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ARTICLE

Poly (tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) for Anion Exchange Membranes

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Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

A soluble perfluorinated polymer poly(tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) (PFSO₂NH₂) was successfully synthesized and used for preparation of perfluorinated anion exchange membranes (AEMs). PFSO₂NH₂ is soluble in many solvents and owns excellent alkaline stability. The perfluorinated AEM (PFSO₂NH-MGMC-OH) which was synthesized by the reaction of PFSO₂NH₂ with 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC) exhibits the hydroxide conductivity of 60.4 mS.cm⁻¹ at 80 °C and 13.8 mS.cm⁻¹ at 30 °C, respectively. The transport numbers of the membrane is 0.91 for Cl⁻ and 0.06 for Na⁺. The membrane shows good alkaline stability that it maintained 79.3% hydroxide conductivity and 85.6% ion exchange capacity (IEC) value after immersion in 8 M KOH over 30 days at 60 °C. This soluble PFSO₂NH₂ with high thermal and alkaline stability could be used as precursor for other perfluorinated functional polymers and membranes.

Introduction

Anion exchange membrane fuel cells (AEMFCs) have received tremendous attention for their potential applications with nonplatinum electrocatalysts or carbon-free supports within their electrode structures. The anion exchange membranes (AEMs) play a key role in the AEMFCs that conducts hydroxide ion from cathode to anode. A variety of polymers, such as polysulfone¹⁻³, poly(arylene ether)^{4,5}, poly(vinylidene fluoride) (PVDF)⁶, partially fluorinated aromatic polymers, poly(vinylidene fluoride) (PVDF) and poly(ethylenecotetrafluoroethylene) (ETFE) have been investigated for AEMs applications^{7,8}. Compared to the benchmark polymer, perfluorinated sulfonic acid, for proton exchange membrane, these AEMs exhibited some disadvantages in alkaline environments. Polysulfone based AEMs became brittle in alkaline media as well as ether hydrolysis were observed^{9,10}. The cleavage of aryl-ether linkages in quaternized poly(arylene ether) was proved¹⁰. Polymer backbone of PVC and PVDF were also turn out decomposition under alkaline environments¹¹. It is desirable to develop new type of alkaline stable polymers which offer the potential of improving the AEMs long-term stability.

Due to their high thermal, chemical and mechanical stability,

perfluorinated polymer such as Nafion precursors (Nafion-SO₂F) have been explored as starting materials for the synthesis of AEMs. To our best knowledge, the first study involves the reaction of Nafion-SO₂F with the 1,4-dimethylpiperazinium (1,4-DMP)^{12,13}. However, the obtained AEMs were verified to be unstable in case of aqueous work up and does not yield stable anion-exchange membranes based on 1,4-DMP¹⁴. Additionally, different head-group chemistries based on Nafion-SO₂F with trimethylammonium, and 1-methyl-pyrrolidine were also performed, but the residual -SO₂F groups in the membrane can react with the water in the presence of the alkaline and form the proton-exchange membrane (Nafion membrane)¹⁵. Perfluorinated sulfone guanidinium functionalized ionomer was also synthesized by Nafion-SO₂F with 1, 1, 3, 3-tetramethylguanidine (TMG). Unfortunately, the ionomer degraded almost completely after soaking in 0.5 M NaOH at 80 °C for 24 h¹⁶. On the other hand, due to insolubility of perfluorinated sulfonyl fluoride precursor, solid-liquid heterogeneous react process has to be adapted in the reaction of PFSO₂F with amine, which may result in incomplete and uncontrolled reaction and not uniform hydroxide distribution throughout the thickness of the membrane. Vandiver and Herring prepared perfluoro quaternary ammonium from perfluorinated 3M sulfonyl fluoride ionomer with various quaternary ammonium cations attached with sulphonamide linkage¹⁷. The unreacted -SO₂F was found in the membrane, which leads the low IEC of the membrane (0.33–0.72 meq g⁻¹) as well as low conductivity. The perfluorinated AEMs from both Nafion-SO₂F and 3M-SO₂F suffered significant degradation when exposed to

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hydroxide^{18,19}. Despite great efforts, the synthesis of perfluorinated anion exchange membranes still remains a great challenge.

In this work, a soluble perfluorinated polymer poly(tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) (PFSO₂NH₂) was synthesized from perfluorinated sulfonyl fluoride precursor (PFSO₂F) and applied for perfluorinated AEM. PFSO₂NH₂ was characterized by FT-IR, elemental analysis, NMR and XRD. The thermal stability and alkaline stability of PFSO₂NH₂ were assessed. Finally, a new perfluorinated AEM (PFSO₂NH-MGMC-OH) was successfully synthesized by the reaction of PFSO₂NH₂ with 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC) in solution under mild heating condition. The hydroxide conductivity, water uptake, swell ratio, permselectivity, transport numbers, thermal stability and alkaline stability of PFSO₂NH-MGMC-OH membranes were also investigated in detail.

Experimental

Materials and chemicals

The perfluorinated sulfonyl fluoride (PFSO₂F) resin with equivalent weight (EW) of 909 g mol⁻¹ was supplied from Dongyue Shenzhou New Materials Company Ltd., China. Nafion 115 (EW=909 g mol⁻¹) was purchased from DuPont with a wet thickness of 136 μm as sheets. Tokuyama®A201 samples were provided by Tokuyama (Tokuyama Corporation). N, N-dimethylformamide (DMF, anhydrous) was purchased from J&K Scientific Ltd.. 4-methylmorpholine (MML), acetonitrile and epichlorohydrin (ECH) were purchased from Sigma-Aldrich Chemical Reagent Co., Ltd.. Deionized water was used throughout the experiments. Other materials were used as received.

Synthesis of 4-methyl-4-glycidylmorpholin-4-ium chloride (MGMC)

The quaternized intermediate, MGMC, was synthesized via the reaction of ECH and MML²⁰. To a dried 250 ml three-necked flask, MML (0.432 mol) and ECH (0.518 mol) were dissolved in 12 ml of acetonitrile under nitrogen flow to form a homogeneous solution. After stirring for half an hour at room temperature, the mixture was heated at 45 °C for 55 h. The resulting white solid was filtered, washed thoroughly with anhydrous ether, and dried at 65 °C under vacuum for 10 h.

