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ARTICLE

Novel Hydroxide-Conducting Polyelectrolyte Composed of an Poly(arylene ether sulfone) Containing Pendant Quaternary Guanidinium Groups for Alkaline Fuel Cell Applications

Junhua Wang,[†,‡] Shenghai Li,[†] and Suobo Zhang*[,†]

[†]*Key Laboratory of Advanced Ecomaterials, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, Changchun 130022, China, and* [‡]*Graduate School of Chinese Academy of Sciences, Beijing 100039, China*

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ABSTRACT: Poly(arylene ether sulfone)s were functionalized with quaternary guanidinium groups in order to investigate their properties as novel polymeric hydroxide exchange membrane materials. The quaternized polymers were synthesized via chloromethylation of poly(arylene ether sulfone)s, followed by reactions with pentamethylguanidine. The resulting quaternized polymers PSGCl-*x* (where *x* represents the number of the quaternary guanidinium groups/repeat units) presented an elevated molecular weight and exhibited an outstanding solubility in polar aprotic solvents. Consequently flexible and tough membranes of PSGCl-*x* with varying ionic content could be prepared by casting from the DMSO solution. Novel anion exchange membranes, PSGOH-*x*, were obtained by an anion exchange of PSGCl-*x* with 1 M NaOH at room temperature. The membranes displayed a high ionic conductivity and an excellent chemical stability. The obtained alkaline anion exchange membranes (AEMs) showed conductivities almost above 10^{-2} S cm^{-1} at room temperature; the hydroxide conductivity of PSGOH-1.4 was for instance found to be 6.7×10^{-2} S cm^{-1}.

Introduction

Polymer electrolyte fuel cells (PEFCs), which convert chemical energy to electrical energy, are regarded as promising future power sources owing to their advantages, such as their high efficiency, high energy density, quiet operation, and environmental friendliness.[1−3] Up until now, the most advanced PEFCs are based on proton exchange membranes (PEMs), in particular Nafion membranes. Although the PEMs exhibit excellent chemical, mechanical, and thermal stabilities as well as high ionic conductivity, some specific limitations exist for PEMs which impede the commercialization of PEMFCs. Limitations of the use of acidic polymeric electrolytes include (1) slow electrode kinetics, (2) CO poisoning of Pt and Pt-based electrocatalysts at low temperatures, (3) high costs of the membranes and catalysts, and (4) high fuel permeabilities.[4−6]

To overcome these hurdles, there has been a growing interest in developing alkaline anion exchange membranes (AEMs) for fuel cell applications.[7−10] AEMs are designed to provide sufficient hydroxyl ions for ion exchange during electrochemical reactions in alkaline fuel cells. AEMFCs have numerous advantages over PEMFCs, including performance and cost. In a basic environment, the cathode oxygen reduction overpotential can be significantly reduced, leading to high fuel cell efficiencies. Moreover, catalysts in basic medium are more durable,[7] and the inherently faster kinetics of oxygen reduction reactions in an alkaline fuel cell renders it possible to employ non-precious metals as catalysts, thereby leading to the use of noble metals such as Pt and Ru, being avoided.[8] Further, AEMFCs offer fuel flexibility (e.g., methanol, ethanol, ethylene glycol, etc.) due to their low overpotentials for hydrocarbon fuel oxidation and reduced fuel crossover.[9,10]

Recently, many kinds of anion exchange membranes based on polymers containing quaternary ammonium groups applied for the alkaline fuel cells have been developed, such as quaternized poly(ether sulfone),[11−19] quaternized poly(2,6-dimethyl-1,4-phenylene oxide),[20] quaternized poly(phthalazinone ether sulfone ketone),[21] quaternized poly(phenylene),[22] and radiation-grafted PVDF, ETFT, and FEP,[23−25] etc. The quaternized polysulfone is typical of these AEMs and has been researched extensively. The first anion exchange membranes based on the polysulfone, Udel 1700 (Amoco), were reported by Zschocke and Quellmalz, who described the material's alkaline stability and demonstrated its use in electrodialysis.[11] They were prepared by chloromethylation of the parent polysulfone and followed by reaction with trimethylamine to form benzyltrimethylammonium groups. Zhuang et al. further developed this kind of quaternized polysulfone and used this material to produce H_2/O_2 alkaline fuel cells successfully.[18] However, compared with PEMs, the low ionic conductivity of quaternary ammonia polysulfone has become an obstacle of the further development for alkaline fuel cell applications.

One of the approaches to promote the hydroxide conductivity of quaternized polymers is to increase the basicity of the functional groups. For the quaternary ammonium hydroxide unit, an increase in its basicity leads to an augmentation of both the number of dissociated hydroxides and the water uptake, thus facilitating the ion conductivity under similar humidified conditions. Recently, Yan et al. synthesized a new quaternary phosphonium based ionomer that is highly hydroxide conductive and is soluble in low-boiling-point water-soluble solvents: tris(2,4,6-trimethoxyphenyl)polysulfone−methylene quaternary phosphonium hydroxide.[26] Pentaalkylguanidine is another kind of organic superbase. For example, the simplest member, pentamethylguanidine, possesses a pK_a value equal to 13.8 while the value of trimethylamine is only 10.8.[27] The strong basicity of pentamethylguanidine suggests that quaternary guanidinium hydroxide is a very strong base. Additionally, the positive charge

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*To whom correspondence should be addressed. E-mail: sbzhang@ciac.jl.cn.

in the guanidinium hydroxides is delocalized over one carbon and three nitrogen atoms, which gives them a high degree of thermal and basic stability.[28] However, to the best of our knowledge, the potential of this or related polymers as a hydroxide-conducting material has not been investigated so far. As a consequence, the objective of this study was to synthesize and characterize novel poly(arylene ether sulfone)s containing quaternary guanidinium hydroxide groups and evaluate their properties as alkaline anion exchange membrane materials.

