Characterization of Anion-Exchange Membranes Containing Pyridinium Groups

Moon-Sung Kang, Yong-Jin Choi, and Seung-Hyeon Moon
Dept. of Environmental Science and Engineering (Engineering and Science),
Kwangju Institute of Science & Technology, (K-JIST), 1 Oryong-dong, Buk-gu, Gwangju, 500-12, South Korea

A poly(vinyl chloride) (PVC)/glycidyl methacrylate (GMA)-divinyl benzene (DVB)-based membrane was prepared via monomer sorption, and then pyridium or its derivates (that is, 4-ethyl pyridium, 4-tetrabutyl pyridium) were introduced into the PVC/poly(GMA-DVB) base membrane. The effects of pyridinium anion-exchangeable sites on the water splitting and the electrochemical properties of the membrane were investigated. The electrochemical properties and the water splitting on the anion-exchange membranes were compared with selected commercial membranes containing quaternary ammonium groups. The pyridium membranes showed good electrochemical properties, comparable to those of the commercial membranes, with electrical resistances of less than $3.0 \times 10^{-4}\ \Omega \cdot m^2$ *in 0.5 mol* dm^{-3} *NaCl and high ionic permselectivities (the transport number of* Cl^- *ions being 0.96). Moreover, water splitting indicated by the proton transport numbers of the membranes containing pyridinium or its derivates, were about two or three orders of magnitude lower than those of the commercial membranes (such as AM-1) at the same current density because the resonance effect in the quaternary pyridinium groups contributed to their molecular stability.*

Introduction

Water dissociation in ion-exchange membranes is a well-known phenomenon, which takes place at the membrane/solution interface above the limiting current density (LCD). In electrodriven processes, water dissociation causes significant problems, such as loss in current efficiency and increase in power consumption (Jialin et al., 1998; Kemperman, 2000; Strathmann et al., 1997; Taky et al., 1992). Interestingly, it has been reported that the behavior of water dissociation in anion-exchange membranes is significantly different from that in cation-exchange membranes. Nearly all of the current was carried by cations through a cation-exchange membrane, even under overlimiting current conditions. In the anion-exchange membranes, however, significant pH changes were observed in many cases (Jialin et al., 1998; Krol et al., 1999; Rubinstein et al., 1984; Strathmann et al., 1997; Simons, 1979, 1985). The difference between the two membranes cannot be explained by the classic electric-field-enhanced model (that is, the second Wien effect). To explain the enhancement of water dissociation in the anion-exchange membranes, Simons suggested a catalytic proton transfer reaction of weakly basic groups, that is, tertiary amines, as follows (Simons, 1979, 1985)

$$2H_2O \underset{k-1}{\overset{k1}{\Leftrightarrow}} H_3O^+ + OH^- \tag{1}$$

$$B + H_2O \underset{k-2}{\overset{k_2}{\Leftrightarrow}} BH^+ + OH^- \quad \text{(Protonation)} \tag{2}$$

$$BH^+ + H_2O \underset{k-3}{\overset{k_3}{\Leftrightarrow}} B + H_3O^+ \quad \text{(Deprotonation)} \tag{3}$$

where B is a neutral base group such as tertiary/secondary amines generated by the degradation of quaternary ammonium groups. Moreover, Rubinstein et al. (1984) reported that water dissociation was indeed determined by the characteristics of the charged groups in the anion-exchange membrane. They examined anion-exchange membranes containing crown ether complexed with alkali metals instead of classic quaternary ammonium groups, and the results showed a significant

---

Correspondence concerning this article should be addressed to S.-H. Moon.

Table 1. Specifications of the Commercial Membranes*

Grade	AM-1	AMX	AFN
Type	Strongly basic anion permeable (quaternary ammonium group)	Strongly basic anion permeable (quaternary ammonium group)	Strongly basic anion permeable (quaternary ammonium group)
Characteristics	Low electrical resistance	High mechanical strength	High acid diffusion coefficient
Ion-exchange capacity (eq./kg)	1.8–2.2	1.4–1.7	2.0–3.5
Transport number for Cl^-	0.98 <	0.98 <	0.98 <

*From Tokuyama Corporation.

reduction in water dissociation. Although the alkali metals are excellent candidates for an alternative anion-exchangeable group, as mentioned in their study, a significant problem is that the immobilized metal is unstable under the strong electric field.

Recently, the preparations of anion-exchange membranes having pyridinium derivatives as anion-exchangeable groups have been investigated. For example, Sata et al. (1998) prepared anion-exchange membranes containing pyridinium-derivative groups and characterized them. Although their results showed reasonable electrochemical properties, the effects of the functional groups on the water-splitting behavior were not investigated.

The aim of this work was to develop novel anion-exchange membranes having a very low water-splitting effect by introducing pyridinium groups into a base membrane. A poly(vinyl chloride) (PVC)/poly(glycidyl methacrylate) (GMA)-divinyl benzene (DVB) base membrane was prepared by the monomer sorption method (Choi et al., 2002), and then pyridine, 4-ethyl pyridine, and 4-tetrabutyl pyridine were introduced into the base film to form quaternized ion-exchange groups. The membranes prepared were characterized in terms of their water dissociation capabilities and electrochemical properties, and compared with selected commercial membranes.

