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Research article

Preparation and investigation of high-temperature proton exchange membranes based on phosphoric acid doped imidazolium polysilsesquioxane crosslinked poly(vinyl chloride)

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Abstract. Developing high-performance and low-cost polymer membranes for high-temperature proton exchange membrane fuel cells is a big challenge to the polymer design. Herein, high-temperature proton exchange membranes are prepared based on the low-cost thermoplastic resin of poly(vinyl chloride) (PVC). However, the methylimidazolium PVC exhibits significantly low phosphoric acid (PA) doping content and low conductivity due to the compact structure. Thus, the *N*-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (SiIm) is employed as a dual functionalized reagent for PVC. On the one hand, SiIm is used to quaternize PVC through the S_N2 nucleophilic substitution between chloride and imidazole. On the other hand, the crosslinked siloxane network is formed via the hydrolysis reaction of SiIm in a dilute sulfuric acid solution. The obtained polysilsesquioxane crosslinked membranes (PVC-*x*%SiIm) display good thermal stability, excellent PA doping ability, superior proton conductivity, and moderate tensile strength. For instance, the PVC-17%SiIm membrane achieves a high PA doping content of 243% after immersing in 85 wt% PA solution and exhibits the highest conductivity of 0.111 $S\cdot cm^{-1}$ at 180 °C without humidifying and tensile strength of 6.0 MPa at room temperature.

Keywords: *polymer membranes, high-temperature electrolyte membrane, crosslinking, poly(vinyl chloride), fuel cell*

1. Introduction

In recent years, high-temperature proton exchange membrane fuel cells (HT-PEMFCs) as a kind of power generation devices have attracted people's attention owing to their advantages of the simple hydrothermal management system, increased tolerance of anode fuel to CO concentration, and faster electrode dynamics at temperatures above 100 °C [1–3]. Among the state-of-the-art high-temperature proton exchange membranes (HT-PEMs), the phosphoric acid (PA) doped polybenzimidazole (PBI) membrane is considered as the best candidate for HT-PEMFCs, which possesses excellent thermal stability, excellent oxidative stability, low gas permeability and superior mechanical stiffness due to its fully aromatic heterocyclic chain [2, 4–6]. The more PA molecules doped in PBI membranes, the higher conductivities can be achieved because of the more formed hydrogen-bonding networks for proton transport, however, at the expense of mechanical strength [7, 8]. Thus, various approaches have been adopted to overcome the trade-off effect of high PA doping content and low tensile strength, including synthesis of PBI derivatives [9, 10], PBI blends [11], crosslinked PBIs [12, 13] and PBI composites [14, 15]. Nonetheless, the poor solubility of high molecular weight PBIs in

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*Corresponding author, e-mail: yjs@mail.neu.edu.cn polar solvents leads to poor processability, while the toxicity of the 3,3′,4,4′-tetraaminobiphenyl monomer severely limits their further application [2, 6]. Recently, exploration of alternative polymeric materials for HT-PEMs with superior properties is desired.

Alternatively, pyridine [16], quinolone [17], piperidine [18], pyrrolidone [19, 20] and imine [21, 22] based polymers have been widely synthesized and chosen as HT-PEMs recently. Besides, side-chain basic group grafted HT-PEMs have been developed based on quaternary ammonium [23, 24], tertiary amine [25], azole [26, 27] and imidazolium [28–33] grafted poly(arylene ether)s. It can be seen that lots of efforts have been made to graft imidazole groups onto polymers because of the wide range of chemical structure designs and the stable conjugated structure of imidazole-type compounds. The pendent imidazolium groups also facilitate the PA doping through the acid-base interaction and form hydrogen bonds, thus achieving the transport of protons. As to the polymer matrix, chloromethylation or bromomethylation of polymers is normally first carried out, followed by quaternization of functional groups. However, it is inevitable to use highly toxic halomethylating reagents in the process of halomethylation, and the degree of halomethylation is difficult to control as well. Thus, developing membrane materials with a simple synthesis process, low cost and non-toxic reagents is still a challenge for HT-PEMs.

Polymers naturally containing chloromethyl or chlorine groups can avoid the chloromethylation process. Poly(vinyl chloride) (PVC) is such a polymer containing chlorine in its repeat unit, which is widely commercialized in various fields for its low price, easy processing, excellent dielectric properties, and superior chemical robustness [34–36]. Recently, PVC-based membrane materials have been prepared for CO_2 capture [37] and fuel cells [34, 38–40]. Recently, we adopted various imidazole compounds as functionalized reagents for PVC [41–43]. It is found that the PVC membranes grafted by imidazole compounds with flexible linkage and a terminal group of imidazole/amino (*i.e.*, 1,4-bis(imidazolyl)butane [42] and 1-(3-aminopropyl)imidazole [41, 43]) exhibited significantly higher PA uptake than those grafted by mono-imidazoles and bis-imidazoles with short linkage. The above investigations indicate that the introduction of 1,4-bis(imidazolyl)butane and 1-(3-aminopropyl)imidazole could generate more free volume for PA doping, while the compact structure of PVC membranes grafted with mono-imidazoles would hinder PA doping.

In our previous work, we employed *N*-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (SiIm) as the functionalized reagent for poly(epichlorihydrin) (PECH) [44] and poly(phenylene oxide) (PPO) [32]. It is found that the grafted SiIm could form a crosslinked structure via the hydrolysis of triethoxysilyl groups in SiIm, which not only enhanced mechanical and dimensional stabilities but also improved the PA doping content due to the increased free volume and hydrogen-bonding interaction. Herein, we extended our work by using SiIm as the grafting reagent for PVC. Both the grafted imidazolium group and the generated siloxane crosslinking structure are expected to enhance the PA doping content of the PVC membrane. The structure-property relationship of PVC-SiIm membranes was investigated systematically.

