Fabrication of a High-Stability Cross-Linked Quaternized Poly(epichlorolydrin)/PTFE Composite Membrane via a Facile Route

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ABSTRACT: A novel cross-linked quaternized composite anion-exchange membrane based on poly(epichlorohydrin) (PECH) was prepared by a facile route. First, PECH was cross-linked with 2-methylimidazole and combined with a poly(tetrafluoroethylene) (PTFE) membrane to form cross-linked PECH/PTFE (CPECH/PTFE). Then, CPECH/PTFE was quaternized by 1-methylimidazole to obtain cross-linked quaternized PECH/PTFE (CQPECH/PTFE). ^{1}H NMR and Fourier transform infrared spectroscopic data indicated that CQPECH was successfully synthesized, and the CQPECH/PTFE membrane had a dense and homogeneous structure demonstrated by the field-emission scanning electron microscopy. The results showed that the use of 2-methylimidazole as the cross-link agent could avoid the solubility of the composite membrane in water and dimethyl sulfoxide. With an increase of 2-methylimidazole, the solubility of the PECH ionomer was decreased. M-3, one of the CQPECH/PTFE membranes, showed good thermal properties (stable below 250 °C under an N_2 atmosphere), excellent mechanical strength (a tensile strength of 67.3 MPa), moderate water uptake of 45.3%, and very low swelling degree of 9.01% at 30 °C. Besides, M-3 showed a hydroxide conductivity of up to 27 mS/cm and good long-term stability in a 1 M KOH solution at 60 °C for 15 days. In addition, a single H_2/O_2 fuel-cell test using M-3 at 50 °C indicated a peak power density of 23 mW/cm^{2}. These results suggested that the CQPECH/PTFE membrane had a good perspective for application in an alkaline fuel cell.

KEYWORDS: poly(tetrafluoroethylene), cross-linked quaternized poly(epichlorohydrin), 2-methylimidazole, composite membrane, stability
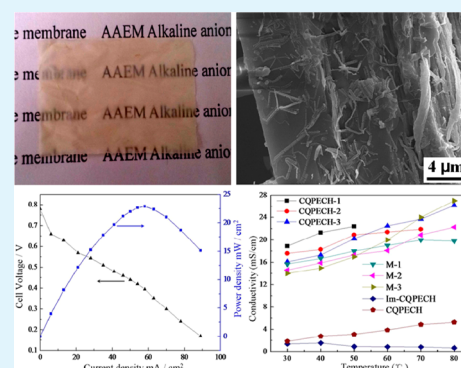
1. INTRODUCTION

Alkaline fuel cells (AFCs) are widely thought of as the environmentally friendly energy sources for the 21st century.[1] As a crucial component of AFCs, alkaline anion-exchange membranes (AAEMs) simultaneously serve as a hydroxide conductor and a fuel/oxidant separator[2] and have been extensively investigated for the past decade. However, one of the challenging issues for the current development of AFCs is to synthesize AAEMs that feature the simultaneous requirements of high hydroxide anion conductivity, good mechanical integrity, and robust alkaline stability under electrochemical conditions.[3] To date, the current synthesis of AAEMs can be categorized into two types: functionalization of existing polymers and bottom-up synthesis of functional monomers.[4] Compared with the latter, functionalization of existing polymers is a simpler and more efficient method to synthesize AAEMs. Most typically, using functionalization of existing polymers to fabricate AAEMs is generally through the chloromethylation and quaternization of benzylchloromethyl groups. However, on the one hand, the chloromethylation reaction is not easy to handle. Generally, the chloromethylation reaction has low productivity. Although the use of chloromethyl methyl ether

has high yield, the reagent is highly toxic and carcinogenic.[5] On the other hand, quaternization usually utilizes extremely volatile reagents like trimethylamine, resulting in an environmentally unfriendly synthetic process. Besides, this quaternary ammonium type of AAEMs has too low alkali thermochemical stability because of the strong nucleophilicity of the OH⁻ anions, which induces displacement and Hofmann elimination reactions.[6] So, finding a new environmental and efficient way to fabricate AAEMs has become the goal of scientists.

Recently, poly(epichlorohydrin) (PECH) is adopted as a polymer matrix to fabricate AAEMs for AFCs.[7,8] PECH exhibits very high gas impermeability and chemical resistance, especially to base.[9] Moreover, it is possible to carry out a S_N2 nucleophilic substitution on chlorine dangling atoms to functionalize them into quaternary ammoniums, and then the chloridion counterions are replaced by hydroxides.[10] Thus, the chloromethylation reaction and highly toxic and carcinogenic reagents can be avoided. Besides, 1-methylimidazole (MIm) is used as

Scheme 1. Fabrication Strategy for the CQPECH/PTFE Membrane
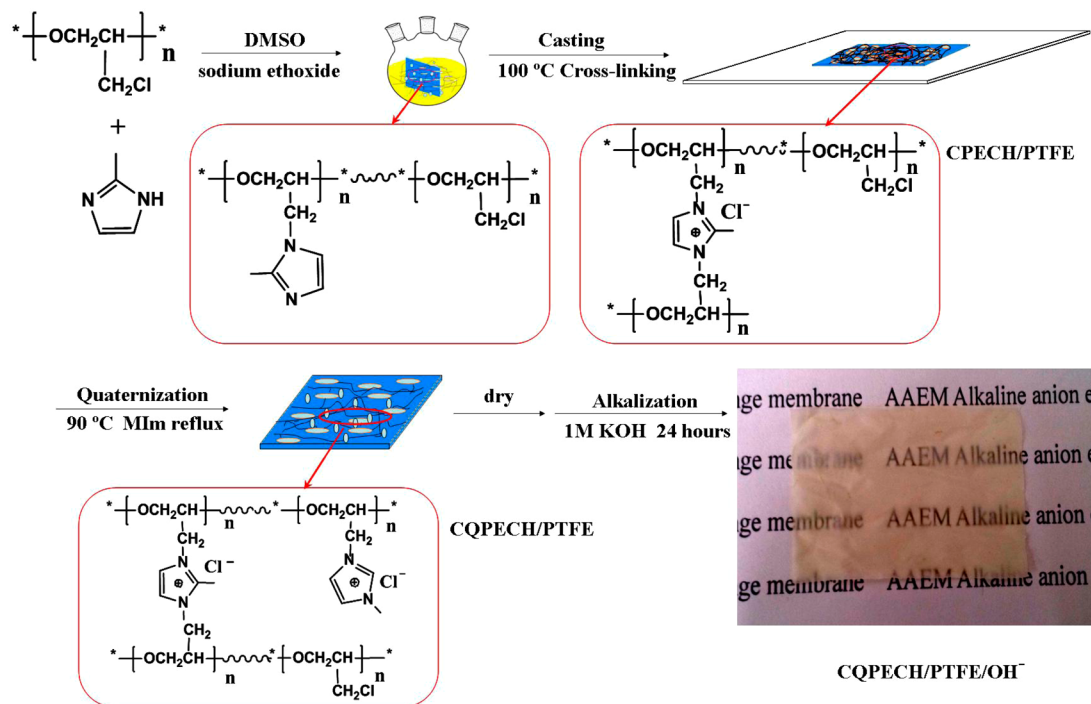
quaternization reagent. Because of the presence of steric hindrance and the π-conjugated structure of the five-membered heterocyclic ring, degradation of the imidazolium cation in an alkaline environment may be minimized. The recent literature contains an increase in the number of reports that investigate the chemical stabilities of AAEMs containing pendent imidazolium groups. Lin et al. reported that [PVMIm]-[OH]$_{40}$-DVB$_4$ still maintained the hydroxide conductivity, even after immersion in a 1 M KOH solution at 60 °C for 400 h.[11] Likewise, Guo et al. discovered that a poly(styrene-co-butyl methacrylate)-based imidazolium (PS-co-PBMA-Im) AEM could maintain good conductivity even after exposure to 6 M NaOH at 80 °C for 120 h.[12] In addition, it has been reported that the imidazolium cation is thermally more stable than the conventional quaternary alkylammonium cation and has good resistance to oxidation at high temperature.[13,14] The utilization of 1-methylimidazole can also avert the employment of extremely volatile reagents like tetramethylammonium (TMA). Nevertheless, because the polyether backbone of PECH is a linear polymer, its ionomers still undergo high swelling in water even when they are dissolved in hot water, which can affect the mechanical property of the membrane.[15]