¹H-NMR (400MHz, DMSO-*d*₆) δ(ppm) : 2.75-2.95 (2H,CH₂), 3.29-3.41 (4H,1×CH,1×CH₃), 3.43-4.01 (10H,5×CH₂).

Synthesis of poly(tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) (PFSO₂NH₂)

PFSO₂NH₂ was synthesized by nucleophilic substitution of PFSO₂F resin (10 g) with the excess liquid NH₃ (50 mmol) in the presence of anhydrous DMF (90 g). The reaction was carried out at room temperature with continuous stirring until a transparent solution was obtained (10 wt. %). The obtained crude PFSO₂NH₂ was washed with deionized water until the pH of the residual water was neutral.

Preparation of PFSO₂NH-MGMC-OH membranes

The graft-onto reaction between PFSO₂NH₂ and MGMC was carried out at the feed mole ratio of PFSO₂NH₂/MGMC=1:1. MGMC (1 mmol) was added to a solution of the PFSO₂NH₂ (1 mmol) in DMF (10 wt. %). The mixture was stirred at 60 °C under nitrogen flow for 24h to get completely reaction. The resulting solution was then cast onto a glass plates and dried in vacuum oven at 80 °C and 160 °C for 2 h, respectively. Upon cooling in oven, the membranes were peeled off from glass plates.

Cl⁻ anions in the as-prepared membranes were converted into OH⁻ by anion exchange. The as-prepared membrane was immersed in 2 M KOH solution at room temperature for 24 h. Then the membranes were taken out and rinsed with N₂-purged deionized water until the pH of the residual water was neutral.

Characterization

Characterization of polymers and membranes

¹H NMR spectra were recorded on a Varian Mercury Plus 400 MHz instrument at room temperature, FT-IR spectra were recorded on a Perkin-Elmer Paragon1000PC Spectrometer, Elemental composition (N) was determined by an elemental analyzer (Elementar-Vario-EL Cube), Thermal gravimetric analysis (TGA) was performed on a TAQ50 instrument under nitrogen with a heating rate of 10 °C·min⁻¹ and scanning range of 50-800 °C. X-Ray diffraction (XRD) patterns were recorded on a D/max-2200/PC (Japan Rigaku Corp.) using CuKα radiation (λ=1.5418 Å). Dynamic Light Scattering (DLS) measurements were performed on the self-assembly aqueous solutions using a ZS90 Zetasizer Nano ZS instrument (Malvern Instruments Ltd., U.K.) equipped with a 4 mW He-Ne laser (λ= 633 nm) at an angle of 90°.

Water uptake, swelling ratio

Water uptake of the PFSO₂NH-MGMC-OH membrane was measured by equilibrating the sample of the membrane with N₂-purged deionized water at room temperature for 24 h. Subsequently, the hydrated membrane was taken out from water, the excess surface water was removed by wiping with a tissue paper and the mass was quickly measured (*M_w*). Then the wet membrane was dried under a vacuum at 80 °C, until a constant dry weight (*M_d*). The water uptake (%) was calculated as follows:

$$\text{Water uptake (\%)} = \left(\frac{M_w - M_d}{M_d} \right) \times 100\% \quad (1)$$

Water content (λ_{H2O}), denoted as the number of water molecules per quaternary ammonium group, was calculated from the following equation:

$$\lambda_{H_2O} = \left[\frac{\text{Water uptake (\%)} \times 10}{IEC \times 18} \right] \quad (2)$$

The linear swelling ratio was characterized by linear expansion ratio, which was determined by the difference between wet and dry dimensions of a membrane sample (2 cm in length and 1 cm in width). The wet sample was measured after the membrane was boiled in N₂-purged deionized water for 1 h. The dry samples were obtained by drying the wet samples in a vacuum oven at 100°C for 2 h. The linear swelling ratios were calculated according to the following equation:

$$\text{Linear swelling ratios} = \left(\frac{L_w - L_d}{L_d} \right) \times 100\% \quad (3)$$

Where L_w and L_d are the length of the soaked membrane and dry membrane, respectively.

The volume swelling ratio (V_s %) is calculated as the length \times width \times thickness of the membrane.

$$V_s\% = \frac{V_w(OH) - V_d(OH)}{V_d(OH)} \times 100\% \quad (4)$$

Where V_w and V_d are the volume of the soaked membrane and dry membrane, respectively.

Ion-exchange capacity (IEC)

The ion-exchange capacity (IEC) of the hydroxide form of the membrane was measured using the typical back-titration method. S-PFSO₂NH-MGMC-OH membrane was immersed into 100 mL of 0.01 M HCl standard solution for 48 h to render the membrane to Cl⁻ form under N₂ atmosphere. Then the solutions were back titrated with 0.01 M NaOH standard solution to pH 7 using phenolphthalein as an indicator. The IEC values were calculated using the following equation:

$$IEC_{OH^-} = \frac{C_{HCl}V_{HCl} - C_{NaOH}V_{NaOH}}{m_{dry(Cl)}} \quad (4)$$

Where C_{HCl} V_{HCl} is the amount (mmol) of HCl solution before titration, and $C_{NaOH}V_{NaOH}$ is the amount (mmol) of NaOH consumed in the titration with membranes, respectively, and $m_{dry(Cl)}$ is the mass (g) of the dried sample.

