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ARTICLE

High Performance Cross-Linked Poly(2-acrylamido-2-methylpropanesulfonic acid)-Based Proton Exchange Membranes for Fuel Cells

Hanbin Diao,[†] Feng Yan,*[,†] Lihua Qiu,[†] Jianmei Lu,[†] Xinhua Lu,[†] Bencai Lin,[†] Qing Li,[†] Songmin Shang,*[,‡] Wenming Liu,[§] and Jianguo Liu[§]

[†]*Key Laboratory of Organic Synthesis of Jiangsu Province, School of Chemistry and Chemical Engineering, Jiangsu Key Laboratory for Carbon-Based Functional Materials & Devices, Soochow University, Suzhou 215123, China,* [‡]*Institute of Textiles and Clothing, The Hong Kong Polytechnic University, Hong Kong, China, and* [§]*Eco-materials and Renewable Energy Research Center, Department of Physics and National Laboratory of Solid State Microstructures and Department of Materials Science and Engineering, Nanjing University, Nanjing 210093, China*

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ABSTRACT: Poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS) has been used for the preparation of proton exchange membranes (PEMs) due to the superior ability of sulfonic acid groups originated from AMPS in supporting proton conduction. Since PAMPS is water-swollen or even soluble in water, it is necessary to copolymerize AMPS with proper monomer oils to control the swelling and mechanical properties of membranes. However, as a water-soluble monomer, AMPS is generally immiscible with hydrophobic monomer oils. To overcome this obstacle, AMPS was converted to an ionic liquid (IL) form by neutralization with a Brønsted base, 1-methylimidazole. The resultant 1-methylimidazolium 2-acrylamido-2-methylpropanesulfonate ([MIm][AMPS]) is miscible with monomer oils and thus could be cross-linked with styrene, acrylonitrile, and divinylbenzene. The produced copolymer membranes in IL form were converted to acid form by treated with acid. Membranes in both IL and acid forms have good thermal stability and mechanical properties which could be further tuned by the content of cross-linking agent. The water uptake, swelling degree, proton conductivity, and methanol permeability of the membranes increased with the PAMPS content while decreased with cross-link agent content. The acid form PAMPS-based membranes showed high proton conductivity of 3.82×10^{-2} S/cm and low methanol permeability of 3.80×10^{-7} cm^2/s at 25 °C. The properties of the samples suggested that this type of cross-linked PAMPS-based membranes were particularly promising to be used as PEMs in direct methanol fuel cells.

Introduction

Direct methanol fuel cells (DMFCs) are promising energy conversion devices that convert the chemical energy stored in the fuel directly into electricity. Recently, DMFCs have been studied intensely because of their high power density, the ease of handling operating conditions, and possible applications in micro fuel cells.[1,2] The proton exchange membrane (PEM) is one of the most important components in DMFCs which serve as proton conductor and also as a separator between the anode and cathode. The most commonly used ionomer membranes, represented by Nafion membranes, have high proton conductivity and excellent chemical stability. However, practical application of Nafion membrane in DMFCs suffered from high permeability of methanol, which led to a decrease in overall cell efficiency and lifetime.[3] Therefore, development of new types of PEMs with high proton conductivity, good methanol resistant, and mechanical properties are in great demand before the commercialization of DMFCs.

New PEMs, such as sulfonated aromatic membranes,[4a−c] graft membranes,[4d] cross-linked,[5] and blend membranes,[6a] have been recently proposed and investigated. In most cases, high sulfonation level is required to achieve the polymer membranes with sufficient proton conductivity. Therefore, a typical anionic polyelectrolyte with sulfonic acid groups ($-SO_3H$) in its chemical structure, poly(2-acrylamido-2-methylpropanesulfonic acid) (PAMPS), has been chosen to produce PEMs. The choice of PAMPS is based on its high proton conductivity comparable to partially hydrated Nafion membrane under the same water content.[6b] In addition, it has also been demonstrated that the proton conductivity of PAMPS increases with water content up to $6H_2O$ per equivalent and then levels off.[6c,d]

Since PAMPS is generally water-swollen or even soluble in water, controlling the morphology of the membranes by either blending PAMPS with other polymers or polymerization of AMPS monomer within a swollen polymeric membrane has been extensively studied.[7−11] However, blends of immiscible polymers generally exhibit poor mechanical properties due to a coarse and unstable morphology, especially when swollen in water.[10] This obstacle could be overcome to a certain degree by copolymerization of AMPS with suitable monomers (such as 2-hydroxyethyl methacrylate (HEMA) and acrylic acid (AA)),[8a,11] and thus a high amount of sulfonic acid groups could be retained to achieve high proton conductivity. However, the produced PAMPS-based copolymers are still excessively water-swollen or even soluble in water. Recently, Texter and co-workers synthesized a reactive surfactant, ionic liquid-AMPS (IL-AMPS), where both the cation and anion are polymerizable.[7a] Polymerization of IL-AMPS produced polymers with high ionic conductivity and offer potential application for sensor, fuel cell, and battery technologies. The resultant poly(IL-AMPS) is not soluble in any solvents; however, extremely large degrees of swelling may be obtained in

*Corresponding authors. E-mail: fyan@suda.edu.cn (F.Y.); shang.songmin@inet.polyu.edu.hk (S.S.).

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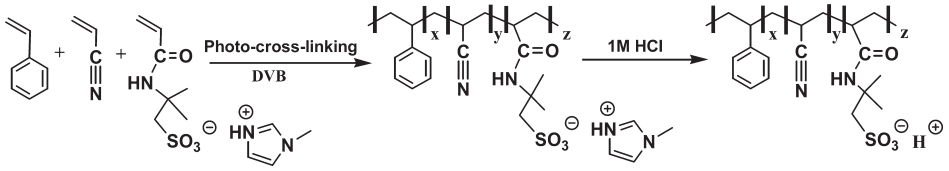
Scheme 1. Schematic Reaction Route for the Preparation of PAMPS-Based Membranes



appropriate solvents.[7a] Therefore, it is desirable to copolymerize or cross-link AMPS monomer with hydrophobic monomer oils to produce the membranes with both high proton conductivity and low swelling degree and good mechanical properties.

