Proton-conducting polymer membrane comprised of a copolymer of 2-acrylamido-2-methylpropanesulfonic acid and 2-hydroxyethyl methacrylate

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Abstract

In order to identify a proton-conducting polymer membrane suitable for replacing Nafion® 117 in direct methanol fuel cells (DMFC), we prepared a cross-linked copolymer of hydrophilic 2-acrylamido-2-methylpropanesulfonic acid (AMPS) and 2-hydroxyethyl methacrylate (HEMA). Fumed silicas were also added in an attempt to increase the amount of water adsorbed by the membrane and to enhance water retention. Hydrated copolymer membranes adsorbed significantly more water than Nafion® 117, but were no better at retaining water during drying under ambient conditions. Films composed of 4% AMPS—96% HEMA had a room temperature proton conductivity of 0.029 S cm^{-1}, which increased to 0.06 S cm^{-1} at 80 °C. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Proton-conducting; Membrane; AC impedance; AMPS; Nafion®; Silica

1. Introduction

Fuel cells are being considered as direct replacements for batteries in Army applications to power soldier-portable devices, as power supplies for recharging batteries, power for silent watch and remotely-placed sensors, and for use in robotics and electric vehicles. A fuel cell can provide uninterrupted power so long as the fuel is continuously supplied. The process involves the conversion of chemical energy (hydrogen and oxygen) directly to electricity, heat and water.

Polymer electrolyte membrane fuel cell (PEMFC) technology is favored as a man-portable system because of its light weight, high power, low operating temperature and fast start-up. Hydrogen is oxidized at the anode to produce electricity and hydrogen ions that migrate through the polymer electrolyte membrane to the cathode. The hydrogen ions combine with oxygen that is reduced at the cathode to produce water. Although, the preferred fuel is hydrogen, difficulties remain with its safe storage, transport and handling in an economical and light weight system. An alternative to hydrogen gas is to reform liquid fuels (e.g. alcohols, gasoline, diesel fuel) or compressed gases (e.g. butane, ammonia) to produce hydrogen. This adds system weight, complexity and cost.

Direct methanol fuel cells (DMFC) oxidize methanol fuel directly at the fuel cell anode (no separate reforming process) to produce electricity and hydrogen ions. However, there is a loss in performance with the present systems. Current technology uses Nafion® 117 as the polymer electrolyte membrane which conducts protons from the anode to the cathode as well as serving as the barrier between these two electrodes.

However, performance is less than desired and requires two primary areas of improvement. Firstly, methanol permeates the membrane to cause a ''chemical short'' at the cathode, where it directly reacts with oxygen, thereby decreasing fuel utilization and oxygen cathode performance, and rendering Nafion® unsuitable for use in DMFCs. Secondly, by improving the proton conductivity of the membrane higher current densities could be realized which could further reduce the size and weight of the fuel cell. Additionally, Nafion® 117 is very expensive, so identifying a less costly material would have significant impact on system cost.

The ionic conductivity of Nafion® is due to the ionization of hydrated sulfonic acid groups that result in solvated protons. Conductivity is generally reported to be in the range of 0.08–0.1 S cm^{-1}, but the extent of membrane hydration is a critical factor in determining conductivity. Conductivity increases with water content, but at temperatures exceeding 100 °C it decreases as water is lost. DMFC

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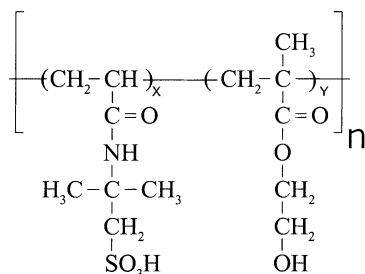*E-mail address:* cwalker@arl.army.mil (C.W. Walker Jr.).

Fig. 1. AMPS–HEMA copolymer.

operating temperatures (60–80 °C), self-heating generated by methanol oxidation, and air flow at the cathode tend to dehydrate the Nafion[R] membrane thereby decreasing proton conductivity. The ability of a membrane to adsorb and maintain significant amounts of water should improve ionic conductivity and stabilize cell operating performance.

