

Photocurable Poly-AMPS-Based Proton Exchange Membranes For Fuel Cells

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Introduction

Polymer electrolyte membrane fuel cells (PEMFC) continue to garner great interest particularly in the automotive sector as eco-friendly and energy efficient alternatives to internal combustion.¹ The heart of any PEMFC is the polymer exchange membrane (PEM) which serves the dual role of separating the anode and cathode as well as transporting protons from the former to the latter.

To stand any chance of successful application in a fuel cell, the PEM must fulfill a number of criteria. The membrane should remain mechanically stable across a range of temperatures and relative humidities. Chemical stability in a highly acidic environment and in the presence of radicals is also important. Proton conductivity should be as high as possible and fuel crossover should be as low as possible. Water management is also very important since it has direct bearing on fuel cell performance. During operation, water is generated at the cathode and an electro-osmotic drag force is produced, which depletes the water content at the anode side. To prevent the anode from drying out, PEMCs are optimally operated from 60 to 80 °C which necessitates a cooling system. Under heavy load however, cooling may not be sufficient and indeed the membranes are expected to operate up to 100 °C. These difficult criteria greatly limit applicable materials as PEMs. DuPont's Nafion®, which is a polymer based on a perfluorinated sulfonic acid vinyl monomer, has long been heralded as the polymer de facto in this field although its high cost is a burden.³ Indeed a polymer which offers comparable performance at lower cost can truly help advance the use of PEMs and thus portable fuel cells.

Over the last 30 years, a variety of polymers have been developed and investigated as potential replacements for Nafion®.^{4, 5} As with Nafion®, the majority of investigated polymers are poly sulfonic acids though alternate ionomers based on phosphonic acid^{6, 7} and benzimidazole⁸ are also considered. As a class, sulfonated aromatic polymers⁹ tend to be easier to synthesize and thus less expensive than Nafion®. Polymers synthesized from less expensive strong acid vinyl monomers such as 2-acrylamido-2-methylpropane sulfonic acid (AMPS) are also considered and indeed this monomer is utilized within this paper.¹⁰⁻¹³ An additional benefit of this monomer is that it is amenable to photo induced polymerization which we herein present as a relatively uncomplicated method for preparing PEMs with nevertheless quite high proton conductivity. Further tests are planned to determine the real applicability of such polymers for use in PEMFCs.

Results & Discussion

Polymers from AMPS

AMPS (Figure 1) was selected as a low cost and yet highly acidic acrylate monomer. The linear homopolymer of AMPS readily dissolves in water making crosslinking a necessity. A variety of commercial multi functional acrylate monomers are available to copolymerize with and thus crosslink AMPS. An appropriate crosslinker (XL) should be miscible with AMPS, react at a similar rate, and impart no negative influence on the conductivity of the copolymer membrane.

Crosslinking and conductivity

Before evaluating different crosslinkers, we wanted to know the effect of concentration of both AMPS and the crosslinker on swelling and conductivity. For these investigations, we chose a 700 m.w. polyethylene diacrylate (PEG700DA) as crosslinker because it is flexible, water soluble, and should have comparable reactivity of other commercial diacrylates. PEG700DA was copolymerized with AMPS in different ratios so that concentration of AMPS was adjusted from 0.5 M to 2.0 M while the molar ratio of crosslinker was varied from 4 to 13.3%. Polymerization was conducted within a porous polypropylene membrane to provide support to the gels.

Conductivity increased with AMPS concentration, while the effects of XL concentration were less significant. The thickness of the membrane is primarily attributed to swelling where higher concentration of AMPS increases swelling and higher XL concentration reduces swelling. Although the XL had only a negligible influence on the conductivity, the influence on the thickness was much greater. At low AMPS concentrations, the crosslinker had no influence on the thickness, but at higher AMPS concentrations, a higher concentration of the crosslinker suppressed swelling and reduced membrane thickness.