The chloride form IECs were determined by the Volhard titration method²¹. S-PFSO₂NH-MGMC-Cl membrane immersed in 20 mL of 1 M NaNO₃ salt solution for 48 h. 5 mL of 0.1 M AgNO₃ was added to the beaker containing the solution of chloride and nitrate ions and the solution was then titrated with 0.1 M KSCN to the equivalence point. The difference in 0.1 M KSCN volume used to titrate the control solutions (solutions not exposed to AEMs) and the test solutions was used for calculating the IEC. See eqn (5) below

$$IEC_{Cl^-} = \frac{(V_2 - V_1) \cdot C_{KSCN}}{m_{dry(Cl)}} \quad (5)$$

Where V_2 , and V_1 , NaOH are the volumes of the KSCN consumed in the titration without and with membranes, respectively. C_{KSCN} is the molar concentration of KSCN.

Solubility

Solubility of PFSO₂NH₂ and PFSO₂NH-MGMC-OH membranes were qualitatively investigated by immersing samples (1.5 g) in different solvents (10 mL) for 48 h at different temperatures. Prior to testing, samples were both dried for 24 h at 80°C to remove the water.

Hydroxide conductivity measurements

The resistance value of the membranes was measured over the frequency range from 1 Hz to 1 MHz by two-point probe alternating current (AC) impedance spectroscopy using an electrode system connected with Autolab PGSTA302 electrochemical test system (Eco Chemie, Netherlands) at different temperatures in water. To avoid CO₂ contamination from ambient air, pure N₂ was flowed through the system at a high rate. All samples were equilibrated for at least 30 mins at a given temperature. Repeated measurements were taken with 10 min interval until no additional change in conductivity was observed. The in-plane conductivity ($S \cdot cm^{-1}$) was calculated as follows:

$$\rho = \frac{l}{dwR} \quad (6)$$

Where l is the distance (cm) between two electrodes, d and w are the thickness and width of the membrane, respectively. And R is the membrane resistance value from the AC impedance data (Ω).

Evaluation of transport properties of the anion-exchange membranes

Apparatus

The experimental set-up consisted of two cells separated by the membrane under investigation and the capacity of each compartment was 100 cm³. On one side of the membrane a 0.1 M NaCl solution flowed through the cell and on the other side a 0.5 M NaCl solution was used (Fig. 1). The effective area of the membrane under investigation was 20.3 cm². The temperature was 20 \pm 0.2°C. The voltage drop across the membrane was measured with calomel electrodes and recorded on a multimeter.

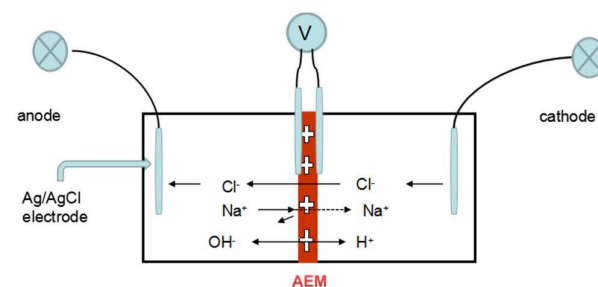


Fig. 1 Schematic diagram of the experimental equipment for determination of the transport numbers and permselectivity.

Transport properties of anion-exchange membranes

The anion transport number (T_{Cl^-}) in a membrane was calculated by a following equation^{22, 23}:

$$E_m = (\Phi_2 - \Phi_1) = \frac{RT}{F} (1 - T_{Cl^-}) \ln \frac{C_1}{C_2} \quad (7)$$

The transport numbers of the water dissociation products can thus be calculated according to

$$T_{H^+} = \frac{FV(dC_{H^+}/dt)}{I} = \frac{FV(dC_{H^+}/dt)}{iA} \text{ or}$$

$$T_{OH^-} = \frac{FV(dC_{OH^-}/dt)}{I} = \frac{FV(dC_{OH^-}/dt)}{iA} \quad (8)$$

The pH measurements were used to convert the pH values into H^+ or OH^- ion concentrations next to the membrane in order to determine the contribution of water dissociation products to the total ion transport through the membranes. Since the sum of transport numbers equals one, the cation transport number (T_{Na^+}) can be calculated from the relation:

$$T_{OH^-} = T_{H^+} = 1 - T_{Na^+} - T_{Cl^-} \quad (9)$$

R is the gas constant (8.314 J/(mol K)), T is the absolute temperature (K), F is the Faraday constant (96,485 C/mol), and C_1 and C_2 are concentrations of electrolytes in each compartment. The theoretical voltage difference per membrane is 80.3 mV.

The permselectivity was determined using a static membrane potential measurement. Prior to an experiment the membrane was equilibrated in a 0.1 M NaCl solution for 24 h. The membrane potential was measured after 20–30 min when steady state was reached. Finally the membrane permselectivity could be calculated as the ratio between the measured membrane potential (ΔV_{meas}) and the theoretical membrane potential (ΔV_{theo}):

$$\alpha(\%) = \frac{\Delta V_{meas}}{\Delta V_{theo}} \times 100 \quad (10)$$

where ΔV_{theo} is the theoretical membrane potential for a 100% selective membrane (V) which can be calculated using the Nerst equation:

$$\Delta V_{theo} = \frac{RT}{ZF} \ln \frac{C_1}{C_2} \quad (11)$$

Z is the electrochemical valence.

Chemical stability of PFSO₂NH-MGMC membrane

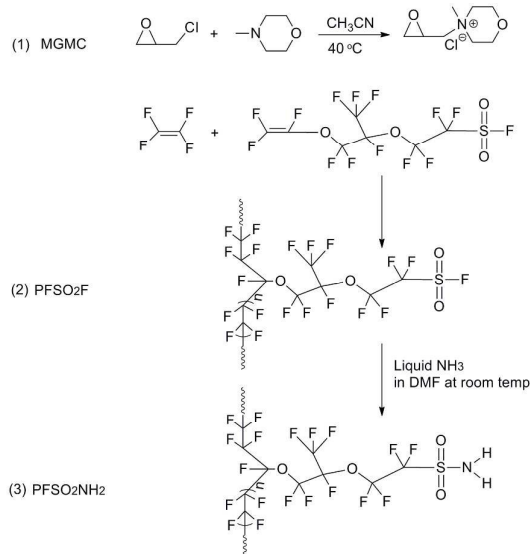
The chemical stability of the membranes was examined by immersing the membrane samples in 8 M KOH solution at 60 °C

over different time. The degradation of the PFSO₂NH-MGMC-OH membranes was evaluated by measuring the changes of FT-IR and NMR spectra, ion transport number, permselectivity, hydroxide conductivity and IEC of the membranes. The chemical stability of the PFSO₂NH-MGMC-Cl was examined by immersing the membrane samples in 8 M KOH solution at 60 °C over different time and later exchanged back to the chloride form.

