Proton-Conducting Polymer With Methanol-Inhibiting Copolymer

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Direct methanol fuel cells suffer performance losses due to methanol cross-over through the polymer electrolyte membrane (PEM) which is usually Nafion®. A free-standing PEM was developed having lower permeability to methanol while permitting high water permeability, but having lower proton conductivity. A two-polymer composite formed an interpenetrating polymer network (IPN) composed of a proton-conducting copolymer of 2-acrylamido-2–methyl propanesulfonic acid (AMPS) and 2-hydroxyethyl methacrylate (HEMA) and a second polymer, poly(vinyl alcohol) (PVA), serving as a methanol barrier. Ion conductivity and methanol permeability were controlled by adjusting polymer ratios and the extent of cross-linking of the two polymers.

IPN water adsorption is much greater than that of Nafion. Solvent adsorption and selectivity for IPN's with an AMPS-HEMA-PVA wt ratio of 4-21-75, using 88%, 96%, and 99% hydrolyzed PVA is shown in Figure 1. While Nafion® adsorbs much more methanol than water, all of the IPN's adsorb significantly more water than methanol.

We define selectivity (S) as the ratio of wt% adsorbed methanol to wt% adsorbed water, desiring to achieve a very low selectivity. Because methanol adsorption is restricted and there is a high affinity for water adsorption, the IPN's show a low selectivity for methanol. The IPNs in which PVA was cross-linked least (by treating only 10 minutes with glutaraldehyde) resulted in the best (lowest values) selectivity for methanol. Also, the lowest methanol adsorption occurred with IPNs containing the purest PVA (99% hydrolyzed). The most selective IPN was the 4-21-75 (99% hydrolyzed PVA) membrane, which had a methanol selectivity (S = 0.16) that was 15 times less than Nafion® (S = 2.4). Although longer periods of PVA cross-linking reduces water adsorption, methanol adsorption slightly increases.

Swelling of the IPNs is much greater than Nafion® even for the most highly cross-linked IPNs. Hydrated Nafion® swells about 18%, while IPN swelling ranges from about 28% to 48% depending on composition and cross-linking conditions. Swelling decreases as the extent of hydrolysis of the PVA increases.

IPN's containing 4 wt% AMPS had conductivity about an order of magnitude lower than Nafion (Figure 2). Although increased cross-linking restricts swelling, within experimental error, the degree of PVA cross-linking (and thus swelling) had no effect on conductivity. In general, conductivity of different composition ratios AMPS-HEMA-PVA IPNs varied only slightly, being a little more than one order of magnitude less conductive than Nafion® at room temperature.

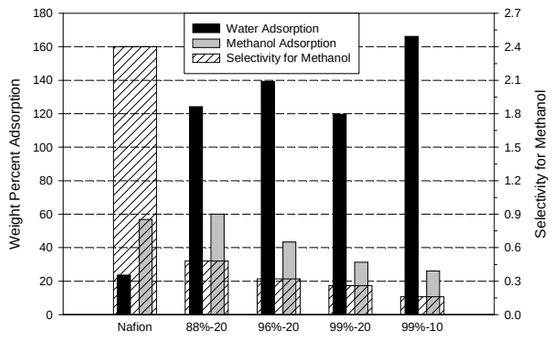

Figure 1. Solvent adsorption and selectivity for methanol for Nafion and four IPNs containing 4% AMPS, 21% HEMA, and 75% PVA. IPNs designated by percent hydrolysis of PVA and period of cross-linking in minutes.

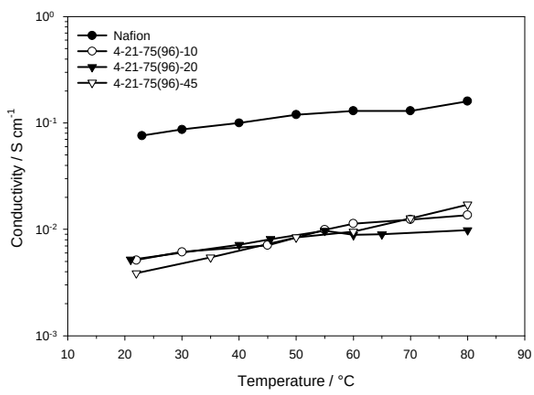

Figure 2. Conductivity vs temperature for Nafion and IPNs where PVA was cross-linked for periods of 10, 20 and 45 minutes.