Evaluation of commercial crosslinkers

Seeing that higher monomer concentrations led to higher conductivity, we utilized higher AMPS concentrations than initially foreseen. AMPS is very soluble in water, which allowed concentrations of 2 M and 4 M to be used in combination with various levels of XL. We chose a 400 m.w. PEGDA as a hydrophilic XL and decane diol diacrylate (DDDA) as a more hydrophobic XL. Since DDDA is not soluble in water we had to find an appropriate solvent to mix it with the hydrophilic AMPS. AMPS is very soluble in water but sparingly so in most organic solvents. We found NMP however to be amenable to both of these monomers. Conductivity of polymers based on DDDA was found to be very low and thus all subsequent investigations were performed with hydrophilic crosslinkers.

By comparison, membranes formed with PEGDA crosslinker showed much higher proton conductivity. Unfortunately, subsequent aging experiments indicated that the PEG-based acrylates were not stable to acid at high temperature. For these stability tests, samples with PEG-based acrylate XL were extracted in DI water for 24 h and then aged for 24 h in fresh DI water at 80 °C. Conductivity measurements before and after the ageing showed a conductivity

loss of 90%. The acidic conditions inside the membrane are thought to accelerate the cleavage of ester bonds of the acrylate matrix. As support to this hypothesis, when we neutralized the AMPS in the membrane to its sodium form we observed no loss of conductivity.

Methacrylamide based XLs

Since methacrylamides are known to be more stable against hydrolysis compared to methacrylates, three new multi functional methacrylamide-based XLs (Figure 1) were synthesized to copolymerize with AMPS.

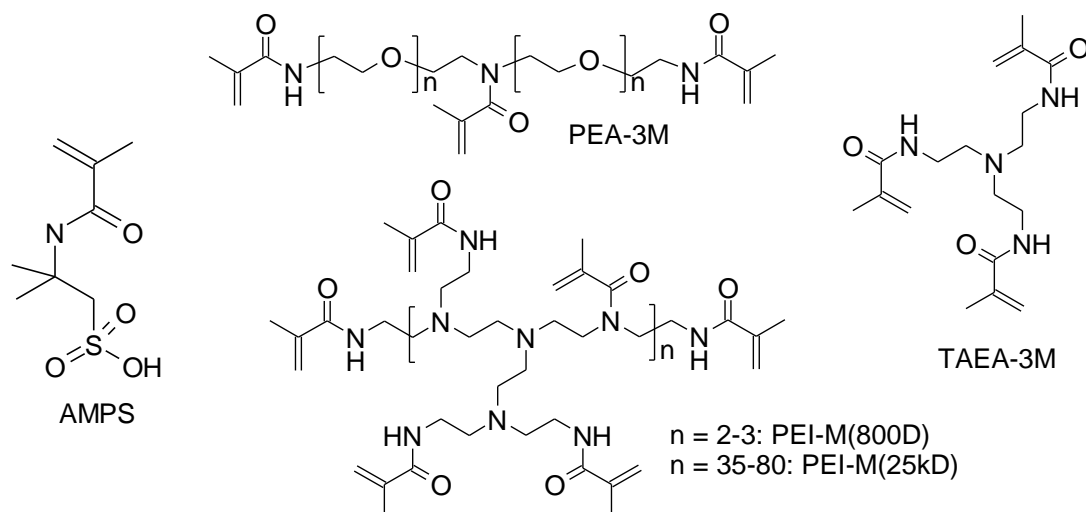


Figure 1. Sulfonic acid monomer AMPS and synthesized methacrylamide-based XLs

The amine-based reagents were converted with an excess of methacrylic anhydride at 0-5 °C to the corresponding methacrylamide. The stated molecular weight for PEI XLs is the M_w of the precursor branched amine and the structure in Figure 1 is deliberately simplified for readability. To decompose residual methacrylic anhydride, a mixture of 50% DI water and 50% saturated sodium carbonate solution was added and the temperature was increased to 60 °C for 3 hours. The products were obtained by extraction with ethyl acetate with a yield between 49% and 96%.

