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공학석사 학위논문

**Poly(arylene ether sulfone) containing
tetra(quaternary ammonium pendant
groups) for alkaline anion exchange
membrane fuel cells**

사차암모늄 펜던트그룹을 갖는
폴리아릴렌이써설피온의
알칼라인 연료전지 음이온 교환막으로서의 특성

2014년 2월

서울대학교 대학원
공과대학 화학생물공학부
최 지 은

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지도교수 성 영 은

이 논문을 공학석사 학위논문으로 제출함
2014년 2월

서울대학교 대학원
공과대학 화학생물공학부
최 지 은

최지은의 석사 학위논문을 인준함
2014년 2월

위 원 장 _____ (인)

부위원장 _____ (인)

위 원 _____ (인)

Abstract

Poly(arylene ether sulfone) containing tetra(quaternary ammonium pendant groups) for alkaline anion exchange membrane fuel cells

Jieun Choi

School of Chemical and Biological Engineering

The Graduate School

Seoul National University

A series of poly(arylene ether sulfone)s containing quaternary ammonium pendant groups is prepared for anion conducting membranes. We synthesize a new monomer that contains four amine groups which are changed to ammonium functional groups. By using the functionalized monomer, it is possible to directly obtain functionalized poly(arylene ether sulfone) for anion exchange membranes. This process allows precise control of the amount of

quaternary ammonium groups and their locations along the polymer backbone. The product is characterized by ^1H NMR, thermogravimetric analysis, water uptake, ion exchange capacity, conductivity and cell performance. The anion exchange membranes formed from these polymers show conductivities above 40 mS/cm at 30 °C. In fuel cell test, the maximum power output of 77 mW/cm² is achieved using hydrogen and oxygen.

Keywords : anion exchange membrane; poly(arylene ether sulfone); quaternary ammonium group; membrane electrode assembly; solid alkaline fuel cell

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1. Introduction

1.1. Alkaline fuel cells

In recent years, studies on ion-conducting polymers have been strongly promoted as a result of a considerable interest in the development of high performance polymer electrolyte membrane fuel cells (PEMFCs) for transportation, stationary and portable power applications.¹ However, since PEMFCs use high-priced perfluorosulfonated polymers like Nafion® and precious Pt catalyst, which put serious limits to commercialization, new type fuel cells are urgently demanded.

By switching from an acidic medium to a basic one, alkaline anion exchange membrane fuel cells are expected to solve those problems. The faster kinetics of oxygen reduction reactions under alkaline condition allows the use of nonprecious metal electrocatalysts, thus drastically reducing the cost of the fuel cell.² Furthermore, ion transport within the membrane is from the cathode to the anode, opposing the direction of methanol crossover from anode to cathode, which will reduce the methanol permeability. Also, AEMFCs use relatively cheap alkaline exchange membrane (AEM).

Unfortunately, AFC systems have been plagued by the presence of CO₂ when air is used as the oxidant. The gas dissolves in the liquid

electrolyte, most commonly a KOH solution, and converts OH^- ions to CO_3^{2-} and then HCO_3^- . The aqueous carbon dioxide also increases solution viscosity, thereby lowering species diffusion coefficients. Even more detrimentally, the CO_2 reaction produces carbonate salts, which precipitate in the electrode pores, blocking reactants from accessing catalytic sites, and destroying the water-proof character of the gas diffusion layer. Solid alkaline exchange membrane fuel cells (SAEMFCs) overcome the issues intrinsic to AFCs by replacing the liquid electrolyte with a solid state, ion-conducting polymer membrane. The membrane possesses covalently attached cationic pendant groups, and anionic counterions. The cationic groups aid in the transport of OH^- anions from cathode to anode.³

1.2. Anion exchange membranes

Among several components for SAEMFC, the AEM is one of the most important parts and determines the whole performance of the fuel cell. There are very few commercially available anion exchange membranes (AEMs) as Nafion[®] does in the field of proton exchange membranes. For anion exchange membrane fuel cell (AEMFC) applications, AEMs need reasonable conductivity, mechanical strength and chemical stability.⁴ AEM materials by the introduction of quaternary ammonium groups to existing polymers such as poly(arylene ether sulfone)⁵, poly(arylene ether ketone)⁶, poly(phthalazinone ether sulfone ketone)⁷, polystyrene⁸, poly(phenylene)⁹, poly(vinyl alcohol)¹⁰ and poly(2,6-dimethyl 1,4-phenylene) oxide¹¹ backbone have been investigated. Among these materials, poly(arylene ether sulfone) was considered as a promising material for AEMFCs application due to its high durability over a broad pH and temperature range with excellent mechanical, thermal and chemical stability.¹²

One of general synthetic methods of poly(arylene ether sulfone) based AEMs typically included a chloromethylation and a quaternization reaction steps.¹³ However, the chloromethylation reaction used toxic chloromethylation reagent, and gelation often occurs during the reaction. For that reason, new alternative synthetic

routes have been performed.^{6, 14-17} Another synthetic method includes the bromination of benzylmethyl group in polymer backbone which is followed by base treatment to get hydroxyl ion exchange membrane. In case of this method, however, the bromination reaction of benzylmethyl group was not complete. Therefore, the final structure of the polymers is not exactly what is designed.¹⁵

In order to avoid the problem as mentioned above, in this study, we synthesized a monomer that has tertiary amine groups that are changed to quaternary ammonium group. In addition, the monomer was successfully polymerized with other linking monomers. Previously, it was reported that a monomer with two tertiary amine groups was synthesized.¹⁸ In case of our system, the hydrophilic channel would be increased because tetra-ammonium functional groups are easily gathered compared to di-functional one.

A series of poly(arylene ether sulfone) containing four amine functional groups was prepared by condensation polymerization. Then, the tertiary amine substituents were converted to the quaternary ammonium group for hydroxyl ion conduction by reaction with iodomethane and KOH treatment, successively. In the research of proton exchange membranes, it had been found that the polymer electrolyte using tetra-sulfonated monomer showed better conductivity than one using di-sulfonated monomer.¹⁹ We are interested in the properties of poly(arylene ether sulfone) containing

tetra(quaternary ammonium group), which could provide the formation of bigger ionic cluster linked by hydrophilic channels than di-functional one. The hydroxide exchange membranes were characterized for SAEMFCs by several different analytical instruments.

2. Experimental

2.1. Synthesis of poly(arylene ether sulfone) containing quaternary ammonium iodide salt (QPES-I-x)

2.1.1. Materials

4,4'-Dihydroxydiphenyl ether and 4,4'-biphenol were obtained from Tokyo Chemical Industry Co., Ltd. Dimethylamine solution (33 wt%), formalaldehyde solution (37 wt%), bis(4-fluorophenyl)sulfone, Cs₂CO₃, iodomethane, and solvents were purchased from Sigma-Aldrich Co. without further purification. Before synthesis, all monomers and polymers were dried under vacuum at 60 °C overnight.

2.1.2. Synthesis of 2,5,2',5'-tetra(trimethylaminemethylene)-4,4'-dihydroxydiphenylether (TADHDPE)

4,4'-Dihydroxydiphenyl ether (60 g, 0.291 mol) was dissolved in 180 mL of ethanol. Aqueous solutions of dimethylamine (10.0 equiv.) and formalaldehyde (10.0 equiv.) were added. The reaction mixture was kept at 70 °C for 24 h.²⁰ Recrystallizations from ethanol gave the product as buff powder (106.3 g, 83.2% yield).

¹H NMR (CDCl₃, ppm): δ 6.67 (s, 4 H, ArH), 3.48 (s, 8 H, -CH₂-),

2.27 (s, 24 H, $-\text{CH}_3$); ^{13}C NMR (CDCl_3 , ppm): δ 152.04, 149.65, 124.25, 118.75, 60.40, 44.93.