Experimental Studies

Materials

Glycidyl methacrylate (GMA, Tokyo Kasei Co., Tokyo, Japan) and divinyl benzene (DVB, Aldrich, Milwaukee, WI) were used without further purification to prepare the base membrane, with benzoyl peroxide (BPO, Fluka, Buchs, Switzerland) as an initiator, which was purified by recrystallizing in a methanol/water mixture at −5°C. Analytical-grade pyridine (Py, Aldrich), 4-ethyl pyridine (EPy, Aldrich), and 4-tetra-butyl pyridine (TBPy, Aldrich) were used without further purification to introduce their quaternary pyridinium groups into the base membrane. Nonporous poly(vinyl chloride) (PVC, LG Chemical Co., Seoul, Korea) film having a thickness of 70 μm was employed as the reinforcing material. Neosepta AM-1, AMX, and AFN (Tokuyama Co. Ltd., Tokuyama, Japan) were selected for comparison with the membranes prepared in this study, and their specifications are summarized in Table 1.

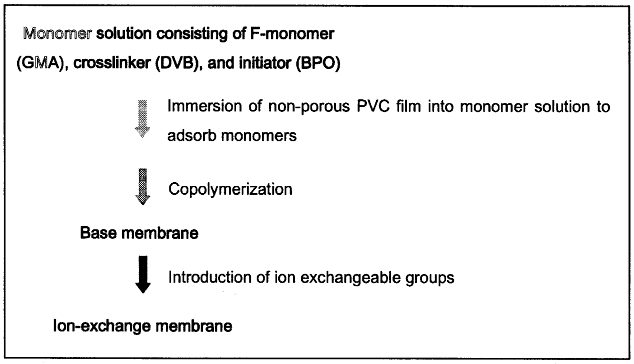

Figure 1. Procedure for PVC-based membrane preparation.

Membrane preparation

The membrane preparation procedure is illustrated in Figure 1. Initially, the monomer solution, consisting of GMA, DVB, and BPO, was prepared. The composition of the monomer solution is summarized in Table 2. Nonporous PVC film was immersed in the monomer mixture and kept at room temperature for 3 h to allow the monomers to be absorbed sufficiently into the PVC film. After soaking, the PVC film is swollen due to the solvent effect of the monomer adsorbed into the PVC network. The swollen PVC film was placed between two glass plates with a separating polycarbonate film, and the glass plates were sealed with aluminum tape to prevent evaporation of the monomers during polymerization. The monomers in the PVC film were then copolymerized in an oven set at 80°C for 0.5–10 h. After copolymerization, the base membrane was dried under atmospheric conditions at room temperature for 24 h to remove any nonreacted monomers. The base membranes were treated with: 0.5 mol dm^{-3} Py in water; 0.5 mol dm^{-3} EPy in water/ethanol (1/1% w/w); and 0.5 mol dm^{-3} TBPy in water/ethanol (1/1% w/w) to introduce the quaternary pyridinium anion-exchange groups. The reactions for the quaternization were carried out for 3–4 h at 50°C and then the membranes were treated with 1 mol dm^{-3} HCl for 2 h. The membranes were alternately washed in 0.5 mol dm^{-3} NH_4Cl and 1 mol dm^{-3} HCl several times. They were then stored in 0.5 mol dm^{-3} NaCl at room temperature. The reaction scheme for the pyridinium membrane is described in Figure 2. Figure 3 shows the introduced

Table 2. Composition of the Monomers

Components	Monomer Content (% w/w)	Weight Part
GMA	99.5	1
DVB	0.5	
BPO		0.02

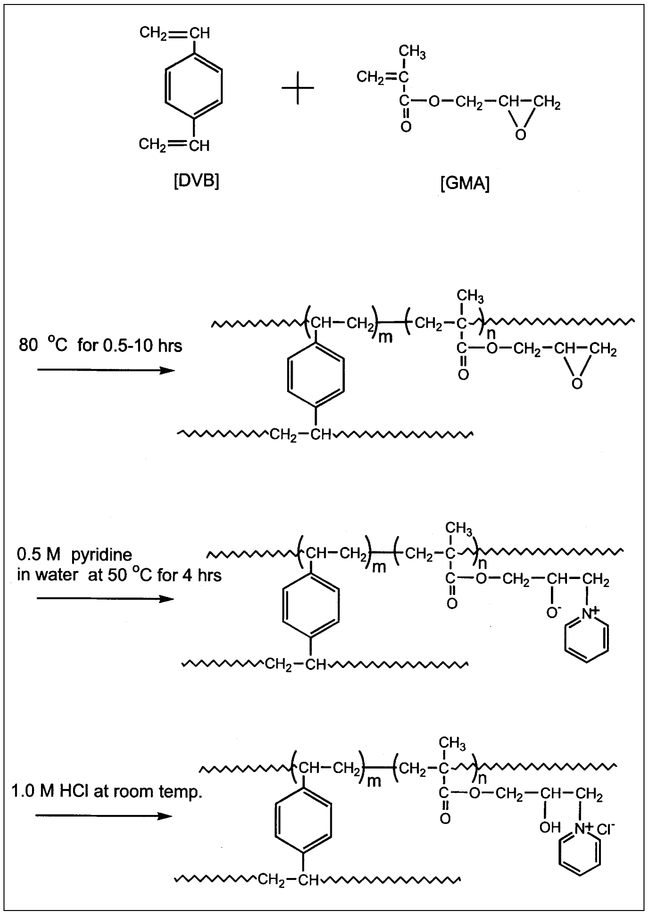

Figure 2. Reaction scheme for the pyridinium anion-exchange membrane.

quaternary pyridinium anion-exchange groups. The confirmation of the chemical structure of the prepared membranes was carried out using FT-IR (460 plus, Jasco, Japan) equipped with an ATR accessory.

