

Effects of Interface Hydrophilicity and Metallic Compounds on Water-Splitting Efficiency in Bipolar Membranes

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Abstract—Bipolar membranes (BPMs) were prepared by using commercial ion exchange membranes and hydrophilic polymer as a binder to investigate the effects of the interface hydrophilicity on water-splitting capacity. In this study, polyHEMA/MPD cross-linked with TMC was used as a binding material to enhance the BPM interface hydrophilicity. The enhanced hydrophilicity of the BPM interface accelerated the water-splitting reaction because the hydrophilic polymer layer increases the water activity by attracting water from the ion exchange layers to the space charge region. In addition, a mechanism of the metal catalytic reaction was proposed. Metal species were immobilized in the BPM in a hydroxide form and possibly react with water molecules and the quaternary ammonium groups reversibly. It was also observed that metal species immobilized in the membrane improved the water-splitting efficiency by increment of the membrane wetness and enhancement of the membrane conductivity, with an apparent optimum metal concentration for the water-splitting reaction.

Key words: Bipolar Membrane, Hydrophilicity, PolyHEMA/MPD, Immobilization of Metallic Compound, Metal Catalytic Reaction

INTRODUCTION

Aqueous salts (e.g. NaCl, KCl, and Na₂SO₄ etc.) are generated from flue gas scrubbing, metal pickling and various chemical processes. Disposing of these waste salts is a significant issue related to environmental pollution and expenditure burden. Conventional treatments, such as evaporative crystallization and discharge into a water system, require a great deal of energy and also are further restricted by environmental protection laws. In addition, disposal of the waste salts is loss of resources that can be recycled. Water splitting electrodialysis (WSED) using a bipolar membrane (BPM) has been proposed as an effective process that can regenerate waste salts to their acid and base [Kim and Moon, 2001; Lee et al., 1998]. WSED process is a clean technology with a high-energy efficiency combining conventional electrodialysis (ED) and unique electrical properties of a bipolar membrane [Nagasubramanian et al., 1977; Liu et al., 1978a, b; Mani et al., 1988; Chiao et al., 1991; Graillon et al., 1996; Cherif et al., 1997].

Bipolar membranes consisting of anion and cation exchange layers can contiguously generate protons and hydroxyl ions under the reverse bias condition. During the current application, all ionic components are removed from the BPM and the water splitting occurs at the interface due to the influence of a strong electric field. Usually, electric field-enhanced water dissociation and catalytic proton transfer reaction are employed to explain the water-splitting mechanism. It has been considered that various physicochemical phenomena (i.e., prepolarization of water molecules, second Wien effect,

chemical reactions etc.) caused by unique bipolar structure originate the non-ideal water dissociation [Ramirez et al., 1992; Tanioka et al., 1996; Mafe et al., 1990; Strathmann et al., 1997; Shimizu et al., 1997; Onsager, 1934; Simons, 1985].

As mentioned previously, water splitting occurs at the bipolar junction; therefore, the BPM performance significantly depends on the interface characteristics. In this sense, many researchers have tried to enhance the water-splitting efficiency by modifying the interface properties. For instance, Simons prepared BPMs having a low water-splitting potential using a solution of inorganic salt (e.g. sodium metasilicate) as a binder [Simons, 1986]. It was considered that the voltage reduction was probably related to the increased wetness of the interface by the introduced hydrophilic substance. However, these BPMs had short lifetimes because the hydrophilic substance was unstable at extreme pH conditions. As another example, Strathmann et al. prepared multilayer BPMs including a very thin intermediate layer consisting of an insoluble polyelectrolyte complex of poly(4 vinylpyridine) and polyacrylic acid [Strathmann et al., 1993a, b].

Another approach to reducing the water-splitting voltage is the introduction of metallic compounds as a water-splitting catalyst. Up to now, polymeric membranes containing metal complex and modified with inorganic substance have been studied in many fields of chemical engineering such as catalysis [Pomogailo, 1988; Choi et al., 2000; Lee et al., 1995; Kim et al., 1995]. Interestingly, metal compounds have been considered as a catalyst for promoting water dissociation reaction in a BPM interface. It is a well known phenomenon that the water-splitting reaction rate is increased drastically in electromembrane systems where soluble salts of Ca²⁺, Mg²⁺ and other metal ions serve as the electrolyte [Simons, 1985; Zabo-

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lotskii et al., 1991; Jialin et al., 1998; Simons, 1993]. Simons reported a new method for preparing bipolar membranes using alkaline solution of a metal salt (e.g. CrCl_3) as a binder [Simons, 1993]. In the study it was suspected that a thin layer of metallic compounds, possibly an oxide or hydroxide, formed at the interface, decreased the water-splitting potential because the interface became more hydrophilic and consequently more conducting to hydrogen and hydroxyl ions. Hanada et al. pretreated the cation exchange membrane with aqueous metallic solution (e.g. FeCl_3) before casting the anion exchange layer [Hanada et al., 1993]. They presumed that the ion-exchanged metal ions affect the water molecules and the bonds of water come loose, so that the water can be dissociated easily. Zabolotskii et al. suggested that complex formation of the transition metal ions with the ion exchangers containing phosphoric acid, carboxyl, and amino groups leads to changes in water dissociation rate by the catalytic reaction [Zabolotskii et al., 1991]. However, the mechanism for the decrease of water-splitting voltage by these metallic compounds is still unclear [Simons, 1993].

