Polysulfone-based Anion Exchange Membranes for Potential Application in Solid Alkaline Fuel Cells

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A B S T R A C T

In present research work, anion exchange membranes based on quaternized polysulfone with ammonium cation moieties (QAPSF) were prepared by chloromethylation, amination and alkalization. The chloromethylated polysulfone were characterized by ^{1}HNMR spectroscopy and functionalization degree was determined according to peak area integration. Ion transport properties (ionic conductivity, ion exchange capacity, activation energy for ion transport) and water content associated properties (water uptake, swelling ratio, hydrated number) were measured for the prepared anion exchange membranes. The ion exchange capacity for these membranes varied from 0.96 to 1.73 meq/gr while the degree of chloromethylation increased from 82% to 143%. The membrane with IEC value of 1.73 meq/gr showed the highest ionic conductivity in the range of 15.87-34.01 mS/cm at 25-80 °C. The activation energy for ion transport, water uptake and swelling ratio of this membrane were measured to be 11.99 kJ/mol, 37.41% and 14.71%, respectively which demonstrated the reasonable performance of the prepared anion exchange membranes. Based on the obtained results, prepared anion exchange membranes could be proposed as good candidates for solid alkaline fuel cells.

1. INTRODUCTION

Fuel cells are known as promising technologies in conversion of chemical energy into electrical energy due to high efficiency and low environmental impacts. Solid alkaline fuel cells (SAFCs) or anion exchange membrane fuel cells (AEMFCs) received more attention among all different types over the last decade. SAFCs have some advantages over proton exchange membrane fuel cells (PEMFCs) such as: high oxygen reduction rate in cathode, use of cheap and non-noble catalysts, low fuel permeability due to the opposite direction of fuel and hydroxide ion and excellent corrosion resistance in the alkaline media [1-3]. Anion exchange membrane (AEM) is core component of SAFC and plays an important role in improving SAFC performance and efficiency. Various kinds of AEMs have been fabricated by changing chemistry of the polymers, cationic moieties and functionalization methods. Based on mode of preparation and precursors, homogeneous AEMs can be prepared with different approaches. These membranes can be made by (co)polymerization of monomers or chemical modification of existing polymer [1, 2]. AEMs with chemical modification structures are more interesting, because the functionalization of existed polymer is an effective and simple method to synthesize AEM [4, 5]. Among different polymers and cationic groups, polysulfone (PSF) and ammonium species can be good candidate for AEM preparation. PSF is a high performance engineering thermo plastic polymer which is highly soluble in wide range of polar solvents and exhibits good thermal, mechanical and chemical stability in different pH values. Quaternary ammonium (QA) groups are the most popular functional groups used in AEM fabrication due to preparation simplicity and high performance in ionic exchange measurements [6-9].

According to the considerable amount of literature has been published, AEMs based on PSF and QA groups with chemical modified structure, can be divided into following categories:

1) AEMs prepared by direct reaction of ammonium groups (monoamine or/and diamines) with CMPSF and AEMs functionalized by immersing the CMPSF film into amination agent solution [10-18].

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2) AEMs synthesized in electrospun fibers and quaternized with ammonium groups [19-21].
3) Quaternized AEMs which have support or nano particles in their structure (composites and nanocomposites) [6, 7, 22, 23].
This paper will focus on AEMs (QAPSFs) preparation by chemical modification method using PSF (base polymer) and TMA (amination agent). Effects of chloromethylation time and amination solvent on AEMs structure and performance were studied. The degree of chloromethylation in chloromethylated PSF (CMPSF) was determined using ^{1}HNMR spectra. Ion transport properties include ionic conductivity, ion exchange capacity (IEC) and ion transport activation energy and the water content associated properties include water uptake (WU), swelling ratio (SR) and hydrated number were measured for the prepared QAPSFs.

2. MATERIALS AND METHODS

2.1. Materials   Polysulfone (PSF)-average $M_w \sim 35000$, $M_n \sim 16000$ and chlorotrimethylsilane-98% were provided by Sigma-Aldrich. Chloroform, paraformaldehyde, N-methyl-2-pyrrolidone (NMP), dimethylacetamide (DMAc), trimethylamine (TMA)-40 wt% solution in H_2O, ethanol-99%, potassium hydroxide (KOH)-84%, sodium hydroxide (NaOH)-99%, hydrochloric acid (HCl)-fuming 37%, phenolphthalein-1% solution in ethanol were purchased from Merck Chemicals. Stannic chloride ($SnCl_4$) was supplied from Scharlau. All chemicals are used without further purification.