In the work reported here, inexpensive, hydrophilic, 2-acrylamido-2-methylpropanesulfonic acid (AMPS) monomer was chosen as a possible candidate for a new electrolyte membrane based on it containing a sulfonic acid group in its chemical structure and on published work where it was prepared as a proton-conductive gel used in electrochromic devices [1–8]. It has also been used as the basis for a humidity sensor [9] and as a lithium ion-conducting polymer electrolyte in a lithium battery [10]. Conductivity of semi-solid poly-AMPS was found to be higher than that of partially hydrated Nafion[R] that was hydrated to 15 water molecules per sulfonic acid group [2]. By contrast, conductivity of poly-AMPS increases with water content only until about 6 molecules per equivalent and then levels off [2]. This suggested to us that this polymer may be more tolerant to fluctuations in water content and drying, and might maintain an ionic conductivity greater than Nafion[R] under conditions of low water content. Because AMPS homopolymers will only produce gels, extensive crosslinking or introduction of a copolymer is required. By choosing a suitable copolymer, and with cross-linking, it may also be possible to control methanol permeability, permitting its use in DMFCs.

Poly(2-hydroxyethyl methacrylate) (HEMA) was chosen as a copolymer (Fig. 1) because it produces a water-insoluble but water-swellable polymer. Although, it is hydrophobic, its water-swellable character means water will not be excluded from the copolymer. In addition to preventing polymer solubility, HEMA will provide structural stability and rigidity that should in turn reduce methanol permeability.

Cross-linking also prevents dissolution of the polymer in solvent and also reduces or prevents swelling, thereby also reducing methanol permeability. Ethylene glycol dimethacrylate (EGDM) was chosen as a cross-linking agent.

2. Experimental methods

The general synthetic procedure, substantially similar to that of Giglia and co-workers [4,5], is to prepare a 50 ml:50 ml:5 ml solution of methanol, ethanol, and water which is deaerated using bubbling nitrogen. While continuously stirring and slowly bubbling nitrogen, the desired ratio of AMPS and HEMA (Aldrich) is added with a total weight of approximately 7–7.6 g. Approximately, 2.5 wt.% EGDM (Aldrich) is then added followed by 1.3 wt.% 2,2′-azobisisobutyronitrile (AIBN) (Aldrich) free radical initiator to catalyze the polymerization reaction. After the solids are completely dissolved, the solution is refluxed at 60 °C with stirring and slow bubbling of nitrogen for 8–13 h, then cooled to room temperature. The polymer is solution cast in a Teflon dish or on a Teflon-coated fiber–glass mat. The solvent is allowed to evaporate in a fume hood at room temperature for 1–3 days, then the film is placed in a 70 °C dry air oven for more complete solvent removal and to initiate the cross-linking reaction.

Additional polymer formulations were prepared to include Nafion[R], which was introduced as a 5% solution (Aldrich), to improve mechanical properties. Dimethyl formamide (DMF, Aldrich) was also used as a co-solvent to alter mechanical properties. In addition, untreated fumed silica (Cabosil EH-5, surface area 380 m^2 g^{-1}) was added in an attempt to increase water absorption and water retention. Fumed silicas are hydrophilic, possessing chain-forming tendencies which form 3-D branched aggregates, with an ability to adsorb moisture that increases with surface area.

Water adsorption studies were performed after drying 1 cm^2 coupons of polymer film under vacuum at 65–70 °C. Coupons were weighed and suspended from the caps of vials with a nickel screen holder attached to the cap. The vials were partially filled with solutions of LiCl which created atmospheres of 15, 35, 50, 75, 90 and 100 percent relative humidity (RH). Coupons were periodically weighed over a period of 1–2 weeks until a stable weight was obtained, from which wt.% water adsorbed was calculated with respect to each sample's dry weight. Drying rate of fully hydrated films was also determined by following weight loss over time under ambient laboratory conditions.

Ionic conductivity was determined by AC impedance measurements taken between 10 Hz and 100 kHz using a Solartron AC impedance system (1260 impedance analyzer, 1287 electrochemical interface, Zplot software). A four-point probe method was employed using a test fixture designed and constructed at Case Western Reserve University [11]. Samples measuring 3 cm × 0.5 cm were first hydrated in deionized water before assembly in the test fixture. The conductivity cell was placed in a sealable container having electrical feedthroughs and containing a small amount of water to maintain an atmosphere of 100% RH. The container was placed in a Tenney chamber to control temperature. Impedance measurements were taken at each temperature after equilibrating for a minimum of 2 h.

Methanol permeability is not reported here but is currently being studied to be included in a future report.