In this work, we studied the composite BPMs containing the hydrophilic intermediate region to investigate the effects of the interface hydrophilicity and the immobilized metallic compounds on water-splitting capacity. The mechanism of the metal catalytic water dissociation was also proposed in terms of pH conditions at the BPM interface.

EXPERIMENTAL

For water-splitting experiments, composite bipolar membranes (CBMs) were prepared by interfacial polymerization. NEOSEPTA® CM-1 and AM-1 (Tokuyama Co. Ltd., Japan) were employed as the cation and anion exchange membranes, respectively, due to the low electrical resistance. The detailed specifications for the ion-exchange membranes used in this study are listed in Table 1. 2-hydroxyethyl methacrylate (HEMA) and m-phenylenediamine (MPD)

Table 1. Specifications of the NEOSEPTA® membranes [Tokuyama Co. Ltd., 1993]

Grade	CM-1 ^a	AM-1 ^b
Type	Strongly acidic cation permeable	Strongly basic anion permeable
Characteristics	Low electric resistance	Low electric resistance
Backing	PVC	PVC
Electric resistance	0.8-2.0	1.3-2.0
Thickness	0.13-0.16	0.12-0.16
Water content	0.35-0.40	0.25-0.35
Exchange capacity	2.0-2.5	1.8-2.2

Measurement basis - Electric resistance: Equilibrated with a 0.5 mol dm^{-3} NaCl solution, at 25 °C ($\Omega \text{ cm}^2$). Thickness: (mm). Water content: Equilibrated with 0.5 mol dm^{-3} NaCl solution ($\text{g} \cdot \text{H}_2\text{O}/\text{g} \cdot \text{dry membrane}$). Exchange capacity: ($\text{meq}/\text{g} \cdot \text{dry membrane}$).

^aCation exchange membrane having sulfonated styrene-divinylbenzene copolymer type, sulfonic acid groups [Hanada et al., 1993; Sata., 1994].

^bAnion exchange membrane having quaternary ammonium groups [Liu et al., 1978].

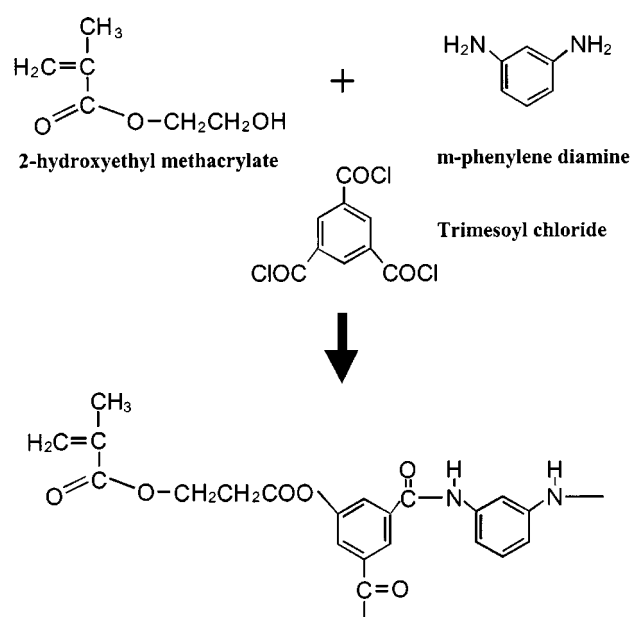


Fig. 1. Cross-linking mechanism of HEMA/MPD with TMC.

were used for the binding materials and trimesoyl chloride (TMC) for the cross-linking agent. Poly(2-hydroxyethyl methacrylate) (PEHMA) widely used in biomedical applications exhibits good chemical stability and resistance to acid hydrolysis [Salamone, 1996]. Therefore, it can be considered as one of the suitable substances for improving the hydrophilicity of BPM interface. Under the constant ratio, MPD was added to the binding material with a cross-linking agent (TMC) to prevent the excessive swelling. The cross-linking mechanism is depicted in Fig. 1. The detailed procedure of the membrane preparation was as follows. First, the cation and anion exchange membranes were immersed in the aqueous solution containing 1 or 2 wt% HEMA/MPD monomers for 12 hrs at room temperature. After they were taken from the solution and dried, cross-linking agent was sprayed on the membrane surface. Then the cation and anion exchange membranes were placed between two Teflon plates and pressed with a hydraulic press for 1 day. The operating pressure was 4,000 psi and the temperature was controlled as 35 °C. During the pressing, HEMA and MPD monomers in the interface of the two membranes were cross-linked with TMC and hydrophilic polymers were formed near the interface. Finally, two membranes were firmly adhered by growth of the hydrophilic polymers. Confirmation of the crosslinking was performed through FT-IR/ATR (460 plus, Jasco, Japan). Moreover, morphological observation of the prepared membranes was performed through an SEM (JEM-2010, JEOL, Japan) after the sample was mounted on a stub and coated with gold by using an ion coater.