Results and discussion

Synthesis and characterization of PFSO₂NH₂

PFSO₂NH₂ was synthesized by the reaction of PFSO₂F and liquid NH₃ in anhydrous DMF (Scheme 1). FT-IR was applied to monitor the reactions. Compared with the PFSO₂F spectrum (Fig. 2A), the peak related to -SO₂F groups at 1467 cm⁻¹ and the peaks at 823 and 796 cm⁻¹ disappeared in the PFSO₂NH₂ spectrum (Fig. 2B), suggesting full reaction of -SO₂F groups. Meanwhile, the emergence of amino group (-NH₂) at 3304–3437 cm⁻¹ and at 1547 and 922 cm⁻¹ (asymmetric N-H of the -NH₂) indicates formation of the -SO₂NH₂. The O=S=O stretching is shift to 1388 cm⁻¹ after the S-F bond is replaced by an S-N bond. Besides, the bands associated with -CF₃, C-O-C and -CF₂ groups keep the same as the PFSO₂F precursor, indicating that the reaction just occurred between the -SO₂F group and the NH₃. Fig. 3 shows the ¹³C and ¹H NMR spectra of PFSO₂NH₂. The fluorocarbon peak appeared at 110 ppm in ¹³C NMR spectrum (Fig. 3A.) and the protons of -SO₂NH₂ appeared at 9.0 ppm in ¹H NMR spectrum (Fig. 3B.). Furthermore, elemental analysis measurement indicates that the contents of N atom in PFSO₂NH₂ is 1.72% which agrees with the theoretical one that calculated by the EW (909 g mol⁻¹).



Scheme 1 Synthesis of the PFSO₂NH₂.

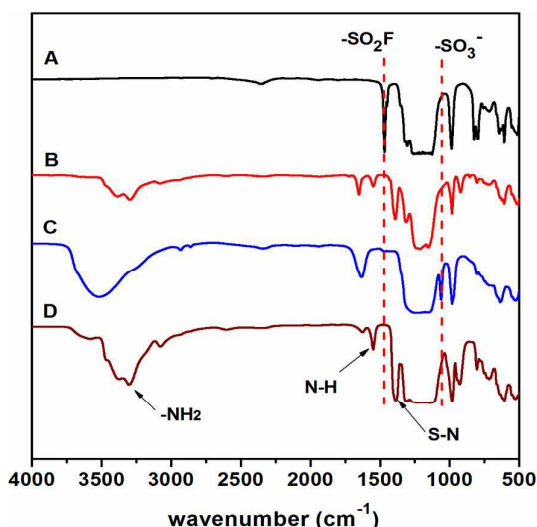


Fig. 2 FT-IR spectra of PFSO₂F (A), PFSO₂NH₂ (B), (C) and (D) were PFSO₂F and PFSO₂NH₂ after treating with 8 M KOH solution at 80 °C for 6 and 48 h, respectively.

PFSO₂NH₂ is very stable in strong base. From Fig. 2D, there is no any alteration in FT-IR spectrum of PFSO₂NH₂ after treating with 8M KOH solution at 80°C for 48 h. However, SO₂F groups of PFSO₂F at 1467 cm⁻¹ is completely converted into the -SO₃⁻ anions at 1063cm⁻¹ (Fig. 2C).

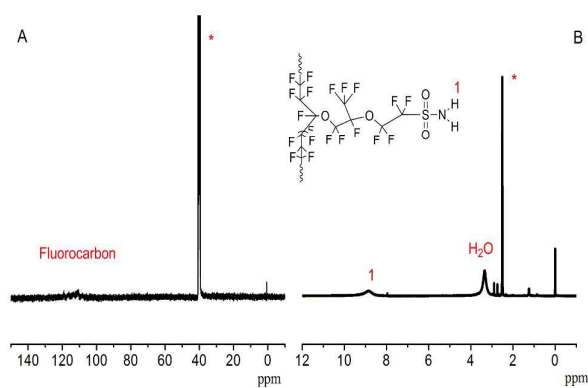


Fig.3 ¹³C NMR (A) and ¹H NMR(B) spectra of PFSO₂NH₂ in DMSO-*d*₆.

On the other hand, PFSO₂NH₂ has a good solubility in common solvents, such as N, N-dimethylformamide (DMF), dimethyl sulfoxide (DMSO), isopropanol and ethanol (see Table 1). DLS was used to measure the solubility of PFSO₂NH₂ in solvents. Fig. 4(A), (B) and (C) show similar size distributions for 5wt. % PFSO₂NH₂ in DMF, DMSO and ethanol, respectively. The number-average diameter of particles is lower than 1 nm which indicates PFSO₂NH₂ chain dissolved well in these solvents. As shown in Fig. 4 (D-F), PFSO₂NH₂ can also dissolve in such solvents with 50 vol. % in water with diameter of 1~10 nm.

Table 1 Solubility of PFSO₂NH₂^a.