Compositing with an other polymer or base membrane that has good mechanical strength is an effective way of overcoming this shortcoming. Stoica et al. fabricated a composite membrane based on the poly(epichlorydrin−allyl glycidyl ether) copolymer and polyamide. Such a supported membrane was very dramatic because of its good thermal stability and mechanical property. However, the polyamide support had a weak influence on the swelling behavior at high temperature.[9] The interpenetrating polymer network (IPN) made by an anionic conducting PECH network entangled within cross-linked poly(2-hydroxyethyl methacrylate) in different mass proportions was prepared by Ghamouss and co-workers. This IPN also had dramatic thermal stability, water management ability, and other good electrochemical properties compared with a

single PECH network.[16] However, the conductivity of the IPN needed to be improved. In this study, a porous poly-(tetrafluoroethylene) (PTFE) membrane had been adopted as the supporting material because the PTFE reinforcement technique was considered to be one of the most effective methods to increase the mechanical strength of the membrane.[17−19] A thin composite membrane based on PTFE and quaternary polysulfone was prepared by Wang and co-workers. This membrane had a low swelling degree (SD) and water uptake (WU), and the highest conductivity of 0.051 S/cm was achieved at 55 °C. The membrane showed a high peak power density of 146 mW/cm^2 at 50 °C. Moreover, a high open-circuit potential, above 1.0 V, indicated that the membrane exhibited low hydrogen permeability.[20] Guo et al. reported a quaternized PECH with PTFE blend membrane for a direct methanol fuel cell (DMFC), the AAEMs exhibited a high hydroxyl conductivity of up to 0.0623 S/cm at 80 °C, and the methanol permeability was comparable to that of the Nafion membrane.[8] Besides, previous reports had suggested that a self-cross-linked alkaline polymer electrolyte owned extraordinary stability in both physical and chemical properties.[21] Thus, in order to achieve membrane stability, a self-cross-linking reaction using 2-methylimidazole as a cross-linking agent was introduced to prepare the AAEMs, which could also make the preparation process of the membrane simpler and did not induct an additional cross-linking agent. The specific benefits of this novel composite AEM include (i) a facile synthetic method, (ii) a dense and uniform structure, (iii) good ionic conductivity and low SD and WU, and (iv) adequate mechanical strength as well as high thermal stability.

2. EXPERIMENTAL SECTION

2.1. Materials. Dimethyl sulfoxide (DMSO) was purchased from Tianjin Fu Yu Chemical Co., Ltd. A poly(tetrafluoroethylene) (PTFE) membrane was supplied by Zhejiang Dongyang San-wei Kongmo Co., Ltd. The average pore size, average thickness, biggest pore size, and

Table 1. Basic Information of the Membranes

film	PECH (g)	2-methylimidazole (g)	1-methylimidazole (mL)	increase of weight after quaternization (%)	thickness (μm) (dry)	SF (wt %) in DMSO
Im-PECH	0.7	0	excess			100
CQPECH-1	0.7	0.063	excess	4.3	70−90	9
CQPECH-2	0.7	0.126	excess	3.5	70−90	8
CQPECH-3	0.7	0.190	excess	2.5	70−90	6
M-1	0.7	0.063	excess	3.6	30−40	8
M-2	0.7	0.126	excess	2.9	30−40	5
M-3	0.7	0.190	excess	1.7	30−40	3
Im-PECH/PTFE/ OH⁻	0.7	0	excess		30−40	
CPECH/PTFE/OH⁻	0.7	0.190	0		30−40	

porosity of the PTFE membrane were 0.5 μm, 18 μm, 2.5 μm, and 80%, respectively. Poly(epichlorohydrin) (PECH) was purchased from Sigma-Aldrich. All other chemicals were supplied from Aladdin Chemistry Co. Ltd.

2.2. Fabrication Strategy of the Membrane Sample. Scheme 1 shows the fabrication strategy for the cross-linked quaternized PECH/PTFE (CQPECH/PTFE) membrane. Briefly, 0.7 g of PECH was dissolved in 7 mL of DMSO at 90 °C, and the mixture was stirred for 2 h to form a homogeneous PECH solution. In order to improve the wettability of the PTFE membrane in DMSO, the PTFE membrane was orderly treated in ethanol and acetone with ultrasound for about 1 h and then immersed in anhydrous ethanol for at least 1 day to obtain swelling of PTFE for standby. Then, the appropriate area of swelling of the PTFE membrane film was immersed in the PECH solution, resulting in PECH penetrating into the pores of the PTFE membrane. Afterward, 2-methylimidazole in a controlled amount and several drops of sodium ethoxide were orderly added, and then the mixture was kept stirring for 12 h at 80 °C. Finally, the PTFE membrane was taken out from the solution and placed on the Teflon plate. The residual solution was cast onto the PTFE membrane, and the cross-linked PECH/PTFE (CPECH/PTFE) membrane was formed by solvent evaporation in an oven at 100 °C for 24 h. Then, the membrane was peeled off of the Teflon plate, washed with ethanol and hot distilled water thoroughly, and dried in a vacuum oven at 80 °C for 24 h. This membrane was then immersed in a 30 wt % 1-methylimidazole solution at 90 °C for 48 h under the conduction of reflux to fabricate the CQPECH/PTFE membrane. Next, the obtained membrane was heated in open air at 60 °C for 24 h and 80 °C for another 24 h to get rid of the unreacted 1-methylimidazole. Then, the membrane was put into a 1 M KOH solution for 24 h. At last, the quaternization composite membrane (CQPECH/PTFE/OH⁻) was washed several times with distilled water and kept in distilled water before testing. Furthermore, a 1-methylimidazole-functionalized PECH (Im-PECH) solution was also synthesized by adding abundant 1-methylimidazole in a PECH solution at 90 °C. In the same way, CPECH/PTFE/OH⁻ and Im-PECH/PTFE/OH⁻ were fabricated. As a result, the CPECH/PTFE/OH⁻ (cross-linked but not quaternized), Im-PECH/PTFE/OH⁻ (quaternized but not cross-linked), and CQPECH/PTFE/OH⁻ (quaternized and cross-linked) membranes were obtained. Besides, according to the different contents of 2-methylimidazole (as shown in Table 1), CQPECH/PTFE/OH⁻ membranes were respectively denoted as M-1, M-2, and M-3. A single PECH ionomer was synthesized in the same way without compositing with the PTFE membrane. According to the different contents of 2-methylimidazole (as shown in Table 1), the membranes were denoted as Im-PECH, CQPECH-1, CQPECH-2, and CQPECH-3, respectively.

