전기투석공정에서 새로운 바이폴라막을 이용한 차염발생 연구

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Study on Hypochlorite Production Using Newly Synthesized Bipolar Membranes in Electrolysis Process

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Abstract: In the current study, both aminated polysulfone (APSf) and poly(ether imide) (APEI) were synthesized in accordance with the amination degree of the anion exchange membranes, and as for cation exchange membrane, sulfonated poly(ether ether ketone) (SPEEK) was synthesized as well. The two types of bipolar membranes of APSf/SPEEK and APEI/SPEEK relative to the amination degree with a double-casting method were prepared to carry out the hypochlorite formation electrodialysis process. It was found that the hypochlorite concentration increased as the amination degree increased. Typically, the hypochlorite production concentration of 124.7 ppm at 5 mA/cm$^2$ was observed for the APSf/SPEEK (3:1) membranes whereas 59.6 ppm concentration was shown at the same current density for APEI/SPEEK (3:1). APSf/SPEEK membranes were superior to APEI/SPEEK membranes from the aspect of hypochlorite formation concentration because the ion exchange capacity (IEC) of APSf/SPEEK is higher than that of APEI/SPEEK.

Keywords: aminated polysulfone, aminated poly(ether imide), sulfonated poly(ether ether ketone), bipolar membranes, hypochlorite, electrodialysis.

Introduction

An ion exchange membrane can selectively transfer anions and cations depending on the types of functional groups in the polymers, and they are classified into cation exchange membrane (CEM) and anion exchange membrane (AEM).1 A cation exchange membrane is connected to the cathode to transfer cations whereas an anion exchange membrane is connected to the anode to transfer anions. The representative functional groups of a cation exchange membrane include -SO$_3$-, -COO$^-$, and -PO$_4^{2-}$, and the functional groups of an anion exchange membrane include -NH$_3^+$, -NRH$^+$, -NR$_2^+$, -NR$_3^+$ and -PR$_3^{3-}$.2 An ion exchange membrane is used in the seawater desalination process using electrodialysis (ED), oxygen/hydrogen production by water electrolysis, the chemical synthesis process for hypochlorite, and the energy conversion and storage process for fuel cells or secondary batteries.3,4 Among the various applications, we focus on hypochlorite production.

In general, electrolyzed water for hypochlorite production can be prepared by adding salt or hydrochloric acid to tap water.5,6 The purpose of electrolyzing water is to disinfect water. Chlorine disinfection for tap water is one of the general...
methods of disinfecting water. Residual chlorine has been widely used as a disinfectant for water at home and abroad. The efficiency of chlorine as a disinfectant depends on the form of chlorine in the solution. The form of chlorine in the solution is classified into hypochlorite and hypochlorous acid. In addition, the chlorine efficiency depends on pH. Hypochlorite is the most effective disinfectant among chlorine disinfectants. The form of most chlorine in the solution is hypochlorite whose effective pH is 5~6.5. Thus, hypochlorite can be maximally obtained in this range. The hypochlorite concentration decreases at pH 6.5~7.6 and hypochlorite is converted to hypochlorous acid at pH 7.6 or higher. It remains molecular chlorine at pH 5 or lower. Therefore, the efficiency of a disinfectant depends on pH and HOCl or OCl- concentration in the solution.

In this study, polysulfone (PSf) and poly(ether imide) (PEI) were aminated to synthesize anion exchange polymers at different amination ratios and poly(ether ether ketone) (PEEK) was sulfonated to make cation exchange polymers. Two bipolar membranes, APSf/SPEEK and APEI/SPEEK, were prepared by using synthesized polymers and a hypochlorite production test was conducted. As shown in Figure 1, we conducted the hypochlorite production test using various bipolar membranes prepared at a fixed flow rate, concentration of feed solution, and reaction temperature as well. Then, we measured hypochlorite production depending on amination degree in the anion exchange membrane and changes in current density.