The membrane electrical resistances (MER) were determined by using a clip cell and the LCZ meter. Prior to the measurement, the samples were equilibrated in 0.25 mol dm^{-3} Na_2SO_4 solution at 25 °C over 1 day. They were inserted in the clip cell prepared in the laboratory and alternating current was applied by 2321 LCZ meter (NF electronic instruments, Japan) with a frequency of 100 kHz. Consequently, we could measure the magnitude of impedance $|Z|$ and the phase angle of impedance (θ) of the membranes and convert them into MER ($\text{ohm} \cdot \text{cm}^2$) using Eq. (1).

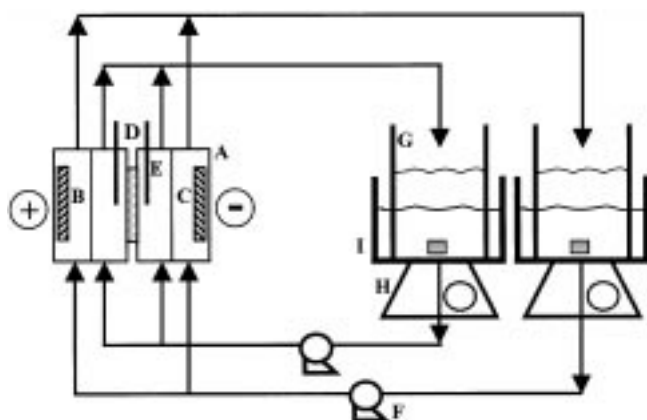


Fig. 2. Schematic diagram of the electro dialysis cell system for measuring membrane potential.

- | | |
|--------------------------|---------------------|
| A. Electro dialytic cell | F. Peristaltic pump |
| B. Anode | G. Reservoir |
| C. Cathode | H. Stirrer |
| D. Membrane | I. Water bath |
| E. Pt-black electrode | |

$$\text{MER} = |Z| \cdot \cos \theta \cdot \text{Area} \quad (1)$$

To determine the degree of swelling, membrane samples were previously equilibrated for 1 day in $0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$ solution. After removing the surface solution, we measured the wet weight of the samples. They were then dried at 60°C under a vacuum condition and weighed with a balance. The membrane water contents (MWC) were calculated from the weight difference between the wet and the dry membranes according to Eq. (2) [Bauer et al., 1988].

$$\text{MWC} = \frac{W_{\text{wet}} - W_{\text{dry}}}{W_{\text{dry}}} \quad (2)$$

The experimental setup for the electro dialytic cell experiments is illustrated in Fig. 2. For the characterization of the BPM, a potential drop across the membrane was measured as a function of applied electric current density in the 4-compartment cell. The membrane effective area was 12 cm^2 and the distance between the two membranes was 2 cm. The two cells containing the electrodes were separated from the other cells by cation exchange membranes. The salt solution ($0.25 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$) and the electrode rinse solution ($0.5 \text{ mol dm}^{-3} \text{ Na}_2\text{SO}_4$) were circulated by peristaltic pumps, and the temperature was controlled constantly at 25°C throughout the tests. The current was supplied by the HP 6674A power supply (Hewlett Packard Co. Ltd., USA) connected to two platinum plated titanium electrodes. The potential drop between the both sides of bipolar membrane was measured by using Pt-black electrodes connected with HP 34401A multi-meter (Hewlett Packard Co. Ltd., USA).

The water splitting efficiency of the prepared BPMs was estimated by using an electro dialytic cell composed of six individual chambers. A schematic of the configuration of the 6-compartment electro dialytic cell is shown in Fig. 3. The concentrations of sulfuric acid and sodium hydroxide were determined by acid/base titration and pH measurement according to time. The current efficiency was calculated from the total current passing through the cell system and the measured acid and base concentrations [The Membrane

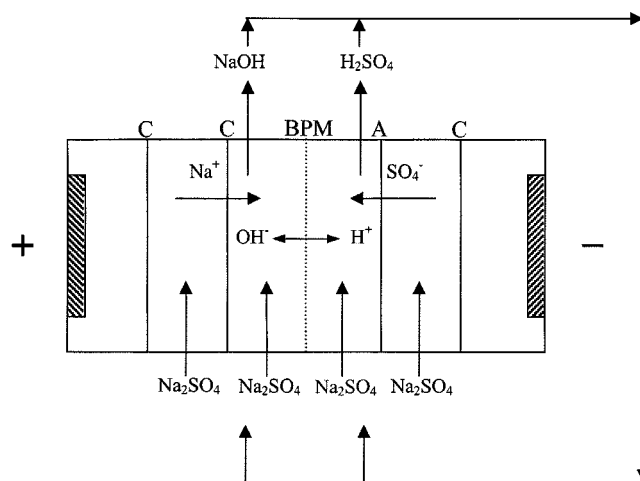


Fig. 3. Configuration of 6-chamber water-splitting electro dialytic cell.