3. Results and discussion

3.1. Physical characteristics

Solution cast copolymer films of AMPS–HEMA were clear and transparent, but brittle in the dry state. When hydrated, the films became flexible. If the content of AMPS is too great (e.g. 50 wt.%), hydration results in a soft gel which is easily broken apart, whereas, an intact flexible film results when using less than 10% AMPS. Films containing 10% AMPS were relatively fragile when hydrated and were unable to withstand rough handling. Decreasing AMPS content to 5% provided a more robust film but was still judged as a little "soft". When AMPS content was 4% or less, hydrated films were more rugged and easily handled. The dimensional change as the polymer swells with hydration was measured to be approximately 16% for a 2% AMPS copolymer. Films with 2% fumed silica added had similar physical characteristics as polymer without silica. Addition of 5% silica resulted in an uneven film noticeably containing silica particles.

Nafion® solution was used as an additive to try to lend mechanical flexibility to the dry polymer. It was introduced by two methods: incorporated with the monomers and refluxed in the synthetic process, or added to the AMPS–HEMA copolymer after refluxing and just prior to casting. Composition of the membrane prepared was 2% AMPS, 5% Nafion® and 93% HEMA. In both preparation methods, a visible phase separation was observed in the cast film. The films were composed of two distinct areas, a clear portion and an opaque, milky white portion. Physical properties, water adsorption, drying rate, and ionic conductivity of this

formulation were equivalent to the AMPS–HEMA copolymer without Nafion® (data not presented).

Another effort to alter the mechanical properties was through the use of an additional solvent, DMF, during synthesis. A 2% AMPS—98% HEMA polymer was prepared in the usual manner except that the amounts of ethanol and methanol were halved, and the difference made up with DMF. Solution cast films were clear and remained as brittle as films prepared without DMF. However, when immersed in water the film hydrated quickly but became cloudy in appearance and disintegrated into small pieces when handled.

3.2. Water adsorption

Proton conductivity depends on the ability of the membrane to remain hydrated, especially as temperature increases. Besides the use of AMPS monomer, fumed silica was added to increase water content and retain water.

Fig. 2 shows water adsorption of various AMPS–HEMA polymer formulations compared with Nafion® equilibrated one to two weeks at various relative humidities. At relative humidities of 75% and below, differences in adsorbed water are very small to negligible, and only a small increase in water content occurs as RH increases. Above 75% RH, adsorbed water increases sharply with increasing content of AMPS as well as for the Nafion® membrane, but the AMPS copolymers adsorb significantly more water than Nafion®. At 90% RH, 10% AMPS contained 23 wt.% water, Nafion® 14 wt.%. At 100% RH and for immersed samples, increases in water adsorption are even more dramatic, with 10% AMPS adsorbing 69–71 wt.% water while Nafion®
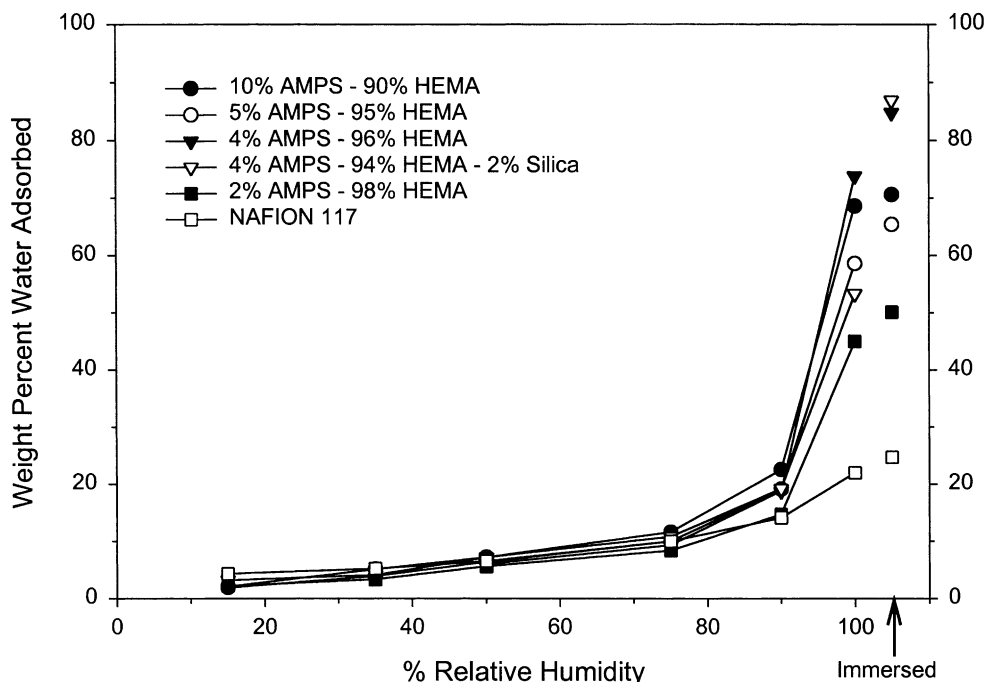

Fig. 2. Water uptake as a function of RH.

adsorption ranges from 22–25 wt.%. Membranes immersed in liquid water adsorbed even more water than those equilibrated in saturated water vapor.