2.2. AEM Preparation   The AEM samples were prepared by chemical modification method in three steps: chloromethylation, amination and alkalization that were shown in Figure 1.

Chloromethylation: Chloromethylation is the most important step in the synthesis of functionalized PSF which makes the chloromethylated groups on the polymer structure. The common method for chloromethylation is performed by chloromethyl methyl ether (CMME) that is toxic and carcinogenic compound. Therefore, in this study chloromethylation step was carried out based on a route reported by Avram and co-workers [24]. 5 g of PSF was dissolved in 250 mL chloroform. After that the solution was transferred to three necked flask equipped with a magnetic stirrer and reflux condenser. When the temperature of the mixture raised to 55°C, 3.38 g of paraformaldehyde and 12.3 g of chlorotrimethylsilane were added to the mixture. Finally, $SnCl_4$ as the reaction catalyst was added dropwise to the solution. After the precursors undergo the reaction in the solution for different times (24, 48 and 72 h), chloromethylation reaction solution was precipitated in ethanol and vacuum filtrated to collect

solid CMPSF particles. The obtained CMPSF was dried in vacuum oven at 50°C for 24 h.
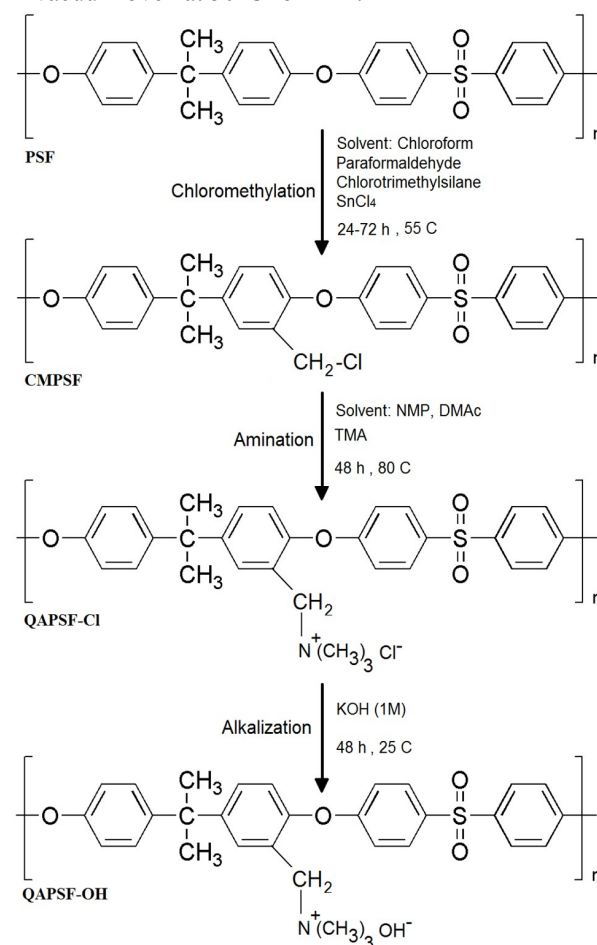

Figure1. AEM preparation route based on quaternized PSF and ammonium groups

Amination: This step starts with dissolving the CMPSF powder in a desired solvent (NMP or DMAc) to prepare 10 wt/vol% solution. After that appropriate amount of TMA was added to the mixture in order to obtain molar ratio of 3:1 for TMA to CH_2Cl. Amination reaction was carried out at 80°C for 48 h. When the reaction completed, the solution was casted on glass plate and dried in 60°C oven to remove solvent. To ensure that all solvent has been evaporated, the AEM film was vacuum dried at 80°C for 12 h. The final product of this step is AEMs in chloride form (QAPSF-Cl) with average thickness of 50-75 μm.