2.3. Characterizations. All samples were quantified and dried up to constant weight under a vacuum at 60 °C for at least 3 days before characterization. The Fourier transform infrared (FTIR) spectra were recorded using a Nicolet Nexus-6700 spectrophotometer (Thermo Electron Corp., Waltham, MA) equipped with attenuated total reflectance with a resolution of 2 cm⁻¹ and a spectral range of 4000−600 cm⁻¹. ¹H NMR spectra were recorded on a DMX 300

NMR spectrometer (¹H resonance at 300 MHz). The morphology was evaluated using field-emission scanning electron microscopy (FSEM) operating at 5 kV; the samples were fractured in liquid nitrogen, sputtered with gold, and examined at 5000× magnification.

2.3.1. Soluble Fractions (SFs). SFs (un-cross-linked components) contained in different single PECH ionomers and M-x were quantified from a known weight of dry material (W_0) extracted in a Soxhlet with DMSO at room temperature for 48 h. After extraction, the samples were dried under a vacuum at 60 °C until constant weight (W_E). The SF was calculated as a weight ratio:

$$\text{SF (\%)} = \frac{W_0 - W_E}{W_0} \times 100 \tag{1}$$

2.3.2. Thermogravimetric Analysis (TGA). A TGA analyzer (Mettler Toledo TGA/SDTA851) was used to test the thermal stability of the membrane. About 5−10 mg of the sample was heated from 30 to 700 °C at a heating rate of 10 °C/min under an N₂ atmosphere (N₂ flow rate: 80 mL/min). The sample was dried for 24 h at 60 °C in a vacuum to remove moisture prior to the test.

2.3.3. Mechanical Property. The mechanical property of the dry membrane was measured using a Zwick/Roell materials testing machine (BTC-FR020TN A50; Zwick/Roell, Ulm, Germany). The membrane was cut into 1 cm × 5 cm pieces for each sample and examined with a test speed of 2 mm/min and a preload force of 0.001 N in isothermal conditions at 25 °C. The tests were made in quintuplicate, and the results were reported as average.

2.3.4. Ion-Exchange Capacity (IEC). The IEC of the membrane was determined by the titration method. The membrane in OH⁻ form was soaked in a 0.01 M HCl solution at 30 °C for 48 h. Subsequently, HCl was titrated against 0.01 M NaOH with phenolphthalein as the indicator. The IEC was calculated as follows:

$$\text{IEC (mmol/g)} = \frac{(V_b - V_s)C_{HCl}}{W_{dry}} \times 1000 \tag{2}$$

where V_b and V_s (mL) are the consumed volumes of the NaOH solution for the blank sample and membrane, respectively. C_{HCl} (M) is the concentration of the HCl solution, and W_{dry} (g) is the mass of the dry membrane sample.

2.3.5. WU and SD. Initially, the weight and dimensions of the dry membrane (dried under a vacuum at room temperature for 48 h) were measured, and then the dry membrane was immersed in deionized water and kept in a tightly sealed container for more than 10 h to ensure full hydration. Subsequently, the weight and dimensions of the wet membrane were measured. The WU and SD could be calculated by the two following equations, respectively:

$$\text{WU (\%)} = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \tag{3}$$

$$\text{SD}_L \text{ (\%)} = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \tag{4}$$

$$SD_T\ (\%) = \frac{T_{wet} - T_{dry}}{T_{dry}} \times 100 \qquad (5)$$

where W_{wet} and W_{dry} are the weights of the wet and dry membrane samples, respectively. SD_L is measured by length changes, and SD_T is measured by thickness changes. L_{wet} and L_{dry} are the lengths of the wet and dry membrane samples, respectively; T_{wet} and T_{dry} are the thicknesses of the wet and dry membrane samples, respectively.

2.3.6. Hydroxide Conductivity. The hydroxide ion conductivity was measured via the electrochemical impedance spectroscopy test with a Solartron 1255B and 1287 frequency response analyzer at an oscillating voltage of 10 mV. The impedance spectra ranged from 1 MHz to 1 kHz. The hydroxide ion conductivity measurement was done using a two-probe method. Before the test, the membrane was cut into 1 cm × 1 cm pieces and then hydrated in degassed deionized water for at least 24 h. The hydroxide conductivity (σ) was calculated as follows:

$$\sigma = \frac{d}{RS} \qquad (6)$$

where R (Ω) is the resistance, d (cm) is the distance between electrodes, and S (cm^2) is the electrode area.

2.3.7. Stability. Composite membranes were kept in pure water and a KOH solution at 60 °C for 15 days. Then, they were washed with deionized water to remove the absorbed KOH and immersed in deionized water for at least 48 h prior to measurement for ionic conductivity analysis and morphology.

2.3.8. Fuel-Cell Testing. The performance of M-3 was evaluated in a single testing cell using a Fuel Cell Testing System (Arbin Instruments, College Station, TX). Pure hydrogen was fed to the anode and air was fed to the cathode, with flow rates of 300 mL/min (hydrogen) and 1000 mL/min (air) under a back-pressure of 20 psig. The fuel-cell test was conducted at 50 °C and controlled at relative humidity RH = 100%. The membrane electrode assembly (MEA) was prepared as follows. A catalyst ink was prepared by mixing the catalyst (20% mass Pt/C, Johnson Matthey) and an Im-PECH solution (5% in DMSO). The mixture was sonicated and then coated onto a PTFE-treated carbon paper until the platinum loading and the content of ionomer in the catalyst layer were 2 and 1 mg/cm^2, respectively. The MEA was prepared by sandwiching M-3 between two electrodes and pressing at 70 °C for 1 min under a pressure of 1 MPa. Its effective electrode area was 4 cm^2. Before the test, M-3 with OH$^-$ form was soaked in a 0.1 M KOH solution for 4 days so that Cl$^-$ was fully exchanged. Then, the membrane was washed several times with distilled water and kept in distilled water at least 1 day to get rid of KOH.

3. RESULTS AND DISCUSSION

3.1. Membrane Preparation and Characterization.
The fabrication route of the CQPECH/PTFE membrane is shown in Scheme 1. Besides, a single PECH ionomer was synthesized in the same way without compositing with the PTFE membrane. All of the CQPECH/PTFE membranes were flexible, yellowish, and transparent. They could be cut into any desired shapes. The essential information of the membrane is shown in Table 1. The weight of the purification membrane was measered before and after quaternization. The results confirmed that the quaternized reaction occurred. In order to check the cross-linking reaction, the amounts of SFs of the CQPECH and composite membrane were determined by Soxhlet extraction with DMSO at room temperature. As shown in Table 1, the SF values were all lower than 9 wt %, which confirmed the correct cross-linking of these polymers. The composite membrane was thinner than the single PECH ionomer membrane under the condition of maintaining the flexibility of the membrane, which was a benefit for the electrochemical performance of the membrane.