Society of Korea, 1996]:

$$\eta(\%) = \frac{FV\Delta C}{nIt} \times 100 \quad (3)$$

where = Current efficiency (%)

F = Faraday's constant ($96,500 \text{ C mol}^{-1}$)

V = Volume of acid/base solution

ΔC = Concentration change of acid/base solution

n = Number of cell pair

I = Current (A)

Iron(III) chloride and chromium(III) chloride were employed as the catalytic substances to enhance the water-splitting reaction. These were reported as an effective water-splitting catalyst in the previous works [Simons, 1993; Hanada, 1993]. The metallic compounds were immobilized in the membranes through two different procedures modified from the conventional method [Simons, 1993]. In the first method, the cation and anion exchange membranes were immersed in alkaline slurry of 1 or 5% (w/v) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ or $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ in $1 \text{ mol dm}^{-3} \text{ NaOH}$ at 60°C for 60 mins. In the second method, the cation exchange membranes were first immersed in 1 or 5% (w/v) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ aqueous solution at 25°C for 24 hrs. Then the membranes were rinsed with distilled water and then immersed in $1 \text{ mol dm}^{-3} \text{ NaOH}$, at 60°C for 60 mins. The pretreated membranes were thoroughly rinsed with distilled water before the BPM preparation. The metal contents of the prepared membranes were analyzed by ICP-AES (Thermo Jarrell Ash, USA). In the 6-chamber electro dialytic cell experiments, the hydroxyl ion flux was determined from the time course of pH values under reverse bias condition (constant voltage (CV) operation).

RESULTS AND DISCUSSION

1. Identification of Crosslinked HEMA/MPD Layer through SEM Image and ATR Spectra

Fig. 4 shows the SEM photographs of CM-1 membrane surface untreated (a) and treated (b) with 1 wt.% HEMA/MPD and 1% (w/v) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ alkaline slurry, respectively. As shown in these figures,

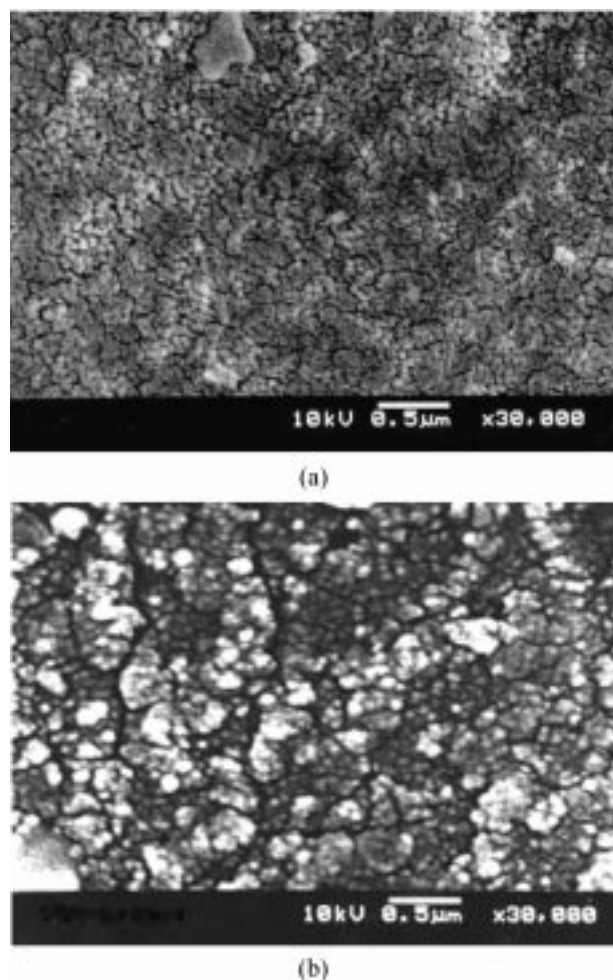


Fig. 4. SEM photographs of the CM-1 membrane surface: (a) untreated (b) treated with 1 wt% HEMA/MPD and 1% (w/v) $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ alkaline slurry.

the surface roughness was developed with the hydrophilic polymer (i.e., the polyHEMA/MPD cross-linked with TMC) layer. In addition, some glitter spots were observed on the membrane surfaces due to the immobilized metallic compounds.

The ATR spectra of cation-exchange membranes are shown in

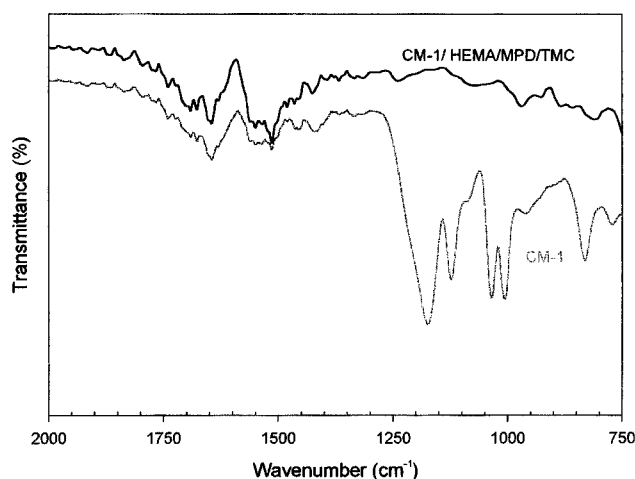


Fig. 5. ATR spectra of CM-1 and CM-1 coated with HEMA/MPD/TMC surfaces.

Fig. 5. The absorption band assigned to sulfonic acid groups was observed at $1,123$ and $1,003\text{ cm}^{-1}$ and the spectra of S=O stretching vibration at $1,369$ and $1,163\text{ cm}^{-1}$ from the surface of non-treated CM-1. Meanwhile, most of these peaks were not observed from the surface of the membrane coated with HEMA/MPD crosslinked with TMC. The absorption peaks of amides were confirmed at $1,550$ and $1,239\text{ cm}^{-1}$, respectively. It was evident that HEMA/MPD layer was formed at the interface between anion and cation exchange layers.