Experimental Section

Materials. 4,4′-Biphenol, 4,4′-dichlorodiphenyl sulfone, chloromethyl methyl ether, and 1,1,3,3-tetramethylurea were purchased from Aldrich. Dimethyl sulfoxide (DMSO) and *N,N*-dimethylacetamide (DMAc) were stirred over CaH_2 for 24 h, then distilled under reduced pressure, and stored over 4 Å molecular sieves under a nitrogen atmosphere. Toluene and acetonitrile were dried by refluxing over sodium or CaH_2 and distilled prior to use. All other reagents were obtained from commercial sources and used as received. The unfunctionalized poly(arylene ether sulfone) was prepared as described by Harrison et al.[29]

Synthesis of 1,1,2,3,3-Pentamethylguanidine (PMG). The Vilsmeyer salt (*C*-chloro-*N,N,N′N′*-tetramethylformamidine) was obtained by reaction of 1,1,3,3-tetramethylurea with oxalyl chloride in toluene.[30] In a nitrogen atmosphere, to a solution of Vilsmeyer salt (34.2 g, 0.20 mol) in dry acetonitrile, excessive methylamine gas was slowly passed through the reaction system under room temperature. After the mixture was refluxed for 2 h, 5 equiv of 8 M NaOH solution was added under vigorous stirring. The mixture was filtered; after removal of the solvent as well as excess methylamine, the residue was distilled under reduced pressure to afford 21.9 g (0.17 mol, yield 85%) of 1,1,2,3,3-pentamethylguanidine as a colorless liquid. ^{1}H NMR (CD_3Cl): δ 2.90 (3H, s), 2.72 (6H, s) and 2.59 (6H, s). ^{13}C NMR (CD_3Cl): δ 161.24, 39.25, 38.64, and 36.48. Anal. Calcd for $C_6H_{15}N_3$ (129.2): C, 55.78%; H, 11.70%; N, 32.52%. Found: C, 55.93%; H, 11.78%; N, 31.96%.

Synthesis of Model Compound. To a 100 mL round-bottomed flak were charged 6.32 g (0.05 mol) of 1-(chloromethyl)benzene, 6.46 g (0.05 mol) of 1,1,2,3,3-pentamethylguanidine, and 20 mL of toluene. The solution was stirred at room temperature for 4 h. The precipitate was filtered, washed with toluene, and dried in a vacuum. The product was obtained in a yield of 96% (12.3 g). ^{1}H NMR (DMSO-d_6): δ 7.45−7.32 (5H, m), 4.52−4.16 (2H, m) and 3.02−2.75 (15H, m). ^{13}C NMR (DMSO-d_6): δ 163.49, 136.60, 130.00, 129.89, 129.30, 56.31, 40.84, and 38.50. Anal. Calcd for $C_{16}H_{36}N_6$ (255.8): C, 61.04%; H, 8.67%; N, 16.43%; Cl, 13.86%. Found: C, 61.01%; H, 8.62%; N, 16.31%; Cl, 13.92%.

Synthesis of Polysulfone Containing Chloromethyl Groups (PSCM-*x*). The DS values of the polymers, where DS represented the degree of substitution (the number of chloromethyl groups/repeat units), were controlled by adjusting the amount of $ZnCl_2$. A typical synthesis procedure of PSCM-1.0, where 1.0 refers to the DS value, was as follows. PS (1.0 g, 2.5 mmol) was dissolved in 30 mL of 1,1,2,2-tetrachloroethane in a three-necked flask equipped with a stirrer, a condenser, and a dropping funnel under nitrogen. Anhydrous zinc chloride (0.33 g, 5 mmol) was dissolved into 8 g of chloromethyl methyl ether (CMME, 40 equiv). The zinc chloride solution in CMME was dripped into the flask by the addition funnel. Because chloromethyl methyl ether is a known toxic, carcinogenic substance, caution must be used to avoid any contact with or inhaling it. The resulting solution was heated to reflux for 4 h in the dark. After cooling to room temperature the reaction was poured into excessive methanol (0.5 L). The fiber-like precipitate was collected by filtration and washed with deionized water and methanol three times prior to being dried under vacuum to produce the final product. Yield: 98%.

Synthesis of Polysulfone Containing Quaternary Guanidinium Chloride (PSGCl-*x*). The following represents a typical procedure for the synthesis of guanidinium of PSGCl-*x*. PSGCl-1.2 (1.0 g, 2.4 mmol) was dissolved in 20 mL of DMSO, and then 1,1,2,3,3-pentamethylguanidine (0.7 g, 4.8 mmol) was added. The reaction mixture was stirred at room temperature for 12 h and then poured into distilled water. The precipitate was filtered off, washed with deionized water thoroughly, and dried in vacuum oven for 24 h at 60 °C to give product with 95% of yield. NMR was used to confirm the synthesis of PSGCl-1.2, and the degree of conversion of $-CH_2Cl$ group was close to 100%.

Membrane Casting and Preparation of Polysulfone Containing Guanidinium Hydroxide (PSGOH-*x*). PSGCl-*x* membranes were cast from DMSO solutions (4 wt %) in a custom-built flat glass dish. The membranes were first dried at 40 °C for 4 h and at 80 °C for 12 h and then vacuum-dried at 100 °C for 24 h. PSGOH-*x* membranes were obtained by treating PSGCl-*x* in 1 M NaOH at room temperature for 48 h to exchange the chloride ions for hydroxide ions. Then, the membranes were washed thoroughly to remove residual NaOH and immersed in deionized water for 48 h prior to analysis.

