18}$, 10wt% $HP2W_{21}$ and 20 wt% HSiW, more than halve the rate of F^- release but that these dopants also increase the operating voltage of the fuel cell under relatively hot and dry conditions. In general, there is very little change in performance between the control and doped MEAS at wetter operating conditions. 10 wt% of $HP2W_{18}$ represents a total mass of 12 mg in the membrane, assuming a density of the film of 1.6 g/cm^3, which is 3 µmols. Clearly some HPA catalyze the decomposition of peroxide in a fuel cell PEM. This is an extremely exciting result because it implies that an immobilized HPA of the correct structure and doping level could double MEA lifetime and enhance operation under elevated temperature drier fuel cell operation. Conversely some HPA dopants degrade cell voltage, 10% HCoW, 10% $HSiAlW_{11}$, and 20% HPW and some, 10% HSiW, actually increase the rate of F^- release. In order to make sense of these differences we will discuss the fuel cell performance in terms of HPA structure, doping level, and the effect of this not only on the performance during the aging test but also during the temperature challenge run immediately before, Figure 3, and post-test area resistance measurements, Figure 4.
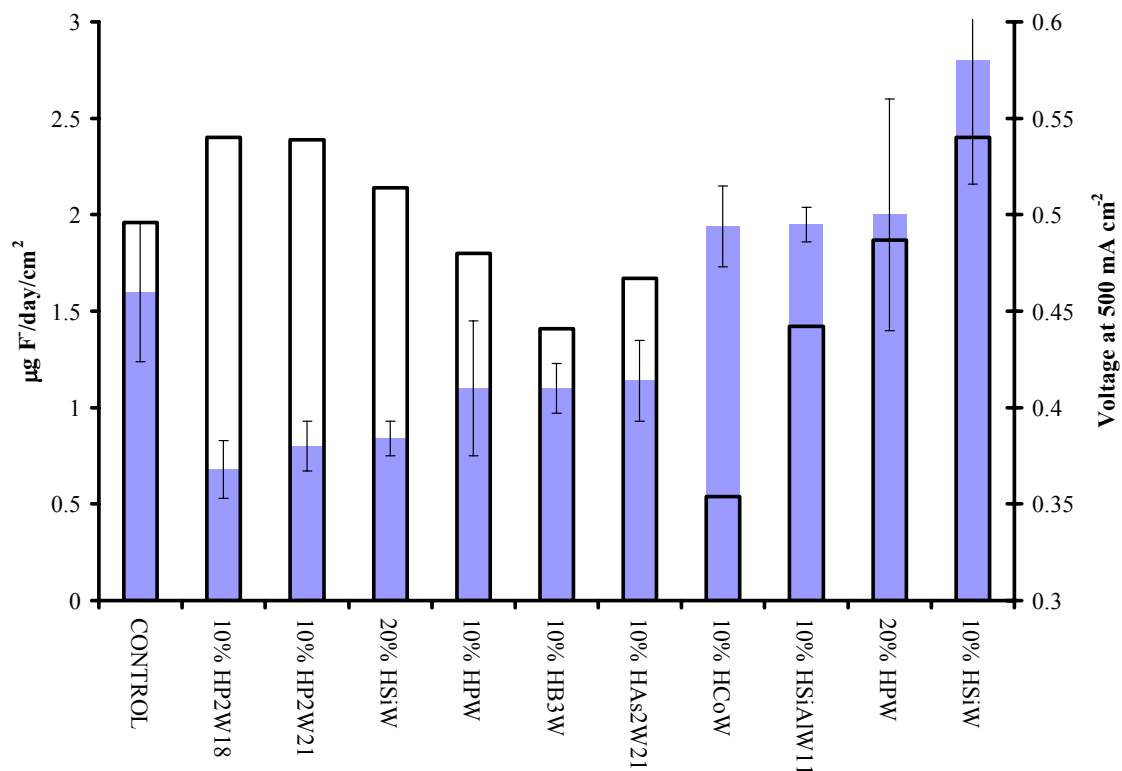

Figure 2. Plot of average F^- release rate for the 40 h accelerated test(solid bars) and average potential at 500 mA cm^{-2}, obtained during hours 2 – 7 of the accelerated test protocol (Open bars).