Water-soluble	Boiling-point / °C	50vol.% in water	Pristine solvent
Methanol	64.7	+	+
Ethanol	78.3	+	+
isopropanol	82.5	+	+
DMF	150.5	+	+
DMSO	189.2	+	+

^a: Soluble

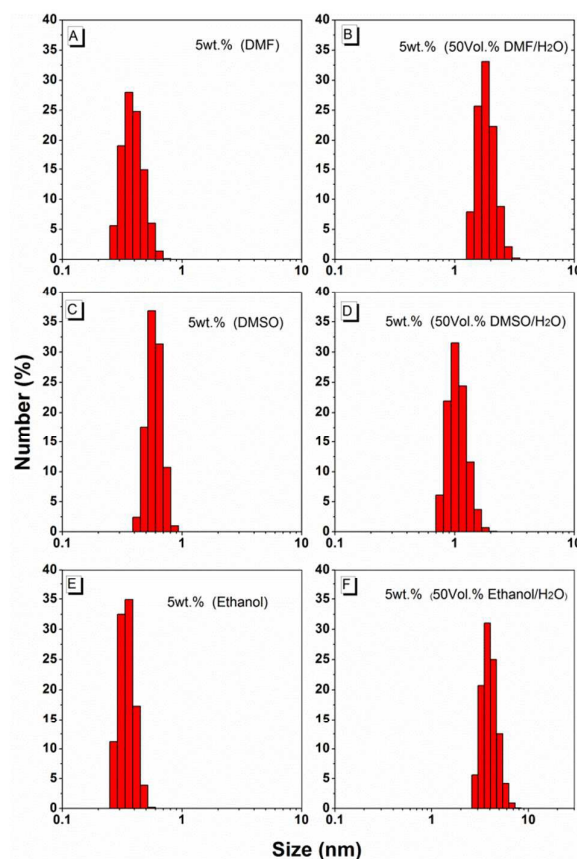


Fig. 4 DLS results of PFSO₂NH₂ solution

The X-ray diffraction was applied to determine the crystallinity of the PFSO₂NH₂. As shown in Fig. 5A, PFSO₂NH₂ display a diffraction peak centred at $2\theta = 8 \sim 20^\circ$. This broad peak can be deconvoluted into two peaks at $2\theta = 16.2$ and 17.6° , corresponding to the amorphous and crystalline regions, respectively^{24, 25}. There is the other broad diffraction peak at $2\theta = 25 \sim 50^\circ$ relating to the amorphous region (Fig. 5A). The relative crystallinity was 8.36% as high as PFSO₂F that calculated from the areas of these two peaks from the XRD spectra²⁶. The thermal stability of PFSO₂NH₂ was determined

through TGA analysis. As shown in Fig. 5B, PFSO₂NH₂ exhibits high thermal stability with the degradation temperatures (T_d , at which a sample loses its 5% weight) of 410 °C.

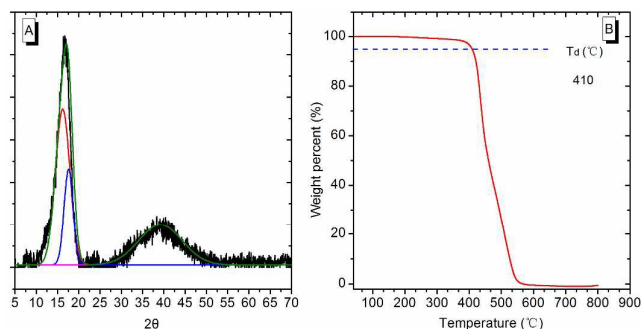
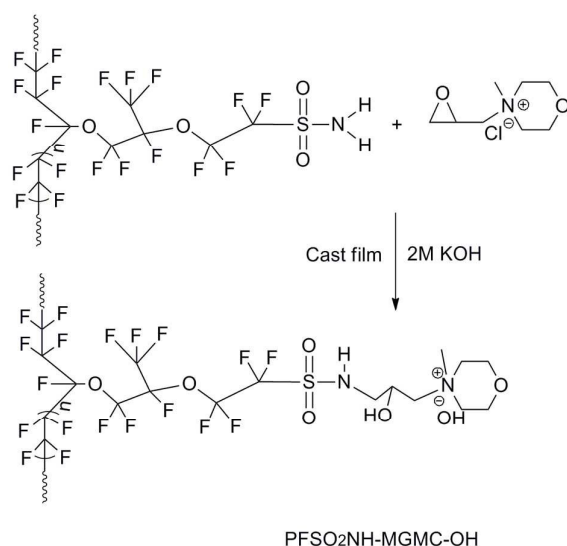


Fig. 5 XRD and TGA patterns of PFSO₂NH₂.

Synthesis and characterization of PFSO₂NH-MGMC-OH



Scheme 2 Synthesis of the PFSO₂NH-MGMC-OH

Due to high thermal and alkaline stability as well as high solubility, PFSO₂NH₂ are suitable for use in AEMs applications. By grafting MGMC to the PFSO₂NH₂, a new perfluorinated AEM (PFSO₂NH-MGMC-OH membrane) was synthesized (Scheme 2). Firstly, the quaternized intermediate, MGMC was synthesized via the reaction of epichlorohydrin and 4-methylmorpholine. Furthermore, PFSO₂NH-MGMC-OH membrane was synthesized via an epoxide ring-opening reaction of MGMC with PFSO₂NH₂ in DMF solution followed by anion exchange in KOH solution. Fig. 6 shows the FT-IR spectra of MGMC and PFSO₂NH-MGMC-Cl. Compared to MGMC and PFSO₂NH₂, for PFSO₂NH₂-MGMC-Cl, disappearance of the amino group(-NH₂) bands at 3304-3437 cm⁻¹, 1547 cm⁻¹ and 922 cm⁻¹ and the epoxy band at 924 and 764 cm⁻¹ suggested that the epoxides of MGMC were opened to reacted with the amino group

of PFSO₂NH₂. Meanwhile, in the spectrum of PFSO₂NH₂-MGMC-Cl, the characteristic peaks of quaternary ammonium groups of the morpholine ring, the CH₃ and CH₂ stretching, the vibration of the hydroxyl groups and S-N band of the -SO₂NHCH₂- group appear at 1470 cm⁻¹, 2873 cm⁻¹, 3100-3500 cm⁻¹ and 1388 cm⁻¹, respectively, further proving the formation of PFSO₂NH₂-MGMC-Cl. In comparison with liquid-solid heterogenous reaction systems which were applied to prepare perfluorinated AEMs from PFSO₂F, the synthesis of PFSO₂NH₂-MGMC-Cl is in homogenous solution, which makes the reaction be complete and be controllable by the feed mole ratio of PFSO₂NH₂ and MGMC.