Alkalization: In alkalization step the AEM films in chloride form were soaked in 1M KOH solution for 48 h at room temperature. The KOH solution was refreshed several times throughout this period to ensure exchange of all chloride ions with hydroxide ones. Subsequently, the AEM films (QAPSF-OH) were washed and immersed in deionized water for 48 h to remove residual KOH.

2.3. Characterization of CMPSF and AEM

^{1}HNMR Spectra: The degree of chloromethylation (DC) of CMPSF was determined by proton NMR (^{1}HNMR) spectroscopy. The DC is average number of chloromethylated groups per PSF monomer unit. The ^{1}HNMR spectra were measured on a 400 MHz Bruker instrument using deuterated chloroform (CDCl$_3$) and deuterated dimethylsulfoxide (d-DMSO) as solvents. The DC was calculated by integration of peak area of chloromethyl (CH$_2$Cl) and isopropylidene (C(CH$_3$)$_2$) groups according to following equation:

$$DC(\%) = \frac{number\ of\ CH_2Cl\ sites}{1\ PSF\ monomer} \times 100 = \frac{3 \times A_{CH_2Cl}}{A_{C(CH_3)_2}} \times 100 \qquad (1)$$

where A_{CH2Cl} is the peak area of CH$_2$Cl protons at 4.4-4.6 ppm and $A_{C(CH3)2}$ corresponds to the peak area of C(CH$_3$)$_2$ protons at 1.6-1.8 ppm in ^{1}HNMR spectra.

Hydroxide Conductivity and Activation Energy Measurement: The Through plane ionic (hydroxide) conductivity was measured by electrochemical impedance spectroscopy (EIS) using Bio-Logic Science Instruments (SP-150 potentiostat). The EIS tests were performed at oscillating voltage of 10 mV and the frequency ranging from 1 MHz to 1 Hz. Before starting the measurements, AEMs were kept in deionized water for 24 h to minimize their exposure to ambient CO$_2$. The membrane samples were taken out quickly, and then sealed between two stainless steel electrodes. The conductivity was measured within the temperature range of 25 to 80 °C under 100% relative humidity (RH). The membrane resistance was determined from the intercept of the Nyquist plot with the real impedance axis obtained at high frequency. Finally, the ionic conductivities were calculated based on the membrane resistance according to equation (2):

$$\sigma = \frac{l}{R \times A} \qquad (2)$$

where l is the membrane thickness (cm), A is the membrane area (cm^2), R is the membrane resistance (Ω or 1/S) and σ is the ionic conductivity (S/cm). Furthermore, while temperature dependency of hydroxide conductivity was governed by Arrhenius form, equation (3), apparent activation energy for ion transport was determined using a linear Arrhenius relationship between lnσ and 1000/T as shown in equation (4) [25, 26]:

$$\sigma = \sigma_0 \exp\left(\frac{-E_a}{RT}\right) \qquad (3)$$

$$E_a = -b \times R \qquad (4)$$

where σ_0 is the pre-exponential factor, E_a is the apparent activation energy (kJ/mol), R is the gas constant (8.314 J/mol.K), T is temperature (K) and b is the slope of the linear regression of lnσ vs. 1000/T plots.

Ion Exchange Capacity Measurement: The IEC (number of functional cationic sites per gram of dry membrane) was determined by back titration. The AEM samples were immersed in 0.1M HCl solution for 24 h. Subsequently, the HCl solution was titrated with 0.1M NaOH solution using phenolphthalein as an indicator. The IEC was calculated from equation (5):

$$IEC = \frac{M_1 V_1 - M_2 V_2}{m_{dry}} \qquad (5)$$

where M_1 (M) and V_1 (mL) are the concentration and volume of the initial HCl solution. M_2 (M) and V_2 (mL) are concentration and volume of the NaOH solution used for titration. m_{dry} (g) is the weight of the dry AEM sample.