2.1.3. Synthesis of poly(arylene ether sulfone) containing tertiary amine group (TPES-x)

The polymerization procedure of TPES-20, where 20 refers to the feed mole percent of TADHDPE in dihydroxyl compounds, is described as follows: TADHDPE (2.610 g, 6 mmol), 4,4'-biphenol (4.514 g, 24 mmol), bis(4-fluorophenyl) sulfone (7.705 g, 30 mmol) and anhydrous NMP 72 mL were added to a 250 mL three-necked round-bottomed flask equipped with a Dean-Stark trap, argon gas inlet and thermometer. After dissolving the mixture, anhydrous Cs_2CO_3 (20.547g, 63 mmol) and 30 mL of toluene were added. The reaction bath was heated to 115 °C for 6 h to dehydrate the reaction mixture. As toluene and water had been distilled off, the temperature was raised gradually to 130 °C and allowed to react at this temperature for 10 h to give a viscous solution. The solution was poured into a large excess of ethanol with stirring. The precipitate was washed with ethanol and hot deionized water several times (14.5 g, 98.1% yield). ^1H NMR (CDCl_3 , ppm): δ 8.04–7.80 (br, 40 H, ArH_c and ArH_c), 7.72–7.53 (br, 32 H, ArH_g), 7.27–7.01 (br, 40 H, ArH_d and ArH_d), 6.98–6.81 (br, 8 H, ArH_a), 3.32–2.98 (br, 16 H,

Ar-CH₂-N-), 2.46–1.94 (br, 48 H, -N-CH₃). In the same way, TPES-30 and TPES-40 were prepared.

2.1.4. Synthesis of poly(arylene ether sulfone) containing quaternary ammonium iodide salts (QPES-I-x)

The conversion from TPES-x to QPES-I-x was performed as follows: To a solution of the polymer TPES-x (10.0 g) in 150 mL of DMAc, iodomethane (2 equiv. of the tertiary amine groups) was added. The reaction mixture was stirred at 30 °C for 6 h, and then poured into ethanol to obtain the yellow powder (10.7 g, 84.6% yield). ¹H NMR (DMSO-*d*₆, ppm): δ 8.12–7.83 (br, 48 H, ArH_a, ArH_e and ArH_{e'}), 7.82–7.60 (br, 32 H, ArH_g), 7.33–6.94 (br, 72 H, ArH_f, ArH_d and ArH_{d'}), 4.72–3.97 (br, 16 H, Ar-CH₂-N⁺-), 3.38–2.89 (br, 72 H, -N⁺-CH₃).

2.2. Membrane fabrication and counter ion exchange from QPES-I-x to quaternary ammonium hydroxide salt (QPES-OH-x)

A series of QPES-I-x membranes was obtained by casting polymer solutions in NMP onto a glass dish. The membrane was dried under vacuum at 100 °C for 48 h. After cooling to room temperature, deionized water was poured onto the glass dish to peel off the membrane. The thickness of the membranes was controlled as $30 \pm 3 \mu\text{m}$. The membranes were immersed in 1 M KOH solutions for 48 h at room temperature to convert the membranes of QPES-I-x (I⁻ form) into those of QPES-OH-x (OH⁻ form). After that, the membranes were washed with deionized water and stored in deionized water for at least 24 h prior to analysis.

2.3. Characterization of QPES-OH-x for alkaline anion exchange membranes

2.3.1. Thermogravimetric analysis

Thermogravimetric analysis (TGA) was performed under nitrogen atmosphere with a Q50 apparatus (TA Instruments) at a heating rate of 10 °C/min. Before testing, all the polymers were dried in a vacuum oven at 60 °C for 24 h.

2.3.2. Water uptake and dimensional stability

Water uptake and dimensional stability of the membranes were determined by measuring the change in weight and length of the membranes before and after immersing in deionized water. The water uptake and dimensional stability were calculated using following equations.

$$\text{Water uptake (\%)} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \times 100\% \quad (1)$$

where W_{wet} is the weight of the wet membrane, and W_{dry} is the weight of the dry membrane.

$$\text{Dimensional stability (\%)} = \frac{V_{\text{wet}} - V_{\text{dry}}}{V_{\text{dry}}} \times 100\% \quad (2)$$

where V_{wet} is the volume of the wet membrane, and V_{dry} is the volume of the dry membrane.

2.3.3. Ion exchange capacities (IEC)

Ion exchange capacity (IEC) was determined by a back titration method. The 30 mg of a dried OH⁻ form membrane was immersed into 35 mL 0.01 M HCl standard solution for 48 h to completely exchange OH⁻ to Cl⁻. The 0.01 M NaOH solution was used for back titration to determine the ion exchange capacity. The end point was observed with phenolphthalein.²¹ The IEC values were calculated as followed:

$$\text{IEC (meq/g)} = \frac{V_{0\text{NaOH}}C_{\text{NaOH}} - V_{x\text{NaOH}}C_{\text{NaOH}}}{W_{\text{dry}}} \quad (3)$$

where $V_{0\text{NaOH}}$ and $V_{x\text{NaOH}}$ are the volume of the NaOH consumed in the titration of the HCl solution without and with membranes respectively, C_{NaOH} is the mole concentration of the NaOH solution which is titrated by the 0.05 M oxalic acid standard solution, and W_{dry} is the weight of the dried membranes.

2.3.4. Ionic conductivity

A four-point probe technique was used for membrane conductivity measurement. Impedance measurements were carried out in galvanostatic mode with a perturbation amplitude of 5 μA over a frequency range from 1 Hz to 1 MHz, using a ZAHNER IM6

impedance analyzer. The impedance (R) of a membrane was measured in controlled humidity and temperature chamber via a Nyquist plot. The membrane was immersed in deionized water for at least 24 h prior to the test. The conductivity (σ) was calculated as followed:

$$\sigma = \frac{L}{RA} \quad (4)$$

where L is the distance between the reference electrode and the sensing electrode and A is the cross-sectional area (thickness \times width) of a membrane.

2.3.5. Preparation of MEA and fuel cell tests

Catalyst ink for both anode and cathode were prepared by dispersing Pt/C electrocatalyst (45.9 wt%) from Tanaka Kikinzoku Kogyo K.K. and AS-4 ionomer solution from Tokuyama Co. with a mixing combination using mechanical stirring and sonication. The catalyst ink was coated on both sides of the membranes prepared in this study by a spraying method. The Pt loading amount was 0.5 mg/cm² on each electrode, and the ionomer amount in dry basis of each electrode was 32 wt.%. The catalyst coated membranes were sandwiched by a pair of gas diffusion layers (Sigracet® 10BA, SGL Carbon Inc.) and bipolar plates with serpentine flow field under the assembling pressure of 60 kgf/cm².²²

The current–voltage polarization curves and impedance spectra of each assembled MEA were obtained in a single cell with an effective area of 9 cm² at 50 °C. H₂ and O₂ gases humidified by 100% RH at a flow rate of 454 and 303 mL/min were fed to anode and cathode, respectively. After the assembled MEAs were activated by repeatedly measuring the current–voltage polarization curves until reaching steady–state, the current–voltage polarization curves and impedance spectra of each assembled MEA were measured.