In situ chemical cross-linking is a feasible and effective method for the preparation of PEMs, which could not only suppress water swelling and but also improve the mechanical strength of membranes.[9b,12] Since AMPS monomer is immiscible with most of the monomer oils, bulk copolymerization of AMPS with hydrophobic monomer oils has been seldomly reported. Qiu et al. recently synthesized poly(AMPS-*co*-MMA) via copolymerization of AMPS and methyl methacrylate in water.[13] Solution casting of the resultant poly(AMPS-*co*-MMA) produced the membranes with high conductivity and low methanol permeability. However, one drawback of the solution-cast membranes is that the mechanical properties are generally poorer than these of cross-linked membranes. In addition, treating of hazardous chemical solvent is also a tedious problem.

The objective of this study is to synthesize new PEMs with high proton conductivity, low methanol diffusion coefficient, and good mechanical properties. To achieve this aim, PEMs were synthesized via in situ cross-linking of AMPS monomers with proper monomer oils. Since AMPS monomer is immiscible with most of monomer oils, it was first derived by converting the acid (H^+) form to an ionic liquid (IL) form by neutralization with a Brønsted base, 1-methylimidazole. The resulting 1-methylimidazolium 2-acrylamido-2-methylpropanesulfonate ([MIm][AMPS]) is miscible with some monomer oils and thus makes it possible to be bulk cross-linking with proper monomer oils (such as styrene and acrylonitrile). The obtained membranes in IL form were then converted to acid form by ion exchange with an acid to regenerate sulfonic acid groups, as shown in Scheme 1. In the resultant copolymer membranes, the hydrophilic region (sulfonate groups) facilitates the transport of proton while the hydrophobic region offers good mechanical strength.[14] The proton conductivity and mechanical properties of the membrane can be balanced by adjusting the content of PAMPS and cross-linking agent. The properties of the membranes such as water uptake, swelling degree, ionic exchange capability (IEC), proton conductivity, and methanol permeability were investigated in this work.

Experimental Section

Materials. Styrene, acrylonitrile, 2-acrylamido-2-methylpropanesulfonic acid (AMPS), 1-methylimidazole, divinylbenzene (DVB), benzoin isobutyl ether, diethyl ether, and ethyl acetate were used as purchased. All of the vinyl monomer oils were made inhibitor-free by passing the liquid through a column filled with basic alumina to remove the inhibitor and/or antioxidant and then stored at −5 °C. Deionized water was used for all experiments.

Synthesis of 1-Methylimidazolium 2-Acrylamido-2-methylpropanesulfonate ([MIm][AMPS]). [MIm][AMPS] was synthesized by mixing of AMPS with overdose molar amount of 1-methylimidazole in an ice−water bath. The mixture was stirred overnight, and the resultant viscous oil was washed with diethyl ether and ethyl acetate three times and then dried in dynamic vacuum at room temperature for 24 h. The chemical structure of the compound was confirmed by ^{1}H NMR (400 MHz, $CDCl_3$): 8.13 (s, 1H, C═O−N−H), 7.7 (s, 1H, N═CH−N), 7.2 (s, 1H, C═CH−N−C), 7.0 (d, 1H, N−CH═C−N), 6.1 (m, 2H, H−C═C, C═CH−), 5.5 (d, 1H, H−C═C), 3.82 (s, 3H, N−CH_3), 3.16 (s, 2H, CH_2−S), 1.5 (s, 6H, C−$(CH_3)_2$).

Preparation of Membranes. A mixture of styrene/acrylonitrile (3:7 molar ratio, 90−30 wt %), [MIm][AMPS] (10−70 wt %), divinylbenzene (4−20 wt % to the formulation based on the weight of monomer), and 0.5 wt % of photoinitiator benzoin isobutyl ether was stirred and ultrasonicated to obtain a homogeneous solution, which was then cast into a glass mold and photo-cross-linked by irradiation with UV light of 250 nm wavelength for 30 min at room temperature. The thickness of the membranes was controlled at around 50 μm by using standard spacer bars. The resultant membranes in IL form were immersed in 1 M HCl for 24 h to convert to acid form. Membrane samples were washed with deionized water and vacuum-dried at 80 °C for 24 h to remove the absorbed water before the characterization.

Characterization of Membranes. Fourier transform infrared (FT-IR) spectra of the polymers were recorded on a Varian CP-3800 spectrometer in the range of 4000−400 cm^{-1}. Dynamic mechanical analysis (DMA) measurements of membranes were conducted on a TA DMA Q800. The samples were heated from 30 to 120 °C at a heating rate of 5 °C/min. The sample chamber was purged with nitrogen at 20 mL/min throughout the test. Thermogravimetric analysis (TGA) measurements were made using a Perkin-Elmer. Samples were heated at 10 °C/min in a flowing nitrogen atmosphere. The amount of free water in fully hydrated membranes was determined by differential scanning calorimetry (DSC, Perkin-Elmer Diamond DSC) with a low-temperature measuring head. The samples were first cooled from room temperature to −50 °C and then heated to 40 °C at a rate of 5 °C/min in a flowing nitrogen atmosphere. Calculation of the amount of bulk water in the samples was done by integrating the peak area of the melt endotherm. An empty aluminum pan was used as a reference. The tensile properties of membranes were measured by using an Instron 3365 at 25 °C at a crosshead speed of 10 mm/min.

