

바이폴라막 제조를 위한 폴리에테르이미드의 아민화 합성 및 표면불소화를 통한 차아염소산 생성

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Synthesis of Aminated Poly(ether imide) for the Preparation of Bi-polar Membranes and Their Application to Hypochlorite Production through the Surface Direct Fluorination

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초록: 폴리페닐렌옥사이드(PPO)와 폴리에테르이미드(PEI)에 대해 각각 설폰화(SPPO) 및 아민화(APEI) 반응이 이루어졌다. SPPO와 APEI의 특성평가를 위하여 FTIR, 열무게분석(TGA), 팽윤도, 이온교환용량(IEC) 및 이온전도도 등에 대한 측정을 하였다. 표면불소화를 실시한 후 표면불소화된 SPPO와 APEI 막과 불소화하지 않은 막과의 차이 점을 알아보기 위하여 위에서 실시한 특성평가를 다시 수행하여 비교하였다. SPPO막의 이온교환용량을 고정시킨 후 APEI의 이온교환용량을 변경하면서 전체적으로 3개 유형의 바이폴라막을 제조하였고, 이를 차염소산 발생을 위하여 여러 전류밀도 하에서 저농도 및 고농도 소금용액에 적용하였다. 표면불소화된 막의 차염소산 생성 농도는 APEI의 이온교환용량에 의존하며 80 mA/m²에서 차염소산 농도 491-692 ppm의 결과를 얻었으며, 5 mA/m²에서 18-28 ppm의 차염소산 농도를 나타내었으며 내구성이 매우 상승된 것을 보여 주었다.

Abstract: Poly(phenylene oxide) (PPO) and polyether imide (PEI) were sulfonated and aminated to create sulfonated poly(phenylene oxide) (SPPO) and aminated polyether imide (APEI), respectively. Characterization of the SPPO and APEI were performed via measurements of FTIR, thermogravimetry (TGA), swelling degree, ion exchange capacity (IEC), and ion conductivity. Next, the surfaces of these membranes were modified by surface fluorination at room temperature. The surface fluorinated SPPO and APEI membranes underwent characterization again for the mentioned measurements to determine any differences. The 3 types of bi-polar membranes were prepared by varying the IEC of the APEI at a fixed SPPO IEC value, which were applied to the low and high NaCl concentration of feed solution at the different current density, respectively. The hypochlorite concentration derived from the surface fluorinated membranes was dependent on the IEC of the APEI and ranged from 491 to 692 ppm at 80 mA/m². At low current density of 5 mA/m², the hypochlorite concentrations ranged from 18 to 28 ppm for the 4 hrs surface fluorinated membranes and their durability increased greatly.

Keywords: hypochlorite production, bi-polar membrane, sulfonated poly(phenylene oxide), aminated polyether imide, surface fluorination.

Introduction

Conventionally, ion exchange membranes are classified into cation exchange membranes (CEM) and anion exchange mem-

branes (AEM), which are determined by their type of ionic functional groups on the polymer backbones. Typical types of ionic groups include -SO₃⁻, -COO⁻, and -PO₃²⁻ for CEM, and -NH₃⁺, -NRH₂⁺, -NR₂H⁺, -NR₃⁺, and -PR₃⁺ for AEM, respectively.¹

There are numerous industrial applications for ion exchange membranes available due to their ecological safeness and com-

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parative low energy consumption.² The application areas can be grouped into three categories: (1) Mass separation processes, such as desalination of sea or brackish water by electrodialysis, Donnan or diffusion dialysis, etc.; (2) Chemical synthesis processes, such as chloro-alkali electrodialysis, production of oxygen and hydrogen by water electrodialysis, and hypochlorous acid (HOCl) etc.; and (3) Energy conversion and storage processes, such as fuel cell or electrical batteries.³

In this paper, bi-polar membranes (BPM) equipped in the electrodialysis (ED) process will be applied to produce hypochlorites. BPM consists of laminar functional compositions with an ion exchange structure of a CEM (with negative fixed charges) layer joined to an AEM (with negative fixed charges) layer through an intermediate layer and is commonly used in dissociation processes.¹ ED with BPM is regarded as one of the most promising fields in the ED industry with many superior advantages over conventional dialysis such as the ED without any membranes⁴ and the ED with CEM⁵ or AEM.⁶ These advantages include, but are not limited to¹:

- low running cost and no gases generated (water is directly dissociated into H^+ and OH^-)
- no oxidation and/or no reduction species that may produce undesirable products (no electrochemical reaction)
- low initial cost and low space consumption (no electrode is needed in the repeating cell)

When both electrodes are applied with voltage (Figure 1), protons and hydroxyl ions are yielded from the CEM and AEM, respectively. In the anode chamber, dissociation of water produces hydronium ions and oxygen while oxidation of chlorine ion produces chlorine gas; however, overall neutrality is maintained due to the dissociation of water yielding an equal number of hydroxyl ions at the AEM and the initial pH does not change. The generated chlorine gas dissolves in the caustic

soda solution, producing sodium hypochlorite. Meanwhile, in the cathode chamber, dissociation of water produces hydrogen gas and hydroxyl ions. In theory, this yields the same number of protons at the CEM.

Various ion exchange polymers are available for use in bi-polar membranes layers. These are well summarized by Wilhelm.⁷ For anion exchange layers, polystyrene and its derivatives, polysulfone, polyvinylidene fluoride blends, polyether sulfone and polymethyl methacrylate and its derivatives are utilized in AEM. Amines are most often used as the ion exchange group. And for cation exchange layers, the very same polystyrene and its derivatives, polysulfone, polyether sulfone, and polybutadiene and its derivatives, polyphenylene oxide, polyether ether ketone, and nafion are used in CEM. Sulfonic group as the ion exchange group is most utilized in this case, as well as polystyrene's phosphoric acid group.

In the current literature, synthesis of aminated polyether imide (APEI) has not been investigated as an anion exchange layer of bi-polar membranes. The aim of this study is to examine the APEI as an anion exchange layer of bi-polar membranes and characterize the novel derivatives including the direct surface fluorination. Double-casting method was conducted to prepare the bi-polar membrane between the APEI and sulfonated polyphenylene oxide (SPPO) and its surface fluorination. These were, then, applied to production process.

Experimental

Materials. Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) and polyether imide (PEI) (UltemTM-1000, M.W. 55000) were purchased from Aldrich Co. and Sabic Co., respectively. Concentrated sulfuric acid of 96 wt% was obtained from Fisher Scientific. Chlorosulfonic acid, zinc chloride ($ZnCl_2$), and trimethylamine (TEA) used in the sulfonation and amination reactions were obtained from Junsei Co., Japan. Chloroform, methanol, dichloroethane, and dimethyl acetamide were provided by Sigma-Aldrich Co (Milwaukee, USA). No further purification was made and all reagents and solvents were used in unadulterated forms.

Membrane Synthesis. The sulfonation of PPO was carried out in accordance with previously reported experimental procedures.⁸⁻¹⁰ The PPO was dissolved in chloroform to produce a homogeneous solution. To sulfonate the PPO to the desired ion exchange capacity, a predetermined amount of chlorosulfonic acid was introduced while the solution was stirred vig-

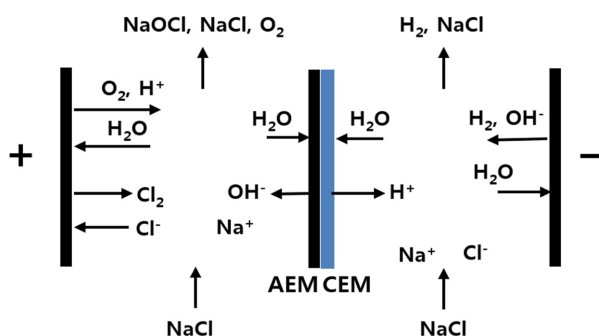


Figure 1. Schematic diagram of electrodialysis with BPM for the production of hypochlorites.

orously. Separation of precipitated polymer by the sulfonation was achieved. The liquid from sulfonation was discarded. The precipitated polymer was dissolved in methanol. Its resulting solution was, then, poured into a tray. This formed about 1–2 mm thickness film of sulfonated PPO. It was dried in air for 24 h at room temperature and was stored in a vacuum oven until needed.