The two apparent regions of water adsorption have previously been observed and explained for Nafion® and seem appropriate for the AMPS copolymers as well. In the region of little increase in water content (<75% RH), uptake of water is involved in the solvation of the protons and sulfonate ions in the membrane [12,13]. In the region above 75% RH, water is involved in filling the pores and swelling of the polymer [12,13]. Two explanations have been offered for differences in water content for membranes equilibrated with water vapor and with liquid water [13]. The first involves several experimental difficulties such as obtaining a truly saturated vapor phase. The second is that adsorption from the vapor phase involves condensation of water on the hydrophobic surfaces of the polymer, which is less favorable than imbibing liquid water.

Nafion®–silica hybrid membranes have shown decreased methanol uptake [14–16] and lower methanol permeability [14] than pure Nafion®. Silica-containing Nafion also provides increased water content at temperatures below 120 °C [14–17]. Other polymers such as poly(vinylidene fluoride-co-hexafluoropropylene) blended with styrene [18] showed increased conductivity with the addition of silica. Watanabe and co-workers also claim the use of silica with various polymers including Nafion® to increase water content and conductivity [19,20]. However, Miyake et al. [17] found conductivity of Nafion® to decrease with the addition of silica. We added untreated fumed silica (2 and 5 wt.%) to polymer solutions prior to casting, anticipating enhanced conductivity by increasing water content. In addition, fumed silicas form 3-D branched chain aggregates. This entanglement could enhance mechanical strength of the polymer, and in fact has been used by others [10] to improve mechanical properties of gel electrolytes containing AMPS.

Comparison of water adsorption for a 4% AMPS copolymer with and without 2% silica shows similar water uptake, with the silica-containing polymer adsorbing about 1–1.5 wt.% more water. There is one exception at 100% RH, where the silica-containing film adsorbs significantly less water, but again exceeds the "plain" films in water-adsorbing capacity when immersed. The experiment was repeated several times to confirm this unexpected incongruity. No explanation for this anomaly is offered.

Increasing the silica content to produce a 4% AMPS—91% HEMA—5% Silica membrane did not improve water adsorption capacity. Actually, water adsorption was slightly less than films containing 2% silica (not shown). The improvement seen by adding silica to Nafion® may occur because relatively little water is normally adsorbed, so silica is effective in increasing the total amount of adsorbed water. In contrast, high levels of water are already adsorbed by AMPS copolymers without silica, so silica does little to increase the overall uptake of water. At higher concentrations (e.g. 5 wt.%), silica effectively reduces the ability of the films to adsorb water, probably by restricting the ability of the polymer to swell.

A plot of adsorbed water as a function of percent AMPS contained in the copolymer is shown in Fig. 3. We expected water uptake to increase with increasing wt.% of AMPS in the copolymer, but a maximum unexpectedly occurred for membranes containing only 4% AMPS either immersed in water or equilibrated at 100% RH. This suggests that this
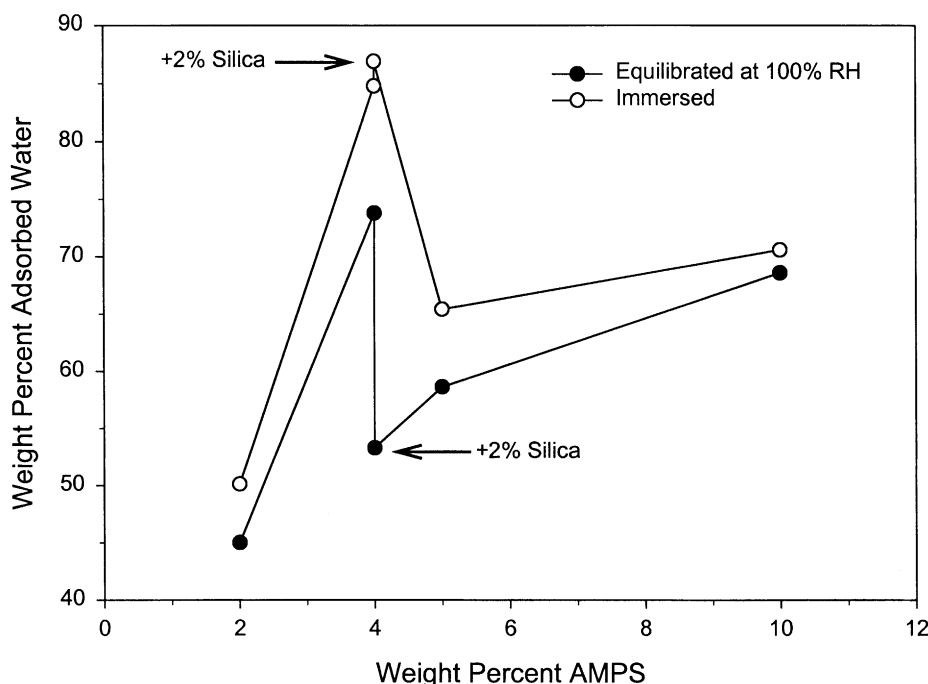