Water Uptake and Ion-Exchange Capacity (IEC). The membrane samples in both IL and acid forms were soaked in deionized water at room temperature for 24 h. The hydrated polymer membranes were taken out, and the excess water on the surface was removed by wiping with a tissue paper and weighed immediately. The water uptake W was calculated by the following equation:

$$W = \frac{W_w - W_d}{W_d}$$

where W_d and W_w are the mass of the dry and water-swollen samples, respectively.

The ion-exchange capacity value of the membranes in acid form was measured by the classical titration technique. The membranes were first converted to sodium form by immersing the membranes in 0.1 M sodium hydroxide for 24 h. Then the residual sodium hydroxide was titrated with HCl solution. The IEC value was calculated using the expression

$$\mathrm{IEC} = \frac{V_{\mathrm{NaOH}} C_{\mathrm{NaOH}} - V_{\mathrm{HCl}} C_{\mathrm{HCl}}}{m_{\mathrm{dry}}}$$

where V_{NaOH} and V_{HCl} are the volume of the NaOH and HCl consumed in the titration, respectively, C_{NaOH} and C_{HCl} are the molar concentration of the NaOH and HCl, which are titrated

by the standard oxalic acid solution, and m_{dry} is the mass of the dry membranes.

Swelling Ratio. The swelling ratio was characterized by linear expansion ratio (LER), which was determined by the difference between wet and dry dimensions of a membrane sample (3 cm in length and 1 cm in width). The calculation was based on the following equation:

$$\text{swelling } (\%) = \frac{X_{wet} - X_{dry}}{X_{dry}} \times 100$$

where X_{wet} and X_{dry} are the lengths of wet and dry membranes, respectively.

Proton Conductivity. The resistance of the polymer membranes was measured using the ac impedance method over the frequency range 1 Hz−1 MHz on electrochemical workstations (CHI604C, CH Instruments). Prior to the measurement, the rectangular piece of membrane was fully hydrated with deionized water and sandwiched between two gold electrodes in a glass cell.

Methanol Permeability. Methanol permeability measurements were conducted using a two-chamber glass diffusion cell.[14] The polymer membranes were equilibrated in deionized water for 24 h before being tightly clamped between two compartments. One compartment of the cell (V = 130 mL) was filled with 10 M methanol solution, and the other one (V = 130 mL) was filled with deionized water. A magnetic stirrer was used in each compartment to ensure solution uniformity throughout the measurements. The increase of methanol concentration with time in the water compartment was monitored using a gas chromatograph (Nicolet 6700, Thermo). Methanol permeability was determined from the slope of the plot of methanol concentration in the water compartment versus time. The methanol diffusion coefficient P was determined from the following equation:

$$c_B(t) = \frac{A}{V_B}\frac{DK}{L}C_A(t - t_0)$$

where C is the methanol concentration; A and L are the membrane area and thickness, respectively; D, K, and t_0 are the methanol diffusivity, solubility, and the measurement time lag, respectively. The product DK is the membrane permeability. C_B is methanol concentration at time t. The permeability P (cm^2/s) was calculated from the slope of the linear plot of C_B against using the following equation:

$$\text{slope} = \frac{dC_B(t)}{dt} = \frac{A}{V_B}\frac{DK}{L}C_A$$

$$P = DK = \text{slope} \times \frac{V_B L}{AC_A}$$

Chemical Stability. Oxidative stability of the membranes was examined by immersing the membrane samples in 3% H_2O_2 solution and Fenton's reagent (3% H_2O_2 aqueous solution containing 2 ppm $FeSO_4$) at 60 °C, respectively. The degradation of polymer membranes is evaluated by measuring the weight loss, proton conductivity, and visual observation.

Results and Discussion

FTIR Study. As a commercially available thermoplastic copolymer, poly(styrene-*co*-acrylonitrile) has been recently used for the preparation of polyelectrolyte for fuel cells[16,17] and dye-sensitized solar cells[18,19] because of their ease of processing, good chemical resistance, and excellent mechanical properties. Our previous studies demonstrated that chemical stability of the cross-linked poly(styrene-*co*-acrylonitrile) is even comparative to that of Nafion-117 membranes in Fenton's reagent under the same measuring conditions.[16] Therefore, styrene and acrylonitrile were chosen as monomer oils to copolymerize with [MIm][AMPS] for the preparation of polymer membranes in this work.

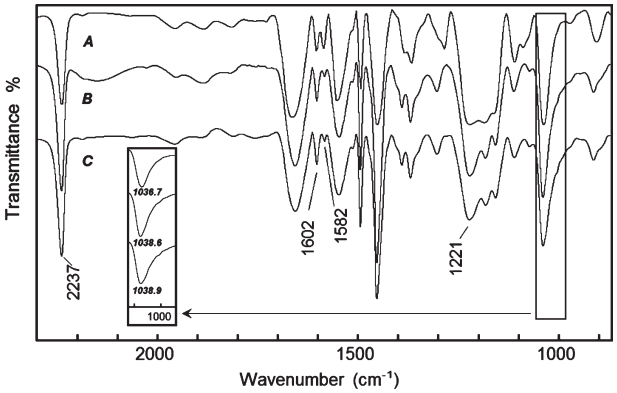


Figure 1. FT-IR spectra of $PAMPS_{60}$−DVB_{10} membranes in (A) IL form, (B) acid form (after 24 h treatment in 1 M HCl), and (C) acid form (after 36 h treatment in 1 M HCl). The inset shows the shift of symmetric stretching vibrations of sulfonate ($-SO_3^-$) groups.

A mixture of styrene/acrylonitrile (3:7 molar ratio, 90−30 wt %), [MIm][AMPS] (10−70 wt %), divinylbenzene (4−20 wt % to the formulation based on the weight of monomer), and 0.5 wt % of photoinitiator benzoin isobutyl ether was stirred and ultrasonicated to obtain a homogeneous solution and photo-cross-linked in a glass mold. The resultant membranes in IL form were converted to acid form by immersing the membranes in 1 M HCl. The produced membranes are denoted as $PAMPS_x$−DVB_y, the subscripts x and y indicate the weight ratio of PAMPS and DVB in the membrane, respectively.