To test conductivity, porous support membranes were filled with an aqueous solution of AMPS, the methacrylamide-based XL and photoinitiator. Concentration of the XL was varied from 5 to 20 mol% (based on functional groups) and AMPS concentration was held at 4M. Following photopolymerization, residual monomers were removed by repeated washing with DI water. Conductivity of the polymers is shown in the following figure.

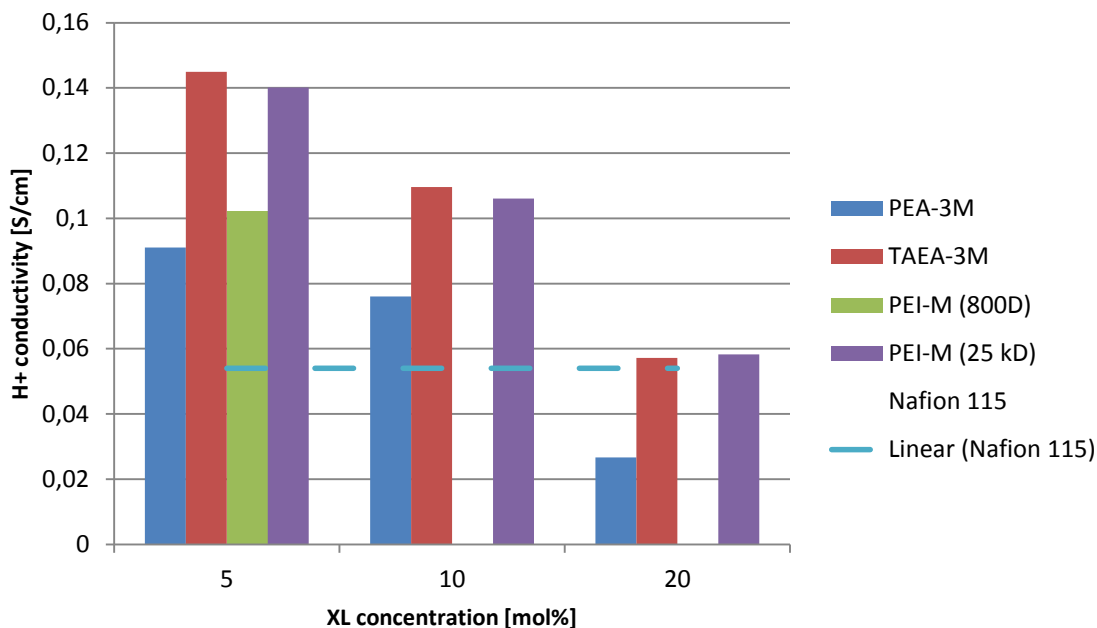


Figure 2. Conductivity as a function of the XL concentration (mol% of AMPS) in different formulations

Figure 2 shows that contrary to the case of the ester-based XLs, conductivity decreased with increasing XL concentrations. This might be explained by the fact that the tested methacrylamide XLs were multifunctional while the acrylate XLs were difunctional. This allows lower amounts of XL to reach the optimum crosslink density. Membranes prepared with 5% of all four of the methacrylamide XLs provided conductivity in excess of all the tested membranes based on acrylate XLs. As had been expected thermal stability was also greatly improved. PEA-3M was more thermally stable than the acrylate XLs, but still after ageing showed signs of degradation with conductivity diminishing by 70%. Since amides are known to be very stable, we consider degradation of ether bonds to be a more likely culprit leading to conductivity loss.

The PEI-M XLs are based on branched oligomers of ethylene diamine and are structurally similar to TAEA-3M although they have higher molecular weights. The PEI-M monomers increase the viscosity of the formulation while conductivity as a function of the XL concentration behaves quite similarly. While PEI-M(800D) showed promising conductivity when used at 5%, membranes formed using higher percentages had mechanical properties not amenable to conductivity measurements. On the other hand, membranes formed with equal percentages of TAEA-3M and PEI-M(25kD) exhibited nearly the same conductivity. Membranes with 5% of either of these XLs showed higher conductivities than those with PEA-3M and more than 2.5 times higher than Nafion®. However, PEI-M polymerized at a slower rate than PEA-3M which necessitated longer irradiation times.