Many studies of HPAs in Nafion[®] membranes have been conducted with the commercially available HPW and HSiW of the Keggin structure, Figure 1, with the general conclusion that these HPAs improve the performance at hotter drier operating

conditions (4, 5, 14). This conclusion is certainly borne out for 10 wt% HSiW doped 3M PFSA before the accelerated test where it out performs all of the other membranes tested >90 ºC, Figure 3, showing an improved performance at a cell temperature of 100 ºC with drier gases, humidifier 70 ºC; potential of 0.43 V over the control, 0.27 V, at 500 mA cm^{-2}. This improved power performance was borne out in the accelerated test where the average voltage at the set point improved to 0.54 V, Figure 2, and in the post mortem analysis where the area resistance of the 10% HSiW doped membrane was consistently lower over all temperatures, Figure 4. However, this membrane shows the highest degradation rate as measured by F$^-$ release, 2.8 µg F$^-$/day/cm^2. Interestingly, when the doping level is increased to 20 wt% HSiW, the performance of the membrane drops to *ca.* that of the control, Figure 2 – 4, but the F$^-$ release rate is 3 x lower, 0.84 µg F$^-$/day/cm^2, half that of the control. Clearly there is a complex trade off between decreasing F$^-$ release, increasing cell voltage and decreasing cell area resistance. Steady state polarization curves (cell 80 ºC, humidifier 70 ºC), Figure 5, taken at the beginning of the testing protocol show that 20 wt% HSiW doped membrane improves performance at high current densities, possibly a critical mass of this HPA is needed for system optimization.
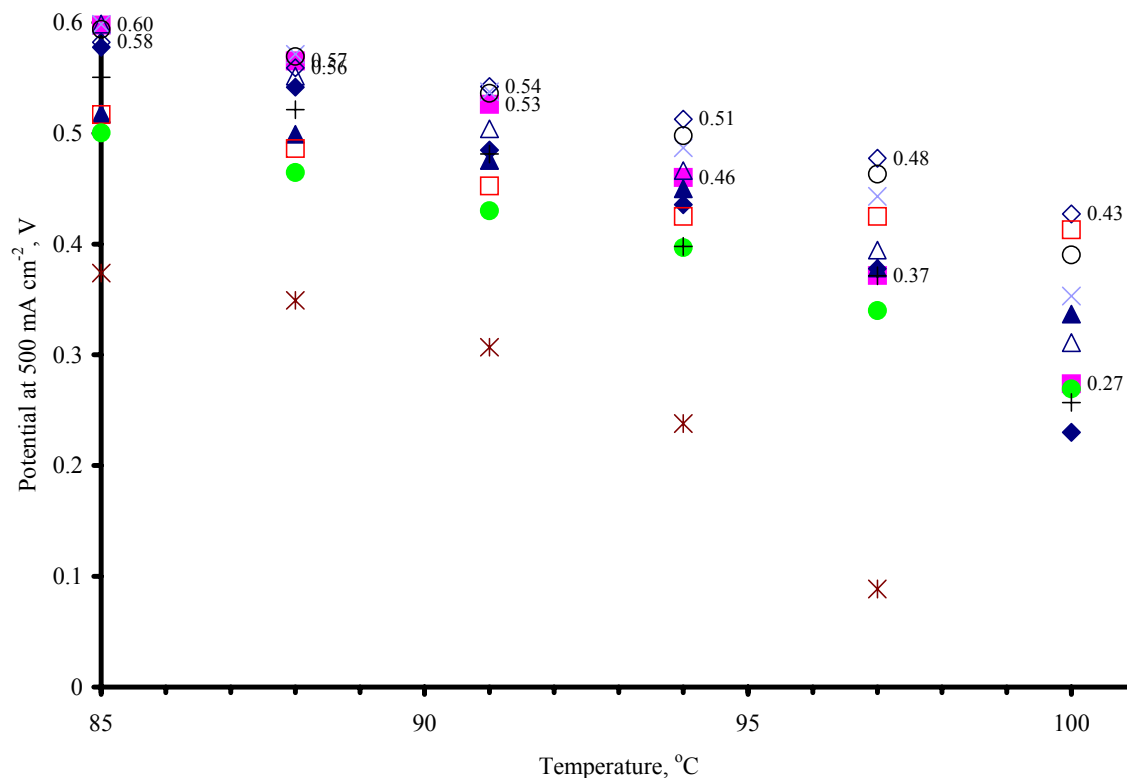