2. Experimental

2.1. Materials

Poly(vinyl chloride) (PVC, $M_W = 80\,000\ \text{g}\cdot\text{mol}^{-1}$) and *N*-[3-(triethoxysilyl)propyl]-4,5-dihydroimidazole (SiIm) were obtained from Sigma-Aldrich (Shanghai, China). Other chemicals were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shenyang, China).

2.2. Fabrication of membranes

A series of SiIm functionalized PVC membranes were prepared by a solution casting method. Under magnetic stirring at 80 °C, PVC and SiIm were separately dissolved in DMAc. Then SiIm/DMAc (2.0 wt%) was added dropwise to the PVC/DMAc solution (2.0 wt%) according to molar ratios (SiIm:PVC) of 0.5:1, 0.7:1, 0.9:1 and 1:1. Each mixture was magnetically stirred at 80 °C for 2 h, then the solution was poured into a Petri dish. After evaporating the solvent at 80 °C, the membrane was peeled from the Petri dish and boiled in deionized water to remove the remaining solvent. Finally, the prepared SiIm grafted membrane was soaked in 1 M H_2SO_4 at 80 °C for 24 h to obtain a crosslinked structure via the hydrolysis of siloxane moieties as described elsewhere [32]. The obtained crosslinked membrane is named as PVC-*x*%SiIm, where *x* represents the practical molar ratio of SiIm to PVC (*i.e.*, the degree of functionalization) and is determined by a gravimetric method (*i.e.*, calculating the weight increase of PVC

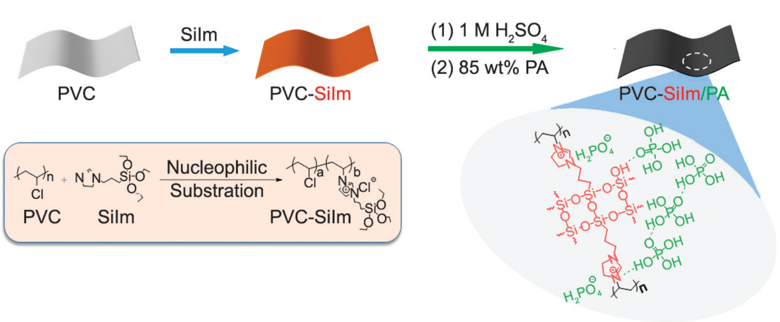

Figure 1. Schematic diagram of the chemical structure and fabrication procedure of PA doped PVC-*x*%SiIm membrane.

before and after the functionalization procedure). Figure 1 shows the chemical structure and fabrication procedure of the PVC-*x*%SiIm membrane.

2.3. Phosphoric acid doping and swellings

The dried membranes were immersed in the PA solution with a concentration of 85 wt% at 60 °C for 72 h to complete the acid doping. The acid doping content (*ADC%*) of the membrane is defined as the weight percent of the adsorbed PA to the dry membrane as calculated by Equation (1). By measuring the size change of the membrane before and after the PA doping treatment, the area and volume swelling (*S%* and *V%*) of the membrane caused by acid doping can be determined as depicted in Equations (2) and (3):

$$ADC\% = \frac{m_1 - m_0}{m_0} \cdot 100 \ [\%] \tag{1}$$

$$S\% = \frac{S_1 - S_0}{S_0} \cdot 100 \ [\%] \tag{2}$$

$$V\% = \frac{V_1 - V_0}{V_0} \cdot 100 \ [\%] \tag{3}$$

where m, S and V represent the mass, area and volume of the membrane before (0) and after (1) immersing in the PA solution.

2.4. Characterizations

The chemical structure of samples was characterized in terms of ^{1}H-NMR (Bruker AVANCE 600 MHz, Bruker Instruments, Germany) and Fourier transform infrared (FT-IR, Bruker VERTEX70, Bruker Instruments, Germany) spectra according to our previous work [43]. Using a scanning electron microscope (SEM, Ultra Plus, Zeiss, Germany), the surface morphology of the membrane was observed. In order to eliminate the charging phenomenon of non-conductive samples, gold was sprayed on the surface of the sample. Thermogravimetric analysis (TGA, Mettler-Toledo Instruments, Switzerland) curves were collected on the METTLER-TOLEDO (HT/808) in an air atmosphere ranging from 30 to 800 °C. Differential scanning calorimetry (DSC, Q2000, TA Ltd, USA) was used to study the glass transition temperature under a nitrogen atmosphere with a scan rate of 10 °C·min^{-1} and temperatures ranging from –20 to 120 °C. The mechanical stress-strain curve of the PA doped membrane was recorded by an electronic tensile strength machine (CMT6502, SANS, China), and measured at a tensile speed of 5 mm·min^{-1} at room temperature and 120 °C in the ambient atmosphere. Before the test, the membrane sample was cut into a dumbbell shape (4 mm × 25 mm). The proton conductivity of the PA doped membrane was measured by using a four-probe conductivity cell with a frequency of 4 kHz. Before each testing, the PA doped membrane was dried at 100 °C for 2 h to eliminate the moisture effect. The calculation equation of the proton conductivity is as Equations (4):

$$\sigma = \frac{L}{RS} \tag{4}$$

where L [cm] and S [cm^2] are the length and area of the membrane, while σ [S·cm^{-1}] and R [Ω] are conductivity and resistance, respectively. The membrane electrode assembly (MEA) was made according to our previous work [44, 45]. The loading of Pt/C catalyst was 1.0 mg·cm^{-2}, and un-humidified hydrogen and oxygen were applied to the fuel cell setup.