Thermal and hydrolytic stability of polymers crosslinked with TAEA-3M and PEI-M was assessed by the same method used for PEGDA membranes. In these tests however conductivity was found to remain high. Therefore TAEA-3M and PEI-M(25kD) are preferable XLs for use in fuel cells, because they provide membranes with both conductivity and high stability against hydrolytic cleavage at elevated temperatures. It was found that formulations with higher concentrations of PEI-M(25kD) became cloudy when polymerized and TAEA-3M containing formulations remained clear. Since solubility is an important parameter in membrane preparation, the smaller TAEA-3M was chosen as XL for further studies.

Asymmetric AMPS-based membranes with TAEA 3M as XL

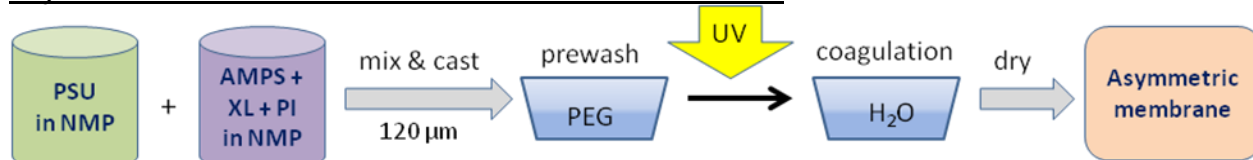


Figure 3. Steps to prepare asymmetric membrane

In a previous publication,¹⁴ methods are described for preparing asymmetric membranes with interpenetrating proton-conducting morphology which lends itself to higher conductivity values. The method consists of multiple steps as shown in Figure 3. In the first step the support polymer polysulfone (PSU) is dissolved in NMP and to this is added the other components (AMPS, XL, and photoinitiator PI also in NMP). This viscous mixture is cast onto a glass plate and then spread with a Bird bar to a thickness of 120 μm . The film is rapidly prewashed in a polyethylene glycol (PEG) solution followed by UV irradiation to polymerize and crosslink the AMPS. The resulting interpenetrating network (IPN) is then submerged in a water bath where solvent NMP leaches out.

Confocal laser scanning microscopy (CLSM) images of the top and bottom surfaces of the wet membranes demonstrate the asymmetric morphology of the system. Larger pores are preferred for the bulk of the material to facilitate water and proton while smaller pores on the top surface help reduce fuel crossover.

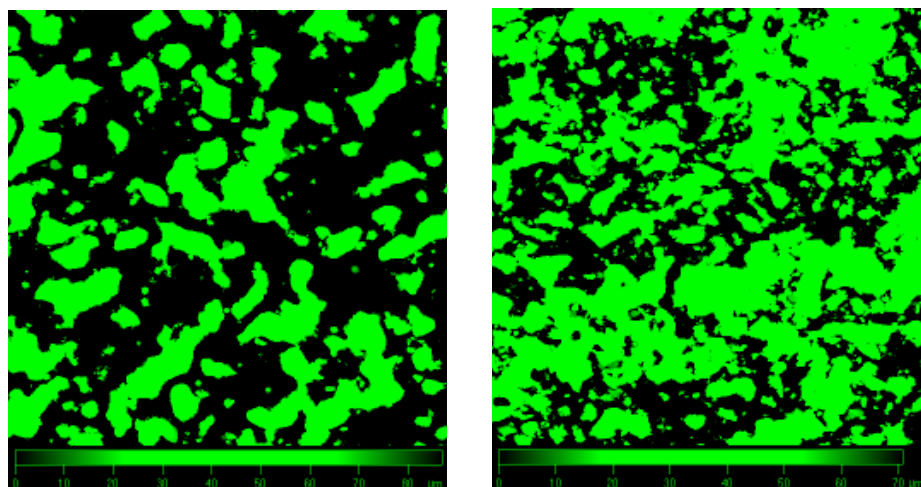


Figure 5. CLSM of asymmetric membrane: topside (left) and bottomside (right)

TAEA-3M was used as XL in the membrane fabrication process since it had shown the best results in the preliminary experiments. The PSU polymer concentration was 16 wt% or 18 wt%, the AMPS concentration was 1.2 and 1.8 mmol/g and the XL concentration was varied between 3, 15, 30 and 60 mol% (based on polymerizable groups relative to AMPS). Figure 4 shows the proton conductivity of these asymmetric membranes.