2. Membrane Electrical Resistance (MER) and Membrane Water Content (MWC)

The electrical resistances of the prepared BPMs are listed in Table 2. It was expected that the electrical resistances of these BPMs are similar to the sum of the resistances of sample 1 (AM-1) and 2 (CM-1). Indeed MERs of the membranes without metallic compounds were almost equal to the expected value from the two membranes. However, the resistances for the BPMs treated with metal catalyst were significantly lower than the sum of the two membranes. Moreover, it was also observed that the MERs diminished with the increase of the metal content fixed inside the membrane. These results indicate that the fixed metal species enhanced the membrane con-

Table 2. Membrane Electrical Resistance (MER)

No	Descriptions	MER (ohm cm^2)
1	AM-1 (Tokuyama Co. Ltd., Japan)	3.50
2	CM-1 (Tokuyama Co. Ltd., Japan)	3.41
3	BP-1 (Tokuyama Co. Ltd., Japan)	6.25
4	(HEMA/MPD 9:1) 1 wt%	7.40
5	(HEMA/MPD 1:9) 1 wt%	9.07
6	(HEMA/MPD 9:1) 1 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 1% (w/v) aqueous	4.75
7	(HEMA/MPD 9:1) 2 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 1% (w/v) aqueous	4.65
8	(HEMA/MPD 9:1) 1 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 5% (w/v) aqueous	3.71
9	(HEMA/MPD 9:1) 2 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 5% (w/v) aqueous	3.69
10	(HEMA/MPD 9:1) 1 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 1% (w/v) alkaline slurry	4.72
11	(HEMA/MPD 9:1) 2 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 1% (w/v) alkaline slurry	4.69
12	(HEMA/MPD 9:1) 2 wt%, ($\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$) 5% (w/v) alkaline slurry	4.50

Table 3. Membrane Water Content (MWC)

No	Descriptions	MCW (g·water/g·dry memb)
1	(HEMA/ MPD 9:1) 1 wt%	0.289
2	(HEMA/ MPD 1:9) 1 wt%	0.273
3	(HEMA/ MPD 9:1) 1 wt%, (FeCl ₃ ·6H ₂ O) 5% (w/v) aqueous	0.312
4	(HEMA/ MPD 9:1) 2 wt%, (FeCl ₃ ·6H ₂ O) 5% (w/v) aqueous	0.324
5	(HEMA/ MPD 9:1) 1 wt%, (FeCl ₃ ·6H ₂ O) 1% (w/v) alkaline slurry	0.307
6	(HEMA/ MPD 9:1) 2 wt%, (FeCl ₃ ·6H ₂ O) 1% (w/v) alkaline slurry	0.349
7	(HEMA/ MPD 9:1) 2 wt%, (FeCl ₃ ·6H ₂ O) 10% (w/v) alkaline slurry	0.362

ductivity. The mechanisms for the reduction of electrical resistances are not clearly understood. It is suspected that the decrease in MERs resulted from the increased water content by the hydrated metal compounds, the existence of free metal ions, and the complexation of metal species with ion-exchange groups. Whereas the hydrophilic polymer (polyHEMA/MPD), used as the binding material, had no significant effects on the MERs.

Table 3 shows the water contents (water swelling ratio) of the prepared bipolar membranes. An increase in the MWCs is observed with increasing the quantity of hydrophilic monomer (HEMA). This observation proves that the polyHEMA/MPD layer modified the interface characteristics. Moreover, the MWCs increased with an increase of the metal content in the membrane. This phenomenon seems to occur because the metal species were present in the membrane as a hydrated form and enhanced the wetness of the membrane interface or matrix. The MWCs of prepared BPMs were correlated with the MERs in Fig. 6. This result shows that the MWCs increased with an increase of the metal contents, whereas the MERs decreased.

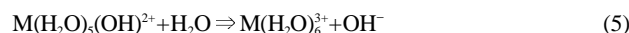
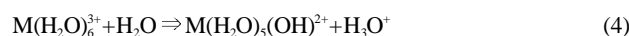
3. Immobilization of Metallic Compound in the Membrane

In this study, two modified methods for immobilizing the metal species in the membrane were applied as previously described. In the first method, the anion and cation exchange membranes were immersed in heated metal hydroxide slurry. Therefore, the metal species can be immobilized by the diffusion of ultrafine metal hydroxides (i.e., angstrom scale in size) into the membranes. In the

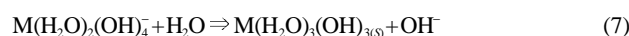
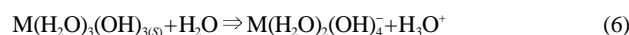
second method, the cation exchange membranes were immersed in an aqueous metal solution and in a heated alkaline solution successively. In this condition, the cations of alkaline solution substitute the previously ion-exchanged metal ions and the hydroxyl ions diffuse into the membrane simultaneously. Consequently, the metal ions are precipitated as a hydroxide form in the membrane. This immobilization mechanism was also reported in the earlier study [Pineri et al., 1985]. The effects of the two immobilization methods on the water splitting are discussed later in this study.