Preparation of the APEI followed a two-step reaction: (1) chloromethylation of PEI using chloromethyl methyl ether (CMME) in the presence of ZnCl_2 , a Friedel-Crafts catalyst, and then (2) amination by means of TEA.^{11,12} Initially, PEI was chloromethylated by dissolving PEI in dichloroethane while stirring to form a 8 wt% solution. Then, the catalyst ZnCl_2 was added at 10 wt% of the PEI and a desired amount of CMME was introduced very slowly while stirring at 60 °C for 3 h. Once completed, the solution was washed with methanol numerous times and dried at 50 °C for 24 h in a forced convection oven. Next, molar ratios of 1:1, 2:1, and 3:1 of TEA against CMME were added into the chloromethylated PEI that had been dissolved in dimethyl formamide. This was kept for more than 12 h at room temperature. The resulting APEI was stored at room temperature under nitrogen environment in a forced convection oven.

The double casting method was used to prepare the bi-polar membranes. First, APEI was cast on the glass plate, where upon the SPPO dissolved in chloroform was cast onto the APEI membrane. Each thickness was about 80–100 μm , making the total thickness about 160–200 μm . Direct fluorination was carried out in a closed reactor at room temperature. The air and water vapor were removed from the reactor, at which point the bi-polar membranes were loaded with the fluorinating mixture of 2000 ppm F_2 against N_2 gas. Then, an F_2/N_2 gas mixture was used to modify the membrane surface. The duration of fluorination was fixed at 60 and 240 min.¹³

Membrane Characterization. The Fourier transform infrared spectroscopy (FTIR) of the membranes were measured by a Nicolet IR 860 spectrometer (Thermo Nicolet, Madison, WI, USA) operating in waveranging between 4000–500 cm^{-1} .

Thermogravimetry (TGA) (TA Instruments TGA 2050, New Castle, DE, USA) was used to investigate the degradation process and the thermal stability of the membranes. The TGA measurements were carried out under a nitrogen atmosphere with a heating rate of 10 °C/min from room temperature to 600 °C.

In order to measure the water content, the films were soaked in ultra-pure water for more than 24 h. After this period, they

were wiped quickly with filter paper, immediately weighed, and then dried under vacuum oven until a constant weight was obtained. To determine their water content (g H_2O /g membrane), the following equation was used:

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

where W_{wet} and W_{dry} are the wet and dry membrane weights, respectively. At least ten measurements were made and averaged prior to reporting their values, with an average estimated error of $\pm 8\%$.

To examine the membrane surface characteristics, static contact angles were measured, providing the operational definition of wettability of the surface against water. These angles at which the liquid interface meets the solid surface were measured using a goniometer (CA-X, Kyowa, Kaimenkagaku Co., Tokyo, Japan) and its procedure followed dropping 1 μL ultra-pure water on the membrane surface. Measurement of the static contact angle was repeated over 10 times and averaged for all values within a standard deviation of $\pm 8\%$.

Classical titration techniques were used to measure ion exchange capacity (also known as IEC value). For PPO cationic exchange membranes,¹⁴ ultra-pure water was used to immerse the films, which were then soaked in a large volume of 0.1 mol/L HCl solution to enable change to the H^+ form. Subsequently, the excess HCl was removed from the samples with distilled water. The samples were, then, equilibrated with 100 mL of 0.1 mol/L NaCl solution for 24 h. Next, using phenolphthalein as an indicator, the remaining liquid was titrated with 0.1 mol NaOH solution. The following equation was used to compute the IEC value (in meq/g):

$$\text{IEC(CEM)} = \frac{M_{\text{O,NaOH}} - M_{\text{E,NaOH}}}{W_{\text{dry}}} \quad (2)$$

Where $M_{\text{O,NaOH}}$ is the milli-equivalent (meq) of NaOH in the flask at the beginning of the titration, $M_{\text{E,NaOH}}$ is the meq of NaOH after equilibrium, and W_{dry} is the weight of the dry membrane (g). Measurement of IEC was repeated at least 5 times and averaged with estimated error of $\pm 3\%$. For anion exchange membranes, 0.1 M NaCl solution was used to immerse the membranes in order to exchange the functional groups to Cl^- . Then, the membranes surfaces were washed several times with distilled water to remove the excess NaCl solution. Next, 0.5 mol Na_2CO_3 was used to immerse the membrane samples for exchange of Cl^- to CO_3^{2-} . Titration with AgNO_3 determined the measurement of the quantity of free Cl^-

in the solution.¹⁵ Finally, the ion exchange capacity was obtained using the following equation:

$$\text{IEC(AEM)} = \frac{2 \times N_{\text{AgNO}_3} \times V_{\text{AgNO}_3}}{W_{\text{dry}}} \quad (3)$$

where N_{AgNO_3} is the concentration of AgNO_3 standard solution, V_{AgNO_3} is the titrated volume of meq of AgNO_3 standard solution, and W_{dry} is the weight of the dry membrane (g).