FTIR spectra of PTFE and M-3 are shown in Figure 1. As can be seen, the intense peaks at 1205 and 1150 cm^{-1}
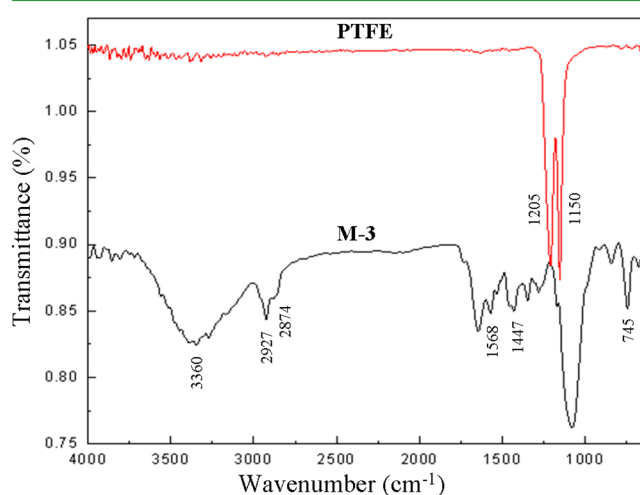

Figure 1. FTIR spectra of the PTFE membrane and M-3.

originated from the C−F bond of PTFE. Compared with that of pristine PTFE, the spectrum of M-3 showed several characteristic peaks. The peaks at 2927 and 2874 cm^{-1} were assigned to the vibration of the aliphatic C−H bond on the methyl or methylene groups. The sharp peaks at 1568 and 1447 cm^{-1} were ascribed to the stretching vibration of C=N and the vibration of the C−N bond on the imidazolium group, and absorption at 745 cm^{-1} was assigned to the bending vibration of the imidazolium ring. Furthermore, a broad absorption peak at around 3360 cm^{-1} was observed in the spectrum of M-3. This absorption, derived from the stretching vibrations of the O−H bond, was due to the presence of water in the AAEMs. These results indicated the successful introduction of imidazolium functional groups into CQPECH.

Further confirmation of the successful synthesis of CQPECH was based on ^{1}H NMR data (Figure 2). For the base PECH, the signals with chemical shifts of δ 3.8 and 3.68 were respectively assigned to methyne (CH) and methylene (CH$_2$) of the main chain, and the peaks at around δ 3.64 were attributable to the protons of methylene (CH$_2$) of the chloromethyl groups. After reaction with 2-methylimidazole, this peak belonging to the proton of methylene was located at higher chemical shift (δ 4.2), as a result of the induction effect. In addition, new peaks appeared that indicated a successful reaction with 2-methylimidazole: the peak at δ 2.6 was due to the protons of methyl of 2-methylimidazole, and the peaks within δ 7.5−8.0 were ascribed to the protons of methylene of the imidazolium ring. After quaternization, new signals arose at δ 3.4 and 9.5, which were ascribed to the protons of the methylimidazolium cations.

Figure 3a shows the surface morphology of the PTFE membrane. It can be seen that the surface of the PTFE membrane was a network structure and the pores inter-connected to form channels. Figure 3b shows that the pores were completely filled after compositing with polymer and the surface became very smooth, which was attributed to the fact that CQPECH penetrated into the pores of the PTFE membrane. Figure 3c for the cross section shows that the inner part of the composite membrane had a dense and uniform structure without any phase separation and pore. The FSEM images indicate that the porous matrix of PTFE was fully
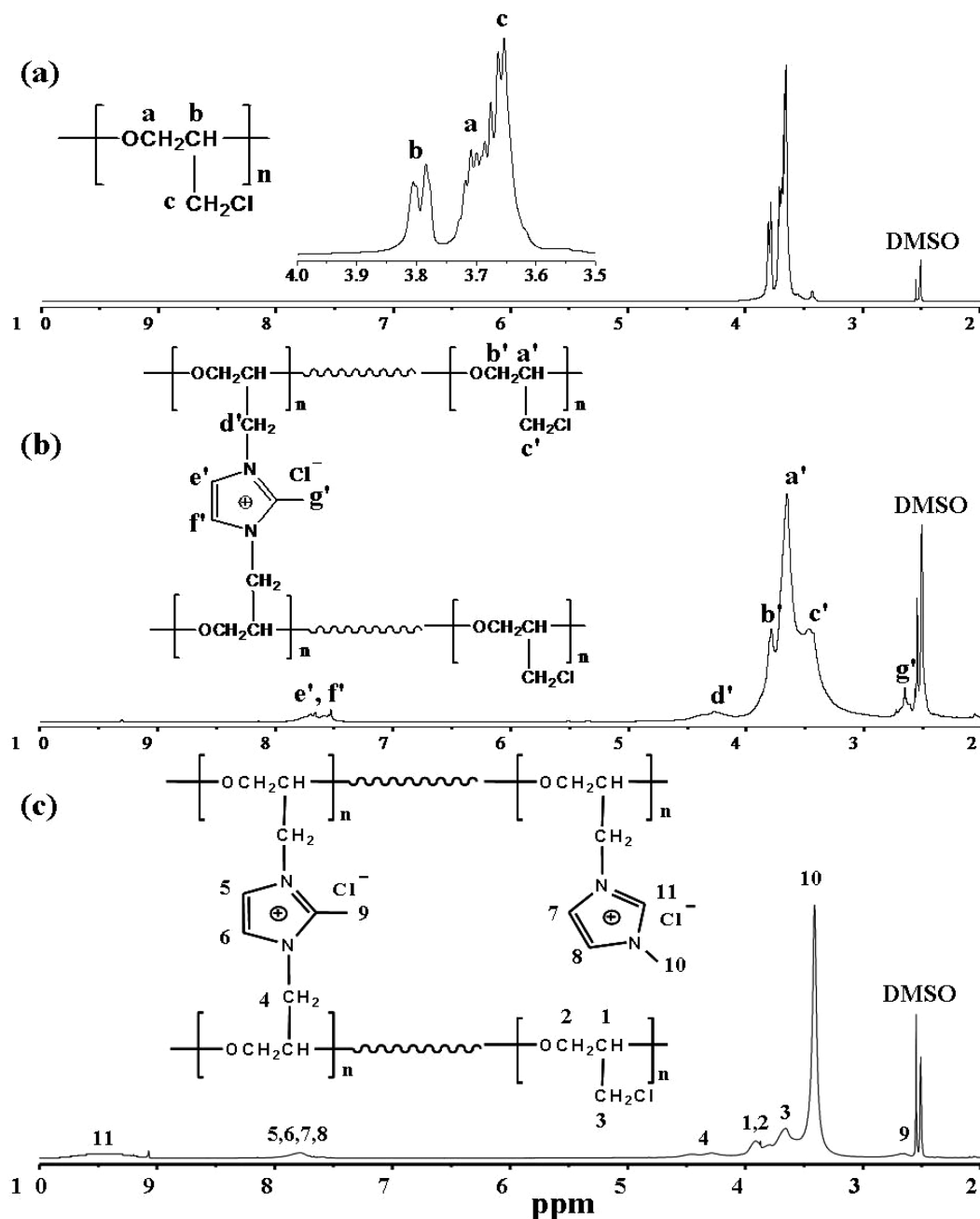
Figure 2. ^{1}H NMR spectra of (a) PECH, (b) CPECH, and (c) CQPECH.

filled with CQPECH and the composite membrane was homogeneous.

3.2. OH⁻ Conductivity. The ionic conductivities of the CQPECH membrane and composite membrane as a function of the temperature in deionized water are shown in Figure 4.

It can be seen that the Im-PECH/PTFE/OH⁻ membrane had very low ionic conductivity at any temperature, and the ionic conductivity decreased with an increase of the temperature. In this report, we added abundant 1-methylimidazole to a PECH solution to achieve a high yield of Im-PECH. Moreover, it was discovered that Im-PECH had very good solubility in water even at room temprature, and the solubility of Im-PECH increased with an increase of the temperature (Table 2).