3. Results and discussion

3.1. ^{1}H-NMR

The PVC-*x*%SiIm was synthesized through the nucleophilic substitution between the dangling chlorine atom of PVC and the imidazole group of SiIm as depicted in Figure 1. Using the solution-casting method, a series of PVC-*x*%SiIm membranes were fabricated by adjusting the initial adding molar ratios (*i.e.*, SiIm to PVC) of 0.5:1, 0.7:1, 0.9:1, and 1:1, respectively. The practical degree of functionalization was determined by a gravimetric method, which was 5%, 8%, 12%, and 17% for above each PVC-*x*%SiIm membrane. Those results suggest that the conversion rate of chloride groups into SiIm groups was less than 20%, which is probably due to the low activity of the chlorine groups in PVC compared with highly reactive chloromethyl groups [39, 43]. Maiti *et al.* [39] previously reported that the final functionalization degree of 1,2-dimethylimidazole to poly(vinyl chloride-*co*-vinyl acetate) was 11.4% when the initial weight ratio of 8:1 was adopted. Our recent work demonstrated that the practical degree of functionalization was around 19% when the initial adding molar ratio of 1-(3-aminopropyl)imidazole to PVC was 1:1 [43].

The chemical structure of PVC-17%SiIm (without hydrolysis) is confirmed by ^{1}H NMR spectra, as shown in Figure 2. As to PVC, the chemical shifts at 2.2 (H_a) and 4.5 (H_b) ppm are assigned to the hydrogen atoms in $–CH_2–$ and –CH–Cl groups, respectively [36, 39, 43, 46]. After grafting SiIm into PVC, several new peaks can be observed in the NMR spectrum of PVC-17% SiIm. For example, the peak at 8.1 ppm belongs to imidazolium groups in the SiIm moiety [31, 47, 48]. The results indicate the successful nucleophilic substitution reaction of PVC and SiIm.

3.2. FT-IR

Figure 3 depicts the FT-IR spectra of PVC and various PVC-*x*%SiIm membranes to identify the chemical structure of membranes further. For crosslinked membranes, the absorption band at about 3390 cm^{-1} results from the stretching vibration of the O–H bond [30, 43, 48], since the introduction of SiIm increased the hydrophilicity of the membrane. The characteristic peak at 1645 cm^{-1} is assigned to the C=N bond originating from the imidazolium groups [44, 49, 50]. The sharp peak at 2848 cm^{-1} is due to the stretching vibration of the $–CH_2–$ group in the SiIm side chain [30, 51]. Additionally, the peak at 611 cm^{-1} results from the C–Cl bond in PVC [43, 52], whose intensity decreased in the spectra of PVC-*x*%SiIm membranes. Thus FT-IR results also demonstrate that the SiIm side chain has been successfully grafted into the PVC backbone through nucleophilic substitution.

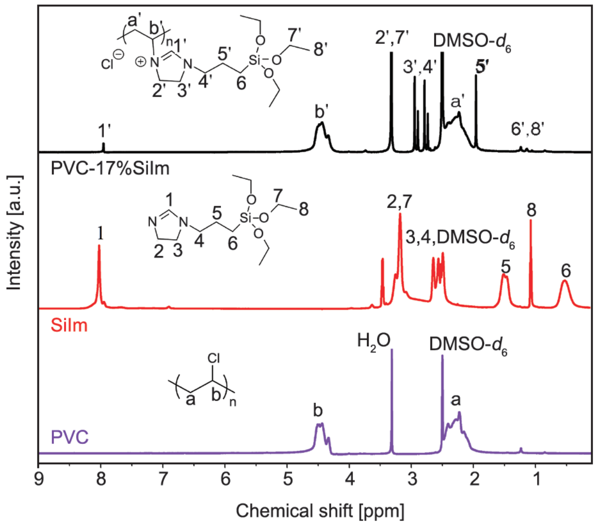

Figure 2. ^{1}H-NMR spectra of PVC, SiIm, and PVC-17%SiIm.

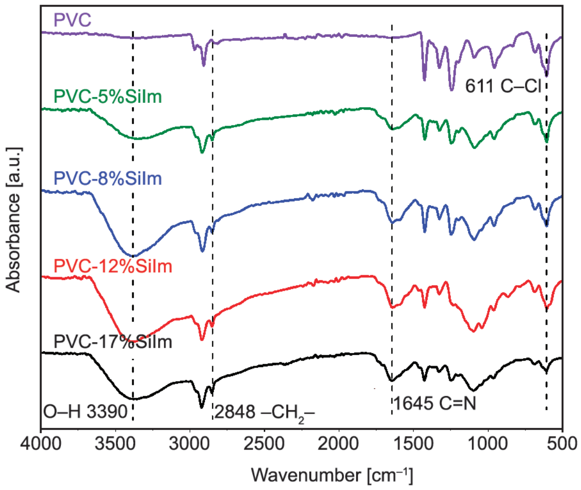

Figure 3. FT-IR spectra of PVC and various crosslinked PVC-*x*%SiIm membranes.

3.3. Solubility test of membranes

Due to the hydrolysis of triethoxysilyl groups in SiIm, the crosslinked structure can be produced in the PVC-*x*%SiIm membrane. The crosslinked PVC-*x*%SiIm membranes and the PVC membrane were immersed in DMAc and kept at 80 °C for 24 h, while the solubility testing result is depicted in Figure 4. Obviously, the whole crosslinked membranes maintained their original shape without significant mass loss after 24 h. In contrast, the pristine PVC membrane totally dissolved in DMAc under the same testing condition. As previously reported, the solubility of membranes in polar solvents is an effective method to demonstrate the formation of the crosslinked network [12, 24, 43, 53]. Thus, it can be concluded that the crosslinked structure has been successfully constructed in the PVC-*x*%SiIm membranes based on the solubility test results.