Ion conductivity of the membranes was obtained using the normal four-point probe technique at relative humidity (RH)=100%. The impedance of the membranes was measured using a Solatron Analytical Full Material Impedance System 12608 W consisting of a frequency response analyzer 1260 and electrochemical interface 1287 unit. Each sample was mounted on the cell upon cutting it into $4 \times 1 \text{ cm}^2$ sections. The ion conductivity (σ) was calculated by the following equation:

$$\sigma = \frac{l}{R \cdot S} \quad (4)$$

where σ is the ion conductivity (in S/cm), and l is the distance between the electrodes used to measure the potential (1 cm). R is the impedance of the membrane (in Ω). S is the surface area required for anion to penetrate the membrane (in cm^2). To ensure good data reproducibility, the impedance of each sample was measured five times.

Hypochlorite Generation. In this study, two feed concentrations of 3.5 and 0.5 wt% NaCl were used to produce high and low hypochlorite concentration, respectively. During hypochlorite generation, concentrations were feed continuously at 42 and 30 mL/min for high and low feed concentration, as indicated in Figure 2. 80 and 5 mA/m^2 were used as current densities and 1270 and 125 mA were set as currents, respectively. The size of the electrode was 15.89 cm^2 with a 4.5 cm diameter. All experiments were performed at 25°C .

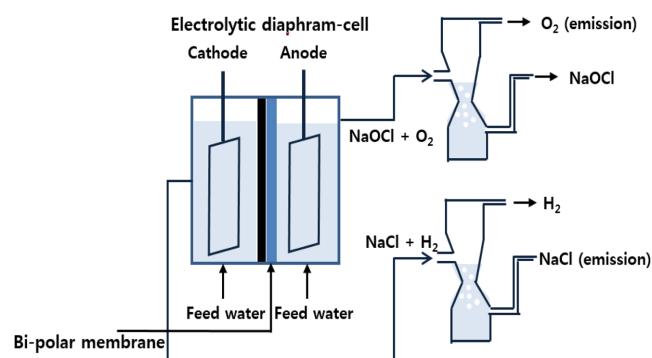


Figure 2. Schematic diagram of sodium hypochlorite generation.

Results and Discussion

Characterization of Synthesized APEI. FTIR spectra of the APEI membranes are illustrated in Figure 3. The characteristic peak at 3300 cm^{-1} is attributed to $-\text{NH}_2$ owing to N-H stretching.¹⁶ As the TEA content increases, i.e., the molar ratio of TEA against CMME rises to 1:1, 2:1, and 3:1, the peak intensity increases, also. This suggests that the APEI was successfully synthesized.

TGA was used to investigate the thermal properties of membrane. It was programmed from room temperature to 600°C at a heating rate of 10°C/min under N_2 gas. The TGA curve of the membranes was fitted using three main degradation stages arising from the processes of thermal solvation, thermal deamination, and thermo-oxidation of the polymer matrix, which is shown in Figure 4. The first weight loss is closely associated with the loss of absorbed water molecules, demarcated up to 180°C . Most of these absorbed water molecules are supposed to exist in a bound state, rather than in the free molecular state,¹⁷ and seem to be bound directly to the polymer chains and/or the $-\text{NH}_2$ groups via hydrogen bonds. The second weight loss region corresponds to the loss of amine group by deamination, which occurs between temperatures of 200 – 300°C though it does not appear in PEI curve. The bond energies of C-H and C-N are known as 414 and 305 kJ/mole, respectively.¹⁸ Therefore, since the deamination temperature in APEI becomes lower than the pristine PEI, the temperature of deamination decreases as the amination ratio increases. This means that the amination portion is larger. The third weight loss region ($>400^\circ\text{C}$) denotes further degradation of polymer