So, the low conductivity of the Im-PECH/PTFE/OH⁻ membrane probably occurred because Im-PECH was dissolved in water during the processes of alkalization and measurement.

In the process of measurement, more Im-PECH was dissolved in water with an increase of the temperature, which made the ionic conductivity of the Im-PECH/PTFE/OH⁻ membrane decrease. It was noted that FTIR and ^{1}H NMR data provided information about the reaction of 2-methylimidazole with −CH₂Cl, but no evidence for cross-linking could be obtained in these data. However, the exact cross-linking that occurred during the reaction was too complex to be clarified by ^{1}H NMR. On the other hand, it could be seen that the CPECH/PTFE/OH⁻ membrane had a certain conductivity in Figure 4, which could assist in explaining the success of the cross-linking reaction. For M-x, the ionic conductivities increased with an increase of the temperature, which was due to the free volume in favor of ion transport, and the anion mobility increased as the temperature was elevated. Besides, the conductivities of M-x were much higher than those of the Im-PECH/PTFE/OH⁻
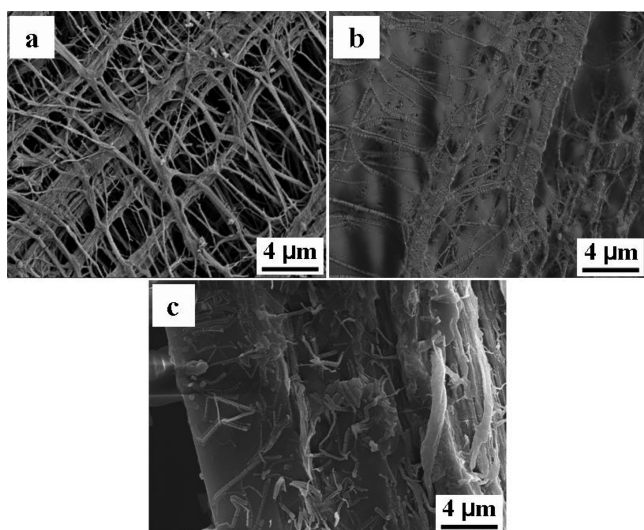
Figure 3. FSEM images of (a) the surface of PTFE, (b) the surface of the M-3, and (c) a cross section of M-3.
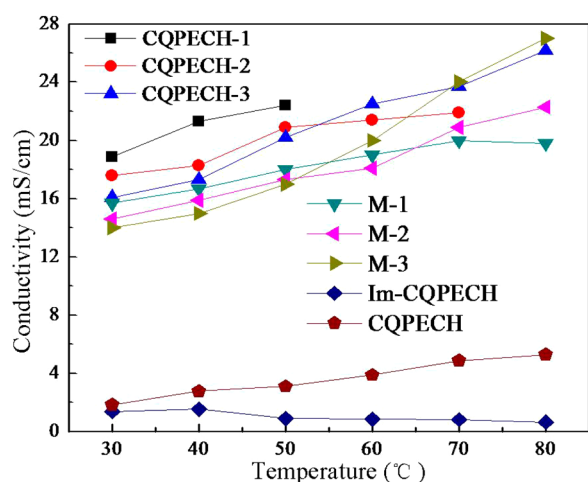

Figure 4. OH⁻ conductivities of membranes at different temperatures.

Table 2. Residual Weight (%) of the Composite Membrane after Conductivity Measurement

film	40 °C	60 °C	80 °C
Im-PECH/PTFE/OH⁻	85	52	27
M-1	96.5	94.6	92.5
M-2	98.1	97.6	95.3
M-3	99.7	99.5	98.8

and CPECH/PTFE/OH⁻ membranes. Compared with the CPECH/PTFE/OH⁻ membrane, M-x had more imidazolium cations that promoted conduction of OH⁻. Moreover,

compared with the Im-PECH/PTFE/OH⁻ membrane, M-x had undergone a cross-linking reaction, which could reduce the solubility of the PECH ionomer in water, which was a benefit for the conductivity of the membrane. M-1 showed conductivity values of 15.7 mS/cm at 30 °C, 20.0 mS/cm at 70 °C, and 19.8 mS/cm at 80 °C, but M-3 had the topmost conductivity of 27 mS/cm at 80 °C. These results indicated that M-1 exhibited poor conductivity at high temperature. Compared with those of M-2 and M-3, the conductivity of M-1 increased more slowly with an increase of the temperature. Besides, M-1 had higher conductivity than M-2 and M-3 when the temperature was lower than 60 °C and exhibited lower conductivity than M-2 and M-3 while the temperatures were respectively higher than 60 and 70 °C. On the one hand, there was less 2-methylimidazole in the reaction, leading to the lower cross-linking density of the PECH ionomers formed and some un-cross-linked PECH ionomers that could be dissolved in water at elevated temperature (as shown in Scheme 2). Therefore, the conductivity of M-1 was increased slowly with an increase of the temperature. On the other hand, the low cross-link density caused the PECH ionomers to have more imidazolium cations, which formed the process of quaternized reaction, and the solubility of un-cross-linked Im-PECH was low at lower temperature (below 60 °C). Thus, M-1 had higher conductivity at low temperature. The same phenomenon occurred in the CQPECH membrane. For CQPECH-1 and CQPECH-2, there was excessive WU and SD, which made the membranes respectively lose their morphology at 60 and 80 °C. Compared with that of the CQPECH membrane, the conductivity of the composite membrane was decreased slightly, which was a benefit for the homogeneous structure of the composite membrane. From the above analysis, we concluded that appropriate cross-linking could enhance the conductivity of the membrane especially at high temperature.

3.3. IEC, WU, and SD. The IEC was a key characterization property of an ion-exchange membrane and played a key role in determining the WU and conductivity. In principle, the IEC of an ion-exchange membrane should be as high as possible to provide maximized ionic conductivity, as long as the WU and physical swelling were not excessive.[22] In Table 3, it can be seen

Table 3. IEC, SD$_L$, SD$_T$, and WU of the Membrane at 30 °C

film	IEC (mmol/g)	SD$_L$ (%)	SD$_T$ (%)	WU (%)
CQPECH-1	1.71	30.2	33.3	92.6
CQPECH-2	1.59	18	19.6	81.3
CQPECH-3	1.39	11.2	11.9	58.9
M-1	1.64	23.8	24.6	75.8
M-2	1.45	10.8	11.4	64.2
M-3	1.31	9.01	9.5	45.3

that in the class of composite membranes, with tunable IECs ranging from 1.31 to 1.64 mmol/g, were achieved via

Scheme 2. Un-Cross-Linked PECH Ionomers
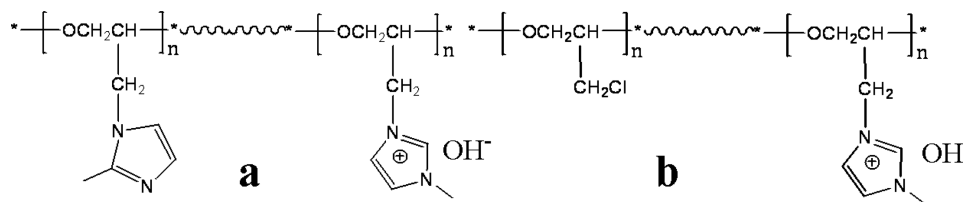
adjustment of the added amount of 2-methylimidazole during the synthesis process. Compared with CQPECH membranes, introducing PTFE to the composite membrane caused the IECs to decrease slightly rather than severely.