Measurements. ^{1}H and ^{13}C NMR spectra were measured at 300 MHz on an AV300 spectrometer. FT-IR spectra were recoded on membrane samples of thickness 10 μm using a Bio-Rad digilab Division FTS-80 FT-IR spectrometer. Elemental analyses were performed on an Elemental Analyses MOD-1106. The reduced viscosities were determined with an Ubbelohde capillary viscometer at 30 ± 0.1 °C on 0.5 g dL^{-1} concentrations of polymer in DMSO. Thermogravimetric analysis (TGA) was performed in nitrogen with a Perkin-Elmer TGA-2 thermogravimetric analyzer at a heating rate of 10 °C min^{-1}. Molecular weights were also determined by gel permeation chromatography (GPC) using a Waters 515 HPLC pump, coupled with a Waters 410 differential refractometer detector and a Waters 996 photodiode array detector operating at a wavelength of 260 nm. $CHCl_3$ was used as eluent. Tensile measurements were carried out with an Instron-1211 mechanical testing instrument at a speed of 1 mm min^{-1}.

Ion Exchange Capacity (IEC). The membranes in the hydroxide form were immersed in 100 mL of 0.1 M HCl standard for 48 h. The solutions were then titrated with a standardized NaOH solution using phenolphthalein as an indicator.

Water Uptake and Swelling Ratio Measurements. The membranes were vacuum-dried at 100 °C for 10 h until constant weight to obtain the dry material. They were then immersed in deionized water at given temperature for 4 h. After this time, the membranes were taken out, wiped with tissue paper, and quickly weighed on a microbalance. The water uptake of membranes was calculated according to

$$\text{water uptake (\%)} = [(W_{\text{wet}} - W_{\text{dry}})/W_{\text{dry}}] \times 100\% \qquad (1)$$

where W_{dry} and W_{wet} are the weight of the dry and the corresponding water-swollen membranes, respectively.

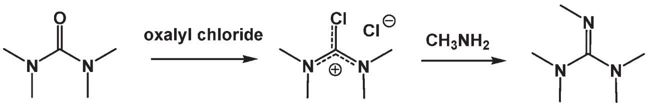
The water swelling ratio of the membranes was investigated by immersing the round-shaped samples into water at given temperature for 4 h, and the swelling ratio was calculated from

$$\text{swelling ratio (\%)} = [(l_{\text{wet}} - l_{\text{dry}})/l_{\text{dry}}] \times 100\% \qquad (2)$$

Here, l_{dry} and l_{wet} are the diameter of the dry and wet samples, respectively.

Hydroxide Conductivity. The hydroxide conductivity (σ, S cm^{-1}) of each membrane coupon (size: 1 cm × 4 cm) was obtained using $\sigma = d/LsWsR$, where d is the distance between reference electrodes and Ls and Ws are the thickness and width of the membrane, respectively. The resistance value (R) was measured over the frequency range from 1 mHz to 100 kHz by four-point probe alternating current (ac) impedance spectroscopy using an electrode system connected with an impedance/gain-phase

Scheme 1. Synthetic Route of 1,1,2,3,3-Pentamethylguanidine (PMG)



analyzer (Solatron 1260) and an electrochemical interface (Solatron 1287, Farnborough Hampshire, ONR, UK). The membranes and the electrodes were set in a Teflon cell, and the distance between the reference electrodes was 1 cm. The cell was placed in a thermo-controlled chamber in liquid water for measurement. Conductivity measurements under fully hydrated conditions were carried out with the cell immersed in liquid water. All samples were equilibrated in water for at least 24 h prior to the conductivity measurement. At a given temperature, the samples were equilibrated for at least 30 min before any measurements. Repeated measurements were then taken at that given temperature with 10 min interval until no more change in conductivity was observed.

Alkaline Stability. PSGOH-*x* samples were kept in a NaOH solution (1 M) at 25 or 60 °C for 48 h. Then, they were washed with deionized water to remove the sorbed sodium hydroxide and immersed in deionized water for at least 48 h prior to measure for ionic conductivity analysis.

Results and Discussion

The synthetic route of 1,1,2,3,3-pentamethylguanidine (PMG) is outlined in Scheme 1. *C*-Chloro-*N,N,N′N′*-tetramethylformamidine (the Vilsmeier salt) was prepared by reaction of 1,1,3,3-tetramethylurea with oxalyl chloride in toluene at a yield of 80%. The Vilsmeier salt reacted quickly with dry methylamine gas at 30 °C, giving pentamethylguanidine (PMG) in 85% yield. The chemical structure and elemental composition of PMG were confirmed by elemental analysis as well as ^{1}H and ^{13}C NMR spectroscopies.

As shown in Scheme 2, the preparation of AEMs involves several chemical reactions: chloromethylation, quaternization, and alkalization. Among them, chloromethylation and quaternization are two key reactions that determine the ionic conductivity.[26] The chloromethylation of polymer is a valuable procedure that was established nearly four decades ago.[31] Chloromethylated polymer is the starting point for the synthesis of polymer-bound reagents for ion-exchange resins due to the high reactivity of the tethered chloromethyl group. As has been reported, the cross-linking reaction often takes place rapidly during chloromethylation of polysulfone resin as the active aromatic ring attacks the chloromethyl group in a Friedel–Crafts alkylation fashion, which in turn causes gelation.[17,19] The formed gel is not useful for further functionalization and membrane preparation. Therefore, it is of high importance to study the effecting factors on chloromethylation and obtain different DS values of chloromethylated polysulfone without gelation.