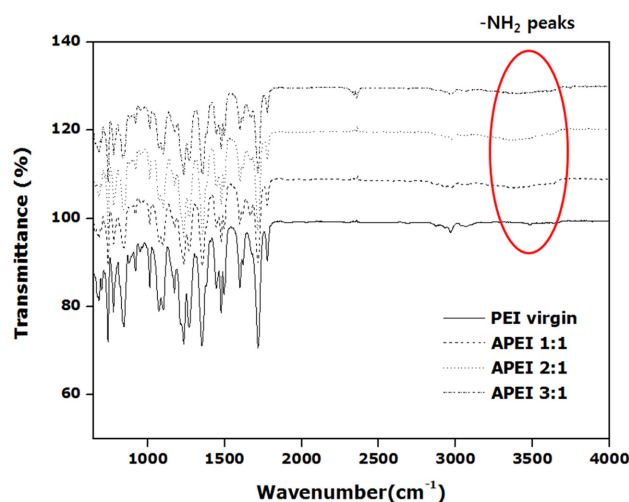


Figure 3. FTIR spectra of APEI membranes.

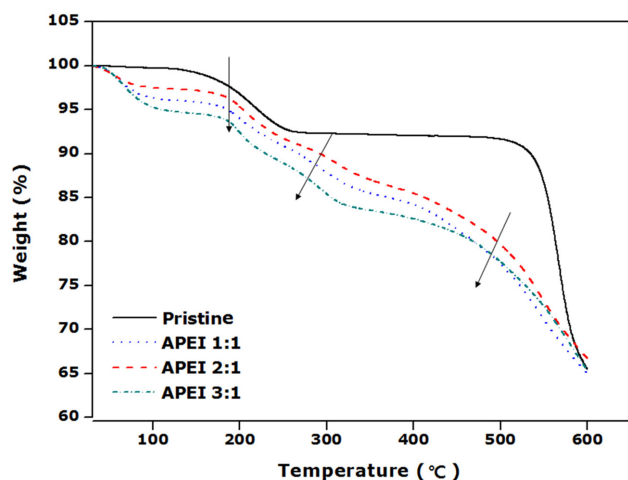


Figure 4. TGA curve of PEI and APEI membranes.

residues at $400^{\circ}\text{C} < T < 500^{\circ}\text{C}$. Here, the main chains of the APEI decompose while the pristine PEI decomposition appears at above 500°C .

Direct fluorination of polymer mixtures (i.e., the treatment of polymeric materials with fluorine of a fluorine-inert gas (nitrogen, helium, etc.)) occur spontaneously at room temperature and can be considered as a surface modification method. This results in polymers with a set of unique properties such as enhanced thermostability, chemical stability, and good barrier properties.¹⁹⁻²¹ In this direct fluorination, hydrogen atoms are substituted for fluorine while double and conjugated bonds are saturated with fluorine. The formation of cross-linking (formation of C-C or C-O-C bonds) and destruction of C-Si bonds are dependent on nature of the polymer and treatment conditions.¹⁹ For hydrogen-carbon based polymers, direct fluorination results in disruption of C-H and C-OH bonds and saturation of double (conjugated) bonds followed by the formation of C-F, C-F₂, and C-F₃ groups. This is because the bond energy of C-F bonds is much higher than that of C-H and C-OH bonds.²¹ Based on these evidences, all the hydrogen atoms in both polymers were expected to be substituted by fluorine and the conjugated bonds in phenyl rings and C=O bonds to be saturated with fluorine. In this experiment, increases in the amination ratio, defined as the molar ratio of TEA against CMME, were also marked by the enhancement of water content (Figure 5) owing to an increase of -NH₂ groups. Additionally, surface fluorination caused the surface to become hydrophobic and hindered water absorption in the fluorinated membrane, lowering the water content of fluorinated membrane as consistently below that of the non-fluorinated (pristine) membrane.

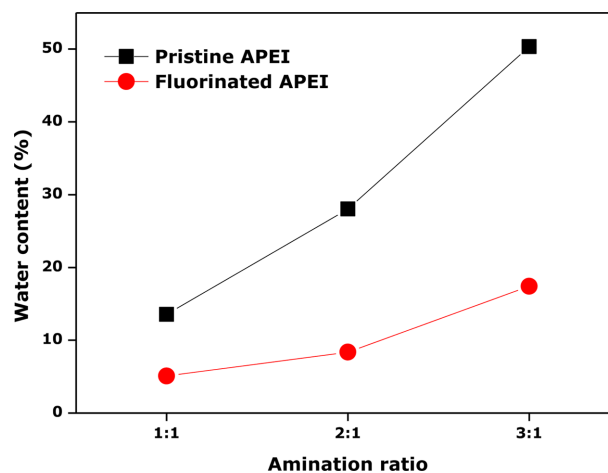


Figure 5. Water content of the fluorinated and non-fluorinated APEI membranes at different amination ratios (molar ratio of TEA against CMME).