Water Uptake, Swelling Ratio and Hydrated Number Measurement: Water uptake (WU) and swelling ratio (SR) were determined by measuring the weight and length difference between the wet and dry AEMs, respectively. The AEM samples in chloride (Cl$^-$) and hydroxide (OH$^-$) form were soaked in deionized water for 48 h at room temperature. Then the membranes were taken out, the surface water was wiped away and the weight and length of membrane were measured (W_{wet} and L_{wet}). After that, the membranes were dried under vacuum at 60°C for a day and their weights and lengths were recorded (W_{dry} and L_{dry}). WU and SR for AEMs were determined from equations (6) and (7), respectively:

$$WU(\%) = \frac{W_{wet} - W_{dry}}{W_{dry}} \times 100 \qquad (6)$$

$$SR(\%) = \frac{L_{wet} - L_{dry}}{L_{dry}} \times 100 \qquad (7)$$

The hydrated number (λ) which is the number of water molecules per quaternized groups can be calculated from WU and IEC according to the following equation [27]:

$$\lambda = \frac{WU}{18.02} \times \frac{1000}{IEC} \qquad (8)$$

3. RESULTS AND DISCUSSION

3.1. Synthesis of CMPSF and ^{1}HNMR Spectra Study

The chloromethylation of PSF was confirmed by ^{1}HNMR spectra. In Figure 2. the ^{1}HNMR spectra of pristine PSF (a) and CMPSF with different chloromethylation times (b-d) were illustrated. As clearly seen in Figure 2 (b-d), the CMPSFs show a new peak at 4.4-4.6 ppm (designated as '5') which is assigned to the hydrogen proton of chloromethyl groups (–CH$_2$Cl). This peak was strengthened by the chloromethylation time. According to the equation (1), the CMPSFs that synthesized in different chloromethylation times of 24 h, 48 h and 72 h have DC(%) values of 82%, 130% and 143%, respectively.
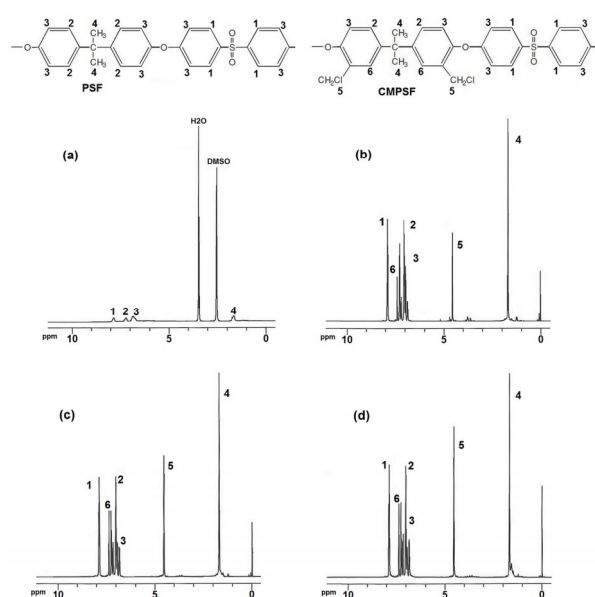
Figure 2. ¹HNMR spectra for pristine PSF (a) and CMPSF with different chloromethylation times: 24 h (b), 48 h (c) and 72 h (d)

3.2. Preparation of AEMs based on QPF-TMA

AEM samples based on quaternized PSF and TMA (QAPSF) were prepared with different chloromethylation times and amination solvents. Four different membranes, denoted as QAPSF-1, QAPSF-2, QAPSF-3 and QAPSF-4, were prepared by chemical modification method according to Table 1.

TABLE 1. Chloromethylation and amination conditions used for AEM preparation

membrane	Chloromethylation			Amination			
	t (h)	T (°C)	DC (%)	t (h)	T (°C)	solvent	TMA:CH₂Cl (mol/mol)
QAPSF-1	24	55	82	48	80	NMP	3:1
QAPSF-2	48	55	130	48	80	NMP	3:1
QAPSF-3	72	55	143	48	80	NMP	3:1
QAPSF-4	72	55	143	48	80	DMAc	3:1

3.3. Hydroxide Conductivity, Activation Energy and IEC for AEMs

The ion transport properties of prepared AEMs including ionic conductivity at 25 and 80 °C, IEC and activation energy are summarized in Table 2. As seen, the membranes with greater DC which were obtained in longer chloromethylation periods, showed more significant ionic conductivity and IEC values. Furthermore, by increasing the ionic conductivity, lower values of activation energy were resulted. Obviously by decreasing the energy barrier for ion transport through the polymer, the ionic conductivity through the AEM increases. As demonstrated in Table 2, while NMP was used as the amination solvent for QAPSF-3, nearly greater ion

transport properties were obtained compared with QAPSF-4 prepared using DMAc as amination solvent. Therefore, it was concluded that NMP can be a good candidate as solvent in amination process.