4. Metal Catalytic Reaction Model

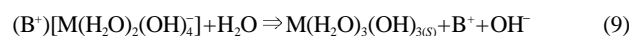
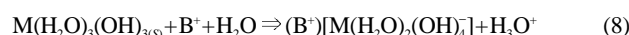
The possible metal catalytic reactions at the membrane interface are as follows.



In the reaction equations, M is a metal ion such as Fe³⁺ or Cr³⁺. This reaction mechanism was modified from the reaction model suggested by R. Simons [Simons, 1985]. Note that the pH in the reaction layer where water splitting occurred varied from about zero, at the boundary in the cation exchange membrane, to about 14, at the boundary region in the anion exchange membrane [Simons, 1986]. Therefore, from the pC-pH relations for hydroxo iron(III) complexes, the reaction (4) and (5) possibly occur in acidic condition near the boundary region of the cation exchange layer. However, the metal ions will be migrated out of the membrane during the current flow, if they are present as an ionic species. We suggest other catalytic reactions occurring in basic condition near the boundary region of the anion exchange layer.



The metal species possibly react with quaternary ammonium group of the anion exchange membrane. The reaction mechanisms are as follows:



where B⁺ is a quaternary ammonium group (-R₃N⁺) in the anion-exchange membrane. This reaction model indicates that metal species immobilized in the BPMs as a hydroxide form and react with water molecules and the quaternary ammonium groups reversibly by the presence of a very strong local electric field. This reaction mechanism seems to be a dominant water-splitting reaction by metal

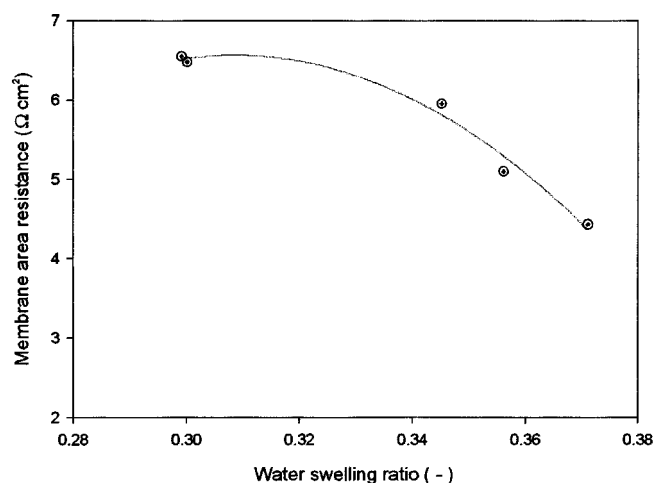


Fig. 6. Relationship between water swelling ratio and BPM electrical resistance.

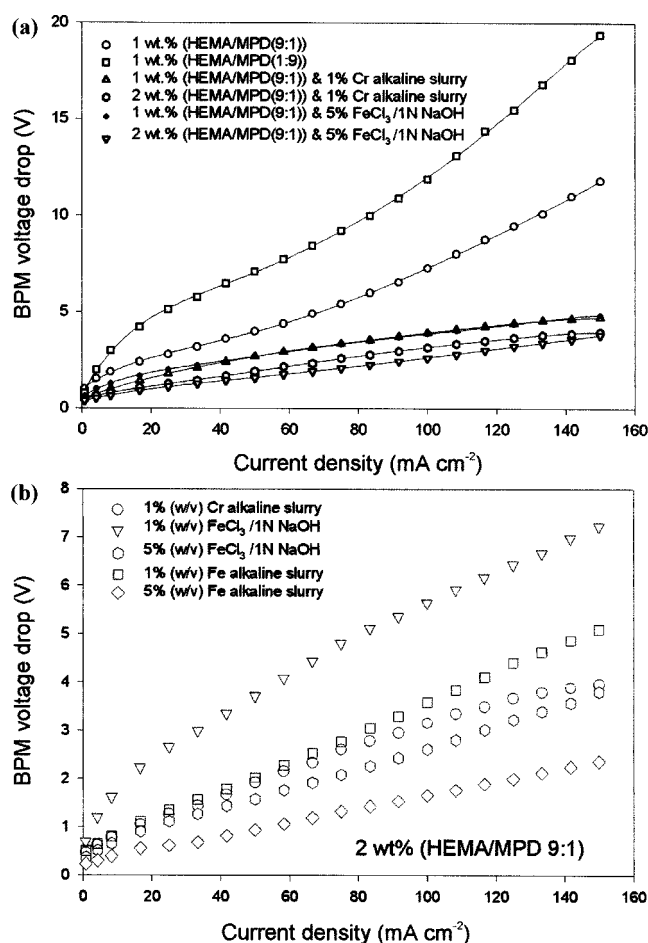


Fig. 7. Current-voltage curves for the prepared bipolar membranes.

species.

5. Voltage-Current (V-I) Relation

Fig. 7 shows the voltage-current (V-I) curves of the prepared bipolar membranes. As shown in Fig. 7(a), the water-splitting voltages decreased with an increase of hydrophilic monomer contents. It is considered that the developed hydrophilicity of the BPM interface accelerates the water-splitting reaction because the hydrophilic polymer layer increases the water activity by attracting water from the ion exchange layers to the space charge region.