3. Results and discussion

3.1. Synthesis and membrane fabrication

2,5,2',5'-Tetra(trimethylaminemethylene)-4,4'-dihydroxydiphenylether) (TADHDPE) was obtained by the reaction with 4,4'-dihydroxydiphenyl ether, dimethylamine and formalaldehyde (Scheme 1). The reaction was carried out at the elevated temperature with excess formaldehyde and dimethylamine to obtain four tertiary amine substituted product. Mannich reaction occurred on the both ortho-positions of hydroxyl group to obtain the compound. The compound was characterized by ^1H NMR (Figure 1) and ^{13}C NMR (Figure 2). The peak position and integration for aromatic and aliphatic hydrogens are well matched to confirm the structure of the monomer.

By using this monomer, we polymerized a series of poly(arylene ether sulfone) (PAES) containing tetra(tertiary amine pendant groups) (Scheme 2). Hedrick et al. employed a solvent with a high boiling point such as NMP in the presence of K_2CO_3 to obtain high molecular weight PAES and to prevent the hydrolytic side reactions that are typical for the synthesis of the polymer.²³ The polymerization of PAES was mostly carried out at the temperature above 160 °C.^{9, 14, 21} However, our monomer, TADHDPE would not be

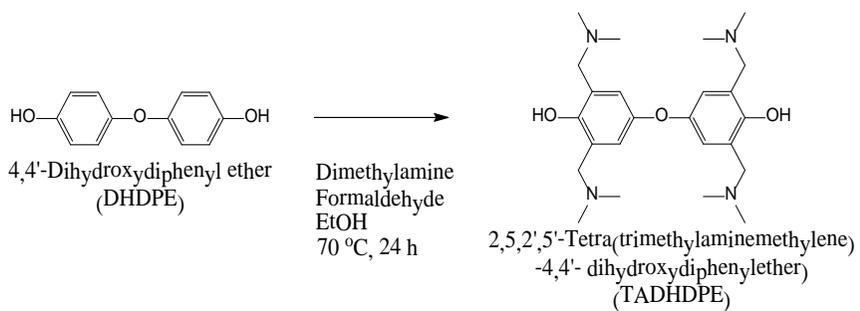
stable at the temperature according to the previous report.¹⁸ Therefore, we could not increase reaction temperature over 140 °C. In order to increase the activity of the polycondensation at such low temperature, we used Cs₂CO₃ instead of K₂CO₃. The excellence of Cs₂CO₃ can be explained in terms of a decrease in the extent of ion-pairing on going from K⁻ to Cs⁻, favoring the nucleophilic reactivity of the associated anion. Moreover, cesium salts are generally more soluble in organic solvents than their potassium counterparts.¹⁸

The chemical structure and compositions of the TPES-x were characterized by ¹H NMR spectroscopy. Figure 3 shows three spectra for the TPES-20, -30, and -40. The peaks at 2.16 and 3.21 ppm are assigned to the chemical shifts of aliphatic protons (-CH₃ (H_c) and -CH₂- (H_b), respectively) on the tertiary amine groups. By the comparison of these peaks with aromatic proton H_g which is well isolated in ¹H NMR spectrum in Figure 3, we can confirm the chemical structure of copolymers. As the feed of TADHDPE was increased in the reaction mixture, the peak integration of H_a, H_b and H_c, which are assigned for TADHDPE, was increased compared to other peaks. The peak ratio of H_b to H_g in ¹H NMR was well matched as theoretical value as shown in Table 1.

The TPES-x was converted to the quaternized by the reaction with iodomethane. After quaternization, the integration ratio of the peak H_b and H_c for TPES-x is changed from 1 : 3 to 2 : 9 (H_b : H_c)

for QPES-I-x, as expected for the composition of quaternary ammonium group (Figure 4). These changes proved quantitative incorporation of quaternary ammonium moieties into poly(arylene ether sulfone).

The QPES-I-x (the iodide form) membranes were prepared by solution casting. To convert them to the hydroxide form, QPES-OH-x, the QPES-I-x membranes were immersed in 1 M KOH at room temperature for 48 h. According to ^1H NMR analysis, a series of the QPES-OH-x was stable after the base treatment (see Figure 5). The stability of the AEMs is one of the most desirable properties. Especially, the stability under strong alkaline conditions is a rather important characteristic. It involves not only the stability of the charged groups, but also the polymer backbone. We also treated the membrane with even severe alkaline condition (4 M KOH at 60 °C for 48 h). Under the severe condition, the QPES-OH-x membranes were still stable (see Figure 6).



Scheme 1. Synthesis of 2,5,2',5'-tetra(trimethylaminemethylene) – 4,4'-dihydroxydiphenylether) (TADHDPE).

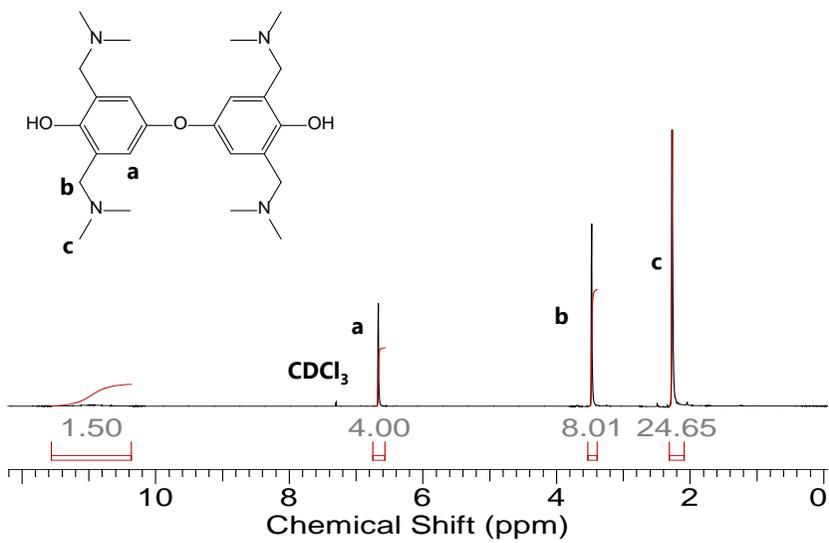


Figure 1. ¹H NMR spectrum of TADHDPE.