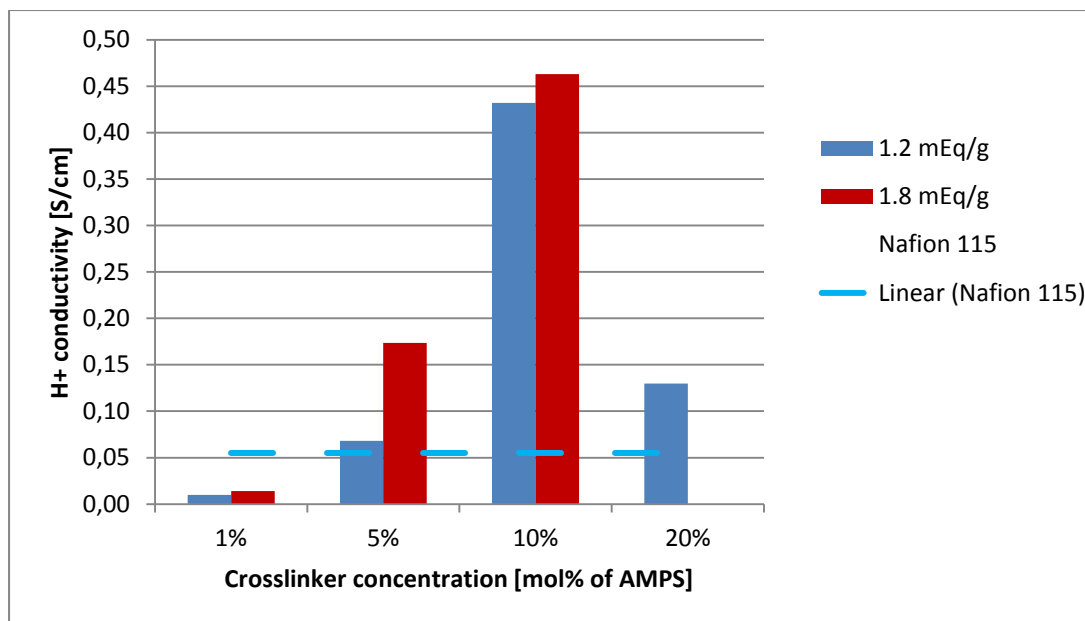


Figure 4. Proton conductivity of asymmetric membranes (TEAE-3M used as XL)

The membranes exhibited very high proton conductivity. XL concentration was adjusted and found to be optimal at 10%. At this concentration, proton conductivity of the membrane was found to be 8 times higher than Nafion®. A low XL concentration led to more swelling and a reduction in the concentration of sulfonic groups per unit volume. At higher concentrations however, the XL diluted the ionomer resulting in a lower concentration of sulfonic groups per unit volume and less mobility and water uptake.

Conclusion

The effects of newly synthesized and commercially available XLs on PEM conductivity have been investigated in membrane-constrained PAMPS gels. Hydrophobic monomers were found to significantly reduce conductivity. PEG-based acrylates exhibited good conductivity, but were easily hydrolyzed in acid at elevated temperature. Acrylamides did not suffer from this disadvantage and, in addition, showed better conductivity than acrylate-based XLs. The best results were achieved with acrylamides having tertiary amino groups in their backbone. Asymmetric membranes based on AMPS and polysulfone as support were fabricated by a multi-step photoinduced IPN method. Asymmetric membranes prepared in this style were found to exhibit conductivity up to 8 times higher Nafion® 115.

Acknowledgements

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