In the cases of BPMs, which were not pretreated with metallic compounds, the water-splitting resistance increased abruptly from about 70 mA cm⁻². This phenomenon possibly occurs because the water-splitting rate was slower than the ion transfer rate. On the other hand, the water-splitting resistance decreased with the increasing current density in the case of metal-treated BPMs. This result indicates that the immobilized metal species in the membrane function as a water-splitting catalyst.

Fig. 7(b) shows the V-I curves for membranes prepared with different metal contents. The current-voltage relations in the figure show different trends with a metal content immobilized in the membrane. The water-splitting resistance decreased with an increase in the metal content of the immersing solution. Also Fig. 7 shows that the BPMs treated by method 1 using alkaline slurry for metal immobilization show lower water-splitting resistance than the BPMs

treated by method 2. This result indicates that the metal catalysts may function in water-dissociation reactions more effectively as a form of hydroxides. The difference in water splitting resistance can be explained by the following reason. In the first method, metal hydroxide can be sufficiently immobilized on the surface of the cation

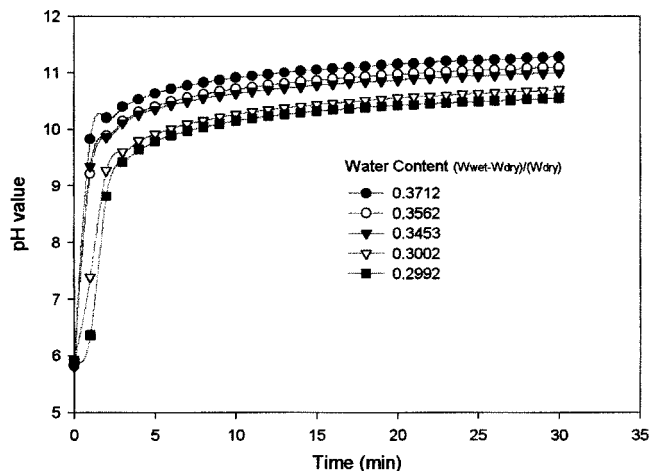


Fig. 8. pH variations of base compartment according to time [25 °C/ CV operation (10 V)].

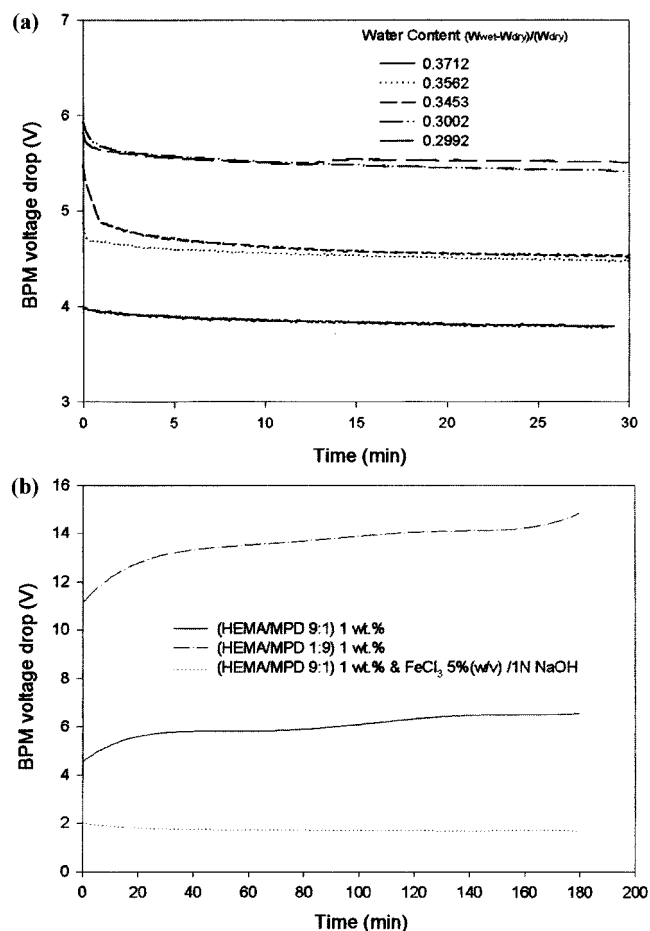


Fig. 9. Time course of membrane voltage for water dissociation (50 mA cm⁻²).

and anion exchange membranes. However, metal hydroxide only exists on the cation exchange layer of the BPMs prepared by method 2. Therefore, the metal compound fixed on an anion-exchange layer could reduce more effectively the water-splitting resistance, and this result supports the catalytic model described before. Meanwhile, no significant difference in the V-I characteristics by ferric and chromium alkaline slurry was observed at the same metal content.

6. Effects of Metal Content and Interface Hydrophilicity on Water Splitting Capacity

Fig. 8 shows the change of pH values in base compartment during constant voltage operation (10 V) for 30 mins. As the water splitting capacity of BPM is higher, the pH increase rate becomes higher. This figure shows the relationship between MWC and water splitting capacity. This result suggests that the hydrophilization of the membrane interface enhanced the water splitting ability.