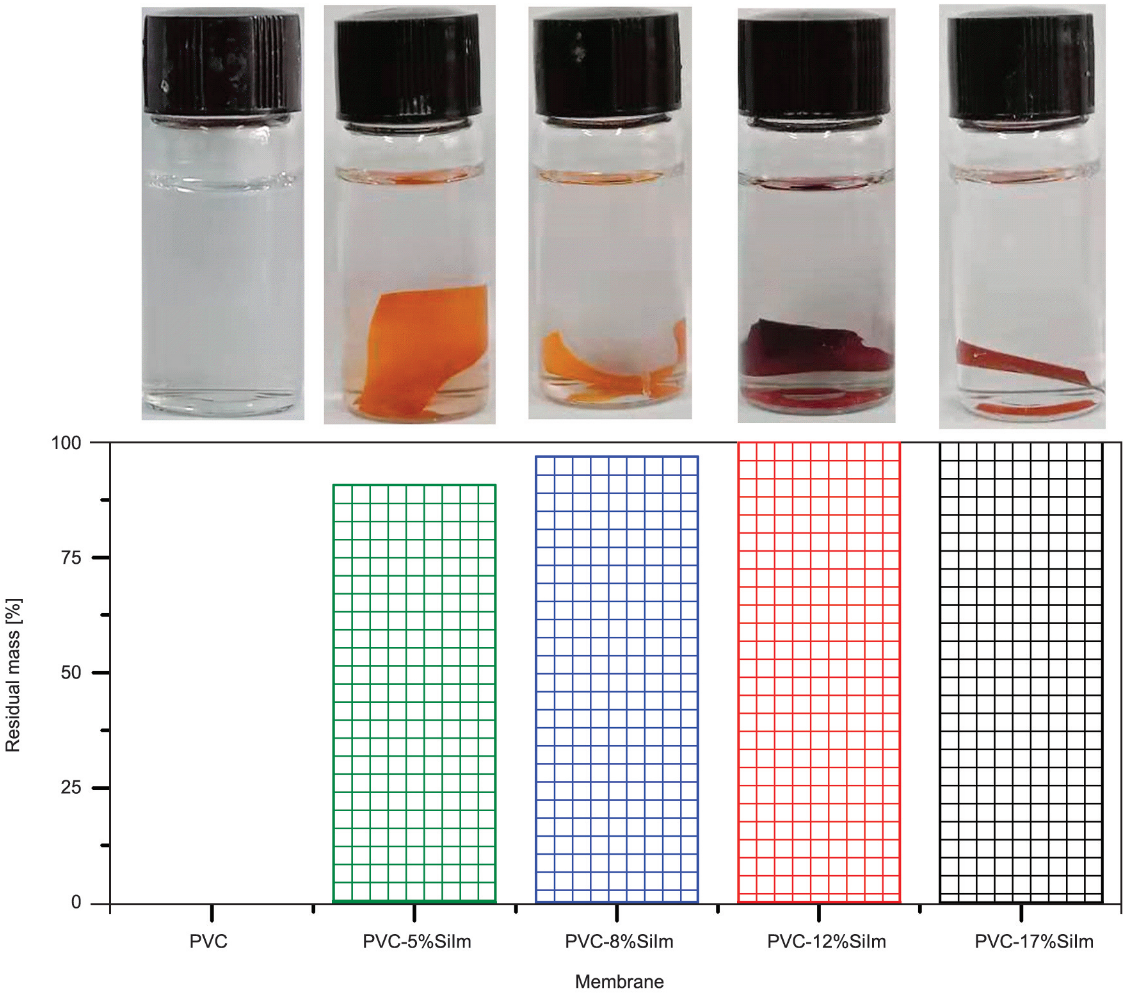

Figure 4. Residual mass and photos of PVC and crosslinked PVC-*x*%SiIm membranes.

3.4. SEM

Figure 5 provides SEM images of PVC, PVC-17%SiIm, and PVC-5%SiIm membranes. Both the surface and cross-section SEM images show that the prepared membranes possessed uniform, non-porous and dense structures. Figure 5 also shows the EDS spectrum of the cross-section image of the PVC-5%SiIm membrane. The peaks at 0.39, 0.53, and 1.74 keV correspond to the elements of N, O, and Si, as shown in Figure 5. These elements did not exist in PVC and obviously came from the side-chain of the SiIm group in PVC-5%SiIm. The EDX result further confirms that the SiIm group was grafted into the PVC matrix.

3.5. TGA

Figure 6a shows the TGA curves of PVC, PVC-5%SiIm, and PVC-17%SiIm samples under an air atmosphere. Pure PVC has good thermal stability under 230 °C, and the decomposition process presents two steps. The first decomposition stage of PVC occurred at around 240 °C due to the mass loss caused by the removal of chlorine radicals from the main chain, while the second weight loss occurred at around 430 °C resulting from the degradation of the polymer main chain [35, 39]. The PVC-*x*%SiIm membranes have three decomposition stages. The first weight loss at around 200 °C is due to the mass loss of moisture or residual solvent adsorbed in the membrane [26, 30]. The second weight-loss stage of the PVC-*x*%SiIm membranes resulted from the decomposition of the grafted imidazolium groups at about 220 °C [39, 44, 54]. Above 400 °C, the degradation plateau is mainly caused by the decomposition of the polymer backbone. Meanwhile, the residual mass of PVC-17%SiIm was slightly higher (about 5.5%) than that of PVC-5%SiIm, which is probably due to the incorporation of the inorganic silica component. A similar phenomenon has been observed for other silica composited membranes [34, 44, 58]. The above TGA results show that the PVC-*x*%SiIm membranes exhibited good thermal stability under