**Experimental**

**Materials.** Polysulfone (PSf, Udel® P-3500, Solvay) and poly(ether imide) (PEI, Ultem™ 1000, Sabic) were used to synthesize anion exchange polymers whereas, poly(ether ether ketone) (PEEK, Victrex® 450PF) was used to prepare cation exchange polymers. Solvents to synthesize ionic polymers included 1,2-dichloroethane (DCE, 99.5%, Junsei), dimethylacetamide (DMAc), chloromethylated PSf, trimethylamine (TMA), and triethylamine (TEA). The synthesis of anion exchange polymers and cation exchange polymers is shown in Figure 2. Polysulfone (PSf) and poly(ether imide) (PEI) were aminated to synthesize anion exchange polymers whereas, poly(ether ether ketone) (PEEK, Victrex® 450PF) was used to prepare cation exchange polymers. Solvents to synthesize ionic polymers included 1,2-dichloroethane (DCE, 99.5%, Junsei), dimethylacetamide (DMAc), chloromethylated PSf, trimethylamine (TMA), and triethylamine (TEA). The synthesis of anion exchange polymers and cation exchange polymers is shown in Figure 2.

**Figure 1.** Schematic diagram of electrodialysis with bi-polar membranes.

**Figure 2.** Schematic block diagram of SPEEK membrane synthesis.

**Figure 3.** Schematic block diagram of synthesis of (a) APSf; (b) APEI membranes.
lacetamine (DMAc, 99.5%, Junsei), N,N-dimethylformamide (DMF, Junsei), and N-methyl-2-pyrrolidinone (NMP, 99%, Junsei). Chloromethylethyl ether (CMEE, 96%, TCI) was used for chloromethylation. Trimethylamine (TMA, 30%, Junsei) and triethylamine (TEA, 99%, Junsei) as amination reagents for PSf and PEI, respectively, were employed. Tin (II) chloride (SnCl₂, Jusei) was used as a catalyst without further purification. Sulfuric acid (H₂SO₄, 95%) was a sulfonation reagent for PEEK.

Membrane Preparation. Cation Exchange Membrane: In order to prepare sulfonated PEEK (SPEEK), powder-type PEEK was dried in a high-temperature vacuum oven for at least 24 h. Then, 10 g of PEEK was added into 200 mL of sulfuric acid and stirred for at least 40 h. The stirred solution was put into 0 °C ultrapure water to finish the sulfonation reaction. After the reaction was completed, SPEEK was repeatedly washed with distilled water until it became neutral. Then, SPEEK was dried in a 100 °C oven for at least 24 h. Dried SPEEK was dissolved in NMP to make an 11 wt% solution and then cast by using a casting knife on the glass plate of 120 µm thickness. The cast membrane was dried in the vacuum oven at 130 °C for 4 h (Figure 2).

Anion Exchange Membrane: Aminated Polysulfone (APSf): PSf polymer was dissolved to be 8 wt% in DCE and then vigorously stirred at room temperature. SnCl₂ as a catalyst was added to this solution with 10 wt% quantity on the polymer basis. Then, CMEE was added over four-fold more than the polymer and stirred at 40 °C for 4 h. The solution was added to methanol for consolidation and dried at 60 °C for 24 h. The dried polymer was dissolved in DMAc and then TMA to CME at 1:1, 2:1, and 3:1 (molar ratio) was added. It was stirred at room temperature for 12 h. The stirred solution was cast on a 120 µm thick glass plate and dried in the forced convection oven at 80 °C for 12 h (Figure 3(a)).

Aminated Poly(ether imide) (APEI): APEI preparation was similarly followed by the APSf synthesis mentioned above. The PEI was dissolved in DMF to form 8 wt% and then TEA to CME at 1:1, 2:1, and 3:1 (molar ratio) was added. It was stirred at room temperature for at least 12 h, cast on glass plates, and fully dried in the thermostatted convection oven at 60 °C (Figure 3(b)).

Characterization of Synthesized Membranes. The swelling degree, ion exchange capacity (IEC), and ion conductivity—which are the basic properties of ion exchange membranes—were measured for the synthesized SPEEK, APSf and APEI. The measurements are referred to in the references and the results are shown in Table 1.

Hypochlorite Generation by the Prepared Bipolar Membranes. APSf/SPEEK and APEI/SPEEK bipolar membranes were prepared by the double-casting method. Six bipolar membranes were prepared, 3 each for APSf/SPEEK and APEI/SPEEK depending on the amination degrees of 1:1, 2:1, and 3:1. The hypochlorite generation test was conducted at room temperature and the flow rate of a feed solution was fixed at 30 mL/min. NaCl (0.5 wt%) was used as a feed solution and the effective membrane area was set to 25 cm². The overall schematic diagram of hypochlorite generation apparatus is shown in Figure 4.