It was well-known that the WU had a profound effect on the hydroxide conductivity and mechanical property of AAEMs. Figure 5 shows the WUs of membranes at different
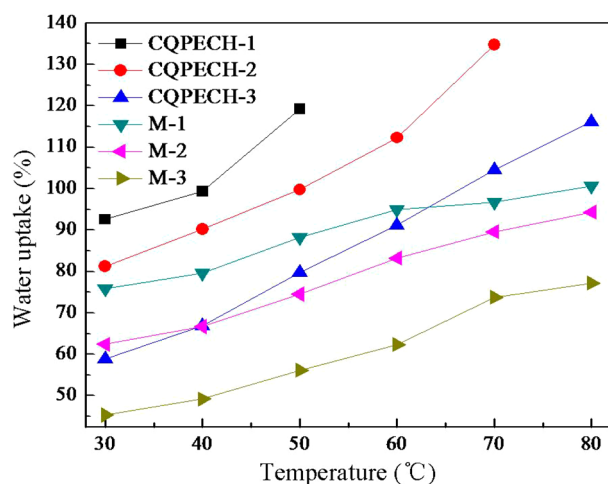

Figure 5. WUs of the membranes at different temperatures.

temperatures. It can be seen that the WUs of the membranes increased with an increase of the temperature. The possible explanation was that elevating the temperature would cause the hydrophilic domains of membrane to be more continuous, which inevitably expanded the overall hydrophilic domains and induced more WU eventually.[23] Compared with the CQPECH membrane, the introduction of PTFE caused the composite membrane to possess lower WU, which helped the membrane maintain its morphology at high temperature.

From Table 3 and Figure 5, we also found that the IECs and WUs decreased with an increase of the addition of 2-methylimidazole for all M-x, respectively. On the one hand, this phenomenon arose from the formation of a cross-linked structure that became more compact with more 2-methylimidazole as the cross-linking reagent. Hence, there was not much space in the composite membrane to contain water molecules and transmit OH$^-$. On the other hand, =N−H in 2-methylimidazole combined with −CH$_2$− in PECH would occupy part of the chloromethyl groups, thereby reducing the location to combine with 1-methylimidazole, which caused the composite membrane to have fewer active sites (imidazolium cations) and led to lower hydrophilicity and ability to transmit OH$^-$.

SDs were divided into SD$_L$ and SD$_T$ ascribed to the different measurement methods. The SD$_L$ values in water of those membranes at different temperatures are shown in Figure 6. Similar to the WU, the SD$_L$ in water also increased with an increase of the temperature and decreased with an increasing in the addition of 2-methylimidazole. The SD$_L$ of the CQPECH membrane was much higher than the that of the composite membrane under the condition of the same cross-linking degree, and CQPECH-1 and CQPECH-2 lost their morphology at temperatures of 60 and 80 °C, respectively. The SD$_L$ of M-1 in water was 23.8% at 30 °C, which was bigger than those of other PTFE composite membranes listed in Table 4. This result might be attributed to the high SD of PECH ionomers.
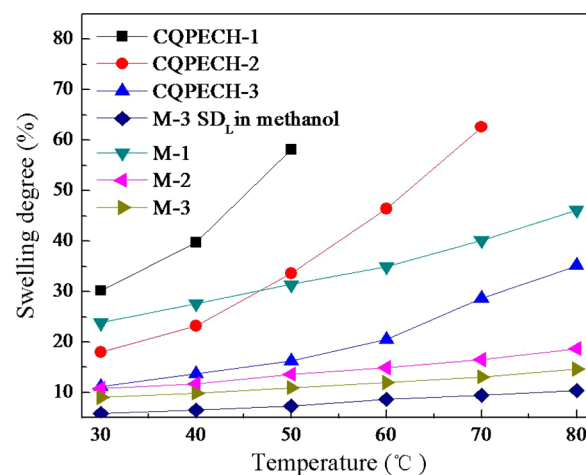

Figure 6. SDs of membranes at different temperatures.

However, M-3 showed 9.01% of SD$_L$ in water at 30 °C, which ranked among the composite membranes with small SD$_L$ values listed in Table 4, indicating that M-3 had good dimensional stability. In addition, those composite membranes were uniformly thick, flexible, and robust. The WUs (≤101%) and SD$_L$ values (≤46%) at 80 °C of those composite membranes were appropriate and satisfactory for potential applications as AAEMs in the AFCs. For M-3, we also investigated the performance of SD$_L$ in methanol. It is worth noting that SD$_L$ of M-3 in pure methanol also increased with an increase of temperature. Moreover, the SD$_L$ value of M-3 was much lower than that of M-3 in water and that of Nafion-117 in methanol (34.5%) at room temperature.[12] This significant result might be due to the different adsorption capacities between liquid molecules and copolymers. The membrane absorbed water more easily than methanol.[13] Because the use of more-concentrated fuels led to higher energy densities, it suggested a feasible approach for practical applications in DMFCs. Furthermore, the SD$_T$ values of the membranes were also measured at 30 °C (as shown in Table 3). It was seen that the SD$_T$ values of the membranes were higher than the SD$_L$ values, which was probably because of the part of the PECH ionomers on the surface of PTFE that could not be limited by the network structure of PTFE.

Table 4 lists the IEC, WU, SD$_L$, and hydroxide conductivity results of various membranes based on different polymeric materials attached with varying anion-exchange groups in typical published works and in this report. It was obvious that the conductivities of composite membranes ranked among those of good conductive PTFE composite membranes. Especially, M-3 had moderate WU and low SD$_L$. In the functional group consisting of imidazolium with close IECs and lower WUs, the membranes had higher dimensional stabilities. The composite membranes demonstrated that the dimensional stabilities were significantly improved and the good conductivities were maintained, simultaneously. Compared with other functional groups such as QATMA and QAPMG, the composite also maintained its superiority.

3.4. Thermal Analysis. The thermal stabilities of PTFE, PECH, CQPECH, and M-3 were analyzed by recording their TGA curves under flowing N$_2$. The TGA profiles of the membranes are presented in Figure 7. Before the tests, the samples were kept in a vacuum oven at 60 °C. The pristine PTFE decomposed at 500 °C, indicating that PTFE had

Table 4. IEC, WU, SD$_L$, and the Hydroxide Conductivity Reported in the Literature and This Report for Different AEMs