Figure 1 shows the FT-IR spectra of the PAMPS-based copolymer membranes in both IL and acid forms. The characteristic absorption band at 2237 cm^{-1} is ascribed to the stretching vibration of cyano groups (C≡N), and the peak at 1602 cm^{-1} is assigned to the skeletal vibration of benzene rings of polystyrene units. In the IL form membrane (Figure 1A), an absorption peaks at around 1582 cm^{-1} was clearly observed based on the vibrational mode of 1-methylimidazolium cations. It should be noted that the intensity of the peak at 1582 cm^{-1} decreased and almost disappeared in the acid form membranes (Figure 1B,C). The absorption peaks at around 1036 and 1221 cm^{-1} were assigned to the symmetric and asymmetric stretching vibration of sulfonate ($-SO_3^-$) groups (Figure 1A).[9b] The absorption peak at 1036.7 cm^{-1} shifted to 1038.6 cm^{-1} in acid form membranes (Figure 1B,C, inset). It has been reported that symmetric stretching vibration of sulfonate groups will shift with the change of the environment around the sulfonic acid groups, such as cation radius and the ionic interaction between sulfonate groups and cations.[20] In the present system, both the reduction of the absorption peak at 1582 cm^{-1} and the shift of 1036.7 cm^{-1} peak indicate the successful cation exchange of sulfonate groups, which changed from 1-methylimidazolium cations to hydrogen cations (H^+).

Mechanical Properties. Parts A and B of Figure 2 show the photograph of the produced PAMPS-based membranes in IL and acid form, respectively. Membranes in both two forms are free-standing, transparent, and flexible and can be easily cut into any desired sizes and shapes or be bent with one pair of tweezers (Figure 2C). Table 1 shows the mechanical properties of acid form PAMPS-based membranes measured at room temperature. The tensile strength of the membranes is in the range of 8−34 MPa. Since all the membranes were highly cross-linked, high Young's modulus and low elongation at break were obtained. To further

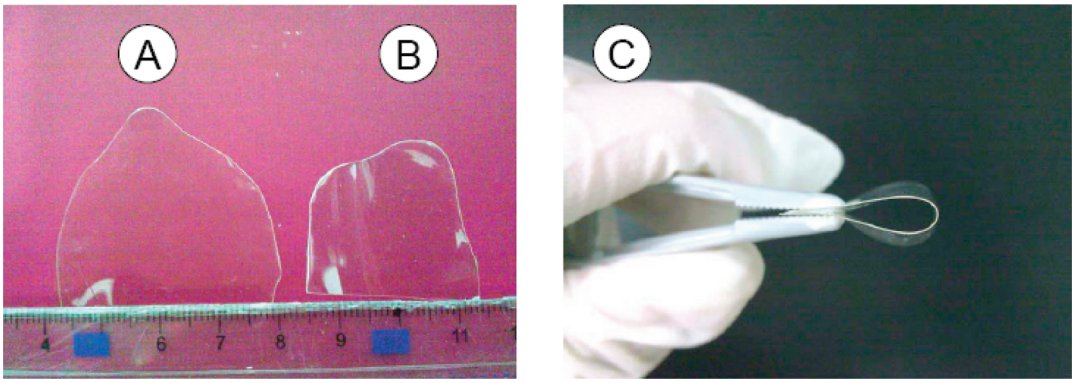


Figure 2. Photograph of the $PAMPS_{60}-DVB_{10}$ membrane in (A) IL form, (B) acid form, and (C) an acid form membrane bent with one pair of tweezers.

Table 1. Mechanical Properties of PAMPS-Based Membranes in Acid Form

polymer membranes	tensile strength (MPa)	Young's modulus (GPa)	elongation at break (%)
$PAMPS_{30}-DVB_{10}$	33.91	1.05	11.87
$PAMPS_{50}-DVB_{10}$	26.56	0.76	10.21
$PAMPS_{60}-DVB_{10}$	14.75	0.47	9.06
$PAMPS_{60}-DVB_{12}$	9.85	0.39	4.45
$PAMPS_{60}-DVB_{16}$	8.00	0.43	3.64

investigate the mechanical properties at a high temperature, DMA measurements at 50 and 80 °C were performed on the membranes, respectively. An acid form membrane of $PAMPS_{60}-DVB_{10}$ (containing 60 wt % PAMPS and 10 wt % DVB) showed a storage modulus of 2750 MPa at 50 °C, which decreased to 2400 MPa at 80 °C. Both two values are about 10 times higher than those of Nafion-117 membrane (300 and 180 MPa at 50 and 80 °C, respectively).[21] Chemical cross-linking is an effective method to improve the mechanical properties of polymer membranes. It is not surprising that increase of DVB content could significantly increase the storage modulus of the membrane. When the content of DVB was increased to 18 wt %, the storage modulus of the membrane was increased to 2840 MPa at 50 °C and 2600 MPa at 80 °C, respectively. These results indicate that the prepared PAMPS-based membranes were strong and tough enough for DMFCs application.