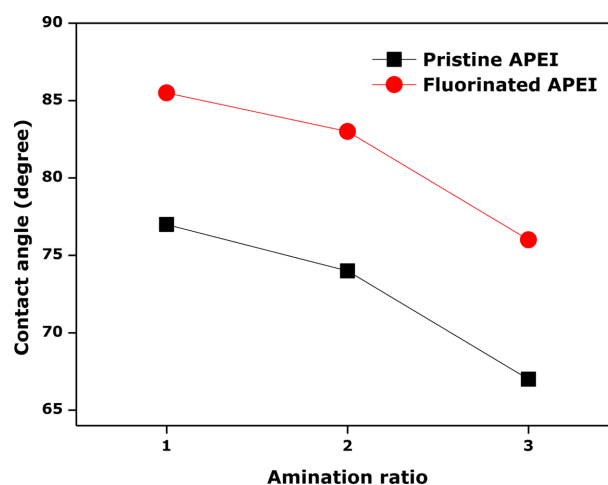


Figure 6. Contact angles of the fluorinated and non-fluorinated APEI membranes at different amination ratios.

Direct fluorination transformed C-H bonds into C-F bonds, changing the membrane surface property. Contact angle measurement is a tool allowing measurements for hydrophilic or hydrophobic properties. The contact angle comparison between the non-fluorinated and fluorinated APEI membranes (Figure 6), determined after fluorination for 1 h with the gas mixture of 2000 ppm F₂ in N₂, indicated increase for fluorinated membranes. Specifically, the contact angle of the 1:1 APEI membrane changed from 77° to 86° after fluorination and 66° to 77° for 3:1 APEI membrane. These increases are considered moderately high.

Ion exchange capacities (IECs) of the non-fluorinated APEI membranes varied from 1.44 to 1.94 meq/g depending on the amination ratio, which differs slightly from the IECs of 1.38 to

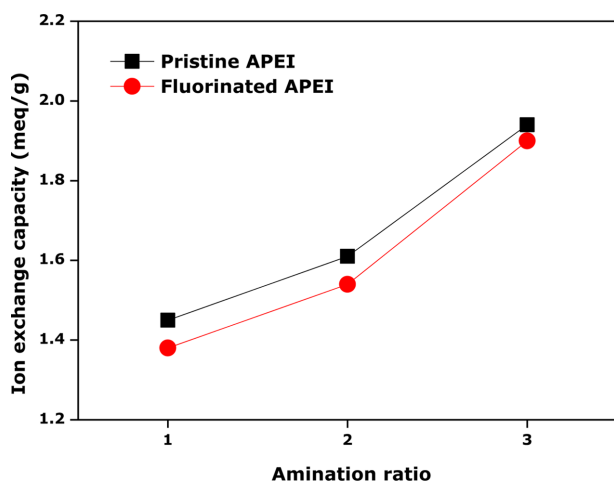


Figure 7. Ion exchange capacity of the fluorinated and non-fluorinated APEI membranes at different amination ratios.

1.89 meq/g for the equivalent fluorinated APEI membranes (Figure 7). The absence of a large change in the IEC values with fluorination is attributed to no difference in the number of $-NH_2$ sites substituted as a result of fluorination.

As the amination ratio increases, ion conductivity also increases (Figure 8). This is due to the increase of the ionic sites, which are necessary for the anionic molecules to pass through the membranes. In a similar manner, as temperature increases, ion conductivity also increases. This is attributed to a rise in the operating temperatures causing the polymer network to become loosened, which in turn enables passing of fairly large sized anion molecules through the membranes.