TABLE 2. Ionic conductivities, IECs and activation energies of prepared AEMs

membrane	σ (mS/cm) at 25 °C	σ (mS/cm) at 80 °C	IEC (meq/gr)	E_a (kJ/mol)
QAPSF-1	6.10	14.96	0.96	14.75
QAPSF-2	9.89	22.57	1.31	13.34
QAPSF-3	15.87	34.01	1.73	11.98
QAPSF-4	14.29	31.29	1.61	12.23

Figure 3. illustrates the ionic conductivity increment with temperature for prepared AEMs. As the temperature increases, the free volume enlarges and the anion transferring channels become wider, which enhances overall mobility of ions and polymer chains and consequently the ionic conductivity increases [28]. The temperature dependency of ionic conductivity is related to the activation energy of ion conduction as observed in Figure 4. and summarized in Table 2. Figure 4. shows that all the prepared AEMs proposed a typical Arrhenius behavior for ionic conductivity, decreasing exponentially with the reciprocal of temperature.
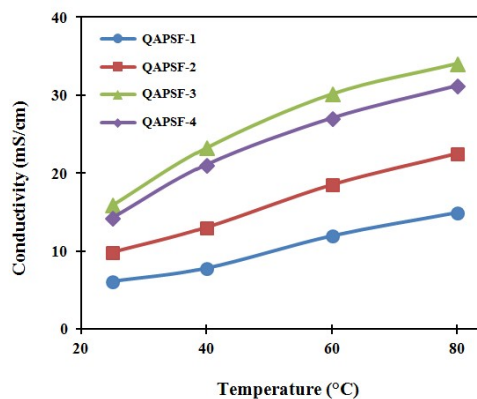

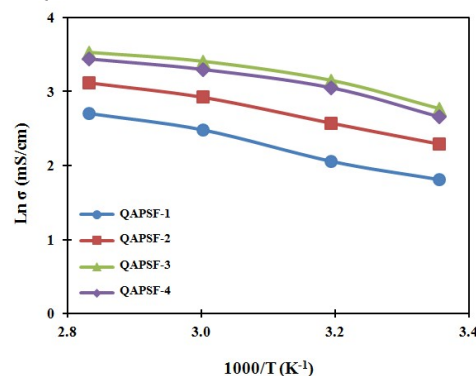**Figure 3.** Temperature dependency of ionic conductivity for prepared QAPSF AEMs

Figure 4. Arrhenius plots of prepared QAPSF AEMs at different temperatures

3.4. Water Uptake, Swelling Ratio and Hydrated Number for AEMs The water content associated properties of prepared AEMs including WU, SR and hydrated number for both chloride and hydroxide forms are reported in Table 3. Generally, these parameters values will increase by enhancement of IEC for AEMs. Since the higher IEC makes the ionic clusters larger and hydrophilic channels more continuous, that enlarges the overall hydrophilic domains and consequently enhances water content associated properties [29, 30]. Furthermore, while DMAc was used instead of NMP as the amination solvent for QAPSF-4, higher values were obtained for WU, SR and hydrated number. These results are in accordance with the results obtained from ion transport properties of AEM. Hence, NMP can be a good choice as the solvent for the amination step which leads to preparation of AEMs with reasonable dimensional stability.