Table 1. Reaction Conditions and Resultant Molecular Weights from the Chloromethylation[a]

sample	time (h)	temperature (°C)	equivalents of CMME	DS[b]	$M_w \times 10^4$ (g mol^{-1})	gelation (%)[d]
1	4	60	20	1.24	133	11
2	4	60	30	1.65	134	6
3	4	60	40	1.96	126	–[c]
4	4	40	40	0.86	121	–
5	4	70	40	2.00	134	35
6	8	60	40	1.96	144	8

[a] Reaction conditions: PS (1 g, 2.5 mmol), $ZnCl_2$ (0.86, 5 mmol), 1,1,2,2-tetrachloroethane (30 mL). [b] Degree of substitution = (number of the chloromethyl groups/repeat units). [c] No gelation. [d] After the reaction finishing, the gel-like precipitates were collected by filtration and dried under vacuum. Gelation was determined by simple weighing.

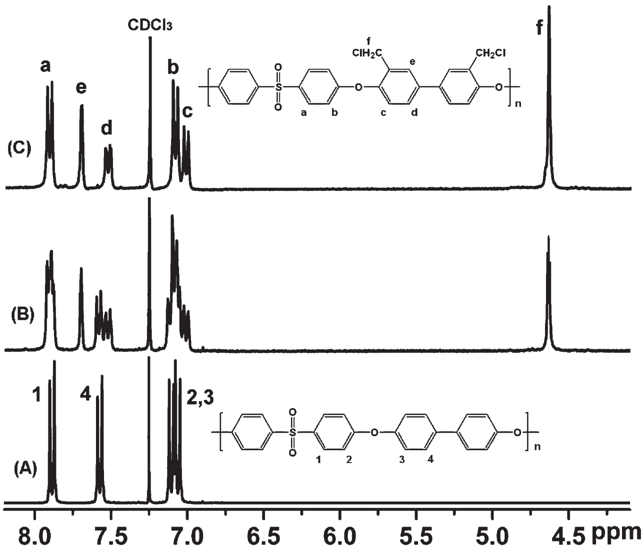
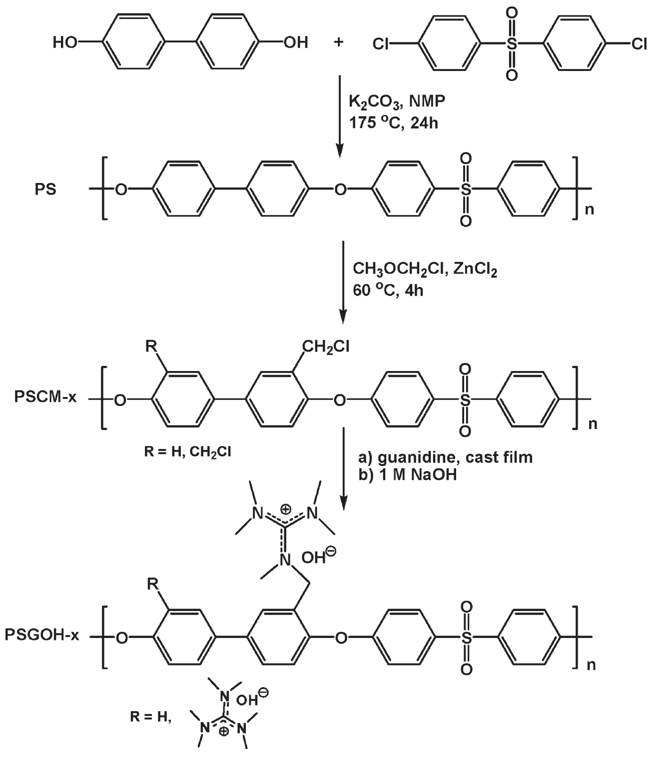


Figure 1. ^{1}H NMR spectra of PSCM-0 (a), PSCM-1.0 (b), and PSCM-1.96 (c) in $CDCl_3$.

The chloromethylation of polysulfone was carried out in 1,1,2,2-tetrachloroethane using chloromethyl methyl ether as a chloromethylation reagent and $ZnCl_2$ as a catalyst. The effects of reaction temperature, reaction time, and the amount of CMME on the chloromethylation were investigated, and the results for six different batches of chloromethylated poly(arylene ether sulfone)s, PSCM-*x*, are summarized in Table 1, where *x* refers to the DS values. ^{1}H NMR analysis (Figure 1) indicated that chloromethylation of PS occurred at the activated positions of the biphenyl moieties. The signals with chemical shifts δ 7.0–7.9 were assigned to the aromatic hydrogen of PSCM-*x*. Resonances due to chloromethyl groups were detected at δ 4.6. The DS values of the polymers were calculated from the ratio of the integration of Hf to Ha. Reaction temperatures higher than 60 °C, reaction times longer than 8 h, or the amount of CMME used less than 40 equiv resulted in gels, presumably because of cross-linking via Friedel–Crafts alkylation by the chloromethyl groups in the presence of a Lewis acid. The optimized reaction conditions was as follows: PS (1 g, 2.5 mmol), CMME (8 g, 100 mmol, 40 equiv), $ZnCl_2$ (0.68 g, 5.0 mmol, 2 equiv), 1,1,2,2-tetrachloroethane (30 mL), 60 °C. Under this optimized condition, the reaction was rather fast; it took ~4 h for the DS to reach 1.96 (close to the theoretical maximum value) without gelating. On the other hand, we noticed that $ZnCl_2$ affected the chloromethylation of polysulfone directly and could determine the DS values by controlling the amount of $ZnCl_2$ used under this reaction condition. As shown in Figure 2, increasing the amount of $ZnCl_2$ increased the number of the tethered chloromethyl group. For example, the gained DS values of PSCM were approximately 0.5, 1.0, and 2.0, with the used equiv of $ZnCl_2$ 0.5, 1.0, and 2.0 in 4 h, respectively.