Membrane characterization

The membrane electrical resistances (MER) were measured using a clip cell and a LCZ meter (NF Electronic Instruments, Tokyo, Japan) with a frequency of 100 kHz. Prior to the measurement, the samples were equilibrated in 0.5 mol dm^{-3} NaCl at 25°C for more than a day. The magnitude of impedance, $|Z|$, and the phase angle of impedance (θ) of the membranes were measured and converted into MER $(\Omega \cdot m^2)$ using the following equation

$$\mathrm{MER} = \left(|Z|_{\mathrm{sample}} \cdot \cos\theta_{\mathrm{sample}} - |Z|_{\mathrm{blank}} \cdot \cos\theta_{\mathrm{blank}}\right) \times \mathrm{area} \tag{4}$$

To measure the water content, after the membrane samples were soaked in 0.5 mol dm^{-3} NaCl for more than a day, they were wiped with a filter paper and immediately weighed. The samples were then dried at 60°C under vacuum until a constant weight was obtained. The water content was determined from the weight difference between the wet and dry membranes (g water/g dry membrane). Meanwhile, the contact angles of the membranes were measured using a contact angle meter (Tantec, IL). The apparent transport number of the counterion through the membranes was determined by the emf method using a two-compartment cell and Ag/AgCl electrodes (Choi et al., 2001a). To ignore the change in the electrolyte's activity coefficient, dilute solutions (0.001 mol dm^{-3} and 0.005 mol dm^{-3} of NaCl) were used. Chronopotentiometric and current–voltage $(I-V)$ curves were obtained via a two-compartment cell (each volume = 230 cm^3) experiment using 0.025 mol dm^{-3} NaCl as an electrolyte (Choi et al., 2001a). To obtain chronopotentiometric curves, a constant current density of 39.0 $A \cdot m^{-2}$ was supplied to the membrane by a potentiostat/galvanostat (AutoLab/PGSTAT30, Eco Chemie, Utrecht, Netherlands) and the potential between the reference electrode (Ag/AgCl) positioned near the membrane–solution interface, and the anode was automatically measured every 0.2 s for 100 s. The detailed procedure for chronopotentiometry was described in a previous study (Choi et al., 2001a). The water-splitting capabilities were evaluated using the six-compartment cell illustrated in Figure 4. Each compartment was separated by a Neosepta ACM anion exchange membrane (Tokuyama Co., Tokuyama Japan), which is known as a proton-blocking membrane, and

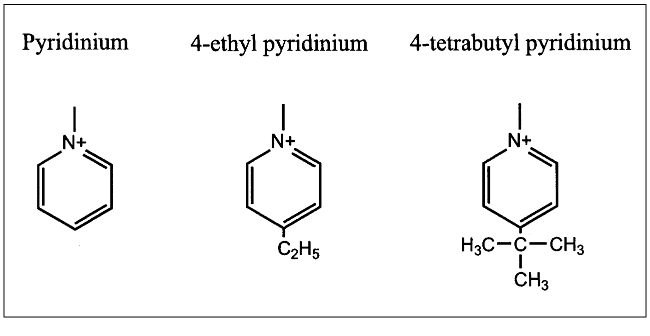

Figure 3. Functional groups introduced into the PVC/poly(GMA-DVB) membrane.

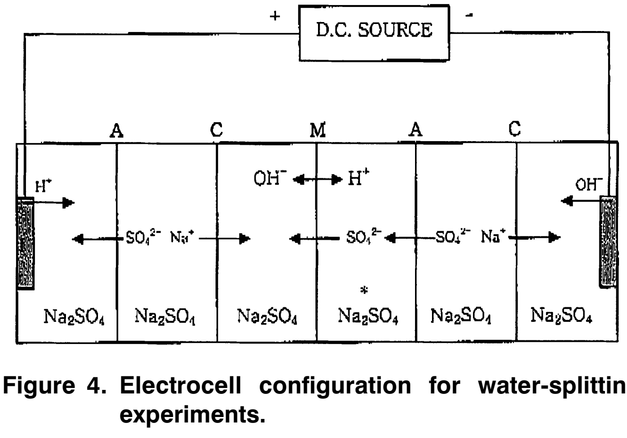

Figure 4. Electrocell configuration for water-splitting experiments.

M: membrane being tested; A: anion-exchange membrane; C: cation-exchange membrane; *pH measurement/acid compartment.

a Neosepta CMX cation-exchange membrane (Tokuyama Co.) Sodium sulfate solution (Na_2SO_4, 0.25/0.025 mol dm^{-3}) was used as an electrolyte solution, and a constant current was supplied by a power supply (6632A, Agilent, CA) into the membrane cell for 30 min. Two hundred milliliters of the test solution was circulated at a flow rate of 25 $mL \cdot min^{-1}$, and the pH of the acid compartment was measured as a function of time. The transport number of hydrogen ions, indicating the occurrence of the water dissociation in the membrane, was estimated from the change in pH according to the following equation

$$t_{H+} = \frac{FV(\Delta C_{H+}/\Delta t)}{IA} \qquad (5)$$

where F is the Faraday constant, V the volume of the solution, C_{H+} the concentration of the proton, t the time, I the current density, and A the membrane area. All experiments were performed at room temperature.