Meanwhile, the difference between the ion conductivity of the pristine and fluorinated membranes varied across all the ranges of the amination ratio and also for different temperatures (Figure 8). Our previous report indicated changes in proton conductivity of a fluorinated poly(vinyl alcohol) cross-linked with poly(styrene sulfonic acid-*co*-maleic acid) membrane from 0.039 to 0.053 S/cm after 60 min fluorination.¹⁴ A fluorine molecule substituted for a hydrogen molecule creates larger space between adjacent atoms in a polymer network than in a non-fluorinated network. This is because the size of the fluorine molecule is much bigger than that of the hydrogen molecule. As a result, protons can pass more easily through the spacious path than the tighter space prior to fluorination, allowing proton conductivity to increase upon fluorination. On the other hand, anions that pass through the anionic exchange membrane such as $-OH^-$ and Cl^- are much larger than protons and may be hindered when passing through the space between the fluorine molecules in the polymer network. This may be

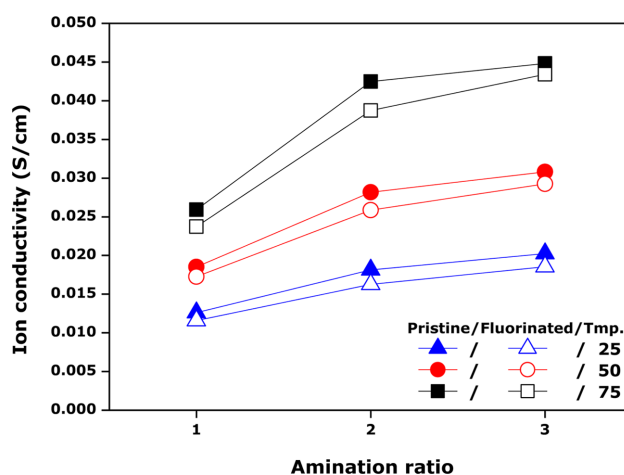


Figure 8. Ion conductivity of the fluorinated and non-fluorinated APEI membranes at different amination ratios and temperatures.

the reason why the ion conductivity of the fluorinated membranes is slightly lower than that of the non-fluorinated membranes across the range of amination ratios.

Generation of Hypochlorites. Table 1 and Table 2 summarize the results from the hypochlorite generation experiments carried out using the SPPO/APEI bipolar membranes. The IEC of the synthesized SPPO was fixed at 0.83 meq/g, while the IEC of the APEI membranes were varied from 1.45 to 1.94 meq/g. The hypochlorite generation experiment was done using the high NaCl concentration of 3.5 wt% at the current density, 80 mA/m² at 25 °C. In the anode chamber, as IEC of the AEM increases, proton formation at the anode increases due to more hydroxyl ions being produced. Hence the pH value declines as the amination ratio rises. In contrast, production of hydroxyl ions is almost constant at the cathode, showing only a slight increase. This near-constant formation may be due to the constant IEC of the SPPO of the CEM, and the slight increase of hydroxyl ions may stem from proton formation in the opposite chamber. Its increased production of protons in the anode chamber leads to the formation of more hydroxyl ions in the cathode chamber, which acts to balance both chambers. Voltage in Table 1 represents resistance, which increases across amination ratios. This increase could arise from the imbalance in IEC values between the CEM and AEM. Consequently, this resistance may be removed by having different IECs that are the same for both the CEM and AEM. The concentration of the formed hypochlorites varied from 533 to 724 ppm. Once the experiment had been in progress for 1 h, elevation in voltage began to occur. This suggests possible membrane surface damage due to attack by the

Table 1. Hypochlorite Production Using Pristine and Fluorinated SPPO/APEI Bipolar Membranes at 80 mA/m²

Membranes	pH at anode	pH at cathode	Voltage	Concentration of produced hypochlorites (ppm)	Experiment duration (min)
*SPPO/APEI 1:1	5.4	13.1	8	533	60
SPPO/APEI 2:1	3.8	13.4	8	637	60
SPPO/APEI 3:1	3.6	13.5	11	724	60
**F2-SPPO/APEI 1:1	7.4	11.8	5	491	240
F2-SPPO/APEI 2:1	6.7	12.9	5	582	240
F2-SPPO/APEI 3:1	6.3	12.7	7	692	240

*Pristine bi-polar membranes. **Surface fluorinated bi-polar membranes (1 h).