The PSCM-*x* was converted to a quaternized poly(arylene ether sulfone)s (PSGCl-*x*) by reaction with 1,1,2,3,3-pentamethylguanidine (PMG). The mole ratio of PMG to the chloromethyl groups was set to be 2:1 to ensure a complete conversion of the $-CH_2Cl$ units into the quaternary guanidinium moieties. In addition, the viscosity of PSGCl-*x* was even greater than the parent polymer in accordance with the reaction. This was due to the positive charges (the quaternary guanidinium groups) located along the polymeric chains that repulsed each other in solution, thereby inducing chain extension. The structure of the ionomers was confirmed by NMR and IR spectroscopies. To obtain precise data regarding the chemical shifts of ^{1}H and ^{13}C NMR, the model

Scheme 2. Synthetic Route of PS, PSCM-*x*, and PSGOH-*x*



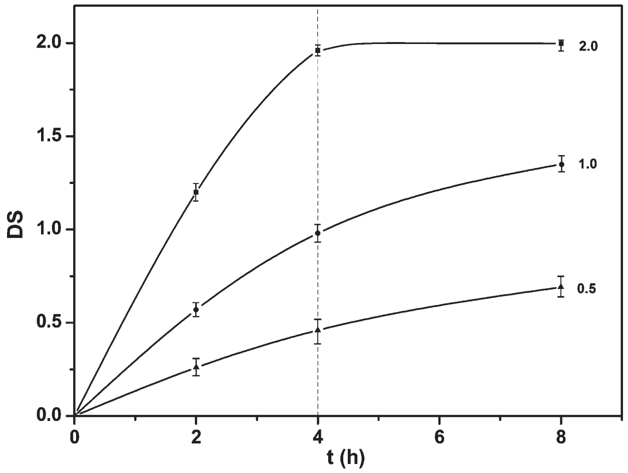
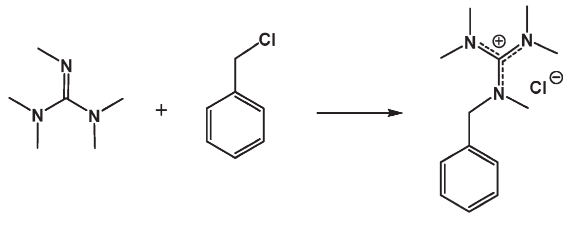


Figure 2. Effect of the amount of $ZnCl_2$ on the DS of PSCM. Reaction conditions: (a) PS (1 g, 2.5 mmol), CMME (8 g, 0.1 mol, 40 equiv), $ZnCl_2$ (0.17 g, 1.25 mmol, 0.5 equiv), 1,1,2,2-tetrachloroethane (30 mL), 60 °C; (b) PS (1 g, 2.5 mmol), CMME (8 g, 0.1 mol, 40 equiv), $ZnCl_2$ (0.34 g, 2.5 mmol, 1.0 equiv), 1,1,2,2-tetrachloroethane (30 mL), 60 °C; (c) PS (1 g, 2.5 mmol), CMME (8 g, 0.1 mol, 40 equiv), $ZnCl_2$ (0.68 g, 5.0 mmol, 2.0 equiv), 1,1,2,2-tetrachloroethane (30 mL), 60 °C.