Results and discussion

Confirmation of polymerization

The ATR/FT-IR spectra of PVC and PVC/poly(GMA-DVB-Py) membranes are shown in Figure 5. In both membranes, the adsorption bands assigned to C–Cl were observed between 830 and 600 cm^{-1}. In the PVC/poly(GMA-DVB-Py) membrane, the absorption band corresponding to aromatic groups was observed near 1,625 cm − 1 and a C–N stretching band near 1,470 cm − 1 (Spiliopoulos and Mikroyannidis, 2001). This clearly shows that DVB and pyridium were introduced into the PVC film. Also, the absorption band (C=O) for carboxylic groups was observed at 1,700 cm^{-1}, indicating that GMA was incorporated into PVC film as well. Meanwhile, the C—O stretching vibration assigned to secondary alcohol groups appears at 1,125–1,100 cm^{-1}. This implies that the epoxides of GMA were opened and that secondary alcohol groups were formed because the epoxides reacted with the pyridine monomers. These results clearly demonstrate that the GMA-DVB copolymer, containing pyridinium groups, was successfully integrated into the PVC film according to the proposed preparation method.

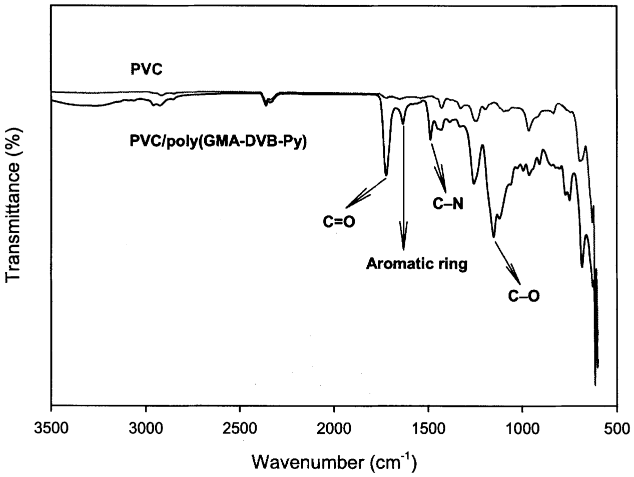

Figure 5. ATR spectra of PVC and PVC/poly (GMA-DVB-Py) films.

Membrane properties

The membrane properties, including the water content, the area resistance, the apparent transport number, and the fraction of surface conducting regions (ϵ) are summarized in Table 3. The pyridinium membranes were more swollen than the commercial membranes, which can be explained as follows: alcohol groups were formed in the base membrane during the quaternization through a reaction between pyridine and epoxide groups of GMA. As a result, increasing numbers of alcohol and ion-exchangeable pyridinium groups in the membrane led to a higher degree of swelling because the alcohol groups readily attract water molecules through hydrogen bonding. The electrical resistances were below 3.0×10^{-4} $\Omega \cdot m^2$ in 0.5 mol dm^{-3} NaCl, and also the transport number for Cl^- ions was over 0.96, indicating high ionic permselectivities. Meanwhile, the MER was affected by the molecular structure and the reactivity of the introduced F-monomers. The pyridinium membranes showed good electrochemical properties, comparable to those of the commercial membranes. The MER was in the decreasing order of GMA-DVB-TBPy > GMA-DVB-EPy > GMA-DVB-Py. The pyridinium derivatives were substituted with different alkyl groups and showed different electrical characteristics. Generally, alkyl groups act as electron-donor (pushing) groups toward the reaction center, and in this way increase the basicity of a molecular structure (Baeten et al., 1994). Therefore, alkyl substitution might increase the reactivity between the epoxide and pyridine derivatives during the quaternization. In spite of the increase in the basicity, however, the MERs of the alkyl-substituted pyridinium membranes were higher than that of the pyridinium membrane. To explain such a contradiction, the effect of steric hindrance, caused by the nature

Table 3. Membrane Properties

Membranes	AM-1	AMX	AFN	GMA-DVB-Py	GMA-DVB-EPy	GMA-DVB-TBPy
Water content	0.31	0.28	0.45	0.64	0.63	0.54
Electrical resistance $\times 10^4$ ($\Omega \cdot m^2$)	2.03	2.90	0.58	2.31	2.78	3.70
τ (s)	32.08	32.25	34.15	34.13	33.11	32.93
$I\tau^{1/2}$	22.09	22.15	22.79	22.78	22.44	22.38
Transport No.*	0.991	0.990	0.979	0.979	0.985	0.986
Transport No.**	0.986	0.983	0.967	0.965	0.966	0.962
ϵ	0.984	0.979	0.965	0.959	0.947	0.934

*Measured by chronopotentiometry.
**Measured by the emf method.

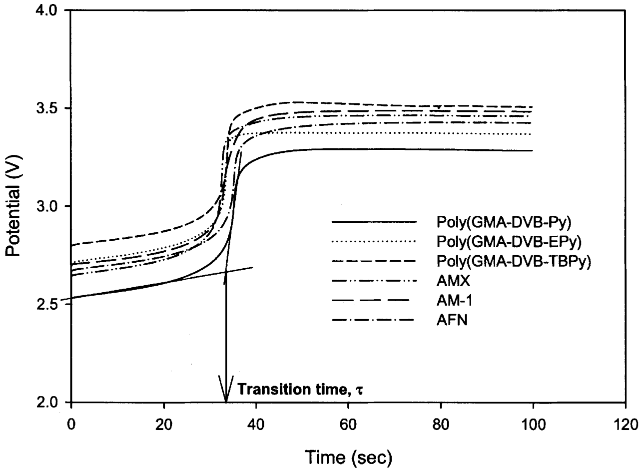

Figure 6. Chronopotentiometry curves.