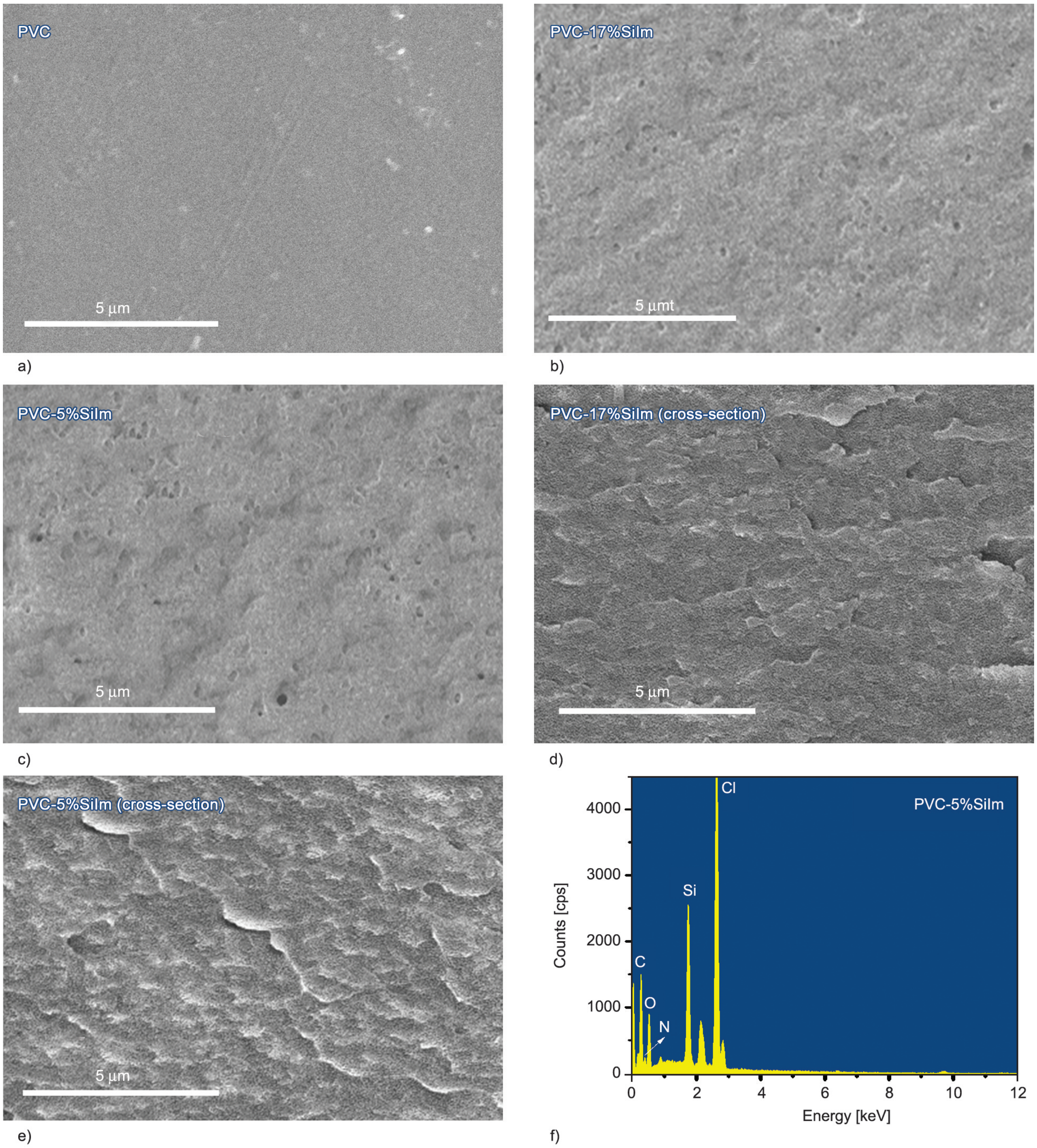

Figure 5. SEM surface images of a) PVC, b) PVC-17%SiIm and c) PVC-5%SiIm membranes; SEM cross-section images of d) PVC-17%SiIm and e) 5%SiIm membranes; and f) EDS elemental analysis spectrum of the cross-section image of PVC-5%SiIm.

200 °C, which is suitable for HT-PEMFC applications.

The glass transition temperature (T_g) is another important criterion of the HT-PEM. Figure 6b depicts the DSC thermograms for pure PVC, PVC-5%SiIm, and PVC-17%SiIm membranes. The T_g of the pure PVC membrane was around 85 °C, which is consistent with the previous report [36, 43]. When the SiIm was grafted onto PVC, PVC-5%SiIm and PVC-17%SiIm membranes displayed slightly increased T_g values, probably resulting from the introduction of inorganic components.

3.6. *ADC%* and swelling

Figure 7 provides acid doping and swelling results of various crosslinked PVC-*x*%SiIm membranes. As widely known, PVC is hydrophobic material and cannot adsorb PA. However, all the PVC-*x*%SiIm