TABLE 3. WU, SR and hydrated number of the prepared AEMs in chloride and hydroxide forms

membrane	WU(%) OH⁻	WU(%) Cl⁻	SR(%) OH⁻	SR(%) Cl⁻	λ OH⁻	λ Cl⁻
QAPSF-1	44.30	17.54	12.20	6.25	25.69	10.17
QAPSF-2	103.32	25.35	23.08	12.50	43.80	10.75
QAPSF-3	143.56	37.41	36.36	14.71	46.02	11.99
QAPSF-4	157.50	40.48	42.11	19.44	54.32	13.96

As represented in Figures 5. and 6. the WU and hydrated number values of the AEMs in hydroxide form is greater than the values of the AEMs in chloride form. This phenomenon can be attributed to the coordination number of hydroxide ion in water molecules network. Each hydroxide ion is surrounded by four water molecules, therefore the AEMs in hydroxide form uptakes more water molecules compared with AEMs in chloride form [1, 31].
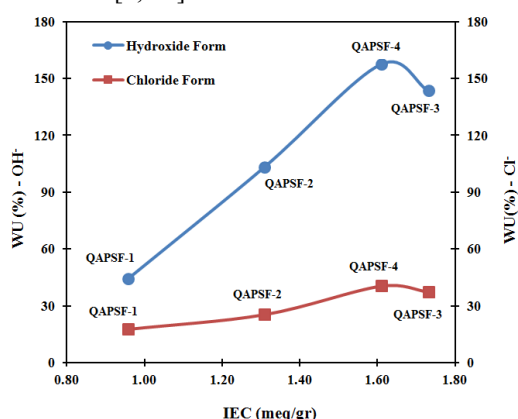

Figure 5. WU of prepared QAPSF AEMs in hydroxide and chloride form versus IEC

3.5. Comparison of Present Study with Literature
A comparison between published data in literature and the data obtained in this study is presented in Table 4.

As observed, performance of the AEMs which prepared in this study is in good agreement with other researchers.
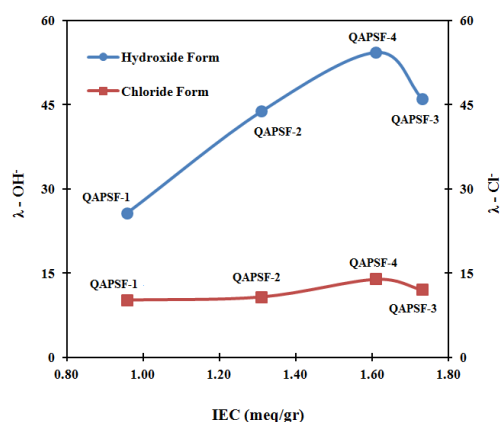

Figure 6. Hydrated number of prepared QAPSF AEMs in hydroxide and chloride form versus IEC

TABLE 4. Comparison of experimental data with published data for AEMs based on PSF and TMA amine group

AEM	Amine group	σ (mS/cm)	IEC (meq/gr)	WU(%)	Ref.
xQAPS-PTFE	TMA	35 (60 °C)	1.23	-	[32]
QAPS-PTFE	TMA	12-27 (20-70 °C)	1.27	55 (30 °C)	[23]
QAPS-OH	TMA	18-34 (20-80 °C)	1.18	230	[33]
PSF-TMA⁺-OH	TMA	17-32 (30-70 °C)	2.05	200 (30 °C)	[13]
QPSF	TMA-TMHDA	11 (25 °C)	-	37 (25 °C)	[12]
PSF-C1	TMA	13-27 (25-60 °C)	3	-	[34]
QAPSF-2	TMA	10-23 (25-80 °C)	1.31	25 (25 °C)	This work
QAPSF-3	TMA	16-34 (25-80 °C)	1.73	37 (25 °C)	This work

4. CONCLUSION

AEMs based on quaternized polysulfone containing ammonium groups (QAPSF) were prepared by chemical modification method using chloromethylation, amination and alkalization. The CMPSF were characterized by 1HNMR spectra and the DC was determined according to the integration of peak area. The properties of resulted membranes including ionic conductivity, IEC, activation energy for ion transport, WU, SR and hydrated number were measured. The experiments results showed that the higher chloromethylation time (the higher DC) and use of NMP as the solvent in the amination step results in the AEMs with greater ionic conductivity and IEC values. Clearly by increasing the ionic conductivity and IEC

values, WU, SR and hydrated number will increase. Therefore, there is a trade-off between the ion transport properties and water content associated properties of the AEMs and both factors should be taken into consideration to obtain membranes with better performance. According to the ionic transport measurements and water content characterizations, the prepared QAPSF AEMs can be denoted as good candidates for SAFC application.

5. ACKNOWLEDGMENT

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