membrane	ionic group	WU (%)	SD$_L$ in water (%)	IEC (mmol/g)	conductivity (×10^{-2} S/cm)
[PVMIm][OH]$_{20}$-DVB$_4$[11]	imidazolium	86.56 (30 °C)	29.37 (30 °C)	0.75 ± 0.06	2.47 ± 0.15 (30 °C)
PSf135-ImOH[24]	imidazolium	92.8 ± 2.8 (20 °C)	25.5 ± 2.8 (20 °C)	2.46 ± 0.25	2.07 ± 0.06 (20 °C)
[VBMI]Cl/styrene copolymer-A[25]	imidazolium	61.9 (30 °C)	not reported	1.45	1.24 (30 °C)
IM-PFEKS[3]	imidazolium	48 (rt)	not reported	1.64	1.71 (rt)
Im-BPPO, M-5[22]	imidazolium	84 (20 °C)	17.5 (rt)	2.40 (20 °C)	3.2 (20 °C)
[PABMHM]$_{30}$[OH]$_2$[26]	imidazolium	40.50 (20 °C)	11.86 (20 °C)	0.998	about 0.5 (20 °C)
PTFE/QDPSU[20]	DABCO^a	61 ± 3 (rt)	17 ± 2 (rt)	not reported	5.1 (55 °C)
PNDB-OH-10[27]	QATMA^b	182.8 (25 °C)	about 20 (25 °C)	1.13	about 0.8 (25 °C)
PTFE/qPVBz/OH$^-$[28]	QADMHDA^c	13 ± 2 (25 °C)	7 ± 1.5 (25 °C)	not reported	1.65 (25 °C)
QPECH/PTFE1[8]	QATMHDA^d	about 70 (30 °C)	not reported	1.1	about 0.5 (30 °C)
QPE-b[29]	QATMA	61 (30 °C)	not reported	1.31	1.2 (30 °C)
poly(ether imide)[30]	QATMA	43.1 (25 °C)	not reported	0.983	0.228−0.351 (25 °C)
PPO/silica[31]	QATEA^e	9−26 (25 °C)	not reported	2−2.3	1.2−3.5 (30−90 °C)
PSGOH-0.6[32]	QAPMG^f	17 (20 °C)	11 (rt)	1.17	1.2 (20 °C)
PSQNOH-40[33]	QATMA	13 (20 °C)	8 (20 °C)	1.47	1.5 (20 °C)
M-1	imidazolium	75.8 (30 °C)	23.8 (30 °C)	1.64	1.57 (30 °C)
M-2	imidazolium	64.2 (30 °C)	10.8 (30 °C)	1.45	1.46 (30 °C)
M-3	imidazolium	45.3 (30 °C)	9.01 (30 °C)	1.31	1.40 (30 °C)

^{a}DABCO = diazobicycloocate (triethylenediamine). ^{b}QATMA = TMA-based quaternary ammonium. ^{c}QADMHDA, QAN = *N*-dimethylhexadecyl-amine. ^{d}QATMHDA = *N′,N′,N,N*-tetramethyl-1,6-hexanediamine-based quaternary ammonium. ^{e}QATEA = triethylamine-based ammonium. ^{f}QAPMG = 1,1,2,3,3-pentamethylguanidine-based quaternary ammonium.
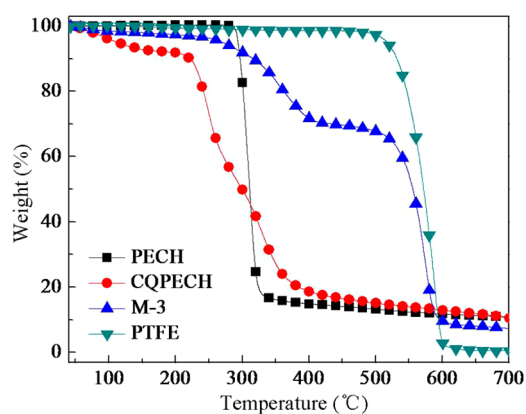

Figure 7. TGA curves of the PECH, PTFE, CQPECH, and M-3 membranes.

excellent thermal stability. The weight of PECH decreased rapidly starting from 300 °C, which was due to decomposition of the chloromethyl groups and aliphatic main chain. Compared with PTFE and PECH, CQPECH exhibited a three-step degradation process. The first weight loss was from 40 to 200 °C, which was mainly due to evaporation of the bound water and some free water absorbed during the preparation of the sample. The second weight loss near 200 °C was attributed to decomposition of the imidazolium groups, which was higher than the typical degradation onset temperature of 120 °C for quaternary ammonium cationic head groups.[34] Hence, over the short term, imidazolium head groups appeared to be more stable than quaternary ammonium-type head groups. The third weight loss above 300 °C was due to decomposition of the unreacted chloromethyl groups and aliphatic main chain of PECH. The TGA curve of M-3 was similar to that of CQPECH. The difference was that M-3 displayed a fourth weight loss at approximately 500 °C. This was attributed to decomposition of the fluorocarbon of PTFE. Further, the first weight loss of M-3 was lower than that of CQPECH. This indicated that PTFE could depress the

hydrophilicity of CQPECH. The second weight loss was about 250 °C, and the third weight loss was near 350 °C, which were decomposition of the imidazolium cations and chloromethyl groups of CQPECH in M-3, respectively. All of them were higher than those of CQPECH probably because the polyfluorocarbon backbone could increase the stability of the chloromethyl and imidazolium groups.[9] The observations indicated that the PTFE matrix could improve the thermal stability of the composite AEM.

3.5. Mechanical Property. It was essential for AAEMs to possess adequate mechanical strength to withstand fabrication of the MEA.[35] The results of stress−strain tests of an alkaline CQPECH membrane, raw PTFE film, and alkaline composite polymer membrane are shown in Table 5. The poor mechanical

Table 5. Key Mechanical Properties of the CQPECH Membranes, PTFE, and Composite Membranes

membrane	tensile strength (MPa)	Young's modulus (MPa)	elongation at break (%)
CQPECH-1	0.317	0.693	57
CQPECH-2	0.526	1.542	43
CQPECH-3	0.793	2.50	32
PTFE	45.2	70.1	110
M-1	53.2	82	82
M-2	59.6	90	71
M-3	67.3	110	54
Nafion-117[36]	28.4	100	329.3
PTFE/ PVBTMAH978[37]	27	381	27
BIm-PPO-0.54[38]	49.9	870	7.6

properties of CQPECH membranes are shown in Table 5, which indicates that the membrane was brittle. The dry PTFE film displayed a tensile strength, an elongation to break and Young's modulus of 45.2 MPa, 110%, and 70.1 MPa, respectively, which indicated that PTFE had excellent mechanical property. For a composite polymer membrane, testing demonstrated a tensile stress at a maximum load of

53.2−67.3 MPa, Young's modulus of 82−110 MPa, and a maximum elongation of 54−82%, which indicated sufficient strength for fuel-cell applications. From Table 5, we can get the following information: (1) With increasing amount of 2-methylimidazole, the mechanical strength of the CQPECH membrane increased, which indicated that a cross-linked network could impove the mechanical property of CQPECH. (2) The introduction of the PTFE support induced a large increase of the tensile strength and Young's modulus, and the mechanical strength was also increased with increasing amount of 2-methylimidazole because the composite could enhance the mechanical strength of the membrane because of the excellent mechanical property of the PTFE membrane and the cross-linked network that restricted the motion of the M-x chain segment. These results indicated that the introduction of the PTFE support induced a large increase of the mechanical property of the membrane and the cross-linked network had improved the mechanical property of the composite membrane. It should be noted that the mechanical properties of M-x were much better than those of Nafion-117 and some reported AEMs. These results demonstrated that these composite membranes were ductile and tough enough to be used as AEMs in fuel cells.