Fig. 3. Water adsorbed as a function of AMPS content.

composition should show the highest proton conductivity because of its higher water content.

3.3. Loss of adsorbed water

Because the AMPS–HEMA copolymer adsorbs a significant amount of water, we hoped that the polymer would retain more water and resist drying or at least dry at a slower rate than Nafion[®] 117. The addition of silica was also used in hopes of improving water uptake and retention. To determine how well adsorbed water was retained, samples of AMPS–HEMA and Nafion[®] were equilibrated at 100% RH or immersed in liquid water, then exposed to ambient conditions. Weight loss was measured as a function of the total time samples were exposed to air. Immersed samples initially retained more water than those equilibrated at 100% RH. However, after 2 h the wt.% adsorbed water was the same for both samples. Surprisingly, both Nafion[®] and the AMPS copolymer lost the bulk of their adsorbed water very quickly. Within 15 min, over 50% of the adsorbed water was lost, and over 80% was lost within 1 h for all but 5% AMPS—95% HEMA, which retained slightly more water (Fig. 4). Loss of water slows after 1 h, approaching a state of equilibrium. Films containing 5% AMPS retained more water than films with 2% AMPS as we expected. In general, the various ratios of AMPS–HEMA copolymer retained less than 10% of the adsorbed water, while Nafion[®] retained about 15%. However, because AMPS copolymers adsorbed much more water than Nafion[®], the wt.% water remaining in the AMPS copolymers is equal to or slightly greater than that of Nafion[®].

The addition of 2% silica with 4% AMPS showed a similar rate of water loss as compared to films containing 4% AMPS without silica. Actually, films with silica lost water at a slightly faster rate than those without silica (Fig. 5), which is contrary to what was expected especially since adsorbed water increased by ~1.5% with the addition of silica. Apparently, water is bound more tightly in the sulfonic acid domains of the copolymer membranes than by the silica particles. The drying rate data for 4% AMPS with and without silica is essentially identical to that for 5% AMPS that had been immersed in water before drying. An increase in silica content to 5 wt.% provided no benefit in water retention. Membranes dried out as quickly as those containing 2 wt.% silica, and overall, lost slightly more water.

3.4. Ionic conductivity

Based on the increased water content of the AMPS copolymers (compared to Nafion[®]) in saturated water vapor, we anticipated ionic conductivity to be high, perhaps exceeding that of Nafion[®]. Conductivity was measured by the four-point probe method with a test fixture designed and constructed by Case Western Reserve University [11]. At 100% RH and room temperature, conductivity of Nafion[®] 117 measured between 0.08 and $0.09\,S\,cm^{-1}$, comparable to results published by others [21–24].