Table 2. Hypochlorite Production at the Low Current Density, 5 mA/m²

Membranes	pH at anode	pH at cathode	Voltage	Concentration of produced hypochlorites (ppm)	Experiment duration (min)
*SPPO/APEI 1:1	4.4	10.5	4	31.2	150
SPPO/APEI 2:1	3.7	11.2	4	36.2	150
SPPO/APEI 3:1	3.7	11.2	4	39.6	150
**F2-SPPO/APEI 1:1	4.3	10.4	3	18.4	480
F2-SPPO/APEI 2:1	3.7	11.2	3	25.4	480
F2-SPPO/APEI 3:1	3.6	11.3	4	28.4	480

*Pristine bi-polar membranes. **Surface fluorinated bi-polar membranes (4 h).

hypochlorites.^{22,23}

The fluorinated polymers have a set of unique properties, such as enhanced chemical stability, thermostability, and good barrier properties.²⁰ Direct fluorination (i.e., treatment with elemental gaseous fluorine) can be used to modify the surface properties of polymers.²⁰ One of the main advantages of direct fluorination is that only a thin surface layer of polymer is affected during modification. Hence the remaining, bulk properties of the polymer are practically unchanged, though the overall physico-chemical properties of the polymer are dictated by its thin modified layer.²⁴ In ordinary direct fluorination, i.e., treatments of polymeric materials with fluorine or fluorine-inert gas (nitrogen, helium, etc.), hydrogen atoms are substituted by fluorine, and double and conjugated bonds are saturated with fluorine.²⁴ The nature and the thickness of fluorocarbon layer depend on reaction variables such as fluorine concentration, reaction time, and reaction temperature. The lower part in Table 1 specifies the results of the hypochlorite production experiments using surface fluorinated SPPO/APEI bipolar membranes. The results indicate similar trends to that of the non-fluorinated SPPO/APEI bipolar membranes; however, the concentrations of the produced hypochlorites are

slightly lower for the surface fluorinated membranes. This is due to the IECs of the fluorinated membranes being slightly lower as mentioned earlier. The pH values at both electrodes and the voltages appear to be better stabilized for fluorinated membranes than the non-treated membranes. Also, even after operating for 4 h, its membrane durability improved considerably as the fluorinated membranes remained intact.

The results for the low feed concentration are shown in Table 2. It is important to find out how much hypochlorites are produced when a low current density is used, defined as 0.5 wt% at the current density 5 mA/m².

As expected, at low current density, the concentrations of produced hypochlorite are noticeably lower than at high current density, 80 mA/m². Surprisingly, due to the lower concentration of hypochlorite, the membrane durability was highly enhanced.

Conclusions

In this study, the poly(phenylene oxide) (PPO) and polyether imide (PEI) were sulfonated and aminated, respectively. The resulting sulfonated poly(phenylene oxide) (SPPO) and ami-

nated polyether imide (APEI) were both characterized via the measurement of FTIR, thermogravimetry, swelling degree, ion exchange capacity (IEC), and ion conductivity. Then the surfaces of these membranes were fluorinated and modified using 2000 ppm F₂ gas against N₂ gas for 1 and 4 h at room temperature. The surface fluorinated SPPO and APEI membranes were characterized again to examine for differences between the pristine and fluorinated membranes in FTIR, thermogravimetry, swelling degree, ion exchange capacity (IEC), and ion conductivity. The 3 types of bi-polar membranes were prepared with 3 different IEC values of APEI values varying from 1.45 to 1.94 meq/g and SPPO with an IEC value fixed at 0.83 meq/g. Then, these bi-polar membranes were fluorinated for 1 h. In general, as the amination ratio increased, its water content, IEC, and ion conductivity increased also. For the fluorinated anionic membranes, each measurement of the 3 properties was relatively lower for surface fluorination compared with non-fluorination across all amination ratios while the contact angle increased.

The hypochlorite generation was carried out using feed concentration of 0.5 and 3.5 wt% NaCl solution at low and high current densities, 5 and 80 mA/m², respectively. At high feed 3.5 wt% and current density 80 mA/m², the generated hypochlorite concentration was dependent on the IEC of APEI and ranged from 533 to 724 ppm, while the surface fluorinated membranes showed a similar hypochlorite generation and a little improvement in durability as they remained intact even after operating for 4 h. In contrast, at low feed 0.5 wt% and current density 5 mA/m², the generated hypochlorite concentration was dependent on the IEC of APEI as well and ranged from 31 to 39 ppm. However, the durability was much highly enhanced for the fluorinated bi-polar membranes. Similarly, pristine bi-polar membranes also showed enhancement for hypochlorite generation.

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