Scheme 3. Synthetic Route of Obtaining a Model Compound



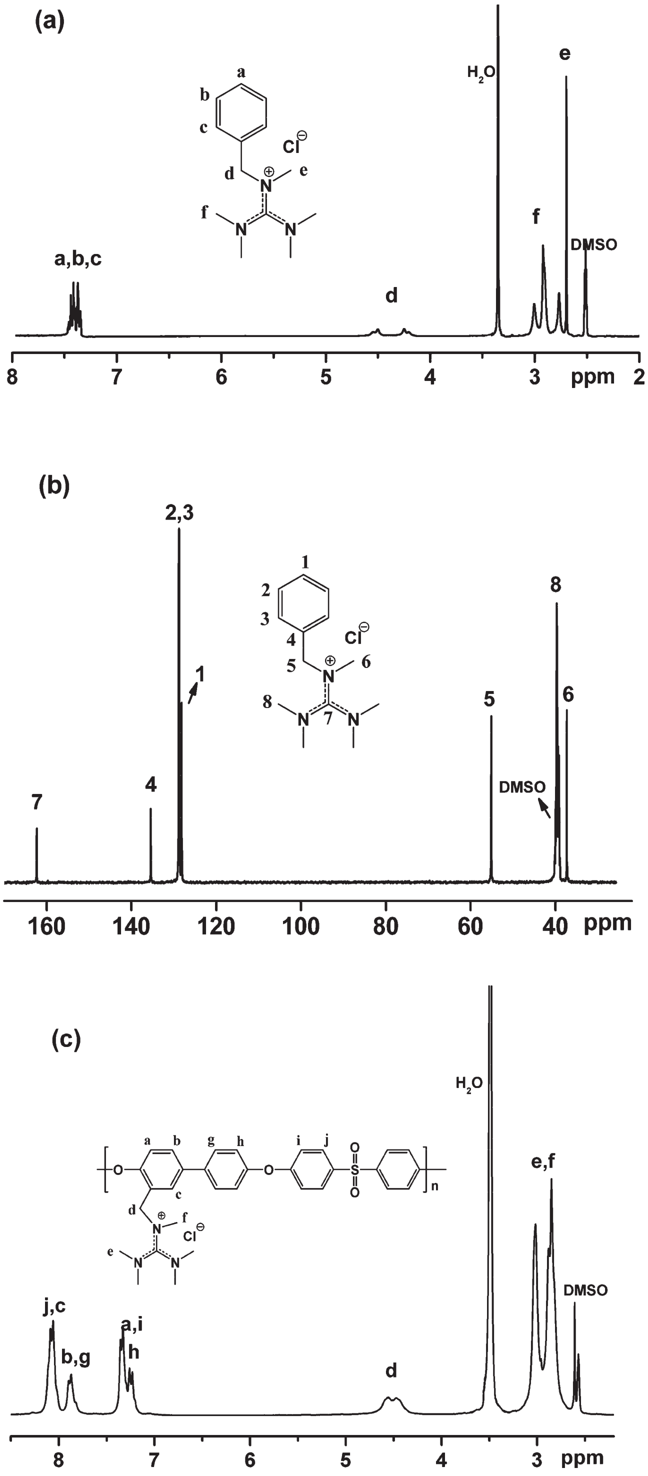


Figure 3. ^1H NMR and ^{13}C NMR spectra of model compound (a, b) and PSGCl-1.2 (c) in DMSO-d_6.

compound was synthesized by the reaction shown in Scheme 3. The PMG reacted quickly with 1-(chloromethyl)benzene at room temperature, giving rise to guanidinium chloride in quantitative yield. As shown in Figure 3a,b, the peaks around δ 4.52−4.16 (2H, m) and 3.02−2.75 (15H, m) could be assigned to the chemical shifts of the protons on the methylene and methyl groups, respectively. The integration ratio of H ($-CH_2-$) to H ($-CH_3$) was close to 2:15, as expected for the composition of the model compounds. In the ^{13}C NMR spectrum, the peak at δ 163.49 ppm was attributed to the chemical shift of the central carbon atom in the guanidinium group, and the peak at δ 56.31 ppm was assigned to the carbon atom in the methylene groups. The two peaks around δ 40.84 and 38.50 ppm were attributed to the carbon atom

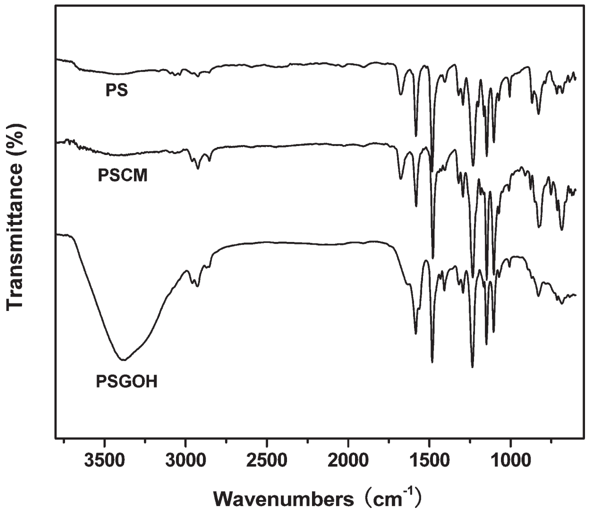


Figure 4. FT-IR spectra of PS, PSCM-1.2, and PSGOH-1.2.

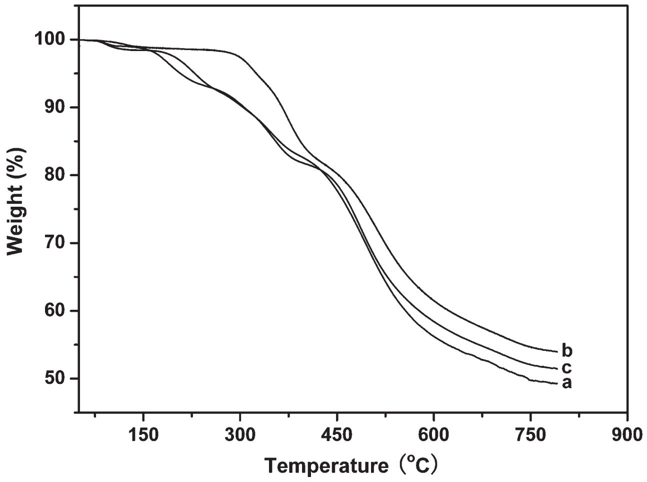


Figure 5. TGA curves for PSGOH-1.2 (a), PSGCl-1.2 (b), and PSQNOH (c) in N_2.

in the methyl groups. These characteristic chemical shifts could all be found in the ^1H spectra of PSGCl-1.2 (Figure 3c).

The FT-IR spectra of PS, PSCM-1.2, and PSGCl-1.2 are shown in Figure 4. The absorption bands at 2977−2850 cm^{-1} were characteristic of the $-CH_2-$ and $-CH_3$ groups. The absorption bands at 723−681 cm^{-1} arise from stretching vibrations of C−Cl bonds. The broad band at 3415 cm^{-1} was assigned to the stretching vibration of O−H bonds, and the band at 1564 cm^{-1} was attributed to vibrations of C=N in the guanidinium groups. After amination, the intensities of the bands at 754−681 cm^{-1} were found to substantially disappear, and new absorption bands appeared at 3415 and 1564 cm^{-1}. This result confirmed the complete conversion of the $-CH_2Cl$ groups; guanidinium units had thus been successfully introduced into the polymers.