Two-compartment cell experiment: electrolyte: 0.025 mol dm^{-3} NaCl; current density: 39.0 A m^{-2}; T: 25°C, without stirring.

of the molecular structure should be considered. Namely, the diffusion of a bulky alkyl-substituted pyridine into the base membrane could be retarded by steric hindrance and this retardation possibly diminished the reaction of pyridine derivates with the epoxides of the base membrane. Consequently, the overall efficiency of the reaction during the quaternization was governed more strongly by the structure of pyridine derivatives than by their reactivities. Also the solvent effects cannot be neglected. Notice that we used a different solvent for the pyridine derivatives [that is, Py in water; EPy in water/ethanol (1/1% w/w); and TBPy in water/ethanol (1/1% w/w)] because the alkyl substituted pyridine derivatives have low miscibility with water. It is possible that the electron donating property of the substituted alkyl groups also slightly decreased the charge intensity of the functional groups.

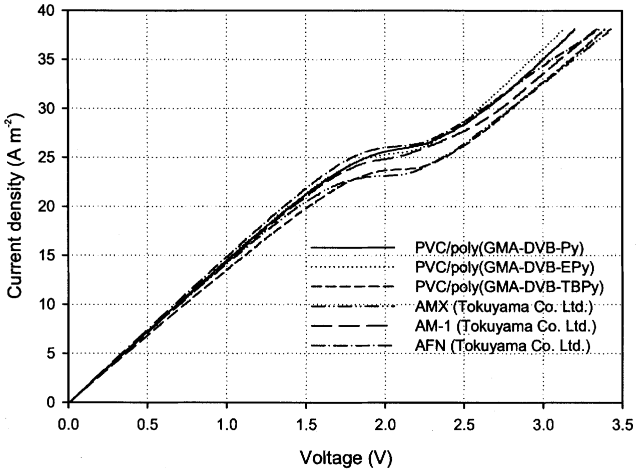

Figure 7. Current–voltage curves.

Two-compartment cell experiment: electrolyte: 0.025 mol dm^{-3} NaCl; T: 25°C, without stirring.

Figure 6 shows the chronopotentiometric curves for the commercial and pyridinium membranes. The fraction of conducting regions, ϵ, was estimated by the chronopotentiometric method proposed by Choi et al. (2001a). Although there is no significant difference in the apparent transport numbers between the commercial and pyridinium membranes, the ϵ values for the commercial membranes were somewhat higher than those of the pyridinium membranes. This implies that the charge intensities of the quaternary ammonium groups are stronger than those of the quaternary pyridinium groups, which are stabilized by the resonance effect.

I–V relationship

Figure 7 shows the comparison between the commercial and pyridinium membranes in terms of their $I-V$ curves. All curves exhibit the typical three-characteristic regions (that is, the first region of approximately ohmic behavior, the second region showing a plateau, and the third region having a rapid current increase (Rubinstein, 1991)). The characteristic values of the $I-V$ curves are listed in Table 4. The resistance ratios (R_{3rd}/R_{1st}) decreased with the increasing ϵ values in the order of AFN > AMX > AM-1; GMA-DVB-TBPy > GMA-DVB-EPy > GMA-DVB-Py). Choi et al. (2001b) suggested that the characteristic values of the $I-V$ curve (that is, R_{3rd}/R_{1st} and plateau length) are closely related with the overlimiting current and electroconvection. Often different membranes with the same permselectivity may exhibit markedly different concentration polarization behaviors, even though the nature of the membrane influences the concentration polarization through permselectivity only (Rubinstein et al., 1988). Therefore, it is thought that the R_{3rd}/R_{1st} values depend on the materials and the surface characteristics, such as heterogeneity, surface charge density, and distribution of charged groups. From the comparison between the commercial and pyridinium membranes, the $I-V$ characteristics of the pyridinium membranes were most comparable to the commercial anion-exchange membranes.

Water-splitting effect

The water splitting on the membranes was evaluated in six-compartment electrocell experiments. Figure 8 shows the

Table 4. Characteristic Values of the *I–V* Curves

Membranes	R_{1st} $\times 10^4$ ($\Omega \cdot m^2$)	R_{3rd} $\times 10^4$ ($\Omega \cdot m^2$)	R_{3rd}/R_{1st}	LCD* ($A \cdot m^{-2}$)	LCD** ($A \cdot m^{-2}$)
AM-1 (Tokuyama Co.)	701.75	723.59	1.031	23.9	312
AMX (Tokuyama Co.)	705.97	778.27	1.102	22.8	310
AFN (Tokuyama Co.)	676.73	911.99	1.348	25.6	323
GMA-DVB-Py	701.75	713.27	1.016	25.0	359
GMA-DVB-EPy	698.32	710.73	1.018	25.0	357
GMA-DVB-TBPy	738.33	757.58	1.026	23.2	318

*Measured using a two-compartment cell/0.025 mol dm^{-3} NaCl/without stirring/25°C.