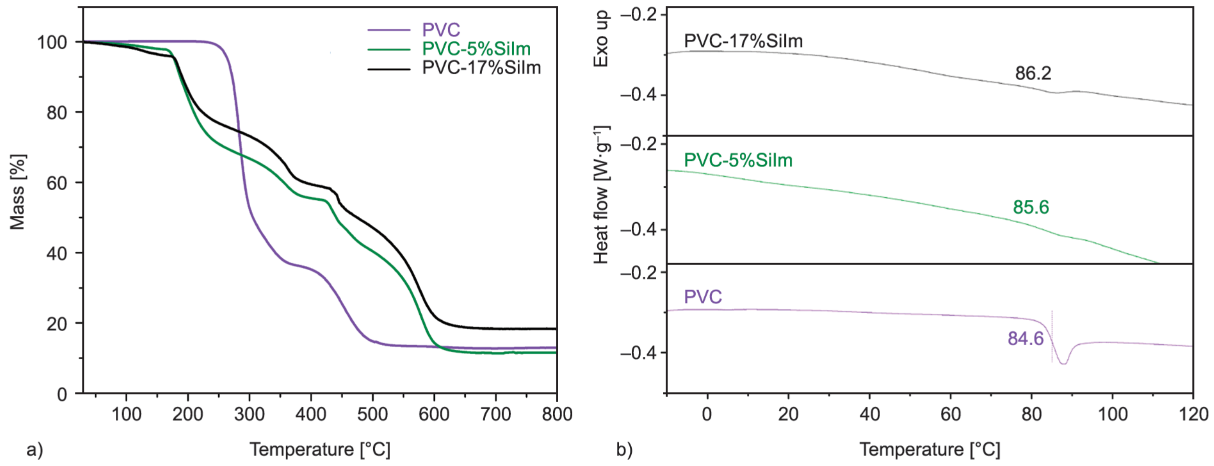

Figure 6. (a) TGA and (b) DSC curves of PVC, PVC-5%SiIm and PVC-17%SiIm membranes.

membranes displayed a high *ADC%* of above 120%. At the same time, as the SiIm content in the membrane increased, the *ADC%* of the PVC-*x*%SiIm membrane increased accordingly. Consequently, the PVC-17%SiIm membrane achieved the highest *ADC%* of 243% after doping in the 85 wt% PA solution at 60 °C. This result shows that the introduction of SiIm groups into PVC significantly enhanced the PA doping capability of PVC-based membranes. Our previous work found that the methylimidazolium group functionalized PVC membrane possessed a quite low PA doping content of below 25%, resulting from the compact structure [42]. Thus, the significant PA doping content of PVC-*x*%SiIm membranes should result from the special chemical structure of SiIm. As previously reported, the formed Si–O–Si network would increase the free volume and hydrogen-bonding interaction sites of the membrane, which benefited the PA doping [32]. Compared with the *ADC%* results in the literature, the PVC-17%SiIm membrane still showed a higher *ADC%* value. For instance, the *ADC%* of poly(aryl ether sulfone) (QPAES)-10 (*N*,*N*-diethyl-3-aminopropyl) trimethoxysilane (EPMS)-90 triethylamine (TEA) membrane and 1-decyl-2-methylimidazole grafted PPO membrane was about 183% [24] and 192% [31], respectively; the ether containing PBI membrane achieved an *ADC%* of 207.4% after doping in 85% PA solution [53]. Normally, higher *ADC%* will bring in increased conductivity, but the dimensional stability of the membrane is sacrificed due to the plasticization of PA molecules. For example, the PBI membrane with an *ADC%* of 183% had a volume swelling of 128% [55]; the 1-(3-aminopropyl)imidazole grafted PVC (PVC-19%APIm) membrane with an *ADC%* of 240% exhibited a volume swelling of 148% [43]; the methylimidazolium polysulfone (MePSU) membrane with an *ADC%* of 180% exhibited a volume swelling of 99% [28]. However, all the PVC-*x*%SiIm membranes in the present work possessed quite low volume swellings of lower than 40%, which was probably attributed to the crosslinked Si–O–Si network [44]. Liu *et al.* [15] observed a similar phenomenon for polyhedral-oligosilsesquioxane nanoparticle bearing sulfuric acid groups (SPOSS) incorporated sulfonated poly (aryl ether ketone) crosslinked PBI membranes. Due to the existence of the silica network, hybrid membranes exhibited higher *ADC%* and lower volume swelling simultaneously compared with the pure PBI membrane. Mukhopadhyay *et al.* [14] also reported that the Metal-Organic Framework (MOF) of UiO-66-NH_2 composited PBI membranes displayed an increased PA loading and

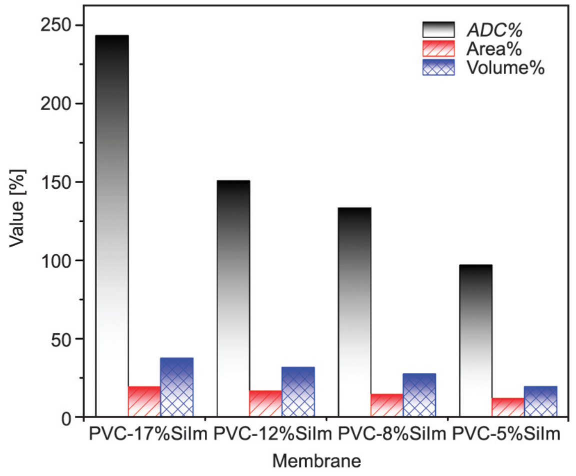

Figure 7. *ADC%*, area and volume swellings of various PVC-*x*%SiIm membranes after soaking in the 85 wt% PA solution at 60 °C.

decreased swelling as increasing MOF content in membranes. As a result, the crosslinked Si–O–Si structure in PVC-*x*%SiIm membranes not only enhanced the PA doping content, but also benefited the dimensional stability and endowed membranes with low volume swelling.