The PSGCl ionomers exhibited outstanding solubility in polar aprotic solvents such as NMP, DMF, DMAc, and DMSO. Then, PSGCl membranes could be cast from DMSO solutions in a flat glass dish. The drying procedure was optimized to produce flat, transparent membranes while quantitatively removing the casting solvent. PSGOH membranes (in the hydroxide form) were obtained by treating PSGCls in 1 M NaOH at room temperature for 48 h. The PSGOH ionomers were soluble in NMP, DMAc, and DMSO; meanwhile, PSGOH-100 was soluble in 2-propanol. In the preparation of alkaline exchange membrane fuel cells (AEMFCs), a required property for AEMs was their solubility in low boiling point solvent such as ethanol and (*n*- or 2-)propanol since a soluble ionomer could be used in the catalyst layer to build an efficient three-phase boundary and thus drastically improve the utilization of the catalyst particles and reduce the internal resistance.[26]

Table 2. Mechanical Properties of PSGOH-*x*[a]

sample	tensile strength (MPa)	tensile modulus (GPa)	elongation at break (%)
PSGOH-0.4	67.6	1.70	10.4
PSGOH-0.6	60.1	1.61	13.5
PSGOH-0.7	55.0	1.53	18.3
PSGOH-1.0	46.3	1.20	26.7
PSGOH-1.2	39.7	0.69	35.5
PSGOH-1.4	15.8	0.33	71.4
PSGOH-1.5	−	−	−

[a] Measured at 30 °C, 50% RH.

The thermal stability of the synthesized PSGCl and PSGOH ionomers was studied under identical drying and heating conditions. The typical TGA curves are shown in Figure 5. As a result of the strong hydrophilicity of the quaternary guanidinium groups attracting water from the atmosphere, a slight weight loss was observed between 80 and 120 °C, corresponding to the evaporation of absorbed water. This behavior has been commonly found in other polymeric ion exchange membranes. The first weight loss (5%) observed for PSGCl-1.2 at 286 °C was related to the degradation of quaternary guanidinium groups, whereas the corresponding value for PSGOH-1.2 was around 185 °C. In comparison, the mass loss for the PSQNOH prepared from trimethylamine and the same PSCM started its mass loss at around 165 °C.[17] This was due to a lower thermal stability of the quaternary ammonium hydroxide as opposed to the quaternary guanidinium hydroxide. The results demonstrate that the PSGOH had a good thermal stability and a higher degradation temperature.

The mechanical properties for the PSGOH membranes over a range of IEC values are shown in Table 2. The samples displayed values of tensile stress at maximum load of 15.8−67.6 MPa, Young's moduli of 0.33−1.70 GPa, and values of elongation at break of 10.4−71.4%. At high IEC values (>2.25 mequiv g^{-1}), gel-like mechanical properties were observed. This was the result of the materials absorbing large amounts of the equilibrium water. The water sorption of these membranes increased with an increasing ion exchange capacity due to the strong hydrophilicity of the guanidinium groups. For example, the tensile stress and Young's moduli of PSGOH-1.4 decreased to respectively 15.8 MPa and 0.33 GPa. This mechanical instability was the result of a morphological change at the percolation threshold in which the hydrophilic domains became interconnected.

The water uptake of sulfonated polymers is known to have a profound effect on the conductivity and mechanical properties of PEMs. The same is true for AEMs. Water molecules dissociate the alkaline functionality and facilitate hydroxide transport. However, excessively high levels of water uptake can result in membrane fragility and dimensional change, which lead to the loss of mechanical properties. Basically, the amount of water uptake of PSGOH-*x* is strongly dependent upon the amount of quaternary guanidinium hydroxide groups and is also related to the IEC values. The water uptake was measured from the ratio of the weight of water absorbed by the membrane when immersed in water, with respect to the dry membrane weight. This data are reported in Table 3 along with the swelling ratios. As expected, the water uptake increased with increasing IEC. The water uptake of the PSGOH-*x* membranes with IEC values between 0.79 and 2.15 was in the range of 12−88%. The results also demonstrate the temperature-dependent water uptake and

Table 3. Ion Exchange Capacity, Water Uptake, Swelling Rate, and Hydroxide Conductivity of PSGOH Membranes

	IEC (mequiv g^{-1})		water uptake (%)		swelling rate (%)		conductivity (S cm^{-1})	
sample	theoretical[a]	experimental	20 °C	60 °C	20 °C	60 °C	20 °C	60 °C
PSGOH-0.4	0.86	0.79	12	15	7	8	0.005	0.008
PSGOH-0.6	1.21	1.17	17	19	11	12	0.012	0.023
PSGOH-0.7	1.37	1.34	24	39	13	16	0.018	0.035
PSGOH-1.0	1.79	1.68	39	65	16	23	0.033	0.051
PSGOH-1.2	2.00	1.89	55	107	20	46	0.045	0.074
PSGOH-1.4	2.25	2.15	88	–[b]	31	–	0.067	–
PSQNOH-1.0	2.45	1.85	44	68	17	22	0.029	0.044

[a] Calculated from ^{1}H NMR. [b] Swelled to gel-like, could not be measured.