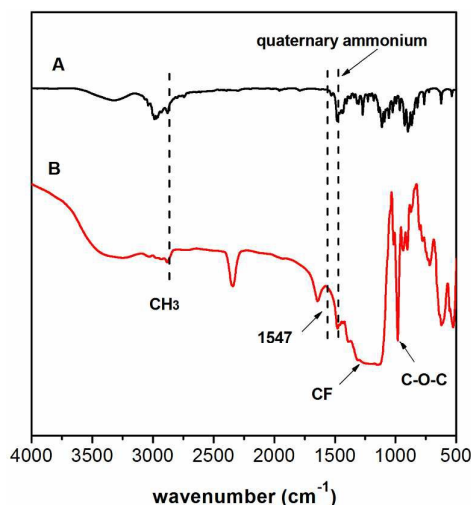


Fig. 6 FT-IR spectra of MGMC (A) and PFSO₂NH-MGMC-Cl (B).

The chemical shift of fluorocarbons in main chain of PFSO₂NH-MGMC-Cl was observed at about 115ppm (Fig. 7A). The two peaks at 2.75 and 2.95 ppm corresponding to the methylene protons of the epoxy group of MGMC disappeared in Fig. 7B. This implied that MGMC has been reacted and no residual MGMC was left in the product. The peaks in the ranges of 4.4-4.5, 3.81-4.12, 3.31-3.72 and 3.10-3.30 ppm were assigned to the OH and the CH, CH₂ and CH₃ of the aliphatic protons of the pendant MGMC units and the protons of the imino groups peak shifted to 8.0 ppm. Hence, from the FT IR and NMR spectra, we can further confirm chemical structure of the membrane. Finally, PFSO₂NH-MGMC-OH was generated through anion exchange of PFSO₂NH-MGMC-Cl with KOH. Fig. S1 shows the pictures of the dry PFSO₂NH-MGMC-OH membranes. It can be seen that the PFSO₂NH-MGMC-OH membrane is transparent and flexible. The IEC value of the PFSO₂NH-MGMC-OH membrane measured using the back-titration method is 0.90±0.2% meq.g⁻¹ which matched the theoretical value of 0.93 meq.g⁻¹ very well. The IEC value for the membranes in chloride form by using the Volhard titration method is 0.88±0.2%, which confirms the structure of PFSO₂NH-MGMC-OH with one substituted ammonium groups on amine group.

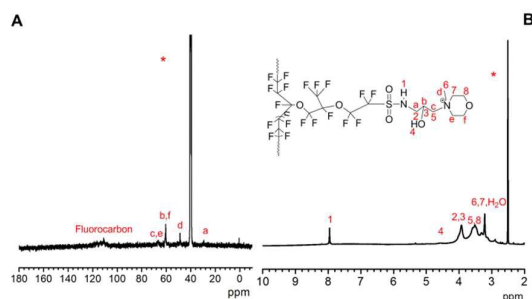


Fig. 7 ^{13}C NMR and ^1H NMR spectra of PFSO₂NH-MGMC-Cl in DMSO-*d*₆.

Ion conductivity, water uptake, swelling ratio

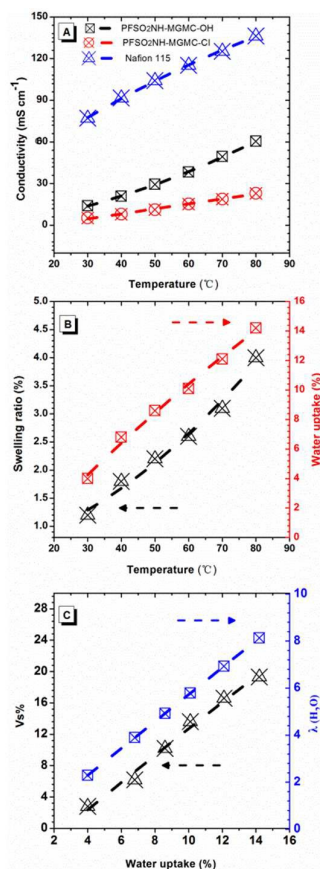


Fig. 8 (A) Conductivities of PFSO₂NH-MGMC-OH, PFSO₂NH-MGMC-Cl and Nafion 115 membrane in water as functions of temperature. Test conditions: the thickness of wet Nafion 115 and S-PFSO₂NH-GCI-OH membrane were 136 and 25 μm; N₂ atmosphere; (B) The change of swelling ratio (%) and water uptake (%) for PFSO₂NH-MGMC-OH membrane with the different temperatures. (C) The volume swelling ratio (*V*_s %) and total water content ($\lambda_{\text{H}_2\text{O}}$) of the membrane versus water uptake (%).

The temperature dependence of the hydroxide conductivity of PFSO₂NH-MGMC-OH membrane is shown in Fig. 8A. The conductivity of fully hydrated Nafion 115 was also tested as comparison. It increased with an increase temperature, since higher