Results and Discussion

Membrane Characterization. The production performance of hypochlorite may be dependent on the number of ion exchange sites in the ion exchange polymers. Also, the ion exchange membrane is known to be very hydrophilic due to

Table 1. Physical Properties of SPEEK, APSf and APEI at 25°C

<table>
<thead>
<tr>
<th>Membranes</th>
<th>Swelling degree (%)</th>
<th>Ion exchange capacity (meq/g)</th>
<th>Ion conductivity (S/cm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEK</td>
<td>13.6</td>
<td>1.8</td>
<td>0.073</td>
</tr>
<tr>
<td>APSf 1:1</td>
<td>6.9</td>
<td>0.9</td>
<td>0.006</td>
</tr>
<tr>
<td>APSf 2:1</td>
<td>19.2</td>
<td>1.3</td>
<td>0.023</td>
</tr>
<tr>
<td>APSf 3:1</td>
<td>25.8</td>
<td>1.6</td>
<td>0.032</td>
</tr>
<tr>
<td>APEI 1:1</td>
<td>5.5</td>
<td>0.44</td>
<td>0.005</td>
</tr>
<tr>
<td>APEI 2:1</td>
<td>15.5</td>
<td>1</td>
<td>0.024</td>
</tr>
<tr>
<td>APEI 3:1</td>
<td>20.8</td>
<td>1.22</td>
<td>0.032</td>
</tr>
</tbody>
</table>

Figure 4. Experimental apparatus for sodium hypochlorite generation.
the hydrophilic ionic groups. The hydrophilic functional
groups stimulate dimensional changes in the ion exchange
membranes so that the intra-molecular spaces become wide
enough for ions to pass into the membrane more freely at a
certain desired adsorption time depending on the IEC values.

The results of the swelling degree, IEC, and ion conductivity
of synthesized ion exchange polymers are presented in Table 1.
To investigate the effect of IEC on the formation of hypo-
chlorite, the IECs of anion exchange polymers, PSf and PEI
were controlled rather than that of cation exchange polymer,
PEEK.

Hypochlorite Generation Using APSf/SPEEK Bipolar
Membranes. The results of hypochlorite generation depend-
ing on current density for 3 APSf/SPEEK membranes are
shown in Figure 5. As the amination degree increased, the
hypochlorite concentration tended to rise at the same current
density. It is considered that the elevated amine groups induced
higher IEC to increase the hypochlorite concentration. In addi-
tion, as current density gradually increased from 2 to 30 mA/cm
(2), the hypochlorite concentrationsheightened. At 2 mA/cm
(the lowest current density), the hypochlorite concentrations
were 28.4 ppm for the APSf/SPEEK (1:1) membrane, 55.3
ppm for the APSf/SPEEK (2:1) membrane and 58.1 ppm for
the APSf/SPEEK (3:1) membrane. At 30 mA/cm (high cur-
rent density), the hypochlorite concentrations of 385.7 ppm
and 469.4 ppm for APSf/SPEEK (1:1) and APSf/SPEEK (3:1),
respectively, were obtained. It may be possible that the break-
down of ions was affected by current density during the break-
down of sodium chloride solution used as the feed solution,
and therefore the hypochlorite concentration increased as cur-
rent density gradually rose to 30 mA/m².

Table 2 shows the results of measurement of pH changes at
both the cathode and the anode, and resistance (voltage), hypo-
chlorite output and operating time (durability) at a constant
5 mA/cm² of current at room temperature. As the amination
degree increased at the cathode, IEC increased, and hydroxyl
ions rose to increase hydrogen ions. The pH at the cathode
decreased from 3.8 to 3.5 and sequentially 3.3 due to the
increase of hypochlorite formation as the ratio of amine
increased. On the other hand, the pH at the anode tended to
increase from 11.5 to 11.7 and 12.2 because the amount of
hydroxyl ions increased. As the ratio of amination rose, the
voltage in the membrane increased from 3 to 4 and 6 V, and
the hypochlorite output tended to increase from 53.7 to 72.3
and 123.7 ppm. However, the operating time as a durability
scale decreased from 250 to 235 and 220 min. Damage to bipolar
membranes could be due to active transfer of ions in
the membranes and the difference in chemical concentrations
between the inside and outside of the membrane as hypo-
chlorite was produced.