AMPS–HEMA copolymer films containing 5 to 10% AMPS were too soft when hydrated to allow rough handling. Consequently, films had to be handled carefully to prevent tearing, and impedance measurements were difficult since the voltage-measuring pins of the conductivity cell could easily penetrate/puncture the films if too much pressure was applied. A few impedance measurements of the 10%
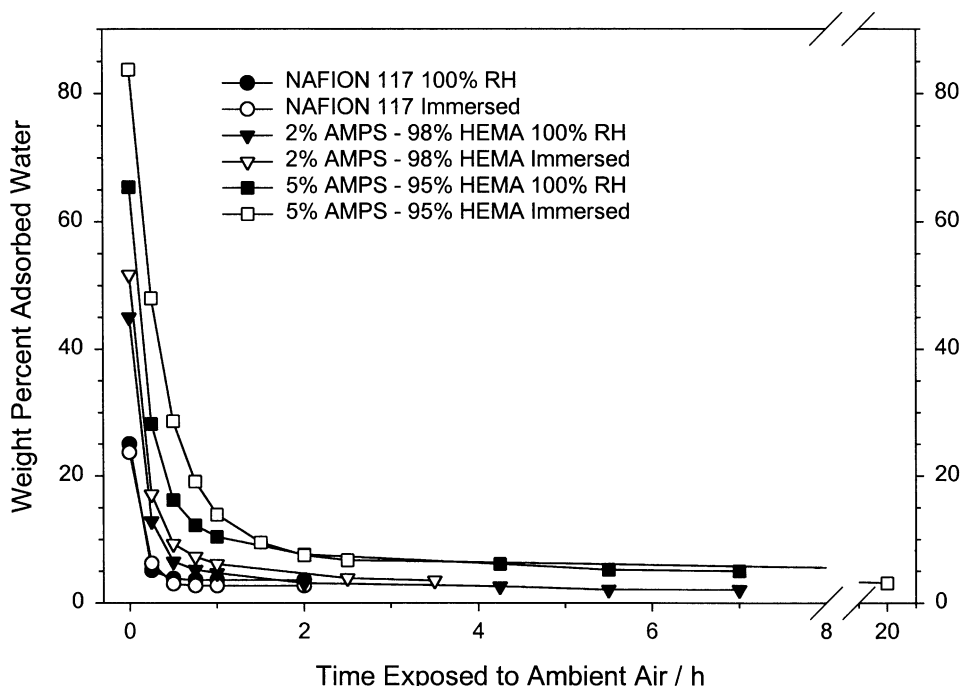

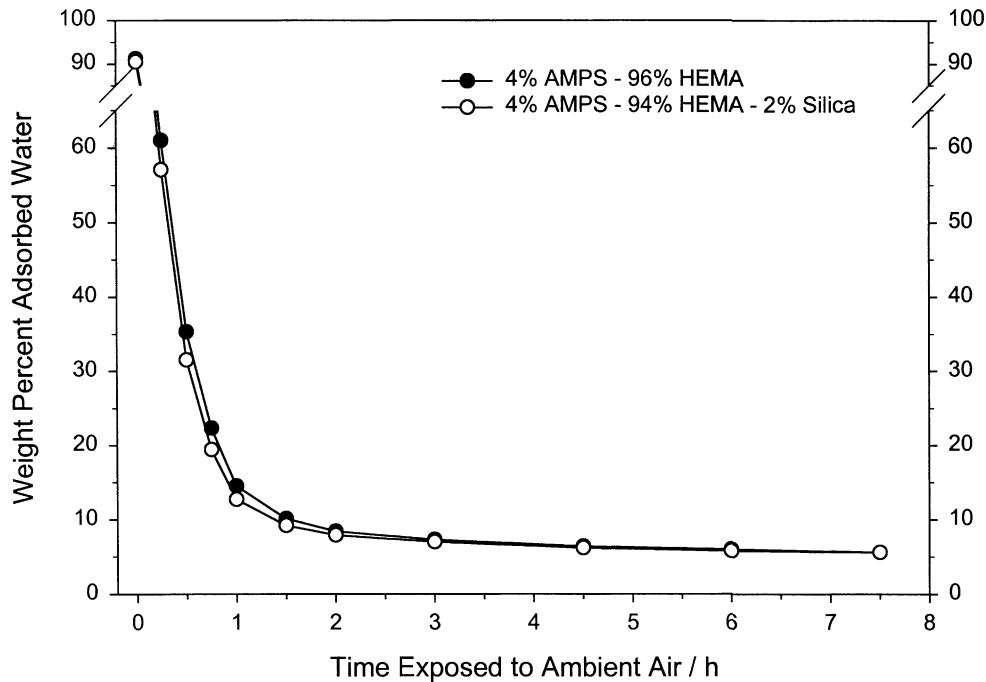Fig. 4. Water loss of hydrated films at ambient conditions over time.

Fig. 5. Water loss of hydrated films with and without fumed silica at ambient conditions over time.