Water Sorption Behavior. Table 2 shows the water uptake, swelling degree, and ion-exchange capacity (IEC) of PAMPS-based membranes. The water uptake and swelling behavior of the membranes are key factors which significantly affect the proton conductivity, methanol permeability, and mechanical properties of membranes. It can be clearly seen that the water uptake increased with the increment of PAMPS content because of more sulfonate groups incorporated within the PAMPS-based membranes. The incorporation of more sulfonate groups could form the larger ion clusters within the membrane and thus led to the absorption of more water. When PAMPS content is high than 40 wt %, the water uptake increased sharply with the rise of PAMPS content. In the case of $PAMPS_{70}-DVB_{10}$ in acid form, the water uptake was as high as 173%. It should be noted that all the membranes in acid form show higher water uptake than the corresponding membranes in IL form, especially at high PAMPS content. Since the amount of sulfonate groups is same in both IL and acid forms, the higher water uptake in acid form is might due to the stronger hydrophilicity of sulfonic acid groups than that of sulfonate 1-methyl imidazolium groups. However, the higher water uptake of the acid form membranes might as well be simply due to the volume-size difference between hydrogen and 1-methylimidazolium cations. Compared with 1-methylimidazolium cations, the volume size of hydrogen cations is relatively smaller.[22] As a result, conversion of the IL form membranes to acid form by replacing the 1-methylimidazolium with hydrogen cations provided membrane with more free volumes or microvoids which therefore enhanced the water uptake capacity, although such a microsturcture could not be observed by SEM.

The effect of DVB content on the water uptake was studied and is summarized in Table 2. The water uptake of membranes in both two forms decreased with the cross-linking agent content increasing. This result is reasonably due to the presence of compact network structures formed in the cross-linked membrane which reduce the free volume to retain water around sulfonate groups and eventually restrict the water uptake. In addition, the cross-linking agent used in this work, DVB, is a hydrophobic compound. The higher amount of DVB, the higher hydrophobicity of the membrane would be. Both two effects may hinder the association of sulfonate groups with water molecules and thus reduce water uptake capability.

Swelling behavior of the membrane is an essential factor influencing the mechanical properties, methanol permeation, and the morphologic stability of membranes. As shown in Table 2, that the swelling degree increases with the increment of PAMPS content because more water has been absorbed within the membrane. The swelling degree of the acid form membranes is higher than corresponding IL form membranes because of the higher water uptake of acid form membranes. Compared with Nafion-117 membrane, most of cross-linked PAMPS-based membranes (except acid form $PAMPS_{70}-DVB_{10}$ membrane) show relatively lower swelling degree because of the compact network structures formed in the cross-linked membranes which restricted the mobility of the polymer chains as well as the free volume in the membrane. In addition, the swelling degree could be notably lowered by the increase of cross-linking agent due to the more compact network structures formed within the membranes.

Ion-exchange capacity (IEC) indicates the amount of the ion exchangeable groups present in a polymer matrix. These ion-exchangeable groups are generally considered responsible for proton transfer and thus are an indirect and reliable approximation of the proton conductivity. The calculated and experimental IEC values of membranes in acid form are compared with Nafion-117 membrane and listed in Table 2. The calculated IEC value of Nafion-117 membrane was 0.97 mmol/g, which was in agreement with that of previously reported by Xu et al.[12] The calculated IEC value increased with the increasing content of PAMPS, and the experimental

Table 2. Water Uptake, Swelling Degree, and IEC of PAMPS-Based Membranes

	water uptake [%]		swelling degree [%]		IEC (mmol/g) acid form	
polymer membranes	IL form	acid form	IL form	acid form	theoretical	titration
$PAMPS_{30}-DVB_{10}$	1.30	3.10	1.12	1.63	0.94	0.66
$PAMPS_{40}-DVB_{10}$	1.39	16.63	2.21	2.97	1.24	0.97
$PAMPS_{50}-DVB_{10}$	34.10	45.60	3.12	8.24	1.57	1.15
$PAMPS_{60}-DVB_{10}$	61.60	80.00	5.67	13.45	1.89	1.63
$PAMPS_{70}-DVB_{10}$	78.00	173.20	10.93	47.60	2.16	1.80
$PAMPS_{60}-DVB_{12}$		74.51		11.56		
$PAMPS_{60}-DVB_{16}$		66.91		10.93		
$PAMPS_{60}-DVB_{18}$		62.52		5.26		
Nafion-117	14.82		17.54		0.97	

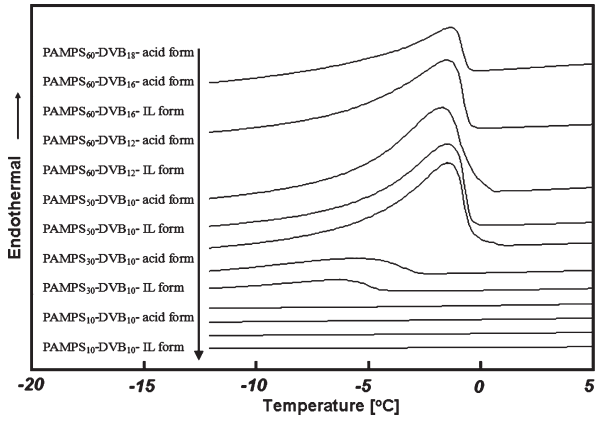


Figure 3. DSC thermograms indicating the melting of water in the fully hydrated membranes in both IL and acid forms.

IEC value increased gradually from 0.66 to 1.80 mmol/g with the PAMPS content increased from 10 to 70 wt %. Since the sulfonic acid groups are the only ionizable groups in the produced membranes, the increase in the IEC value with sulfonic acid content is therefore easily understood.

It is essential to know the states of water confined in the membrane since they play a significant role in determining the transportation of proton and methanol across the membranes. According to its molecular nature, the states of water exist in hydrophilic polymeric networks can be classified into bound water and free water. The water in a "free" state can freeze at the usual freezing point, while some bound water molecules which are associated with the polymeric chains cannot freeze at the usual freezing point. The water states in the membrane could be characterized and analyzed by using a DSC thermodiagram as shown in Figure 3. The samples had a broad endothermic peak ascribed to the melting peaks of fusion of free water. The amount of free water in the membranes could be obtained from an integration of the endothermic peak area and calculated by the following equation:[23,24]

$$X_{aw} = A/H_w$$

Here, A is the heat of fusion at around 0 °C, H_w is the heat of fusion of pure ice (335 J/g),[20d,23,24] and X_{aw} is the amount of free water in the sample. The amount of bound water is calculated by subtracting the amount of free water from the total water.