Figure 3. Potential at 500 mA cm^{-2} for the HPA doped MEAs from 85°C to 100°C, cell temperature, 70°C humidifier temperature: ■ - control, ◆ -10% HPW, ▲ - 20% HPW, ◇ - 10% HSiW, △ - 20% HSiW, ✳ - 10% HCoW, □ - 10% HSiAlW$_{11}$, ● - 10% HB3W, ✕ - 10% HP2W$_{21}$, ＋ - 10% HAs2W$_{21}$, ○ - 10% HP2W$_{18}$, numerical data for control and 10% HSiW annotated on graph.

HPW shows slightly repressed performance compared to the control, Figure 2 – 4, except at the hottest driest conditions. The F$^-$ release rate for the 10 wt% HPW doped membranes are the same as the control within error, but higher for the 20 wt% doped

membrane, Figure 2. HPW is known to be hydrolytically unstable in peroxide and whilst solutions of the degraded rearranged super-oxo HPW in H_2O_2 are peroxide activation catalysts(7) it is possible that the oxide fragments produced during the transformation of the HPW interfere with catalysis and proton transport in the MEA.

The behavior of the other two HPAs studied of the Keggin structure are more easily explained, neither is expected to be especially stable at elevated temperatures. HCoW contains an octahedral Co^{II} in a tetrahedral environment (11), and the Al in the lacunary position of $HSiAlW_{11}$ may be easily removable. The presence of these cations in the PEM almost certainly would be detrimental to the MEA performance. This is especially true of HCoW which has the worst performance of any of the doped membranes studied as shown by lower voltages during the temperatures challenge, Figure 3, and accelerated testing, Figure 2, and higher area resistances, Figure 4, at the end of the testing protocol than any other membrane. $HSiAlW_{11}$ may degrade more slowly as its performance was quite good during the early temperature challenge phase of the testing, Figure 3, but was quite poor at the end of the protocol as shown by a relatively high area resistance, Figure 4. The effect of these two HPAs on the F^- release rate was negligible as no catalyst was present, Figure 2.
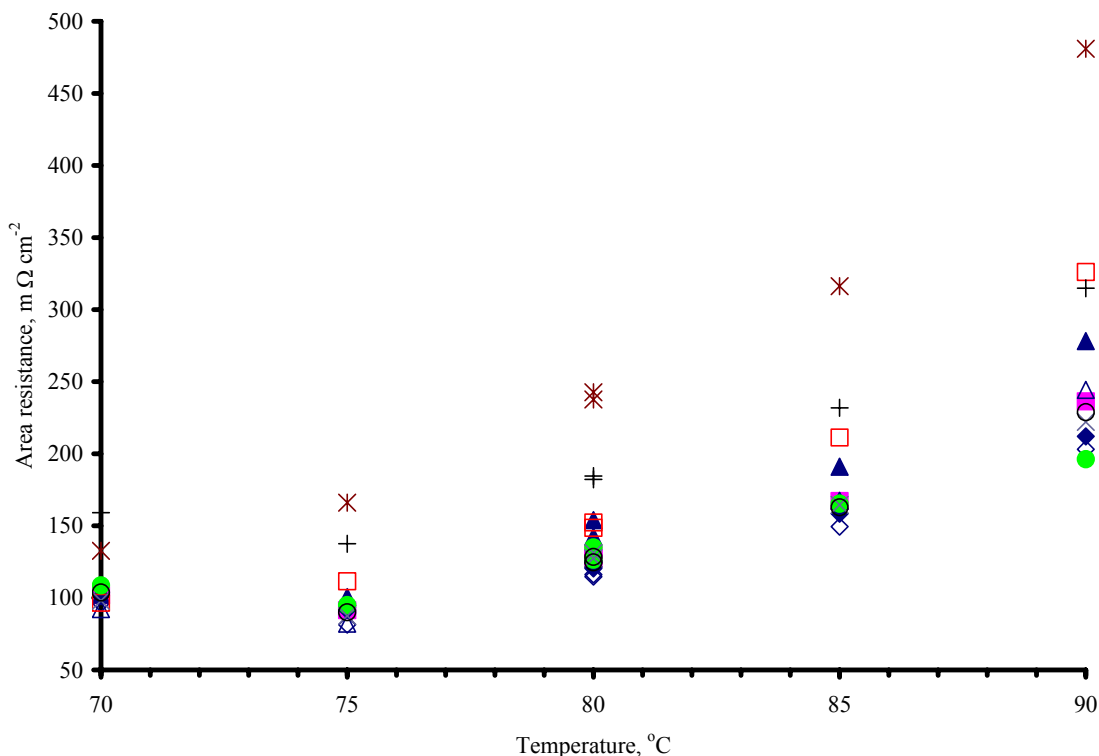