AMPS—90% HEMA films showed conductivity to be nearly equal that of the Nafion® 117 polymer. Because of the difficulty in handling, measurements of 5 and 10% AMPS-containing films were not thoroughly investigated.

Conductivity as a function of temperature for Nafion® 117, 2% AMPS—98% HEMA, and 4% AMPS—96% HEMA are compared in Fig. 6. The conductivity of Nafion® 117 is fairly constant with temperature, showing only a slight

increase with temperature from ambient to 80 °C. Conductivity at 23 °C was 0.076 S cm^{-1}, increasing to 0.160 S cm^{-1} at 80 °C. Conductivity of films containing 2% AMPS was about 500 times lower, measuring 1.55×10^{-4} S cm^{-1} at room temperature, but showed a significant increase with temperature, reaching 1.6×10^{-3} S cm^{-1} at 80 °C.

Doubling the AMPS content to 4% increased the ionic conductivity considerably to 0.029 S cm^{-1} at room
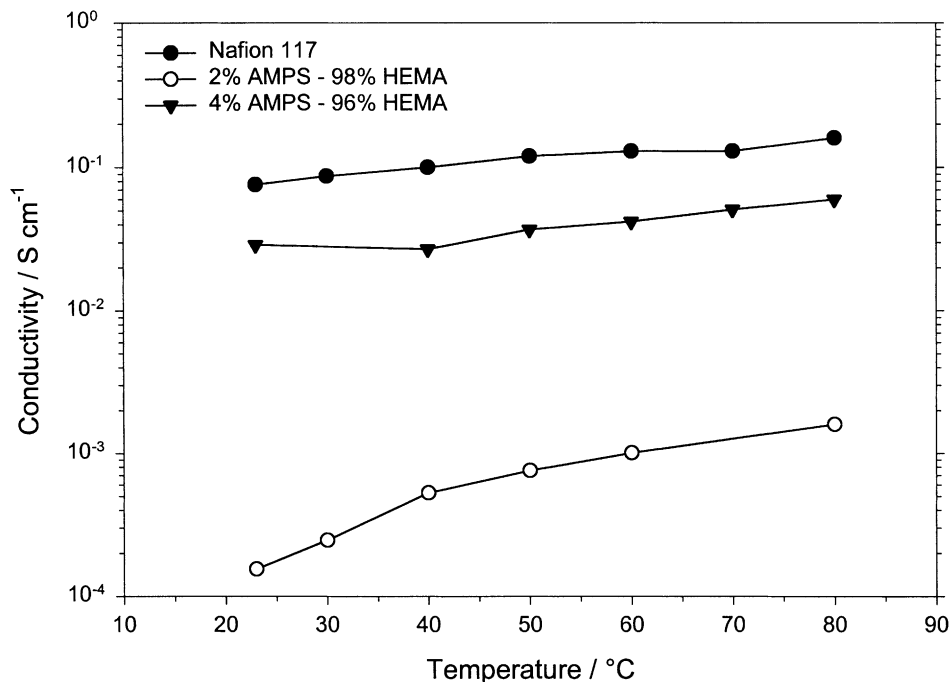

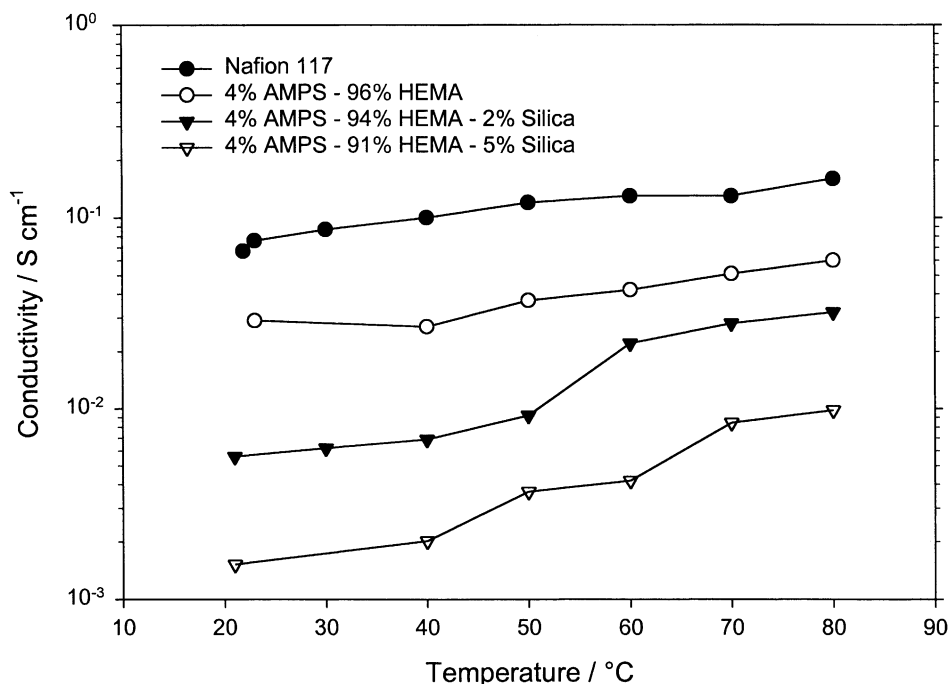Fig. 6. Ionic conductivity as a function of temperature.