Fig. 9 gives the time profiles of the BPM potential measured from 6-compartment cell experiments. From the relationship between MWC and water splitting potential [Fig. 9(a)], it was confirmed that the enhanced hydrophilicity of the membrane interface reduced the water splitting resistance. In the cases of the membranes without metal treatment, the membrane potential increased slightly with time [Fig. 9(b)]. As observed in the previous V-I curves, the water splitting resistance increased with time or current density, because the rate of water splitting reaction is slower than the transport rate of the ions, which were being removed from the membrane. Whereas, the membrane treated with metal showed a significantly lower membrane potential decreased with time by the catalytic effect of the metal.

Fig. 10 shows the variation of cell voltage and cumulative power consumption during constant current operation at 50 mA cm^{-2} . It was demonstrated that hydrophilization of the membrane interface and the enhancement of water splitting capacity caused by metal catalyst decreased the power consumption. The current efficiencies for water splitting of the prepared bipolar membranes were over

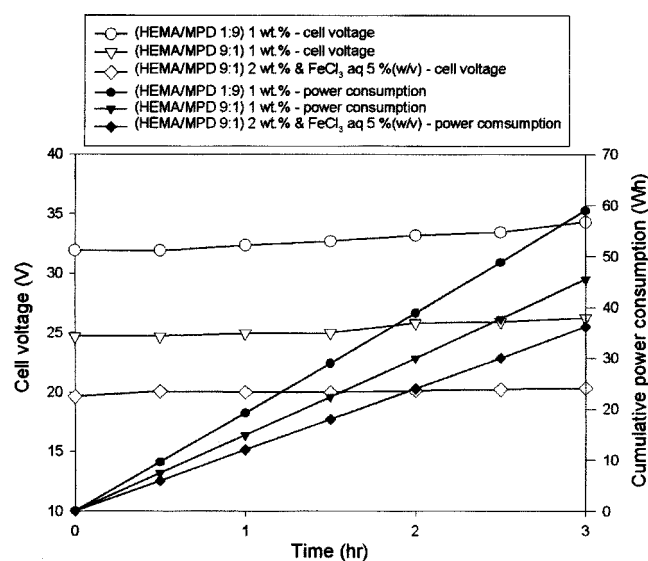


Fig. 10. Variation of the cell voltage and cumulative power consumption for water dissociation measured at constant current density (50 mA cm^{-2}).

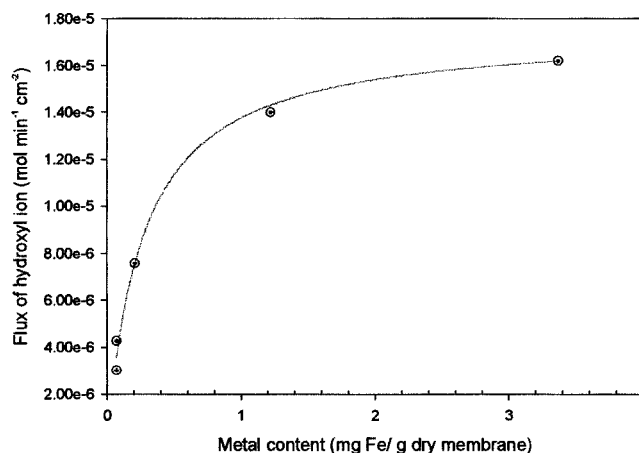


Fig. 11. Variation of hydroxyl ion flux according to metal content [$25^\circ\text{C}/\text{CV}$ operation (10 V)].

93%.

Fig. 11 shows the relation between the hydroxyl ion flux and the metal content under reverse bias condition. It was observed that the hydroxyl ion flux depended on the metal content through the experiments. The water splitting capacity increased linearly with the metal content within ca. $2.10 \times 10^{-4} \text{ g Fe/g dry membrane}$, whereas the increasing rate was reduced at higher contents. It is considered that the excessive metal content interferes with the current flow of the membrane surface where the water splitting takes place and reduces the water splitting capacity. This result indicates that there exists an optimum metal concentration for the water splitting.

CONCLUSIONS

In this study, bipolar membranes were prepared by using commercial ion exchange membranes and hydrophilic polymer as a binder to investigate the effects of the interface hydrophilicity on water-splitting efficiency. In addition, the effects of the metal catalyst on the water splitting capacity were considered.

The prepared membranes were characterized in terms of the membrane electrical resistance, water content, voltage-current (V-I) relations and water splitting capacity. From these experimental results, it was proven that the interface hydrophilicity and the metal content are important factors for improving the water-splitting efficiency. In this study, polyHEMA/MPD cross-linked with TMC was used as a material to enhance the membrane interface hydrophilicity. The enhanced hydrophilicity of the bipolar membrane interface accelerates the water-splitting reaction because the hydrophilic polymer layer increases the water activity by attracting water from the ion exchange layers to the space charge region.

The fluxes of hydroxyl and hydrogen ions generated by metal catalytic reaction depended on the metal contents under reverse bias condition. Metal species are immobilized in the BPM in a hydroxide form and seem to dominantly react with water molecules and the quaternary ammonium groups reversibly by the presence of a very strong local electric field. Moreover, metal species immobilized in the membrane improve the water-splitting efficiency by increment of the membrane wetness and enhancement of the membrane conductivity, with an apparent optimum metal concentration

for the water-splitting reaction.

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