Table 3 summarizes the amount of free and bound water within the produced membranes. When the PAMPS content is lower than 30% in the membrane (such as $PAMPS_{10}-DVB_{10}$ and $PAMPS_{30}-DVB_{10}$ membranes), no endothermic peaks could be observed at around 0 °C, indicating all the water in the membrane could be bound water. However, this result is might due to the very low water content absorbed in the membrane which is undetectable in a normal calorimetric run. The increase of PAMPS content in the membranes increased the water content and also the free water amount; however, it decreased the amount of bound water. The bound water content in IL form membranes is higher than that in corresponding acid form membranes, indicating stronger interaction between water molecules and sulfonate 1-methylimidazolium groups possibly due to the relatively compact structure of IL form membrane. Additionally, the increase of cross-linking content decreased the water content of the membranes while the amount of bound water increased with increasing cross-linking content due to the more compact network structure formed in the membrane, which result in the stronger water−polymer interactions.

Proton Conductivity. In a fully hydrated state, sulfonated polymers may dissociate immobile sulfonic acid groups and the hydronium ions (e.g., H_3O^+, $H_5O_2^+$, and $H_9O_4^+$) were formed via hydrogen bonding around the sulfonic acid groups.[20] The free protons can be transported along the hydrogen-bonded ionic network within fully water-swollen sulfonated polymer membranes. Therefore, proton conductivity will be significantly influenced by the water uptake (related to IEC values) and water state in the membrane. As depicted in Figure 4A, the proton conductivity of PAMPS-based membranes was strongly dependent on the water uptake content and IEC values and exhibited the expected monotonically increasing trend with sulfonic acid group content. The changing trend in proton conductivity was similar to the IEC results and water uptake values. Under the same conditions, polymer membranes in acid form show higher conductivity (about 1.5−3 times) than the corresponding IL form membranes due to the higher water uptake although the amount of bound water in acid form membranes is relatively lower. It should be noted that the proton conductivity of $PAMPS_{60}-DVB_{10}$ and $PAMPS_{70}-DVB_{10}$ membranes in acid form is up to 3.82 and 5.89×10^{-2} S/cm at room temperature, respectively. These values are in the same order of magnitude as the proton conductivity (5.98×10^{-2} S/cm) of Nafion-117 membrane under the same testing conditions. Increase of cross-linking agent content decreased the water uptake and the proton conductivity was thus decreased with cross-linking agent content increasing (Figure 4B).

Figure 5 shows the proton conductivities of Nafion-117 and acid form $PAMPS_{60}-DVB_{10}$ membranes versus temperature at relative humidity (RH) of 30% and 80%, respectively. It can be clearly seen that the conductivities of $PAMPS_{60}-DVB_{10}$ exhibited pronounced increase in proton conductivities with temperature increased at 30% and 80% RH, respectively. Under the same experimental conditions, Nafion-117 membrane showed a similar temperature dependence on conductivities at both RH. However, both are lower in conductivity compared to $PAMPS_{60}-DVB_{10}$ membrane at high

Table 3. States of Water in PAMPS-Based Membranes

sample	T_m (°C)	water content (%)	free water (%)	bound water (%)	bound water degree (%)
$PAMPS_{10}$−DVB_{10}-IL form	N/A	0.7	0	0.7	100
$PAMPS_{10}$−DVB_{10}-acid form	N/A	2.9	0	2.9	100
$PAMPS_{30}$−DVB_{10}-IL form	N/A	1.3	0	1.3	100
$PAMPS_{30}$−DVB_{10}-acid form	N/A	3.1	0	3.1	100
$PAMPS_{50}$−DVB_{10}-IL form	−6.5	23.7	3.6	20.1	87.3
$PAMPS_{50}$-DVB_{10}-acid form	−5.7	31.3	8.1	23.2	74.1
$PAMPS_{60}$-DVB_{12}−IL form	−1.5	36.8	16.0	20.8	56.5
$PAMPS_{60}$−DVB_{12}-acid form	−1.5	42.7	18.8	23.9	56.0
$PAMPS_{60}$−DVB_{16}−IL form	−1.7	35.9	15.4	20.5	57.1
$PAMPS_{60}$−DVB_{16}-acid form	−1.5	40.1	17.4	22.7	56.6
$PAMPS_{60}$−DVB_{18}-acid form	−1.4	38.5	14.8	23.7	61.6

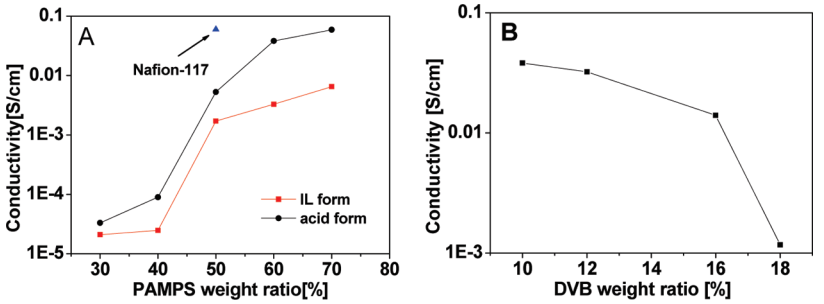


Figure 4. (A) Proton conductivity of the $PAMPS_x$−DVB_{10} membrane in both IL and acid forms as a function of weight content of PAMPS at 25 °C. (B) Proton conductivity of acid form $PAMPS_{60}$−DVB_y membranes as a function of DVB content at 25 °C.