**Measured using a six-compartment cell/0.025 mol dm^{-3} Na_2SO_4/with circulation/25°C.

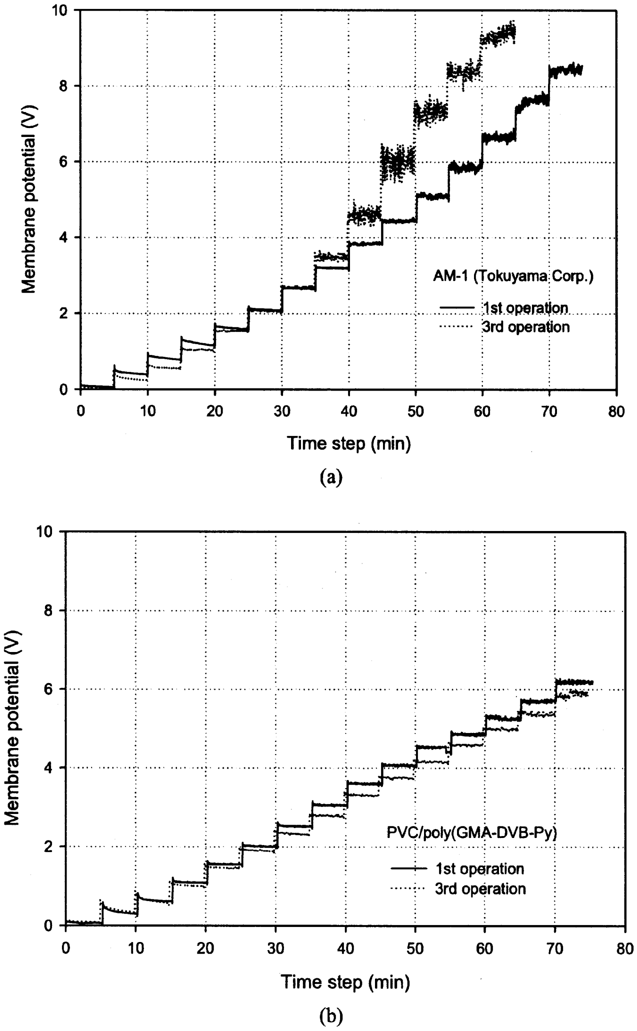

Figure 8. Variations in the membrane potentials according to stepwise increase in the current: effects of the number of operations.

Six-compartment cell experiment: electrolyte: 0.025 mol dm^{-3} Na_2SO_4; the current was increased 4.0 mA every 5 min. (a) AM-1; (b) PVC/poly(GMA-DVB-Py) membrane.

Table 5. Contact Angles of Commercial Membrane Surfaces

Membranes		Contact Angle (degree)
AM-1	Front side	88.3
	Back side	78.8
AMX	Front side	81.3
	Back side	80.6
AFN	Front side	85.7
	Back side	78.7

changes in the membrane potentials with an increase in the current density. Note that the current increased stepwise by 4.0 mA every 5 min. Generally, electrical noise, referring to the hydrodynamic instability near a membrane surface, can be observed near the overlimiting current (Krol et al., 1999; Rösler et al., 1992; Maletzki et al., 1992). In the commercial membranes, electrical noises were observed above the LCD (ca. 310–320 $A \cdot m^{-2}$) during the experiments. However, relatively weak electrical noises were observed in the cases of the pyridinium membranes. It has been reported that the electrical noise is caused by the electroconvection when the current density exceeds the overlimiting current (Krol et al., 1999; Rösler et al., 1992; Maletzki et al., 1992). Therefore, it can be explained that the electroconvection effect on the membranes containing pyridinium groups was diminished because the pyridinium derivatives have relatively weaker positive charge intensities than quaternary aliphatic ammonium groups due to the nature of the aromatic resonance stability. The decreased positive charge intensity might lead to a less active electroconvection.

Figure 8 also contains indirect evidence for the chemical changes on the membrane surface. The membrane potentials of the third operation were higher than those of the first operation when over the LCD region in the commercial membrane, as shown in Figure 8a. This result was probably caused by degradation of the surface-charged groups (that is, quaternary ammonium). On the other hand, the membrane potentials of the pyridinium membrane were nearly unaffected even if the membranes were tested repeatedly under the same experimental conditions, as shown in Figure 8b. Moreover, the contact angles of the virgin and tested commercial membrane surfaces were measured as shown in Table 5. The contact angles of used membrane surfaces (cathodic side) increased, compared to those of virgin membrane surfaces. The result implies that the surface of the tested membranes became more hydrophobic. This observation also indicates the changes undergone on the membrane surface. The mechanism of the chemical change in the quaternary ammonium groups is illustrated in Figure 9. The degradation of quaternary ammonium groups into tertiary amine groups (Figure 9a) occurs on the cathode side of the membrane surface under an electric field. Water dissociation occurs even if there are no tertiary amine groups on the membrane surface, like a cation exchange membrane. It is believed that the Hofmann elimination (Figure 9b) possibly takes place on the surface (Sata et al., 1996) because the previously generated hydroxyl ions can attack the aliphatic alkyl chain of quaternary ammonium groups with the help of the surface temperature, which is increased due to the high electrical resistance caused by the ion depletion at the LCD. The unshared electron pairs of the tertiary amine groups seem to play an important role in the catalytic water dissociation (Figure 9c). The unshared electron pairs attract the hydrogen atoms of prepolarized water molecules (protonation), and then catalytic water dissociation is activated under a strong electric field. Moreover, the prepolarization of water molecules can be accelerated because the tertiary amine is a H-affinity group, while the quaternary ammonium group is a OH-affinity group (Jialin et al., 1998). In the pyridinium membranes, however, the formation of an unshared electron pair is relatively difficult because the ion-exchangeable groups (pyridinium derivatives) are stable due to the nature of the aromatic resonance stability. Although Sata et al. (1966) reported that the membranes containing pyridinium salts could be affected by an alkali solution under very severe conditions, such as a high temperature, the pyridinium salts appear to be more stable than quaternary ammonium groups under normal conditions. Therefore, the water splitting of the anion-exchange mem-

