

Supported 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.¹ 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^{2, 3, 4} 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 long-term endurance of the membrane under rigorous operating conditions. To this end, studies aimed at stabilizing various heteropolyacids in Nafion® without compromising on 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 first supported on different high surface area supports using techniques described in literature.^{5, 6, 7, 8} The supported 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 supports used include silica, alumina, zirconia, zeolites and clays.

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.

RESULTS

The results obtained using Nafion® / supported HPA membranes are very promising. Sample weight measurements before and after immersion in sulfuric

acid and water for a period of 4 hours indicated near zero loss for these membranes, as opposed to a 20% loss for Nafion® / HPA membranes. SEM imaging revealed that the Nafion® / supported HPA membranes had a uniform structure, with the HPA well distributed on the support. SEM images of Nafion® / HPA and Nafion® / supported HPA membranes are shown in Figs. 1 and 2. Preliminary results indicate that the protonic conductivities of the Nafion® / supported HPA membranes (using PTA supported on zirconia) are similar to Nafion® / PTA and Nafion® / STA membranes (Fig. 3). Further results will be discussed in the paper.

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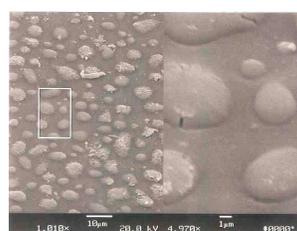


Fig. 1
Nafion®/PTA membrane

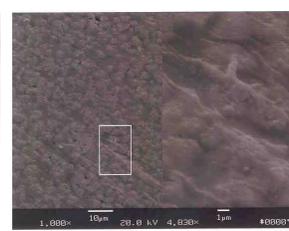


Fig. 2
Nafion®/zirconia supported PTA membrane

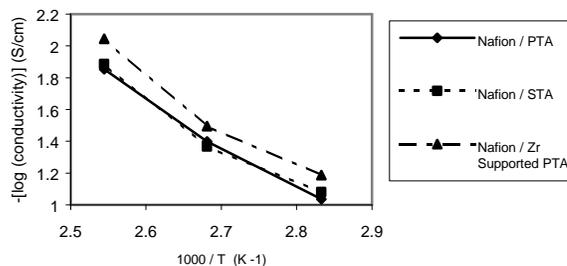


Fig. 3
Conductivities of Nafion® / HPA and Nafion® / supported HPA membranes at different temperatures