

# Modified Heteropolyacid / Nafion® Composite Membranes for High Temperature PEMFCs

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## INTRODUCTION

Proton Exchange Membrane Fuel Cells (PEMFCs) are well suited for transportation applications by virtue of their efficiency and high power densities. From an applications point of view, several advantages result by operating a PEMFC at elevated temperatures (above 100°C) and low relative humidities.<sup>1</sup> Therefore, a significant economic incentive exists to develop and commercialize PEMFCs that operate at under these conditions. Nafion® / heteropolyacid (HPA) composite membranes have been shown<sup>2,3</sup> to provide better proton conductivities at high temperatures. However, heteropolyacids are soluble in water and leach out relatively easily from the host matrix. Stabilizing the additive within the Nafion® is essential for proper membrane processing and for good interfacial stability in membrane electrode assemblies (MEAs) since these involve exposure of the membrane and the MEA to aqueous environments<sup>4</sup>. Additionally, additive stability promotes long-term endurance under rigorous operating conditions. To this end, studies aimed at stabilizing various heteropolyacids in Nafion® without compromising performance were performed.

## EXPERIMENTAL

In this study, Nafion® / HPA membranes were made using two techniques. The first technique involved addition of an appropriate amount of HPA directly to Nafion® and preparing the membrane by solvent casting. In the second technique, the HPAs were chemically modified and converted from a low surface area, water-soluble compound into a high surface area water insoluble compound by a cation exchange process. The chemically modified HPAs were then incorporated into a Nafion® matrix, and membranes prepared by solvent casting. The HPAs investigated include compounds containing phosphorous and silicon as the hetero atom and tungsten and molybdenum as the poly atom. The cations investigated were chosen based upon their ionic radius.

The membranes were characterized by TGA and SEM / EDX analyses. Membrane electrode assemblies (MEAs) were prepared by applying catalyst onto the membrane using an airbrush. The MEAs were evaluated in a fuel cell environment at different temperature and relative humidity conditions, with temperatures ranging from 60 - 120°C and relative humidities from 20 – 100%. The protonic conductivity of the membranes was estimated from resistance measurements obtained using the current interrupt technique. The stability of the additive in the membranes was estimated by evaluating the membranes before and after successive immersions in 0.5 M sulfuric acid and deionized water, and by estimating the weight loss of the membranes during such immersion. The endurance of the membrane was evaluated by performing extended performance runs at elevated temperatures, and monitoring the value of

resistance with time. Optimization of additive loading was done for selected cationic forms of PTA.

## RESULTS

The results obtained using Nafion® / modified phosphotungstic acid (PTA; one of the HPAs studied) membranes are very promising. Sample weight measurements before and after immersion in sulfuric acid and water for a period of 4 hours indicated a reduced loss of additive when compared to traditional Nafion® / PTA membranes. This is shown in Fig. 1. Preliminary results indicate that the protonic conductivities of the Nafion® / modified HPA membranes are similar to Nafion® / PTA membranes (Fig. 2) at 120°C and 35% inlet relative humidity operation. This result, when coupled with the lower loss of additive upon exposure to aqueous environments, suggests that such modified additives represent an advancement in the current state of the art. Further results will be discussed in the paper.

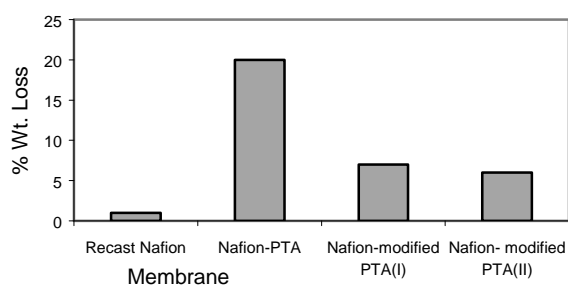


Fig. 1

% Weight loss of Nafion® / PTA and Nafion® / modified PTA membranes – each membrane had 25% by weight of additive prior to immersion in aqueous media

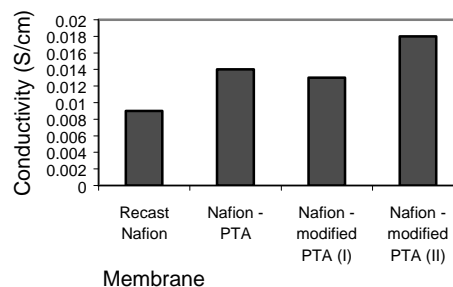


Fig. 3

Conductivities of Nafion® / PTA and Nafion® / modified PTA membranes at 120°C and 35% inlet relative humidity (ambient pressure operation)

## REFERENCES

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