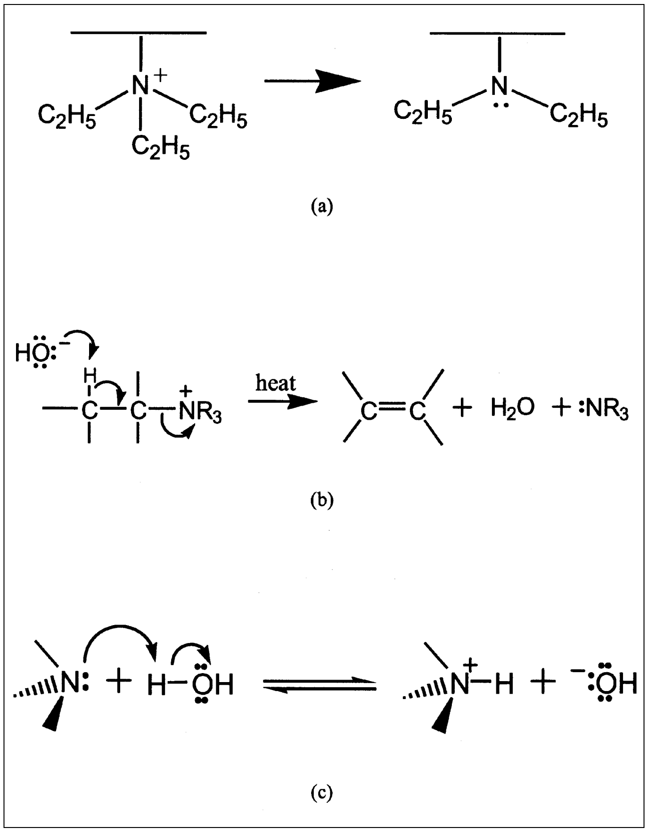

Figure 9. Transformation of quaternary ammonium groups into tertiary amines.

(a) Degradation of the quaternary ammonium group; (b) reaction scheme for Hofmann elimination; (c) water dissociation mechanism: protonation of the tertiary amine group.

branes containing pyridinium derivatives may be lower than those of the commercial membranes. To compare the water-splitting capabilities, the proton transport numbers, t_{H+}were monitored in the six-compartment cell experiments. Figure 10 presents the trends of the t_{H+}values calculated from Eq. 5 according to the applied current densities. In the commercial membrane, the transport numbers increased according to the number of experiments performed, the result being explained by the previous assumptions. However, in the case of the pyridinium membrane, the repeated runs did not cause t_{H+} to increase. Moreover the transport numbers were about two or three orders of magnitude lower than those of AM-1 at the same current density. The average t_{H+} values measured for 30 min at constant current densities (500 and 1,000 A m^{-2}) are listed in Table 6. The results also show that the transport numbers of commercial membranes were much higher than those of pyridinium membranes. The difference between the commercial and pyridinium membranes was attributable to the different ion-exchangeable groups in each membrane. It was reported that the quaternary ammonium groups may be degraded into tertiary or secondary amine forms, and then these functional groups induce catalytic water splitting by reacting with prepolarized water molecules when under a strong electric field (Simons, 1979; Simons, 1985). However, in the cases of the pyridinium membranes, these catalytic reactions seem to be negligible, and water dissociation obeys only the second Wien effect like cation-exchange membranes.

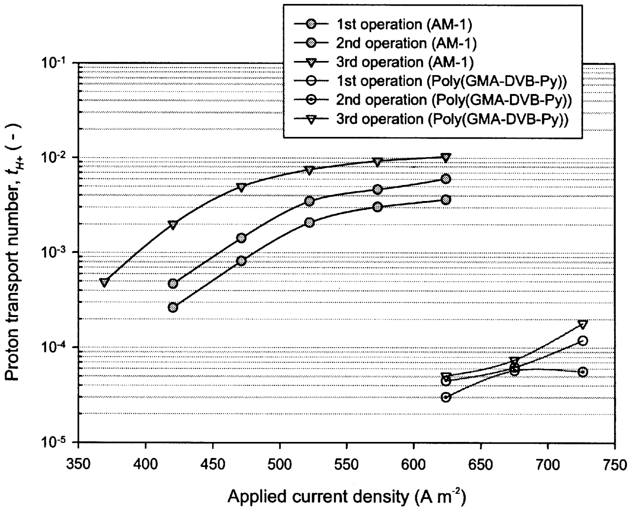

Figure 10. Variations in the proton transport numbers with an increase in the current densities: the effect of the number of operations.

Six-compartment cell experiment: electrolyte: 0.025 mol dm^{-3} Na_2SO_4.

Conclusions

We prepared new anion-exchange membranes containing pyridinium or its alkyl-substituted derivatives as the ion-exchangeable group and evaluated their electrochemical properties and the water-splitting effect. The pyridinium membranes exhibited excellent electrochemical properties comparable to those of the commercial membranes. Moreover, the water splitting of the pyridinium membranes were much lower than those of the commercial membranes. It was concluded that on the surface of the pyridinium membrane, the resonance stability of the quaternary pyridinium and its derivates contributed to their molecular stability. As a result, water splitting in the pyridinium membranes possibly arose via the second Wien effect without a catalytic reaction. In addition, the effect of alkyl substitution on the membrane characteristics was investigated. It was confirmed that alkyl

Table 6. Transport Numbers of the Generated H^+ Ion*

Membranes	t_{H+}**	t_{H+}†
AM-1 (Tokuyama Co.)	5.76e − 3	—
AMX (Tokuyama Co.)	7.31e − 5	—
AFN (Tokuyama Co.)	7.81e − 5	—
GMA-DVB-Py	ND	9.96e-4
GMA-DVB-EPy	ND	1.53e-4
GMA-DVB-TBPy	ND	1.22e-4

*Six-compartment cell experiment: electrolyte: 0.025 mol dm^{-3} Na_2SO_4.