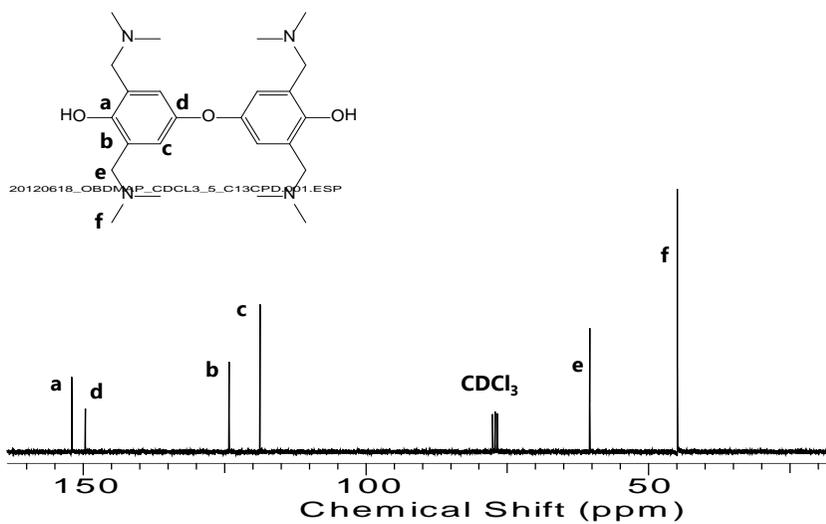
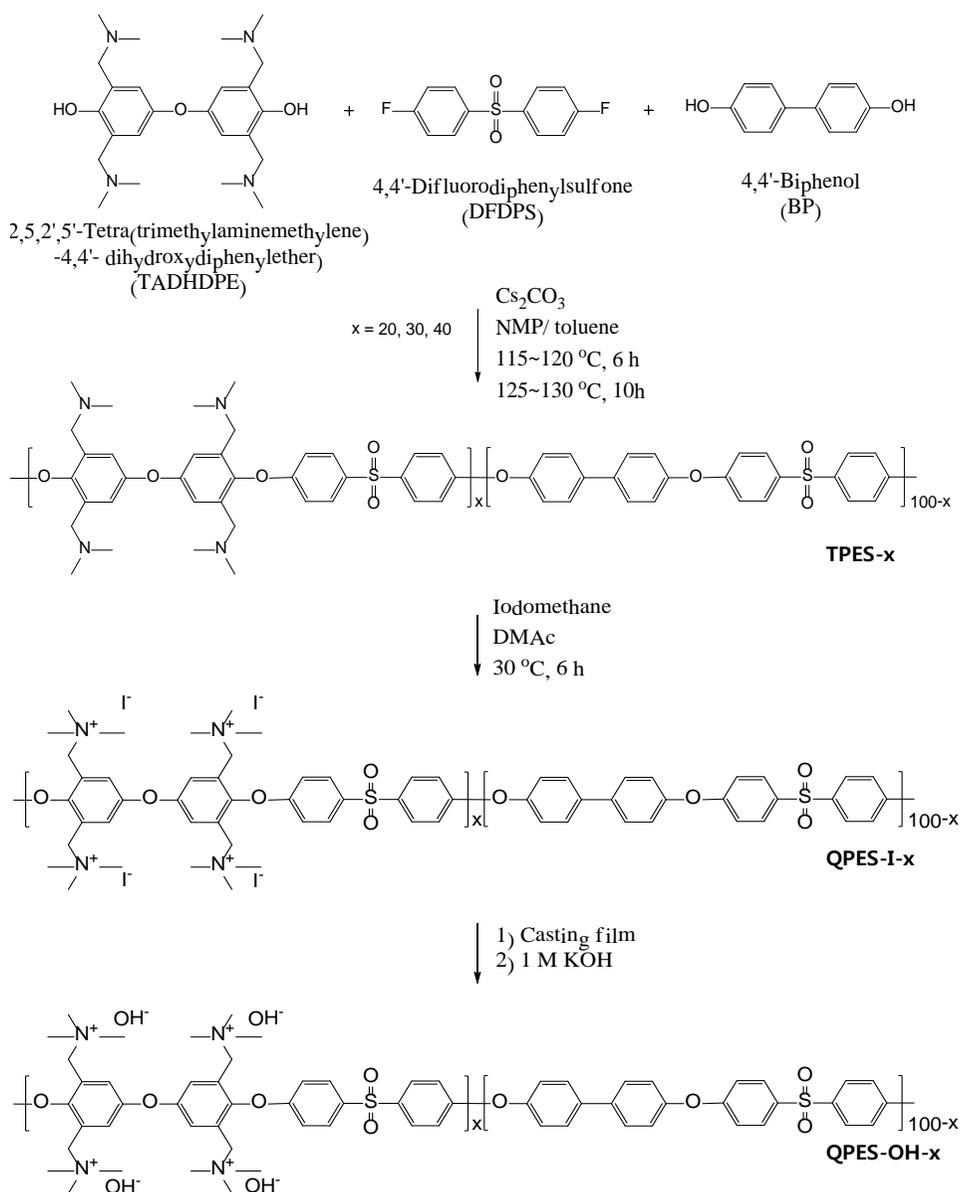


Figure 2. ¹³C NMR spectrum of TADHDPE.



Scheme 2. Synthesis of poly(arylene ether sulfone) containing quaternary ammonium hydroxide salts (QPES-OH-x).

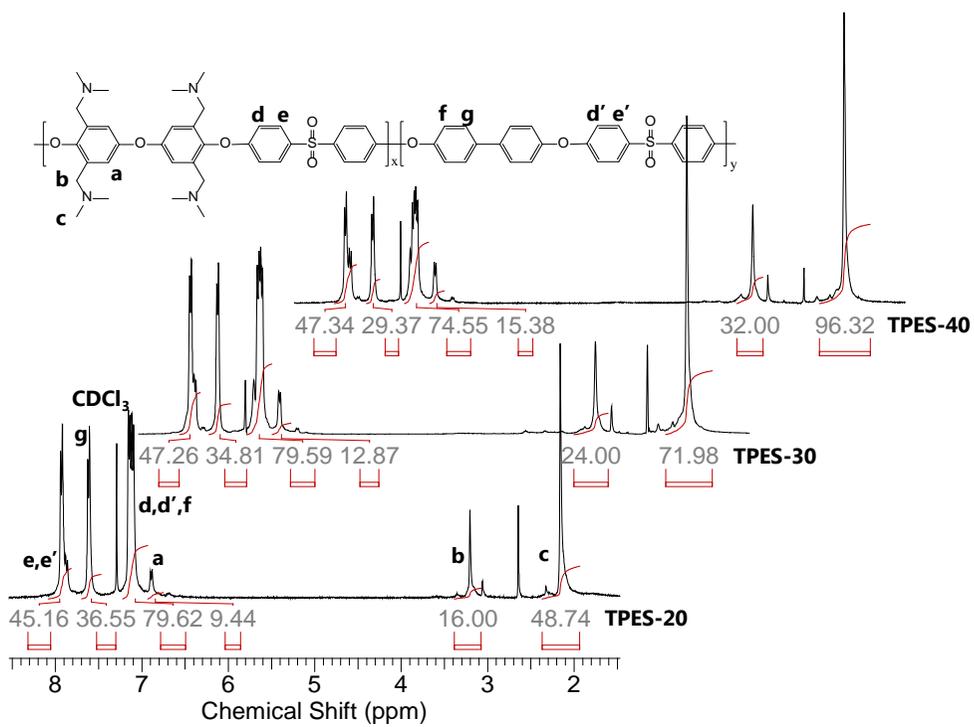


Figure 3. ^1H NMR spectra of TPES-x in CDCl_3 .

Table 1. Comparison of theoretical value and ^1H NMR peak area integration ratio (H_b/H_g) of TPES-x

polymer	H_b/H_g (Theoretical value)	H_b/H_g (^1H NMR)
TPES-20	0.50	0.44
TPES-30	0.86	0.69
TPES-40	1.33	1.09

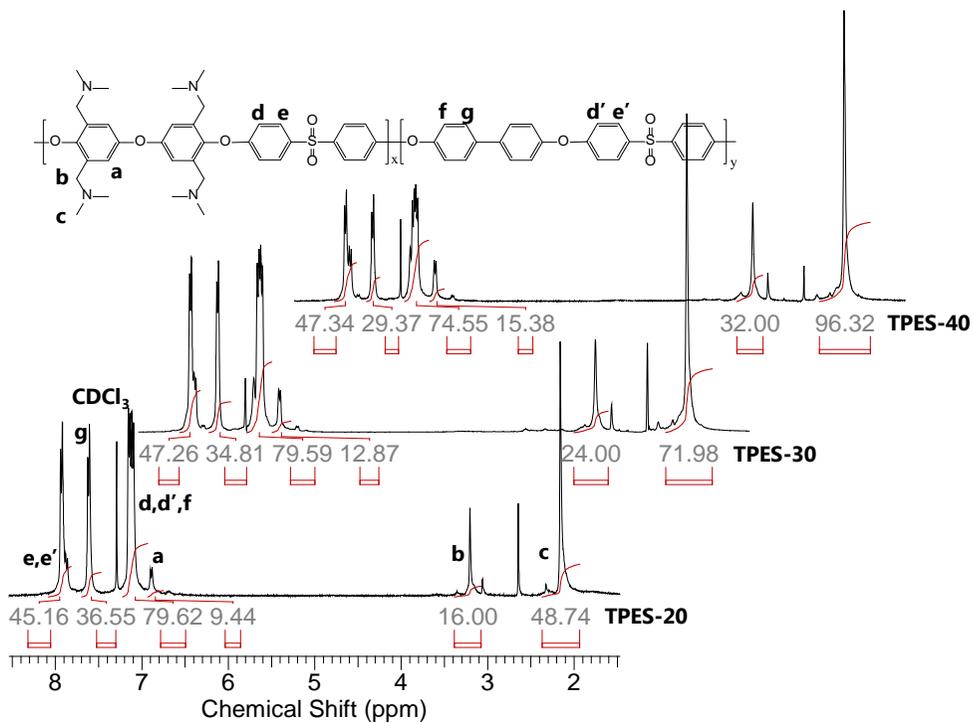


Figure 4. ^1H NMR spectra of QPES-I-x in $\text{DMSO}-d_6$.