3.7. Tensile stress-strain curves

In order to meet the long-time application of membrane materials in fuel cells and electrode assembly requirements, HT-PEMs need to have excellent mechanical properties [5]. The pure PVC exhibits excellent mechanical stability, in which tensile strength and elongation were 37.3 MPa and 5.1%, respectively. The mechanical performance curves at room temperature (RT) and 120 °C of different PA doped PVC-*x*%SiIm membranes are shown in Figure 8. It can be observed from Figure 8a that due to the strong plasticization of PA molecules [23], with the increase of *ADC%*, both tensile stress and elongation at the break of the PVC-*x*%SiIm membranes gradually decreased. As an example, the tensile strength of PVC-5%SiIm/ 97%PA (19.8 MPa) was 3.3 times that of PVC-17%SiIm/243%PA membrane (6.0 MPa) when the latter had a larger *ADC%* than the former. Moreover, the mechanical properties results also indicated that the *ADC%* of membranes has a more significant influence on the rigidity of the membrane compared with the crosslinked network. Compared with the literature results, PVC-*x*%SiIm membranes have comparable mechanical strengths. For instance, Chen *et al*. [56] reported that the tensile stress at break of the PBI/235%PA membrane was about 8 MPa at RT; Zhang *et al*. [25] reported tri-functional group grafted polysulfone membrane with an *ADC%* of 186% had tensile stress at break of 2 MPa. Nevertheless, the tensile strength of PVC-*x*%SiIm membranes at elevated temperatures should be further improved. Figure 8b depicts the tensile stress-strain curves of various membranes at 120 °C. It is seen that the increased temperature greatly degraded mechanical stability. That is because that elevated temperatures softened the membranes and the plasticizing effect of PA molecules became more serious [31, 44]. As a result, the tensile strengths of PVC-5%SiIm/97%PA and PVC-17%SiIm/243%PA membranes decreased to 2.1 and 0.9 MPa, respectively.

3.8. Conductivity

Figure 9a provides proton conductivities of different PA doped PVC-*x*%SiIm membranes under anhydrous conditions. As reported in the literature, the conductivity of one PA doped membrane is related to its *ADC%* and temperature and increases with the increase of both parameters [57, 58]. Taking the PVC-17%SiIm/243%PA membrane as an example, the conductivity of this membrane at 180 °C was 0.111 $\mathrm{S\cdot cm^{-1}}$, which is nearly twice higher than that at 100 °C (*i.e.*, 0.053 $\mathrm{S\cdot cm^{-1}}$). Meanwhile, at the same temperature, the conductivity of PVC-17%SiIm/ 243%PA was much higher than that of other membranes, which is mainly due to the higher *ADC%* of PVC-17%SiIm/243%PA. It has been previously reported that more PA molecules doped in the membrane can produce a more dynamic hydrogen-bonding network, thereby achieving a larger proton transport channel and higher conductivity [2, 7, 8]. As to the PVC-5%SiIm/97%PA membrane, slightly decreased conductivities were observed at temperatures of higher than 160 °C, which possibly

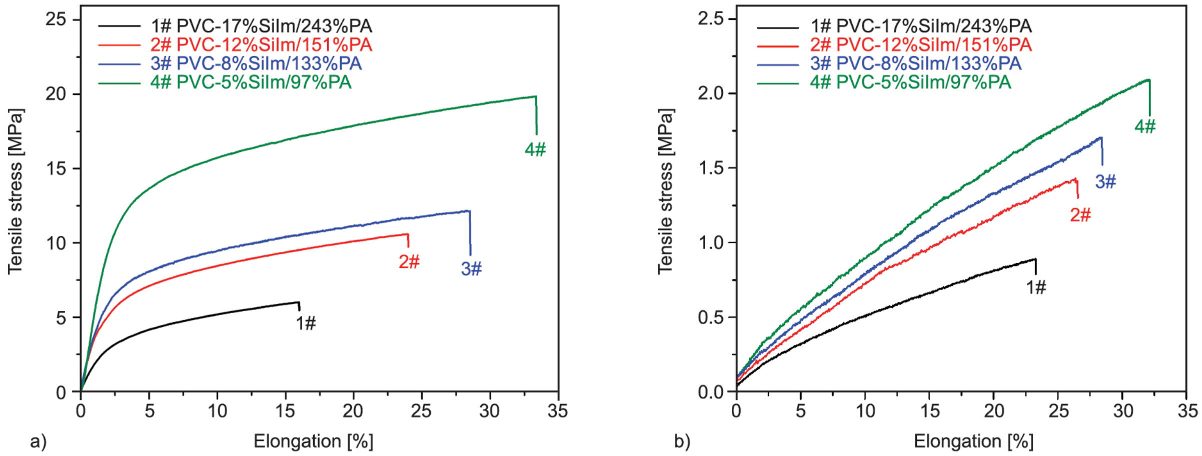

Figure 8. Mechanical stress-strain curves of PA doped PVC-*x*%SiIm membranes at RT (a) and 120 °C (b).

