Particle Size Effects on the Conductivity of Heteropolyacid/Ionomer Composite Membranes for High T/Low RH PEFC Applications

V. Ramani, H. R. Kunz, J. M. Fenton
Department of Chemical Engineering
University of Connecticut
Storrs, CT – 06269, USA

INTRODUCTION

Several advantages result by operating a polymer electrolyte fuel cell (PEFC) at elevated temperatures (above 100°C) and low relative humidities (RH). Nafion®/heteropolyacid (HPA) composite membranes have been proposed for high temperature applications. However, heteropolyacids are soluble in water and leach out relatively easily from the host matrix. Stabilization of the HPA additive within the ionomeric matrix is essential for proper membrane processing and for good interfacial stability in membrane electrode assemblies (MEAs). Such stabilization has been recently demonstrated in Nafion® based systems. Studies aimed at investigating the effect of HPA loading and particle size on the proton conductivities of the Nafion®/HPA and Nafion® stabilized HPA composite membranes as a function of operating temperature and relative humidity were performed. Such effects were also studied in composite membranes prepared using hydrocarbon based ion conducting polymers.

EXPERIMENTAL

Composite membranes were made by first preparing a precursor solution comprising 5% Nafion® dispersion (Solution Technologies, Mendenhall PA), and appropriate amounts of HPA (typically phosphotungstic acid; PTA) and high boiling solvent. The membranes were cast on flat glass plates by evaporating solvent at a desired rate. Particle size control was achieved by controlling the solvent evaporation rate and the composition of the precursor solution. Nafion®112 and recast Nafion® membranes were used as blanks. All data were compared against these membranes.

The HPA particle size was estimated by scanning electron microscopy, and, where needed, by atomic force microscopy. The stability of the additive was verified by comparing FTIR spectra before and after rigorous washing treatments. Proton conductivity measurements were made using a 4 point conductivity cell (Bekktech LLC). Both direct and alternating current techniques were employed. Temperature and humidity were controlled using a fuel cell test system (Scribner Associates, model 890B) and a flow loop (built in-house). Finally, 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. The proton conductivity of the membranes was also estimated in-situ from resistance measurements obtained using the current interrupt technique. The conductivities obtained using different techniques were compared. The effect of the HPA particle size on the proton conductivity of the composite membranes was studied.

RESULTS

The area specific resistances (Ohm-cm²) of two ~33 micron thick Nafion®/HPA membranes (15% by weight HPA loading) with particle sizes of 1-2 microns and 100-150 nm respectively are shown in Fig. 1. These measurements were made in an operating fuel cell environment at 120°C and 35% RH. It is seen that the membrane with smaller particles (which was optically clear) has higher proton conductivity than the membrane with larger particles (opaque). Further results will be discussed in the presentation.

![Fig. 1: Area specific resistances of two 1.25 mil thick Nafion®/HPA membranes (15% by weight HPA loading) with different particle sizes](image)

REFERENCES