Fig. 7. Ionic conductivity as a function of temperature for polymers with and without silica added.

temperature and 0.06 S cm^{-1} at 80 °C. Like Nafion®, there is only a slight increase in conductivity with increasing temperature. Considering the physical characteristics associated with various levels of AMPS, 4% AMPS is the maximum level that provides an easily handled hydrated membrane, and provides the best conductivity we can expect from a copolymer film containing only these two polymers. Consequently, we must rely on other additives (e.g. Nafion®, silica) or additional copolymers to improve ionic conductivity and physical characteristics.

Although, silica had no significant beneficial effect on water adsorption and retention, it was hoped that it could perhaps improve conductivity. Silica itself has been shown to be a proton conductor, with conductivity increasing with temperature and RH [25]. There are conflicting reports that proton conductivity decreased as silica content in Nafion® was increased [17], and that conductivity was increased through the use of silica [19,20]. We prepared AMPS–HEMA copolymers fixed at 4% AMPS and also containing 2 and 5% fumed silica. Conductivity as a function of temperature is shown in Fig. 7. Conductivity of film with 2% silica exhibits significantly lower conductivity than film without silica added. Increasing silica content to 5% further decreased conductivity. Possible explanations are that silica is blocking ion-conducting pathways and slowing ion movement by causing ions to travel around silica particles, or that the silica is restricting the ability of the membrane to swell and is thereby impeding the diffusion of water. Unlike copolymer without silica, conductivity increases dramatically with increasing temperature. However, rather than a linear increase as seen with the other films, the silica-containing membranes exhibit a break somewhere between

40 and 55 °C where conductivity increases sharply and then continues linearly. This suggests that some activation energy is exceeded above 50 °C.

4. Conclusions

In our search for a less expensive alternative to Nafion®, cross-linked AMPS–HEMA copolymers and copolymers containing other additives were investigated to evaluate their possible use as proton-conducting polymer membranes for use in fuel cells. Solution cast films were brittle when dry and very pliable when hydrated, but less rugged than Nafion® 117. AMPS–HEMA copolymer membranes with <5 wt.% AMPS were the most rugged and easily handled in the hydrated state. As wt.% AMPS increases, the tendency is to form softer films that become increasingly gel-like.

Compared to Nafion® 117, water adsorption of AMPS–HEMA copolymer was dramatically higher at 100% RH, and was greatest for compositions of 4% AMPS—96% HEMA. Water loss under ambient conditions was somewhat less for about an hour, but not appreciably different than Nafion® beyond 2 h.

Copolymers containing only 2 wt.% AMPS exhibited poor ionic conductivity. Increasing AMPS content to 4 wt.% greatly improved conductivity, which was slightly less than that of Nafion® at temperatures between ambient and 80 °C. The 4% AMPS—96% HEMA copolymer provided the highest conductivity with reasonable mechanical integrity when hydrated.

Seeking to increase the amount of adsorbed water, to retard membrane dry-out, and to increase ionic conductivity,

fumed silicas were added to the copolymer. Water adsorption was not appreciably affected, and loss of water under ambient conditions was comparable to copolymer without silica. Ionic conductivity was actually worse, probably due to the silica particles interfering with the ion-conducting pathways.

Although, 4% AMPS—96% HEMA copolymer was found to be a good ion conductor, improvements are still needed to be competitive with Nafion® as a polymer electrolyte for a fuel cell. Physical properties also need improving since in the dry state the polymer is too brittle for easy handling and processing of membrane electrode assemblies. Other copolymers are being investigated to improve membrane flexibility and ionic conductivity, and to produce a film that is less permeable to methanol than Nafion® 117. Ongoing work on methanol permeability will be included in a future report.

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