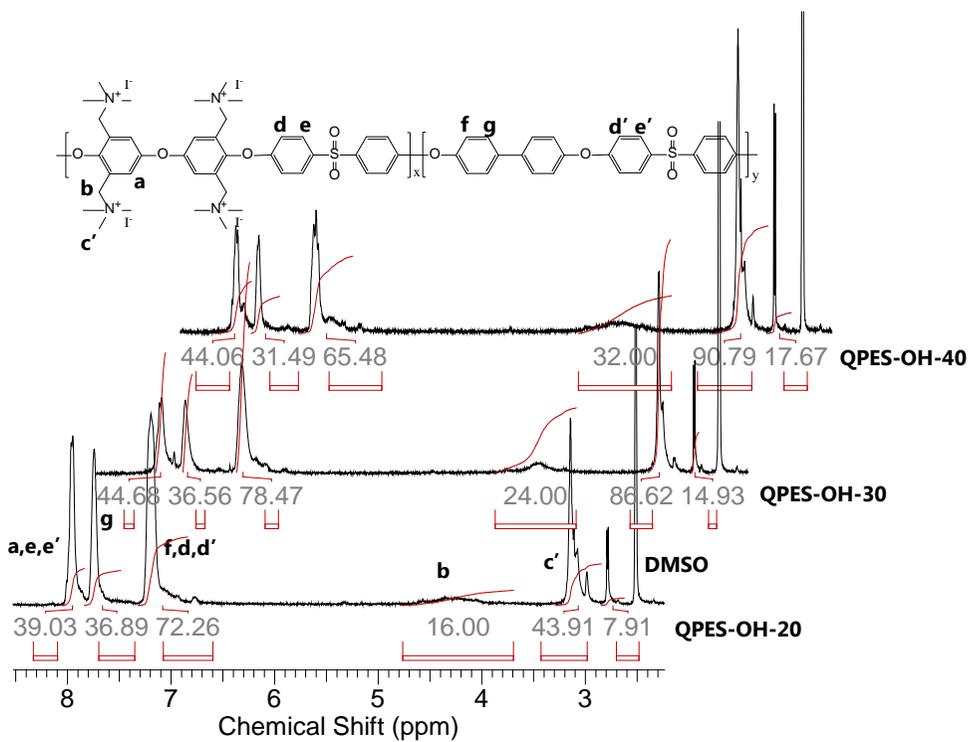


Figure 5. ^1H NMR spectra of QPES-OH-x which were immersed in 1 M KOH at room temperature for 48 h.

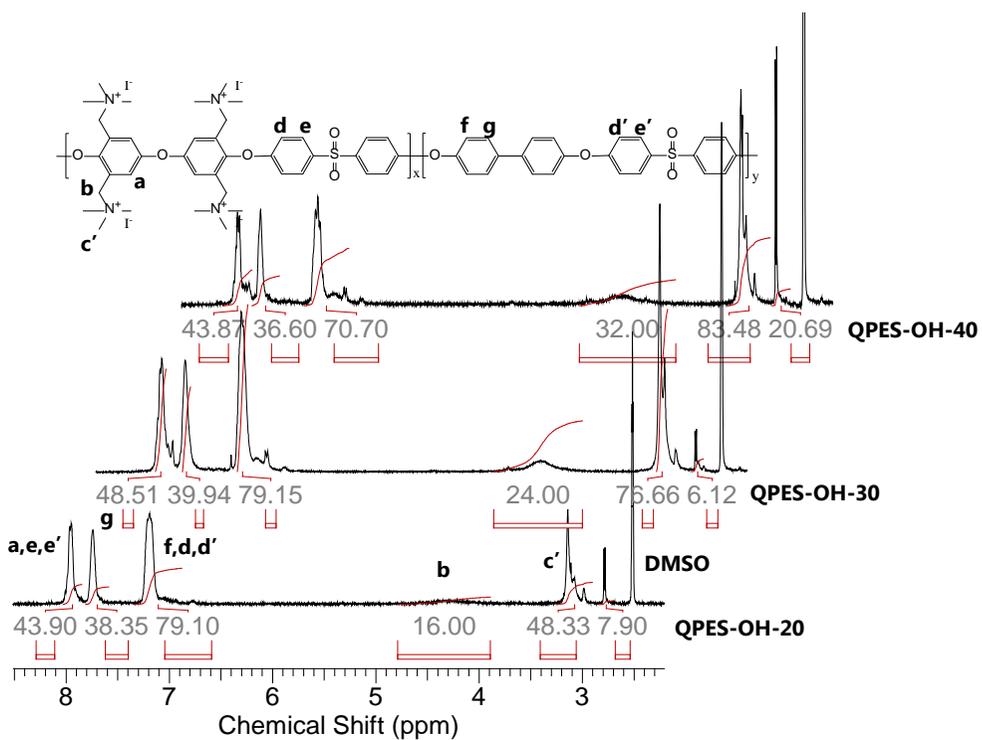


Figure 6. ^1H NMR spectra of QPES-OH- x which were immersed in 4 M KOH at 60 °C for 48 h.

3.2. Characterization of QPES-OH-x for alkaline anion exchange membranes

3.2.1. Thermogravimetric analysis

The thermal stability of all the polymers was determined by TGA technique under nitrogen atmosphere (see Figure 7, Figure 8 and Figure 9). The degradation of the polymers is similar to that of the previously reported polymers.^{16, 22} As shown in Figure 9, all the polymers have three thermal degradation steps. The first weight loss is related to water evaporation. The second loss from 150 °C could be the degradation of quaternary ammonium groups. The third loss from 300 °C is related to the degradation of the polymer backbone.

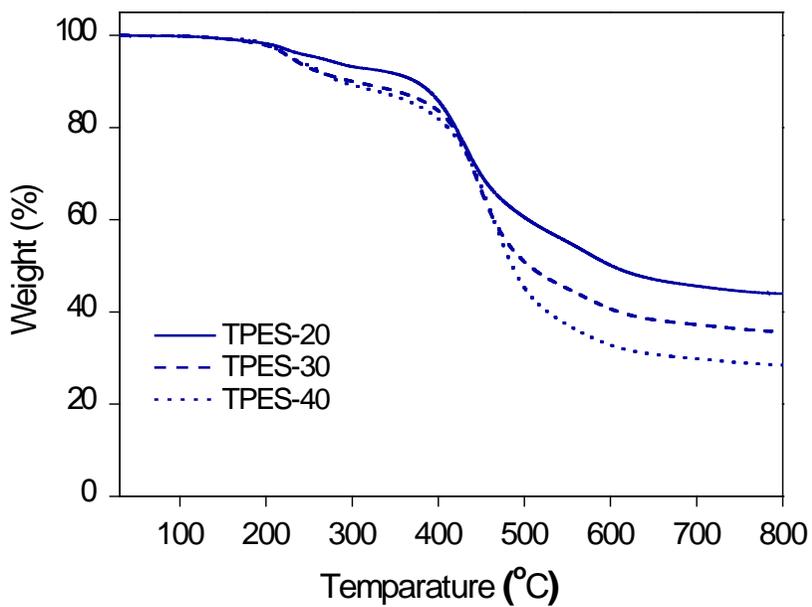


Figure 7. TGA curves of TPES-x.