3.6. Stability of the Membrane. To comprehensively evaluate the critical qualities of composite membranes, we investigated the long-term physical stabilities of conductance of M-1 and M-3 in water at 60 °C. As demonstrated in Figure 8,
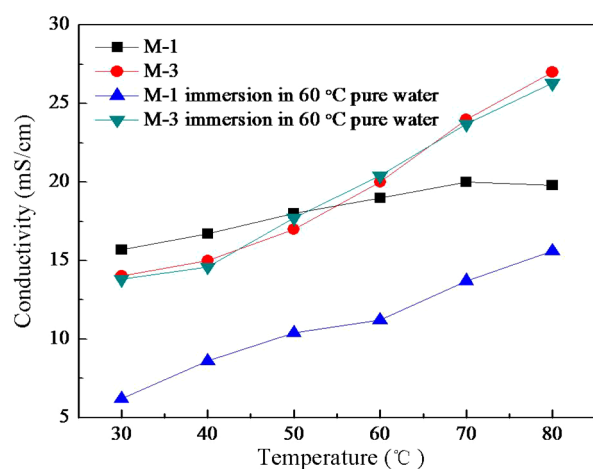

Figure 8. Variations in the ionic conductivities of M-1 and M-3 before and after immersion in pure water at 60 °C for 15 days as a function of the temperature.

the conductivity of M-3 in pure water at 60 °C showed no sign of decreasing over a test period of 15 days. This suggested that there was little dissolution of CQPECH. However, the conductivity of M-1 decreased dramatically under the same condition. One of the reasonable explanations for the results was probably that the un-cross-linked PECH ionomers shown in Scheme 2 were dissolved in water at 60 °C, which made the amount of imidazolium cations decrease, resulting in a decrease of the conductivity. The result also indicated that use of 2-methylimidazole as the cross-linking agent could improve the physical stability of PECH ionomers in hot water, and the physical stability of PECH ionomers increased with an increase of 2-methylimidazole.

From the viewpoint of applications, AEMs should be stable in an alkaline solution, especially at high pH and elevated

temperature. In this report, the stability of M-3 was investigated by conditioning, immersing the sample in a 1 M KOH solution at 60 °C for 15 days to check for changes in the ionic conductivity. Figure 9 shows the hydroxide conductivity of M-3
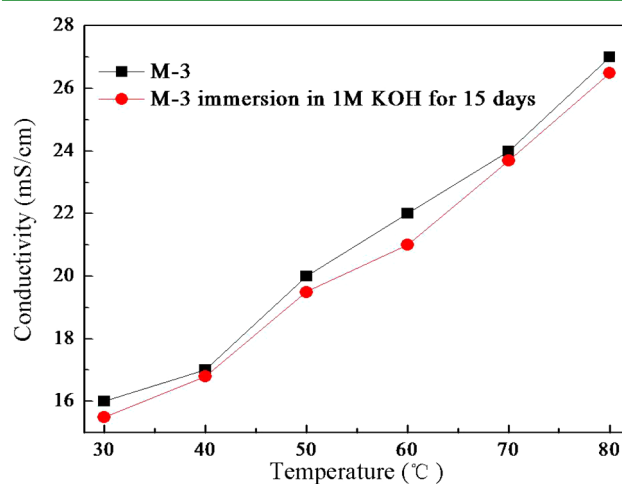

Figure 9. Variations in the ionic conductivities of M-3 before and after immersion in 1 M KOH at 60 °C for 15 days as a function of the temperature.

before and after treatment with 1 M KOH at 60 °C for 15 days. No obvious decrease of the conductivity can be observed. We also explored the surface morphology of M-3 after conditioning with 1 M KOH at 60 °C for 15 days. In Figure 10, it can be
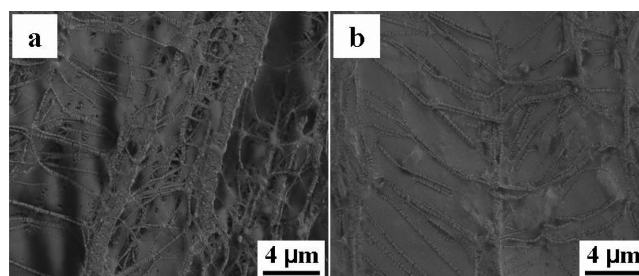

Figure 10. SEM images of (a) the surface of M-3 and (b) the surface of M-3 after the stability test.

seen that there was no obvious change in the surface morphology of M-3 after the stability test and the membrane was still tight and homogeneous, indicating good chemical stability of the M-3 membrane in a KOH solution.

3.7. Fuel-Cell Testing. Figure 11 shows the polarization and power density curves for a H_2/O_2 fuel cell assembled with M-3. The single-cell performance was operated at 50 °C, and the thickness of the membrane was 42 μm (waterish). It could be seen that the open-circuit potential was 0.78 V. The high open-circuit potential indicated that the PTFE pores were filled with CQPECH/OH$^-$ polymer and M-3 had effectively suppressed the rate of methanol crossover. The power density was 23 mW/cm^2 at a current density of 58 mA/cm^2. Generally speaking, the properties of AAEM-based cell behavior could be affected by many factors such as catalyst loading, temperature, and a MEA fabrication procedure. Moreover, the conductivity of M-3 at 50 °C was not very high, which perhaps also affects the single-cell performance. Compared with the previous report about Im-AAEM that exhibited a peak power density of 16
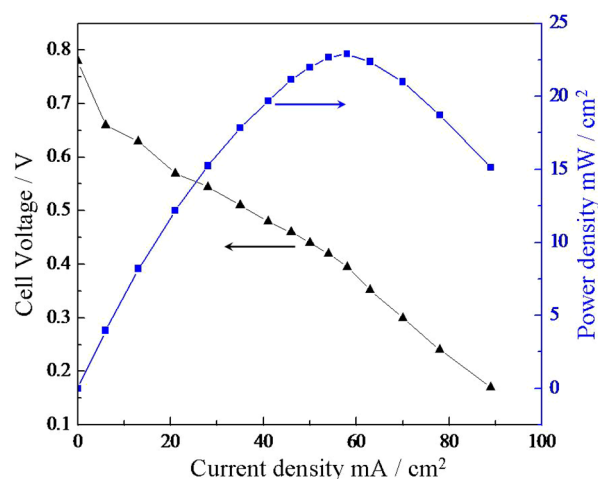
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Figure 11. Polarization and power density curves of a H_2/O_2 fuel cell assembled with M-3. The cell temperature was 50 °C.

mW/cm^2 at 60 °C,[24] M-3 presented more potential electrochemical properties. In the future, we will pay more attention to optimizing the amount of 2-methylimidazole to fabricate the membrane that has a higher electrochemical performance.

4. CONCLUSION

PECH with chloromethyl groups was successfully cross-linked with 2-methylimidazole and quaternized with 1-methylimidazole to obtain CQPECH. The composite AEM was prepared by combining CQPECH with a porous PTFE membrane. FSEM results showed that CQPECH had penetrated into the pores of the PTFE membrane. The dimensional stability of the composite membrane was preferable [M-3 had moderate WU (45.3 at 30 °C) and very low SD (9.01 at 30 °C) in water]. Moreover, the IEC value of M-1 reached a maximum value of 1.64 mmol/g. Besides, the ionic conductivities of the membranes were all above 10^{-2} S/cm and increased with an increases of the temperature and IEC. Furthermore, the WU, SD, IEC, and ionic conductivity decreased with an increase in the addition of 2-methylimidazole. The PTFE reinforcement technique allowed the composite preferable mechanical property and thermal stability. The mechanical strength was also improved by the cross-linked network. Thermal analysis results showed that the PTFE membrane could improve the thermal stabilities of the composite AEMs, which was stable below 250 °C under an N_2 atmosphere. The physical stability of the membrane in pure water at 60 °C was increased with an increase of the 2-methylimidazole content, and M-3 exhibited good chemical stability in a high-pH solution at 60 °C. A single H_2/O_2 fuel cell tested at 50 °C with M-3 yielded a peak power density of 23 mW/cm^2. Such comparable performance and chemical stability revealed the great potential of the cross-linked composite AEM.

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