temperature is in favor of the mobility of anions. The conductivities of the membrane rised up from 13.8 mS cm⁻¹ at 30 °C to 60.5 mS cm⁻¹ at 80 °C. The conductivity of Nafion 115 reached 136 mS.cm⁻¹ at 80 °C. The higher mobility of proton than anions ions contributes to higher conductivity. Meanwhile, the conductivity of the membrane in Cl⁻ form (PFSO₂NH-MGMC-Cl) was also evaluated as a function of temperature (Fig. 8A, red line). The conductivity of the membrane in Cl⁻ form is 22.9 mS.cm⁻¹ at 80 °C, which is about 2.61-2.63 times lower than that of OH⁻ from. Water uptake was described to play a key role in the hydroxide conductivity and mechanical properties of AEMs²⁷. Membrane with adequate water can offer more transport channels for anions which indicates higher hydroxide conductivity. On the other hand, excess water uptake will lead to membrane swelling and uncontrollable deformation. As shown in Fig. 8B, water uptake and swelling ratio of PFSO₂NH-MGMC-OH membrane increased with temperature. The linear swelling ratio of the membrane was controlled below 5%, which reveals that the membrane has excellent length dimensional stability in water. From Fig. 8C, the volume swelling ratio (*V*_s%) of the membrane increased linearly with increasing water uptake and the water content ($\lambda_{\text{H}_2\text{O}}$) was also increases from 2.3 to 8.1. Compared to some of the reported AEMs²⁸⁻³⁰, PFSO₂NH-MGMC-OH membrane demonstrated low water uptake, low volume swelling ratio and high dimensional stability in water. This high dimensional stability in water is particularly important in the context of fuel cell configurations. The IEC, transport numbers and permselectivity for this membrane and Tokuyama A201 are summarized in Table 2. For PFSO₂NH-MGMC-OH membrane, transport numbers for Cl⁻ are 0.91 and 0.06 for Na⁺, and permselectivity is 96.8%, which agree well with Tokuyama A201.

Table 2 Properties of PFSO₂NH-MGMC and Tokuyama A201 at 30 °C

Membrane	IEC (meq.g ⁻¹)		Transport number ^a		permselectivity
	Cl ⁻ form	OH ⁻ form	Cl ⁻	Na ⁺	
PFSO ₂ NH-MGMC	0.88	0.90	0.91	0.06	96.8
A201	1.57	1.62	0.89	0.05	98.9

^a Current density (12 mA/cm²)

Chemical and physical stability of PFSO₂NH₂-MGMC-OH membranes

The chemical stability of the PFSO₂NH₂-MGMC-OH membranes was measured by an accelerated aging method, i.e., the membranes were soaked in 8.0 M KOH at 60 °C for a certain period of time and then the samples were taken out, thoroughly washed with deionized water, and dried. The stability was evaluated by both the variation of hydroxide conductivity and IEC with soaking time. As shown in Fig. 9A, the conductivity of the PFSO₂NH₂-MGMC-OH membranes range from 38 to 31.5 mS.cm⁻¹ at a testing time of 30 days. The IEC values of the AEMs show similar trends during the stability testing period and exhibit a decrease less than 15%, which indicates good alkaline stability of the membrane.

The membranes after immersion in 8 M KOH were further characterized by FT-IR. As shown in Fig. 9B, compared to prior study

^{17,19}, no distinct peak at 1063 cm⁻¹ ascribe to SO₃⁻ band is found in the PFSO₂NH-MGMC-OH membranes, which indicates no hydrolysis of the sulfonyl group occurs. Besides, the peaks of CH₃, CH₂, S-N and quaternary ammonium groups remained unchanged indicating that PFSO₂NH-MGMC-OH membranes is stable or only little degradation when exposed to alkaline solutions.

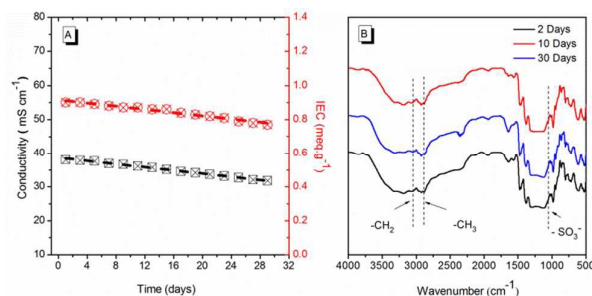
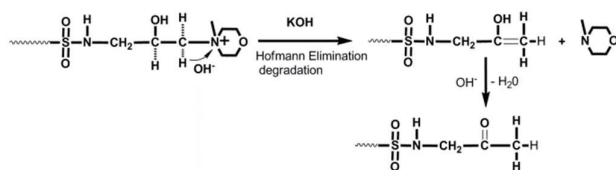


Fig. 9 A, Conductivity and IEC of PFSO₂NH-MGMC-OH membranes after being immersed in 8 M KOH at 60 °C for different time (conductivity measured at 60 °C, 100% RH); B, FT-IR spectra of PFSO₂NH₂-MGMC-OH membranes after being immersed in 8M KOH at 60 °C for different time.



Scheme 3 Degradation mechanism of PFSO₂NH-MGMC-OH membrane in alkaline solution.

Furthermore, the alkaline stability of all the PFSO₂NH₂-MGMC-OH membranes was investigated by ¹H and ¹³C NMR spectroscopy. After being exposed to 8 M KOH solution for 30 days, new weak proton peaks occurred at 8.2 ppm and 2.6~3.0 ppm (Fig. 10A), and ¹³C peaks at 162.9 and 36.0 ppm (Fig. 10B), which indicate the structural change. Scheme 3 shows a possible degradation mechanism of PFSO₂NH₂-MGMC-OH cations in alkaline media. Due to the Hoffman elimination reaction, where hydroxide ions attack a hydrogen atom on the beta carbon relative to the cation and a double bond forms between the alpha and beta carbons resulting in the cation being released.

We also compare the IEC, ionic conductivity, transport numbers and permselectivity values of PFSO₂NH₂-MGMC-OH against Tokuyama A201 after expose the alkaline solutions (Table S1). Tokuyama A201 exhibited a fast degradation within 10 days with 8 M KOH treatment at 60 °C, but the PFSO₂NH₂-MGMC-OH demonstrates relative high stability under the same conditions. The chemical stability of PFSO₂NH₂-MGMC-OH membrane can be related to the steric hindrance of the morpholine ring and incorporation of spacer groups (-NH, CH₃, and CH₂ group) to reduce the electron withdrawing character of the O=S=O group as to improve stability.