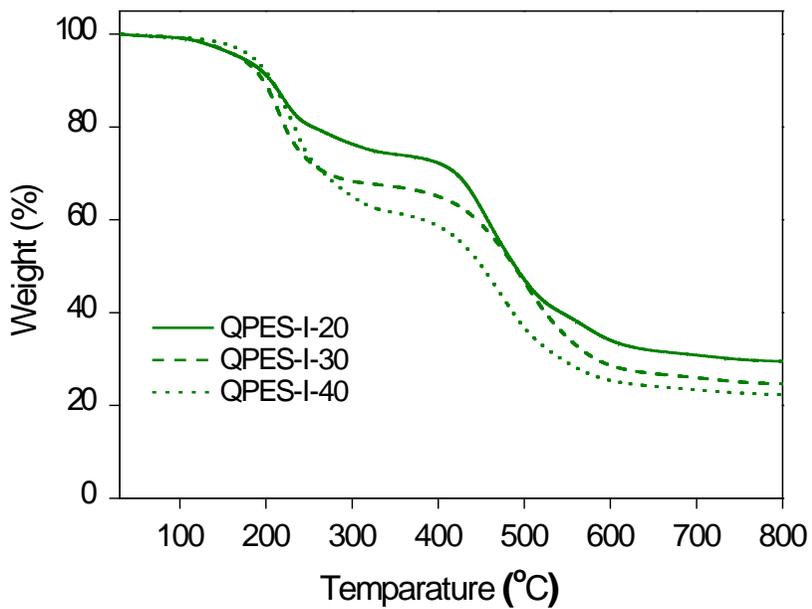


Figure 8. TGA curves of QPES-I-x.

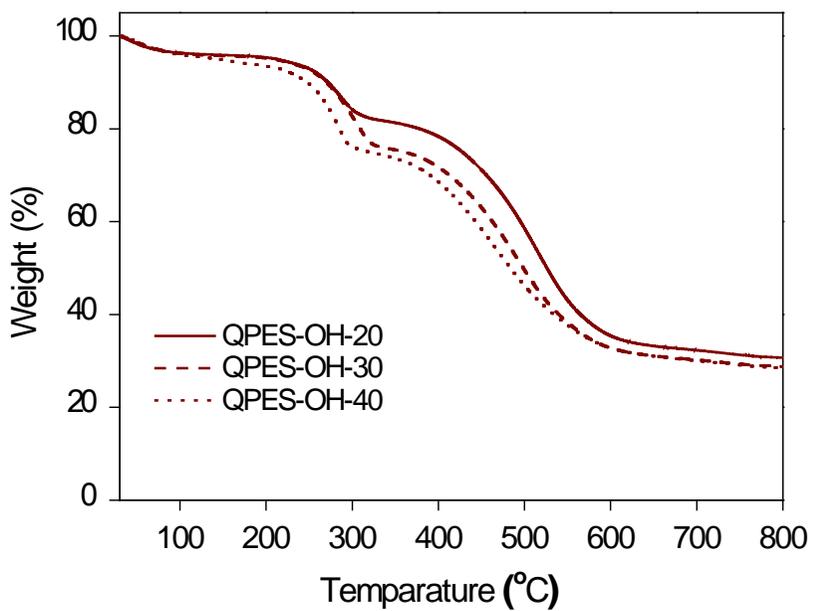


Figure 9. TGA curves of QPES-OH-x.

3.2.2. Water uptake, dimensional stability and ion exchange capacities (IEC)

Water uptake of AEMs is important for hydroxyl ion conductivity, dimensional stability, mechanical strength, and membrane–electrode compatibility. The water uptake is typically a function of the degree of quaternization or the ion exchange capacities (IEC), which is a measure of the exchangeable hydroxide ions in the material. As shown in Table 2, the water uptake values increased in proportion with quaternary ammonium moieties. For instance, QPES–OH–40 showed 34.2%, which was much higher than QPES–OH–20 (5.7%). The IEC values by titration also shows similar trend. As the content of quaternary ammonium moieties increased, IEC is also enhanced.

Table 2. Membrane properties of QPES-OH-x.

membrane	water uptake (%)	dimensional stability (%)	IEC _{titration} (mequiv/g)	comments
QPES-OH-20	5.7 ± 4.8	14.1 ± 6.1	0.57 ± 0.06	ductile film
QPES-OH-30	15.7 ± 7.3	21.7 ± 8.9	0.84 ± 0.07	ductile film
QPES-OH-40	34.2 ± 3.0	36.7 ± 5.5	1.20 ± 0.07	brittle film

3.2.3. Ionic conductivity

The results of impedance measurements were shown in Nyquist plot (Figure 10). The temperature-dependent conductivity under water saturated condition showed that the hydroxyl ion conductivity of these membranes increased with elevated temperature (Figure 11). The conductivity of QPES-OH-20 increased from 45.1 mS/cm (30 °C) to 72.9 mS/cm (60 °C). Their conductivities showed a trend that was similar to that for water uptake. At low IEC values, the conductivity of the membranes was rather low and increased in a gradual fashion. In this case, 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 membrane increased.

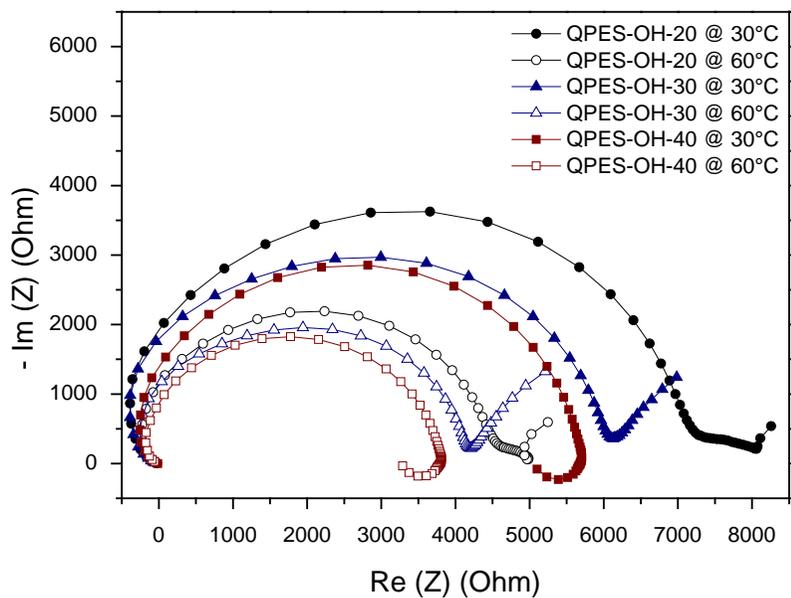


Figure 10. Nyquist plots from the impedance measurement of QPES-OH-x.