Hypochlorite Production in the APEI/SPEEK Bipolar
Membranes. Figure 6 shows the result of hypochlorite pro-
duction depending on current density for the different ratios
of the APEI/SPEEK bipolar membranes. As shown by the result
of the APSf/SPEEK bipolar membranes, as the ratio of APEI
increased for the same current density, the hypochlorite con-
centrations tended to rise. It is considered that the increased
amine groups made the IEC higher and therefore hypochlorite
concentration increased. As current density gradually increased
form 2 to 25 mA/cm² and 30 mA/cm², the hypochlorite concen-
tration tended to increase. At 2 mA/cm² of current density,

![Figure 5](image-url) Hypochlorite concentrations in the APSf/SPEEK bipolar
membranes depending on current density.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>pH at anode</th>
<th>pH at cathode</th>
<th>Voltage</th>
<th>Concentration of produced hypochlorites (ppm)</th>
<th>Experiment duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEK/APSf 1:1</td>
<td>3.8</td>
<td>11.5</td>
<td>3</td>
<td>53.7</td>
<td>250</td>
</tr>
<tr>
<td>SPEEK/APSf 2:1</td>
<td>3.5</td>
<td>11.7</td>
<td>4</td>
<td>72.3</td>
<td>235</td>
</tr>
<tr>
<td>SPEEK/APSf 3:1</td>
<td>3.3</td>
<td>12.2</td>
<td>6</td>
<td>123.4</td>
<td>220</td>
</tr>
</tbody>
</table>
the hypochlorite concentration was 19.6 ppm for the APEI/SPEEK (1:1) membrane, 25.1 ppm for the APEI/SPEEK (2:1) membrane, and 31.4 ppm for the APEI/SPEEK (3:1) membrane. When current density increased from 15 to 20 mA/cm$^2$, the hypochlorite concentration sharply rose in the APEI/SPEEK (2:1) membrane, compared to the other membranes. At 30 mA/cm$^2$ (high current density), the hypochlorite concentration was 298.2 ppm for the APEI/SPEEK (1:1) membrane, 325.0 ppm for the APEI/SPEEK (2:1) membrane and 353.6 ppm for the APEI/SPEEK (3:1) membrane. Therefore, it is concluded that the hypochlorite production was 10-fold higher at 30 mA/cm$^2$ than at 2 mA/cm$^2$.

Table 3 shows the results of the measurement of pH changes at the cathode and the anode, and resistance (voltage), hypochlorite output and operating time (durability) in APEI/SPEEK bipolar membranes at 5 mA/cm$^2$ current at room temperature. When compared with the results for the APSf/SPEEK membranes, pH and voltage changes are relatively similar to each other; however, the hypochlorite concentrations produced are lower than the concentration formed by APSf/SPEEK membranes. It may be considered that the IECs of APEI/SPEEK are lower than those of APSf/SPEEK.

<table>
<thead>
<tr>
<th>Membrane</th>
<th>pH at anode</th>
<th>pH at cathode</th>
<th>Voltage</th>
<th>Concentration of produced hypochlorites (ppm)</th>
<th>Experiment duration (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>SPEEK/APEI 1:1</td>
<td>3.3</td>
<td>11.6</td>
<td>3</td>
<td>36.9</td>
<td>170</td>
</tr>
<tr>
<td>SPEEK/APEI 2:1</td>
<td>3.2</td>
<td>11.6</td>
<td>4</td>
<td>52.5</td>
<td>162</td>
</tr>
<tr>
<td>SPEEK/APEI 3:1</td>
<td>3.1</td>
<td>11.8</td>
<td>5</td>
<td>59.6</td>
<td>150</td>
</tr>
</tbody>
</table>

Conclusions

APSf/SPEEK and APEI/SPEEK bipolar membranes were prepared to investigate the hypochlorite production by the electrodialysis.

As the current density increased, the hypochlorite concentration increased from 28.4 to 385.7 ppm for the APSf/SPEEK (1:1) membrane and from 19.6 to 298.2 ppm for the APEI/SPEEK (1:1) membrane, respectively. At the relatively low current density of 5 mA/cm$^2$, the hypochlorite concentration was 123.4 ppm for the APSf/SPEEK (3:1) membrane while for the APEI/SPEEK (3:1) membrane the concentration was shown to be 59.6 ppm. Because the ion exchange capacity of APSf/SPEEK is higher than that of APEI/SPEEK, hydroxyl ions are produced more, and, as a result, more hypochlorite ions are produced.

In spite of the difference between the two types of bipolar membranes, the other factors such as pH and voltage showed similarity.

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References