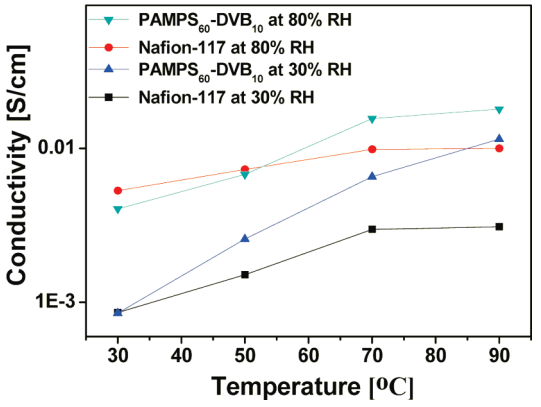


Figure 5. Proton conductivity versus temperature at 30% and 80% RH for acid form $PAMPS_{60}$−DVB_{10} and Nafion-117 membranes, respectively.

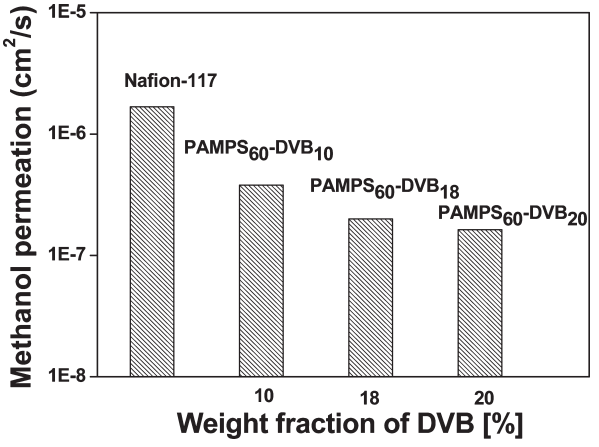


Figure 6. Methanol permeation of acid form $PAMPS_{60}$−DVB_y membranes as a function of DVB content.

temperature (above 70 °C). It has been reported that the conductivity of PAMPS was higher than that of Nafion under the same water content due to the higher tolerance of the PAMPS than Nafion to the fluctuations in water content and drying.[6b,c] Therefore, it can be concluded that the PAMPS-based membranes prepared in this work have relatively higher proton conductivity at high temperature if compared with Nafion-117 membrane.

From viewpoint on practice, membranes with the proton conductivity up to the order of 1×10^{-2} S/cm should have potential applications as PEMs in fuel cells. Therefore, methanol permeation of $PAMPS_{60}$−DVB_{10} and $PAMPS_{70}$−DVB_{10} membranes in acid form was further investigated in this work.

Methanol Permeability. Methanol permeation is a key parameter of DMFCs because high methanol permeation will decrease the efficiency of the fuel cell. Since the acid form membranes of $PAMPS_{60}$−DVB_{10} and $PAMPS_{70}$−DVB_{10} showed comparable proton conductivity to Nafion 117, methanol permeation of these membranes was investigated at 25 °C. Under the same experimental conditions, methanol permeation of Nafion-117 membrane was measured for comparison (Figure 6). As shown in Figure 6, the methanol permeation of acid form $PAMPS_{60}$−DVB_{10} membrane is 3.80×10^{-7} cm^2/S, which is quite lower than that of Nafion-117 membrane (1.68×10^{-6} cm^2/s). However, methanol permeation measurement of $PAMPS_{70}$−DVB_{10} membrane was failed because of its high swelling degree and poor mechanical properties. It has already been reported that the methanol transport behavior of a membrane is dependent on its water uptake, the degree of swelling, and the microstructure of the membrane. Here, the methanol diffusion coefficient of membranes gradually decreased from 3.80×10^{-7} to 1.63×10^{-7} cm^2/s with the increment of DVB content from 10 to 20%. This tendency was the same as the results of water uptake due to the more compact network structures formed in the membranes which suppress the channels to pass methanol molecules.

Thermal Analysis. The thermal degradation of PAMPS-based membranes was studied by TGA as is shown in Figure 7. All the polymer membranes in both acid and IL forms show two main decomposition stages. The first decomposition temperature occurred at 250 °C was assigned to the decomposition of sulfonate groups, propenyl groups, or cross-linking agent. The second thermal degradation that took place at about 380 °C was ascribed to main-chain degradation of polymer. Increase of PAMPS content in the membrane did not affect thermal stability of the prepared polymer membranes. These results suggest that this type of membrane indeed confirms a high thermal stability, far beyond the range of interest for application in DMFCs within the medium operating temperature range.

Membrane Stability. The hydrolytic stability of membranes was investigated by immersing them in water at 90 °C and characterized by measuring the changes in the time when the membranes began to be brittle and could be broken by light bent.[25]

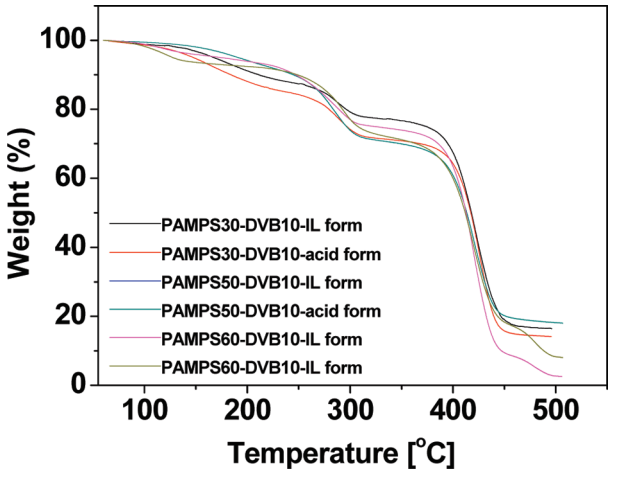


Figure 7. TGA curves of PAMPS-based membranes.