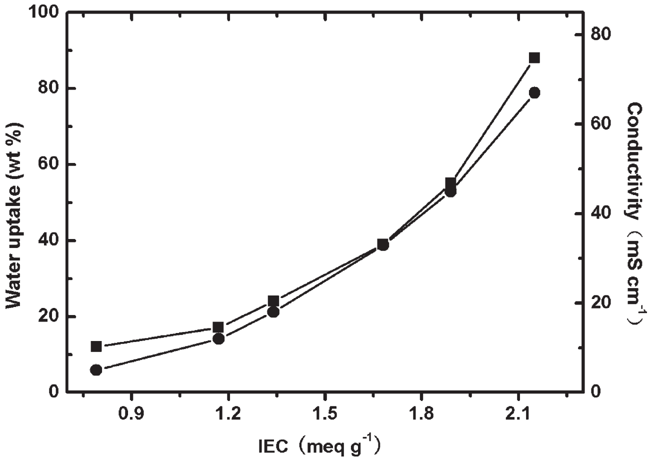


Figure 6. Water uptake and hydroxide anion conductivity versus ion exchange capacity: (■) water uptake; (●) conductivity.

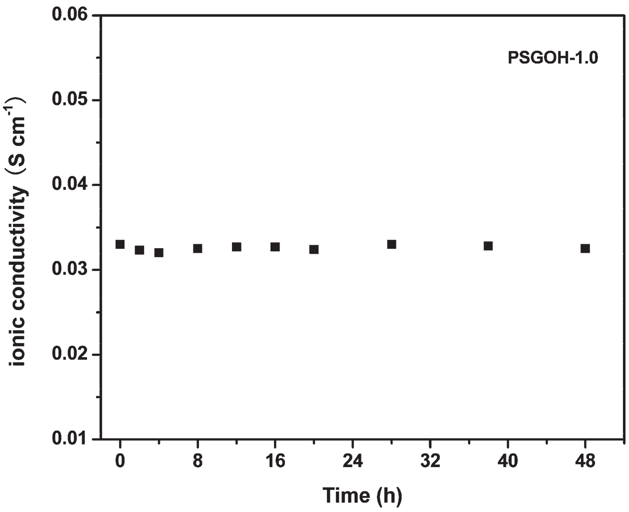


Figure 7. Stability of ionic conductivity in 1 M NaOH at 60 °C.

swelling ratio for the in-plane direction of the PSGOH membranes. An increase in water uptake with increase temperature was also observed. For example, at 60 °C, PSGOH-1.2 showed 107% water uptake and 46% swelling ratio for the in-plane direction, which was much higher than that at 20 °C (55% water uptake and 20% swelling ratio).

The hydroxide conductivities of the PSGOHs were measured after the membranes were initially hydrated by immersion in deionized water for 24 h at room temperature. The hydroxide conductivity values reported in Table 3 are expressed in Figure 6 as functions of the IEC. In general, a conductivity above 10^{-2} S cm^{-1} is required for hydroxide exchange membrane materials used in fuel cells. PSGOH-0.4, 0.6, 1.0, 1.2, and 1.4 presented the hydroxide conductivities ranging from 0.5 to 6.7 × 10^{-2} S cm^{-1} at 20 °C. Their hydroxide conductivities increased with the IEC values and water uptake. At low IEC values, the conductivity of the membranes was rather low and increased in a gradual fashion. In this regime, the ionic conductivity was thought to be limited by the connection between ionic domains, and as the IEC value increased, the conductivity increased rapidly as the volume fraction of water and concentration of ionic groups in the membranes was raised. In comparison, PSGOH-1.2 (IEC = 1.89 mequiv g^{-1}) showed a hydroxide conductivity of 4.5 × 10^{-2} S cm^{-1} at 20 °C, which was higher than that of the aforementioned PSQNOH (2.9 × 10^{-2} S cm^{-1}, IEC = 1.85 mequiv g^{-1}). The reason could be the higher basicity of quaternary guanidinium hydroxides leading to an augmentation of both the number of dissociated hydroxides and water molecules. In addition, the temperature dependence of the hydroxide conductivities of PSGOH-*x* measured in liquid water also is summarized in Table 3. As expected, an increase in temperature resulted in an increase in hydroxide conductivity based on the simplified diffusion mechanism and thermal motion of hydroxides in channels within membranes. For example, the ionic conductivity of PSGOH-1.2 increased from 4.5 to 7.4 × 10^{-2} S cm^{-1}, corresponding to a temperature rise from 20 to 60 °C.

Besides the excellent thermal stability and high ionic conductivity, PSGOHs also had good alkaline stability. The PSGOH membranes maintain their ionic conductivity after immersion in 1 M NaOH solution at 60 °C for 48 h (Figure 7). The thermal stability of PSGOH is high enough for use in AEMFCs, since the operating temperature of current AEMs has typically been limited to 50 or 60 °C. No obvious decrease of ionic conductivity was observed for PSGOHs after immersion in either DI water or 1 M NaOH for 30 days at room temperature, indicating good long-term stability.

Conclusions

In summary, poly(arylene ether sulfone)s were successfully modified with quaternary guanidinium groups through direct chloromethylation followed by reaction with pentamethylguanidine. We synthesized the high DS of chloromethylated polysulfone without gelation and first found that $ZnCl_2$ affected the chloromethylation of polymer directly and could determine the DS values by controlling the amount of $ZnCl_2$ used. The obtained quaternized ionomers exhibited an excellent solubility and formed flexible and tough membranes of varying ionic content by casting from a DMSO solution. These novel AEMs based on quaternary guanidinium hydroxide groups, denoted PSGOHs, presented excellent thermal stabilities, high ionic conductivities, and good alkaline stabilities. The preliminary properties have demonstrated their potential as electrolytes for hydroxide anion exchange membrane fuel cells. The obtained results will aid in designing superior membranes, e.g., the cross-linked or side chain polymers based on varied quaternary guanidinium groups for improved membrane performances.

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