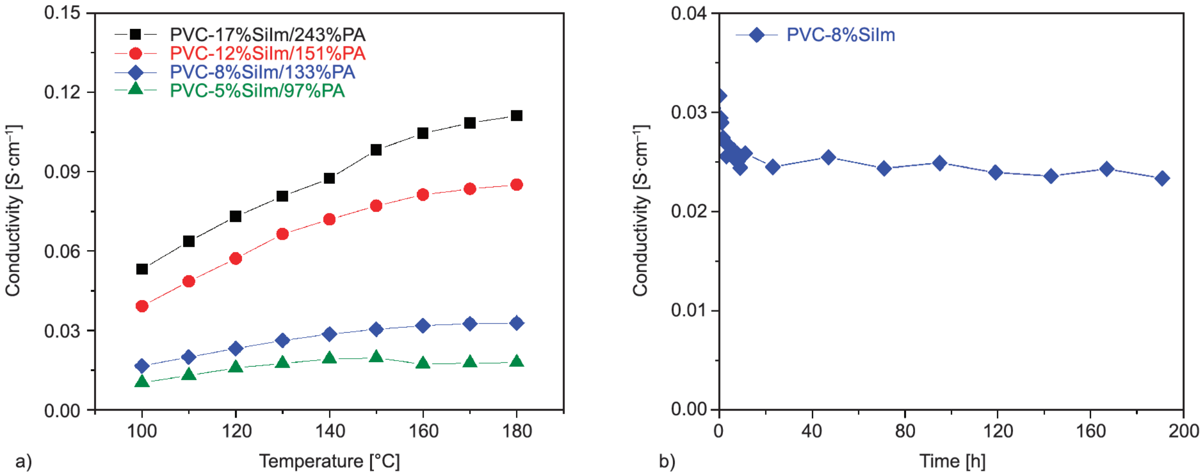

Figure 9. (a) Proton conductivities of PA doped PVC-*x*%SiIm membranes as a function of temperature; (b) the conductivity stability of the PVC-8%SiIm/133%PA membrane at 160 °C for 168 h.

resulted from the dehydration of the doped PA molecules at high temperatures [53]. Thus, a high *ADC%* is necessary for one membrane to obtain upgraded conductivity at elevated temperatures without humidifying. Through comparison with literature, the PVC-17%SiIm/243%PA membrane occupied excellent conductivities. For instance, the 1,2,4-triazole grafted PAEK membrane was synthesized by Bu *et al.* [27] and achieved a conductivity of 51 $mS\cdot cm^{-1}$ at 190 °C; Henkensmeier *et al.* [26] reported that the tetrazole-substituted polymer membrane with an *ADC%* of 112% achieved a conductivity of 25 $mS\cdot cm^{-1}$ at 160 °C; Xiao *et al.* [59] grafted benzimidazole containing compounds to PBI and the prepared PA doped membrane obtained a conductivity of 101 $mS\cdot cm^{-1}$ at 160 °C.

In addition, the conductivity stability of the PVC-8%SiIm/133%PA membrane was evaluated at 160 °C. As shown in Figure 9b, the conductivity decreased during the initial 9 h and then remained constant. The initial significant decrease in proton conductivity of the membrane probably resulted from the exudation of free PA and water molecules from the membrane, as reported for other PA doped membranes [10, 13, 18, 56]. It should be noted that PVC-17%SiIm/243%PA and PVC-12%SiIm/151%PA membranes were not suitable for assembling single cells due to their poor mechanical stabilities at elevated temperatures, although both of them exhibited high conductivities. Thus, the H_2–O_2 fuel cell performance was measured based on the PVC-8%SiIm/133%PA membrane, comprehensively taking into account the conductivity and mechanical properties. As shown in Figure 10, the open-circuit voltage (OCV) and peak power density at 160 °C were 0.81 V and 95 $mW\cdot cm^{-2}$, respectively. These values were lower than those reported in literature recently [18, 45]. As previously reported [2, 60–62], the PA has a disadvantage in the kinetics of oxygen reduction reaction. Firstly, the phosphate anion generated by PA can be adsorbed on the electrode and occupy the Pt sites, reducing the activity of the oxygen reduction reaction. On the other hand, the solubility of oxygen in the PA solution is not high. Thus, optimizations of catalysts type and loading, ionomer binder, and overall MEA fabrication process should be made in future work to improve the fuel cell performance.

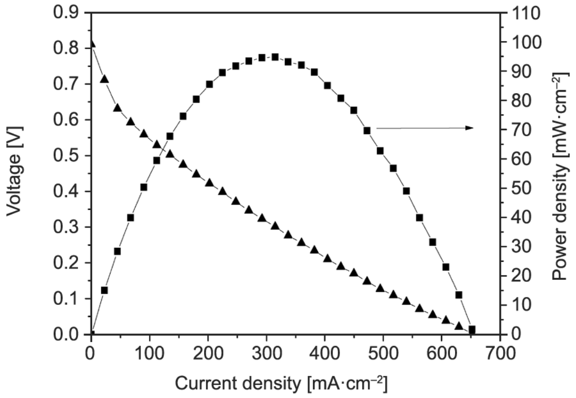

Figure 10. The polarization and power density curves of the H_2–O_2 cell with the PVC-8%SiIm/133%PA membrane at 160 °C. The catalyst loading of Pt was 1.0 $mg\cdot cm^{-2}$ for each electrode.

4. Conclusions

A series of new HT-PEMs were developed based on PVC and SiIm. PVC was chosen due to its low cost, convenient processability, and its natural chlorine atoms in the backbone. Through the S_N2 nucleophilic substitution reaction between the dangling chlorine atom of PVC and the imidazole group of SiIm, the SiIm was successfully introduced into the PVC backbone as confirmed by ^{1}H NMR and FT-IR spectra. Through the hydrolysis reaction of SiIm in a dilute sulfuric acid solution, the crosslinked siloxane network was formed in the PVC-*x*%SiIm membranes. The solubility test confirmed the construction of the crosslinking structure. According to TGA, all PVC-*x*%SiIm membranes showed good thermal stabilities below 200 °C, and the SEM images depicted a uniform and dense microstructure. Due to the presence of the imidazolium group and Si–O–Si network, the PVC-*x*%SiIm membrane displayed excellent PA absorption capacity and thus achieved high proton conductivities. The siloxane crosslinked membranes also exhibited low area and volume swellings and moderate mechanical strength. As a result, the PVC-17%SiIm membrane with a PA uptake of 243% exhibited a low volume swelling of 38%, modest tensile stress at break of 6.0 MPa at RT and high conductivity of 0.111 $S\cdot cm^{-1}$ at 180 °C without humidifying. Results show that the PVC-*x*%SiIm membrane has a potential application in HT-PEMFCs.

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