After 340 h testing period, none of the membranes exhibited any obvious changes in appearance, flexibility, and toughness, indicating that this type of PAMPS-based membrane has good water stability.

Chemical stability of PEMs is of much concern to the lifetime of DMFCs. The oxidative stability of the produced membranes in H_2O_2 or Fenton's reagent (solution containing H_2O_2 and transition metal ions) has been recognized as an important indication of the durability of the membranes in fuel cells. Figure 8 shows the degradation of acid form PAMPS-based membranes tested in 3% H_2O_2 and in Fenton's reagent (3% H_2O_2 solution containing 2 ppm Fe^{2+}) at 60 °C. The degradation of polymer membranes is evaluated by the weight loss and visual observation. As shown in Figure 8, the membranes show a relatively high oxidative durability in H_2O_2 solutions. About 15% weight loss was observed after the $PAMPS_{60}-DVB_{10}$ membrane was immersed in 3% H_2O_2 solution for 120 h. An initial sharp decrease in weight percentage of $PAMPS_{60}-DVB_{10}$ membrane was observed after 24 h test in Fenton's reagent. The sample weight tends to maintain a constant value of about 64% without further weight losses after 120 h testing period. It can be clearly seen that the weight loss of membranes increased with the increment of PAMPS content, indicating that oxidative attack on the membranes by radical species should mainly occur on the PAMPS units. The water uptake of PAMPS-based membranes rises with the increasing PAMPS content, which loosens the compact structure of membranes, and hence some sulfonic acid groups leached into the water during the measurements. It should be mentioned that none of the membranes were broken into small pieces, and all of the samples remained in a good membrane form after the 120 h testing period.

The membrane stability was further confirmed by proton conductivity measurements of the membranes after the oxidative stability testing. Figure 8C shows the conductivity of the $PAMPS_{60}-DVB_{10}$ membrane versus oxidative stability testing time. Although the conductivity decreased after be oxidized, the membrane still showed a conductivity of

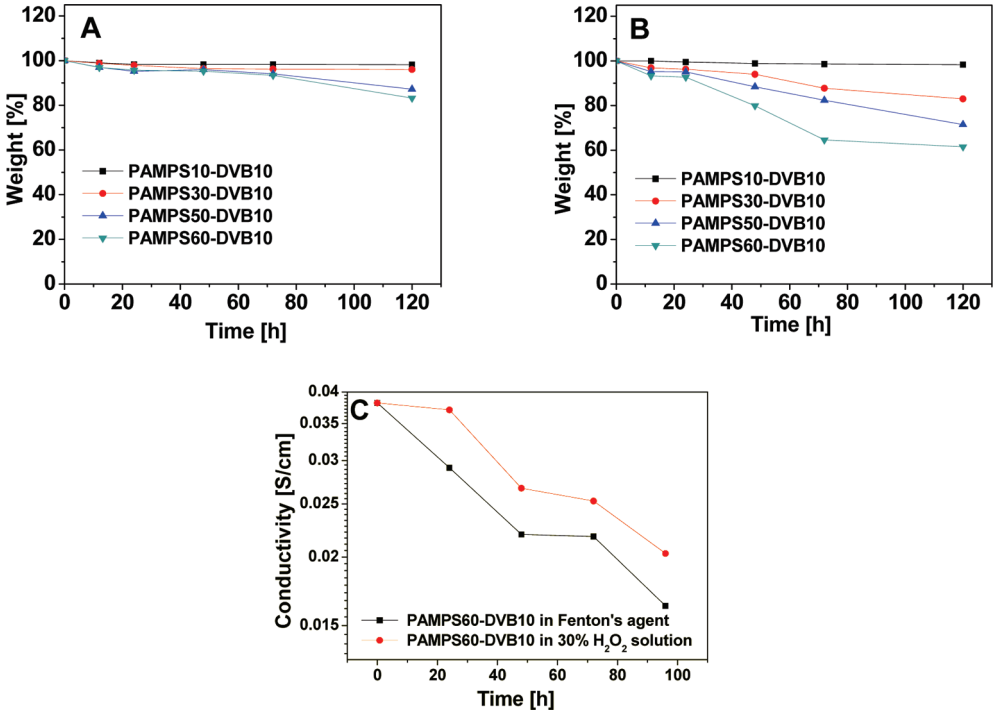


Figure 8. Degradation of acid form PAMPS-based membranes in (A) 3% H_2O_2 and (B) 3% H_2O_2 containing 2 ppm Fe^{2+} at 60 °C and (C) room temperature proton conductivity of the $PAMPS_{60}-DVB_{10}$ membrane versus oxidative stability testing time.

1.68×10^{-2} S/cm after 96 h testing in Fenton's reagent. Theses results further confirmed good chemical stability of the PAMPS-based membranes.

Conclusions

This work reported the synthesis of PAMPS-based polymer membranes via in situ cross-linking of a mixture containing AMPS-based ionic liquid and hydrophobic monomer oils. The resultant copolymer membranes are transparent, flexible, and have good and tunable mechanical properties. The water uptake, swelling degree, IEC, and proton conductivity and methanol permeability of the membranes increased with the PAMPS content while decreased with cross-link agent content. The acid form membrane of $PAMPS_{60}-DVB_{10}$ showed the proton conductivity of 3.82×10^{-2} S/cm and methanol permeability of 3.80×10^{-7} cm^2/s at 25 °C. These results suggested that the cross-linked PAMPS-based membranes reported here meet the claim of easy fabrication, high proton conductivity, low methanol permeability, reasonable swelling, good and tunable mechanical properties, and acceptable chemical stability and thus show a particularly promising to be used as proton exchange membranes in DMFCs. We believe the methodology presented in this work is not limited to the monomer oils considered in this study and should be extendable to some other monomer oils with desirable properties for the preparation of non-fluorinated PEMs.

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