Figure 4. Area resistance for the HPA doped MEAs from 80 – 90 – 70°C, cell temperature, 70°C humidifier temperature: ■ - control, ◆ -10% HPW, ▲ - 20% HPW, ◇ - 10% HSiW, △ - 20% HSiW, ✳ - 10% HCoW, □ - 10% $HSiAlW_{11}$, ● - 10% HB3W, ✕ - 10% $HP2W_{21}$, + - 10% $HAs2W_{21}$, ○ - 10% $HP2W_{18}$.

The two most impressive HPA doped membranes tested were with 10 wt% $HP2W_{18}$ and $HP2W_{21}$, both membranes had superior performance in the steady state polarization curves (cell 80 ºC, humidifier 70 ºC), Figure 5, as did the similarly stable 20 wt% HSiW doped membrane. $HP2W_{18}$ has the well known very stable Dawson structure and

$HP2W_{21}$ a structure related to $HAs2W_{21}$, Figure 1. The stability of these materials in peroxide is inferred as being excellent as related molecules substituted with first row transition metals are used as peroxide and oxygen activation catalysts.(15) These membranes did not have as impressive a voltage at the set point over a range of temperatures as the 20 wt% HSiW doped membrane, Figure 3, and had similar area resistances to the control on post testing, Figure 4. However, both membranes had much higher average voltages at the set point during the accelerated test and the lowest F⁻ release rates observed, 0.54 µg F⁻/day/cm^2.