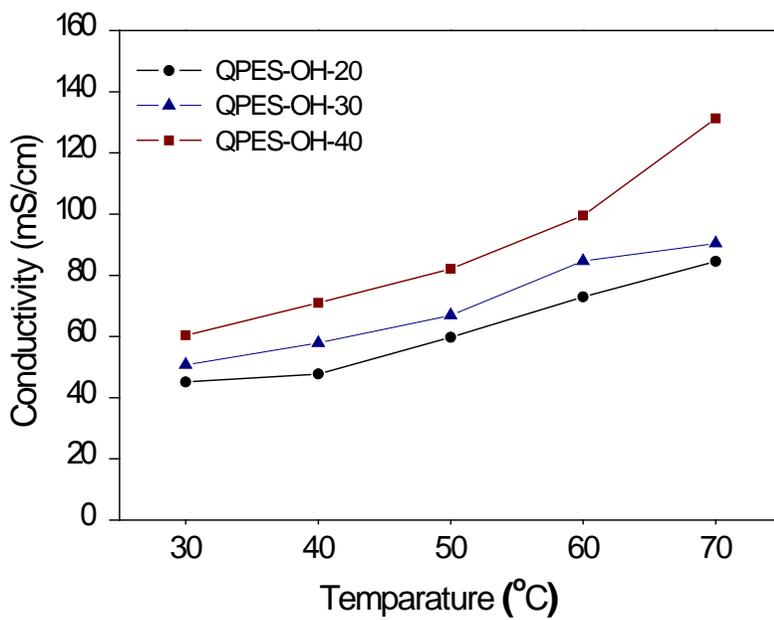


Figure 11. Ionic conductivities of QPES-OH-x.

3.2.4. Preparation of MEA and fuel cell tests

Fuel cell performance data and impedance spectra are shown in Figure 12 and Figure 13. The MEAs using QPES-OH-20 and -30 were only fabricated and evaluated since QPES-OH-40 was too brittle to be fabricated. As shown in Figure 12, the polarization curves show an open circuit potential, above approximately ~ 1.0 V, for a thin membrane ($30\ \mu\text{m}$) which indicates that the membrane had low hydrogen permeability. A peak power density of $77\ \text{mW}/\text{cm}^2$ for the MEA using QPES-OH-30 was achieved using hydrogen and oxygen at $50\ ^\circ\text{C}$ and atmospheric pressure. It results from the less ohmic resistance of the MEA using QPES-OH-30 than that using QPES-OH-20 since the ionic conductivity of QPES-OH-30 was higher than QPES-OH-20 (see Figure 11). It could be also confirmed in impedance spectra of the MEAs using two membranes as shown in Figure 13. The x-intercept of the spectra represents the ohmic resistance of the MEAs. It is observed that the spectrum of QPES-OH-20 is shifted to the right due to higher membrane resistance.

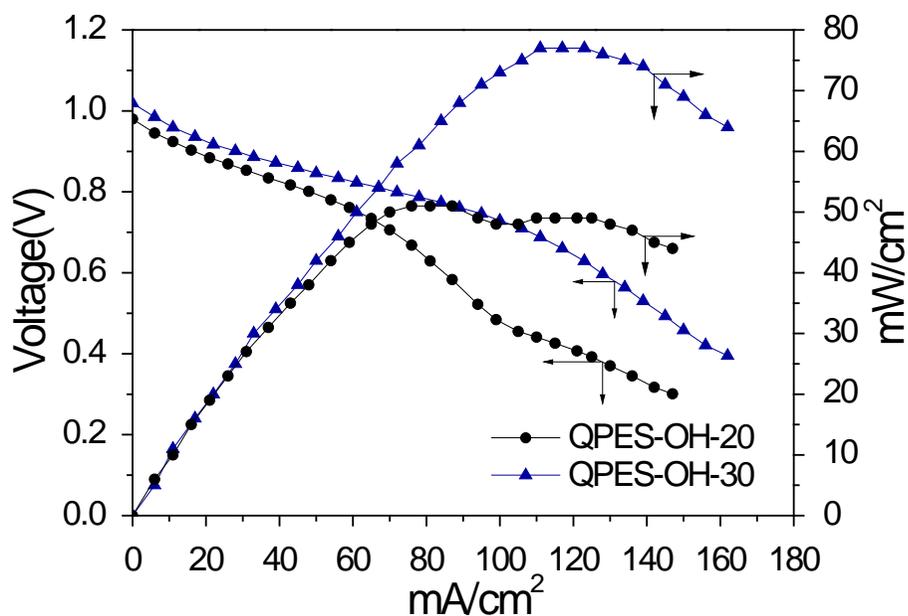


Figure 12. Polarization curves of single cell with QPES–OH–20 and –30. (H_2 and O_2 ; Pt loading: 0.4 mg/cm^2 for the anode and the cathode; 100% relative humidity condition).

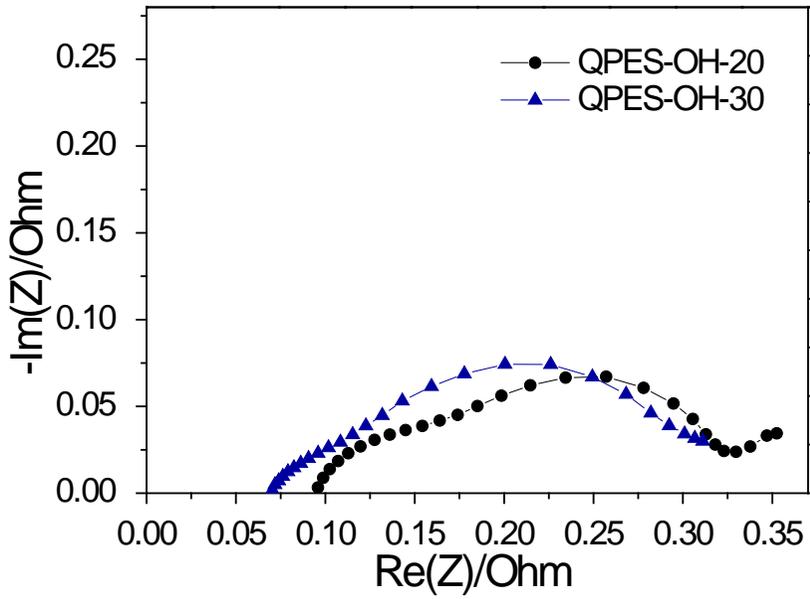


Figure 13. Impedance of a single cell at 0.8 V for QPES-OH-20 and -30.

4. Conclusions

A series of poly(arylene ether sulfone)s containing quaternary ammonium pendant groups was prepared for anion conducting membranes. The reaction procedure was developed for the polycondensation of TADHDPE, BP and DFDPS. We directly obtained functionalized poly(arylene ether sulfone) for anion exchange membranes by using a functionalized monomer. This process allows precise control of the amount of quaternary ammonium groups and their locations along the polymer backbone. The product was characterized by ^1H NMR, TGA, water uptake, ion exchange capacity (IEC), conductivity and cell performance. The anion exchange membranes formed from these polymers showed conductivities above 40 mS/cm at 30 °C. In fuel cell tests, the maximum power outputs of 77 mW/cm² were achieved using hydrogen and oxygen for the MEA using QPES-OH-30. These AEMs, QPES-OH-x, demonstrated excellent solubility, high ionic conductivity, and good alkaline stability. These results will aid in designing better polymer structure, possibly with novel side chains, grafted, or cross-linked polymers, for improving membrane properties.