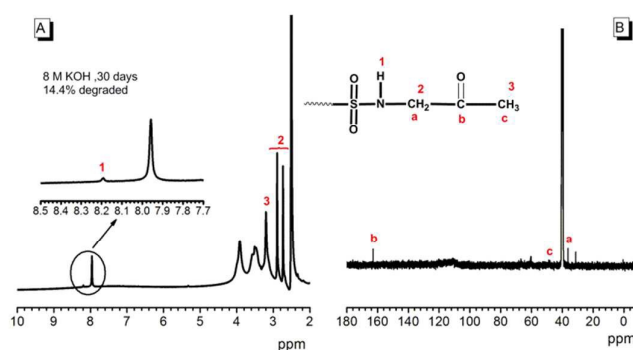


Fig. 10 ¹³C NMR and ¹H NMR spectra of PFSO₂NH-MGMC-Cl in DMSO-*d*₆ after being immersed in 8 M KOH at 60 °C for 30 days.

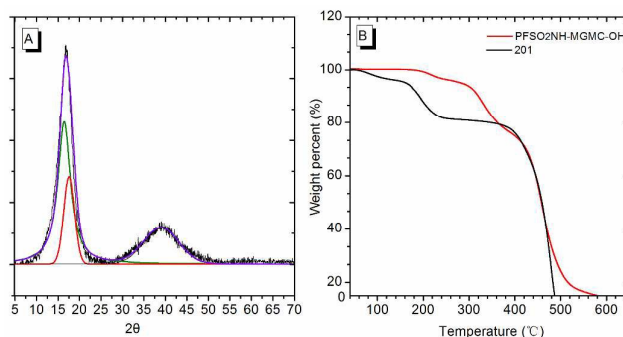


Fig. 11 XRD of PFSO₂NH-MGMC-OH and TGA patterns of PFSO₂NH-MGMC-OH and A201

The XRD pattern of the PFSO₂NH₂-MGMC-OH membranes (Fig. 11A) has crystalline characteristic peak at 2θ = 17.4° that is analogous with the characteristic peaks of PFSO₂NH₂ (Fig. 5A). The relative crystallinity and crystallite size was 6.39 and 5.3 that is litter smaller than PFSO₂NH₂. The thermal stability of the PFSO₂NH₂-MGMC-OH and Tokuyama A201 were evaluated via TGA. As shown in Fig. 11B, for Tokuyama A201, the degradation occurred at around 50 °C. For PFSO₂NH₂-MGMC-OH, the degradation occurred at about 180 °C, which is much higher than that of Tokuyama A201. A three-step weight loss behaviour was observed for the PFSO₂NH₂-MGMC-OH in the Fig. 11B. The first stage weight loss occurred from 180 °C to 270 °C, which is probably caused by the loss of aliphatic component which is grafted onto the polymer backbone, while the second (270~400 °C) stage may be related to the decomposition of the fluorinated side-chain. And the third stage weight loss starting from 400 °C is due to the decomposition of the polymer PTFE backbone^{31, 32}.

Conclusions

An alkaline stable and soluble perfluorinated sulfonamide (PFSO₂NH₂) precursor was synthesized and successfully applied for AEM. PFSO₂NH₂ opens a new paradigm to design and fabricated high performance AEMs. The obtained membranes PFSO₂NH₂-MGMC-OH shows good hydroxide conductivities (>10⁻² S cm⁻¹ at 30-80 °C), high dimensional stability and good alkaline stability. It is

possible to optimize the membrane performance by adopting a varied ammonium groups attached on PFSO₂NH₂.

Acknowledgments

We gratefully acknowledge funding for this work provided by, the National Nature Science Foundation of China (51573090) and the Shanghai Natural Science Foundation (15ZR1422100).

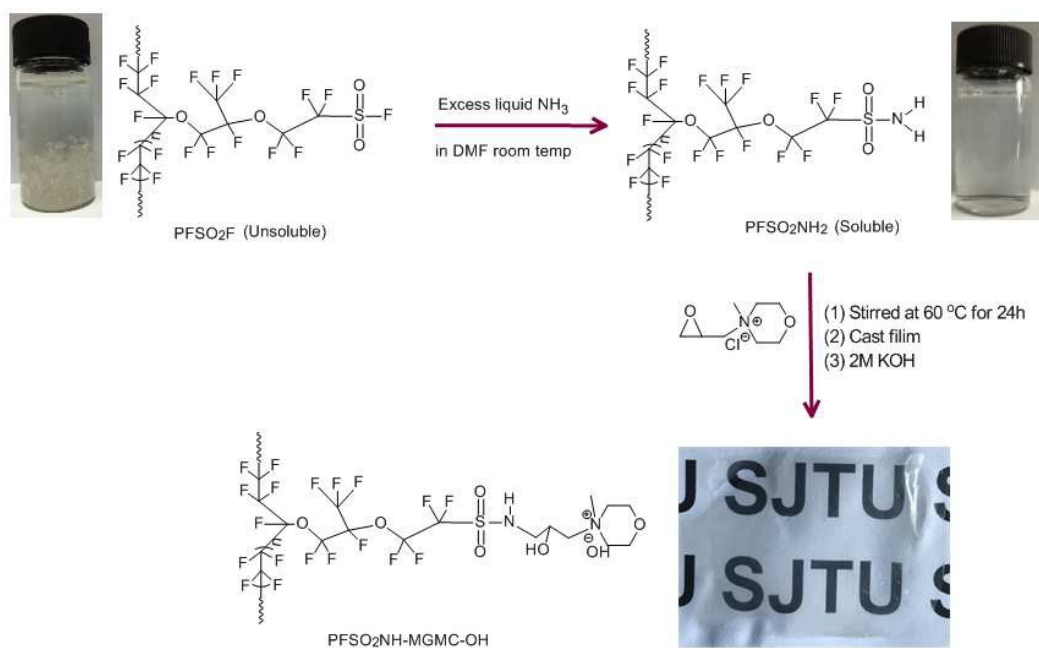
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GRAPHIC ABSTRACT

Poly (tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) for Anion Exchange Membranes

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A soluble perfluorinated polymer poly(tetrafluoroethylene-co-perfluorovinyl ether sulfonamide) (PFSO₂NH₂) was successfully synthesized and used for preparation of perfluorinated anion exchange membranes with good conductivity and alkaline stability.