**Measured at 500 A·m^{-2}.

†Measured at 1,000 A·m^{-2}.

substitution on the pyridine groups affects the properties of the membrane, such as the electrical resistance and the polarization characteristics, by means of the electron donating effect.

Acknowledgment

This work was supported by the National Research Laboratory (NRL) Program of the Korea Institute of Science and Technology Evaluation and Planning (Project No. 2000-N-NL-01-C-185).

Literature Cited

Baeten, A., F. De Proft, W. Langenaeker, and P. Geerlings, "On the Use of Density Functional Theory Based Descriptors for the Interpretation of the Influence of Alkyl Substitution on the Basicity of Amines," *J. Mol. Struct. (Theochem)*, **306**, 203 (1994).

Choi, J.-H., S.-H. Kim, and S.-H. Moon, "Heterogeneity of Ion-Exchange Membranes: The Effects of Membrane Heterogeneity on Transport Properties," *J. Colloid Interface Sci.*, **241**, 120 (2001a).

Choi, J.-H., H.-J. Lee, and S.-H. Moon, "Effects of Electrolytes on the Transport Phenomena in a Cation-Exchange Membrane," *J. Colloid Interface Sci.*, **238**, 188 (2001b).

Choi, Y.-J., M.-S. Kang, and S.-H. Moon, "A New Preparation Method for Cation-Exchange Membrane Using Monomer Sorption into Reinforcing Materials," *Desalination*, **146**, 287 (2002).

Jialin, L., W. Yazhen, Y. Changying, L. Guangdou, and S. Hong, "Membrane Catalytic Deprotonation Effects," *J. Membr. Sci.*, **147**, 247 (1998).

Kemperman, A. J. B., ed., *Handbook on Bipolar Membrane Technology*, Twente Univ. Press, Enschede, The Netherlands (2000).

Krol, J. J., M. Wessling, and H. Strathmann, "Concentration Polarization with Monopolar Ion Exchange Membranes: Current-Voltage Curves and Water Dissociation," *J. Membr. Sci.*, **162**, 145 (1999).

Maletzki, F., H.-W. Rösler, and E. Staude, "Ion Transfer Across Electrodialysis Membranes in the Overlimiting Current Range: Stationary Voltage Current Characteristics and Current Noise Power Spectra under Different Conditions of Free Convection," *J. Membr. Sci.*, **71**, 105 (1992).

Rösler, H.-W., F. Maletzki, and E. Staude, "Ion Transfer Across Electrodialysis Membranes in the Overlimiting Current Range: Chronopotentiometric Studies," *J. Membr. Sci.*, **72**, 171 (1992).

Rubinstein, I., "Electroconvection at an Electrically Inhomogeneous Permselective Interface," *Phys. Fluids*, **3**, 2301 (1991).

Rubinstein, I., E. Staude, and O. Kedem, "Role of the Membrane Surface in Concentration Polarization at Ion-Exchange Membrane," *Desalination*, **69**, 101 (1988).

Rubinstein, I., A. Warshawsky, L. Schechtman, and O. Kedem, "Elimination of Acid-Base Generation ('water-splitting') in Electrodialysis," *Desalination*, **51**, 55 (1984).

Sata, T., M. Tsujimoto, T. Yamaguchi, and K. Matsusaki, "Change of Anion Exchange Membranes in an Aqueous Sodium Hydroxide Solution at High Temperature," *J. Membr. Sci.*, **112**, 161 (1996).

Sata, T., Y. Yamane, and K. Matsusaki, "Preparation and Properties of Anion Exchange Membranes Having Pyridinium or Pyridinium Derivatives as Anion Exchange Groups," *J. Polym. Sci.: Part A: Polym. Chem.*, **36**, 49 (1998).

Simons, R., "Strong Electric Field Effects on Proton Transfer Between Membrane-Bound Amines and Water," *Nature*, **280**, 824 (1979).

Simons, R., "Water Splitting in Ion Exchange Membranes," *Electrochim. Acta*, **30**(3), 275 (1985).

Spiliopoulos, I. K., and J. A. Mikroyannidis, "Poly(pyridinium salt)s with Stilbene or Distyrylbenzene Chromophores," *J. Polym. Sci.: Part A: Polym. Chem.*, **39**, 2454 (2001).

Strathmann, H., J. J. Krol, H. J. Rapp, and G. Eigenberger, "Limiting Current Density and Water Dissociation in Bipolar Membranes," *J. Membr. Sci.*, **125**, 123 (1997).

Taky, G., F. Pourcelly, and C. Gavach, "Polarization Phenomena at the Interfaces Between an Electrolyte Solution and an Ion Exchange Membrane: Part II. Ion Transfer with an Anion Exchange Membrane," *J. Electroanal. Chem.*, **336**, 171 (1992).

Manuscript received Sept. 5, 2002, and revision received Apr. 24, 2003.