HB3W and $HAs2W_{21}$ continue the theme that HPAs that are likely to degrade or rearrange in the MEA under hot and dry conditions have complicated behavior. HB3W is centered on three electron deficient boron centered subunits(13) and $HAs2W_{21}$ as a stretched structure as the As atoms both have facing repulsing lone pairs, Figure 1. So both HPAs are likely to rearrange; HB3W is stable at pH 0 but rearranges to the B centered Keggin structure at pH 1-5 at elevated temperatures. Both HB3W and $HAs2W_{21}$ have slightly lower F⁻ release rates than the control, Figure 2, but their performance is generally poorer in the temperature challenge test, Figure 3 and the average voltage at the set point during the accelerated test, Figure 2. Interestingly at the end of the testing protocol, whilst $HAs2W_{21}$ had a relatively poor area resistance over all temperatures tested, HB3W had the lowest area resistance, 196 mΩ cm^{-2}, at the highest cell temperatures 90 ºC (humidifier 70 ºC)
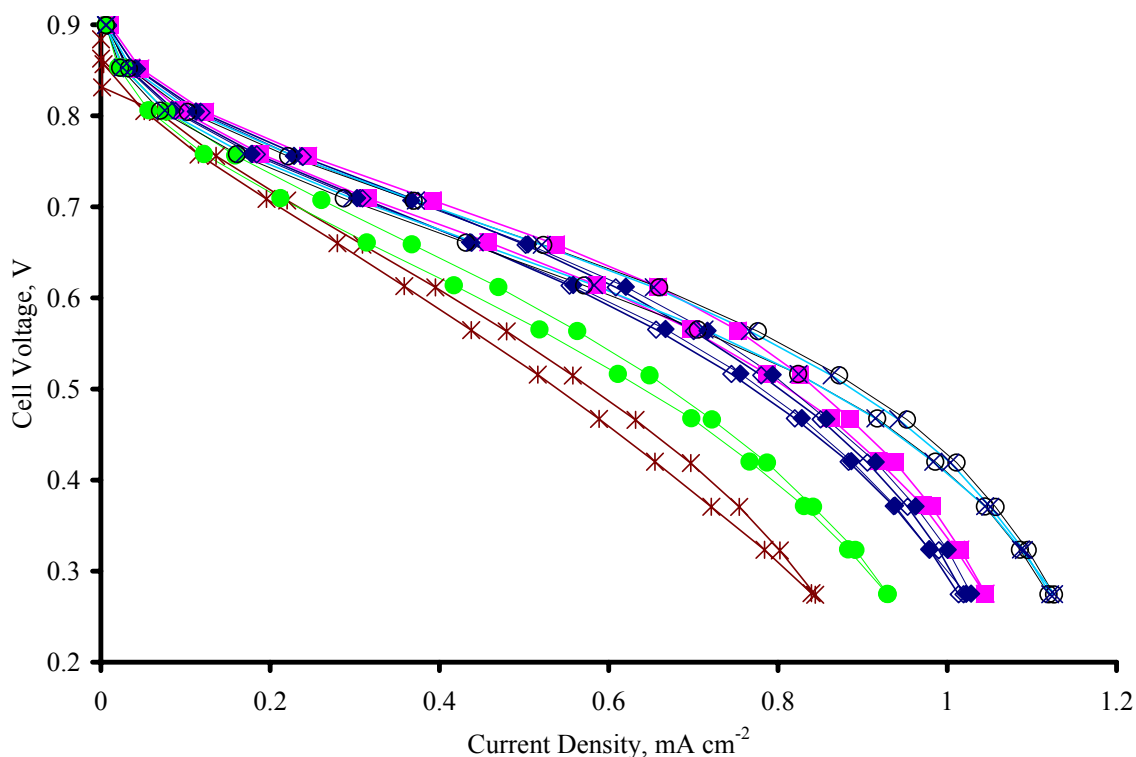

Figure 5. Polarization curves taken during initial incubation after steady state had been obtained, cell temperature, 80°C, humidifier temperature 70°C : ■ - control, ◆ -10% HPW, ◇ - 10% HSiW, ✳ - 10% HCoW, ● - 10% HB3W, ✕ - 10% $HP2W_{21}$, ○ - 10% $HP2W_{18}$.

Conclusions

HPAs that do not rearrange or degrade in peroxide, such as HP2W$_{18}$, HP2W$_{21}$, and HSiW have been shown to dramatically reduce the rate of F$^-$ release from a doped PEM in an operating fuel cell under relatively hot and dry conditions. These same HPA also improve the performance of the MEA under these same conditions, but the doping level is critical to optimum performance. These improvements are expected to translate to dramatically longer lifetimes and improved performance in PEM fuel cells if suitable immobilized HPA can be fabricated for practical fuel cell systems. HPAs that do degrade or rearrange in the presence of peroxide or at elevated temperatures generally do not improve PEM stability and their fragmentation appears to compromise fuel cell performance.

Acknowledgments

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