References

1. Wang, Y.; Chen, K. S.; Mishler, J.; Cho, S. C.; Adroher, X. C., A review of polymer electrolyte membrane fuel cells: Technology, applications, and needs on fundamental research. *Applied Energy*, 2011, 88, 981–1007.
2. Lu, S.; Pan, J.; Huang, A.; Zhuang, L.; Lu, J., Alkaline polymer electrolyte fuel cells completely free from noble metal catalysts. *Proceedings of the National Academy of Sciences*, 2008, 105, 20611–20614.
3. Couture, G.; Alaaeddine, A.; Boschet, F.; Ameduri, B., Polymeric materials as anion–exchange membranes for alkaline fuel cells. *Progress in Polymer Science*, 2011, 36, 1521–1557.
4. Merle, G.; Wessling, M.; Nijmeijer, K., Anion exchange membranes for alkaline fuel cells: A review. *Journal of Membrane Science*, 2011, 377, 1–35.
5. Li, L.; Wang, Y., Quaternized polyethersulfone Cardo anion exchange membranes for direct methanol alkaline fuel cells. *Journal of Membrane Science*, 2005, 262, 1–4.
6. Wang, J.; Wang, J.; Zhang, S., Synthesis and characterization of cross–linked poly(arylene ether ketone) containing pendant quaternary ammonium groups for anion–exchange membranes. *Journal of Membrane Science*, 2012, 415–416, 205–212.

7. Fang, J.; Shen, P. K., Quaternized poly(phthalazinon ether sulfone ketone) membrane for anion exchange membrane fuel cells. *Journal of Membrane Science*, 2006, 285, 317–322.
8. Varcoe, J.; Slade, R., An electron–beam–grafted ETFE alkaline anion–exchange membrane in metal–cation–free solid–state alkaline fuel cells. *Electrochemistry Communications*, 2006, 8, 839–843.
9. Hibbs, M. R.; Fujimoto, C. H.; Cornelius, C. J., Synthesis and Characterization of Poly(phenylene)–Based Anion Exchange Membranes for Alkaline Fuel Cells. *Macromolecules*, 2009, 42, 8316–8321.
10. Nikolić, V. M.; Žugić, D. L.; Maksić, A. D.; Šaponjić, D. P.; Marčeta Kaninski, M. P., Performance comparison of modified poly(vinyl alcohol) based membranes in alkaline fuel cells. *International Journal of Hydrogen Energy*, 2011, 36, 11004–11010.
11. Arges, C. G.; Wang, L.; Parrondo, J.; Ramani, V., Best Practices for Investigating Anion Exchange Membrane Suitability for Alkaline Electrochemical Devices: Case Study Using Quaternary Ammonium Poly(2,6–dimethyl 1,4–phenylene)oxide Anion Exchange Membranes. *Journal of The Electrochemical Society*, 2013, 160, F1258–F1274.
12. Arges, C. G.; Ramani, V., Two–dimensional NMR spectroscopy reveals cation–triggered backbone degradation in polysulfone–based anion exchange membranes.

Proceedings of the National Academy of Sciences, 2013, 110, 2490– 2495.

13. Zhao, Z.; Wang, J.; Li, S.; Zhang, S., Synthesis of multi–block poly(arylene ether sulfone) copolymer membrane with pendant quaternary ammonium groups for alkaline fuel cell. *Journal of Power Sources*, 2011, 196, 4445–4450.
14. Seo, D. W.; Hossain, M. A.; Lee, D. H.; Lim, Y. D.; Lee, S. H.; Lee, H. C.; Hong, T. W.; Kim, W. G., Anion conductive poly(arylene ether sulfone)s containing tetra–quaternary ammonium hydroxide on fluorenyl group for alkaline fuel cell application. *Electrochimica Acta*, 2012, 86, 360–365.
15. Yan, J.; Hickner, M. A., Anion Exchange Membranes by Bromination of Benzylmethyl–Containing Poly(sulfone)s. *Macromolecules*, 2010, 43, 2349–2356.
16. Wang, J.; Zhao, Z.; Gong, F.; Li, S.; Zhang, S., Synthesis of Soluble Poly(arylene ether sulfone) Ionomers with Pendant Quaternary Ammonium Groups for Anion Exchange Membranes. *Macromolecules*, 2009, 42, 8711–8717.
17. Seo, D. W.; Lim, Y. D.; Hossain, M. A.; Lee, S. H.; Lee, H. C.; Jang, H. H.; Choi, S. Y.; Kim, W. G., Anion conductive poly(tetraphenyl phthalazine ether sulfone) containing tetra quaternary ammonium hydroxide for alkaline fuel cell application. *International Journal of Hydrogen Energy*, 2013, 38, 579–587.
18. Wang, J.; Wang, J.; Li, S.; Zhang, S., Poly(arylene ether sulfone)s ionomers with pendant quaternary ammonium

- groups for alkaline anion exchange membranes: Preparation and stability issues. *Journal of Membrane Science*, 2011, 368, 246–253.
19. Li, N.; Shin, D. W.; Hwang, D. S.; Lee, Y. M.; Guiver, M. D., Polymer Electrolyte Membranes Derived from New Sulfone Monomers with Pendent Sulfonic Acid Groups. *Macromolecules*, 2010, 43, 9810–9820.
 20. Song, Y.; Tian, T.; Wang, P.; He, H.; Liu, W.; Zhou, X.; Cao, X.; Zhang, X. L., Phenol quaternary ammonium derivatives: charge and linker effect on their DNA photo-inducible cross-linking abilities. *Organic & biomolecular chemistry*, 2006, 4, 3358–66.
 21. Rao, A. H. N.; Kim, H.-J.; Nam, S.; Kim, T.-H., Cardo poly(arylene ether sulfone) block copolymers with pendant imidazolium side chains as novel anion exchange membranes for direct methanol alkaline fuel cell. *Polymer*, 2013, 54, 6918–6928.
 22. Park, J.-S.; Park, S.-H.; Yim, S.-D.; Yoon, Y.-G.; Lee, W.-Y.; Kim, C.-S., Performance of solid alkaline fuel cells employing anion-exchange membranes. *Journal of Power Sources*, 2008, 178, 620–626.
 23. Hedrick, J. L.; Jelinski, L. W.; McGrath, J. E., Synthesis and Characterization of Deuterated Poly(arylene ether sulfones). *Journal of Polymer Science: Part A: Polymer Chemistry*, 1987, 25, 2289–2300.

국문초록

**Poly(arylene ether sulfone) containing
tetra(quaternary ammonium pendant
groups) for alkaline anion exchange
membrane fuel cells**

사차암모늄 펜던트그룹을 갖는
폴리아릴렌이써설편의
알칼라인 연료전지 음이온 교환막으로서의 특성

최지은

공과대학 화학생물공학부

서울대학교 대학원

사차 암모늄 그룹을 펜던트 그룹으로 갖는 폴리아릴렌이써설편을 음이온 전도성 교환막으로 활용하기 위하여 합성하였다. 먼저 네 개의 아민 그룹을 갖는 단량체를 합성하였고 이 단량체를 이용하여 아민 작용 그룹을 갖는 폴리아릴렌이써설편을 얻은 후 아민그룹을 사차 암모늄그룹으로 전환하였다. 이러한 합성방법을 통해 고분자의 골격에 상당한 양의 사차 암

모늄 그룹을 정교하게 조절하여 도입하는 것이 가능하였다. ^1H NMR로 분자구조를 확인하였으며 열중량변화, 함수율, 이온교환용량, 전도도와 같은 특성을 보았고 셀 성능평가가 이루어졌다. 제조된 음이온 교환막은 $30\text{ }^\circ\text{C}$ 에서 40 mS/cm 이상의 전도도를 보였으며 셀 성능평가에서는 77 mW/cm^2 의 최대출력을 보인 바 있다.

주요어 : 음이온 교환막, 폴리아릴렌이씨설펜, 사차 암모늄 그룹, 고체 알칼라인 연료전지

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