

## 저 물분해 특성을 가진 음이온 교환막의 제조 및 응용

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### Preparation and Application of Anion-Exchange Membrane having Low Water-Splitting Capability

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요 약: 피리디늄(pyridinium) 그룹을 포함한 음이온교환막의 제조 및 전기화학적 특성 평가를 수행하였다. 실험 결과, 제조된 피리디늄 음이온교환막은 상용막과 대등한 전기저항 ( $3.0 \Omega \text{cm}^2$ ), in  $0.5 \text{ mol dm}^{-3}$  NaCl) 및 높은 이온선택도 ( $\text{Cl}^-$  이온수송수 약 0.97)의 우수한 전기화학적 특성을 나타내었다. 또한 피리디늄 그룹을 함유한 음이온교환막에서의 물분해는 상용막(AM-1, Tokuyama Corp., Japan)에 비해 동일한 전류밀도 하에서 약 100배 내지 1000배 가량 낮게 측정되었는데 이는 4차 아로마틱 피리디늄 그룹의 공명효과(resonance effect)가 이온교환기의 분자구조적 안정성에 영향을 미쳤기 때문으로 사료되었다. 또한 피리디늄 음이온교환막의 전기투석 특성이 semi-pilot 스케일에서 평가되었다.

**Abstract:** The preparation and electrochemical characterization of anion-exchange membranes containing pyridinium groups were performed. As a result, the pyridinium membranes showed good electrochemical properties, comparable to those of the commercial membranes, with electrical resistance of less than  $3.0 \Omega \text{cm}^2$  in a  $0.5 \text{ mol dm}^{-3}$  NaCl and high ionic permselectivity (the transport number of  $\text{Cl}^-$  ions being 0.97). Moreover, water splitting in the membranes containing pyridinium groups was about two or three orders of magnitude lower than those in the commercial membranes (e.g. AM-1, Tokuyama Corp., Japan) at the same current density because the resonance effect in the quaternary aromatic pyridinium groups contributed to their molecular stability. In addition, the electro-dialytic properties of the pyridinium membranes were evaluated in a semi-pilot scale.

**Keywords:** anion-exchange membranes, pyridinium groups, water splitting, semi-pilot scale

### 1. Introduction

For many years, electrodialysis (ED) has been utilized in various applications such as water desalination and production of table salt from brackish water[1]. Ion-exchange membranes (IEMs) have been developed to fit the purpose ideally: high permselectivity, even in high concentration, low electric resistance, and discrimination between monovalent and divalent ions[2,3]. The

development of high-performance membranes enables the use of electrodialysis in a number of industrial applications such as demineralization of whey[4], recovery of metals from metal plating rinse waters[5], recovery of inorganic and organic acids[6-9], separation of amino acids from a fermentation broth[10].

To extend the applicable fields of the ED more widely, it is obvious that the economic efficiency should be improved. Since the ED processing cost is dominantly dependent on the membrane area, it is desired to operate at the highest practicable current

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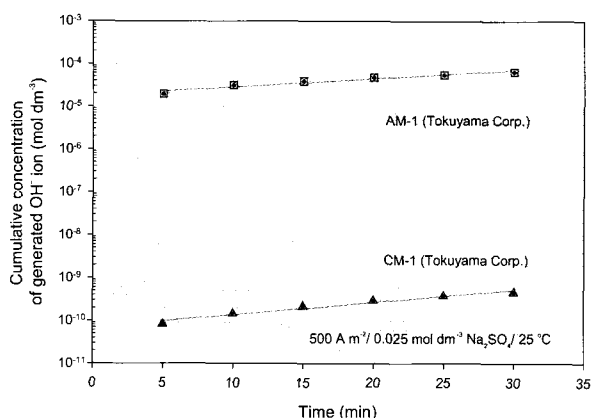
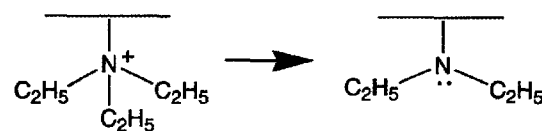


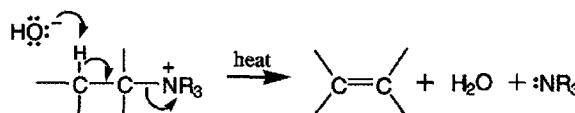
Fig. 1. Comparison of water splitting capabilities between cation-and anion-exchange membranes.

density to get the maximum ion flux per unit membrane area[11]. Operating current levels are, however, restricted by the concentration polarization phenomenon in electrically driven membrane processes. Therefore, it has been traditionally believed that the limiting current density (LCD) is the maximum current allowed to operate an ED process [12]. If the current exceed limiting one, the process efficiency is diminished due to the increase in the electrical resistance and the occurrence of water splitting. To overcome the limitations, therefore, the development of novel ion-exchange membranes exhibiting low water-splitting ability and excellent electrochemical stability under a high electric field is required.

Water splitting in ion-exchange membranes is a well-known phenomenon, which takes place at the membrane/solution interface above the LCD. As mentioned above, water splitting causes significant problems such as loss in current efficiency and increase in power consumption[13-15]. Interestingly, it has been reported that the behavior of water dissociation in anion-exchange membranes (AEMs) is significantly different from that in cation-exchange membranes (CEMs). Nearly all of the current was carried by cations through a cation exchange membrane, even under over-limiting current conditions. In the anion exchange membranes, however, significant pH changes were observed in many cases[13,16-18]. The water splitting capabilities (as the cumulative concentration of



(a) Degradation of the quaternary ammonium group



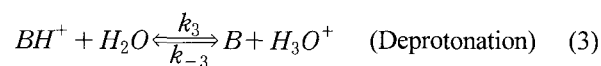
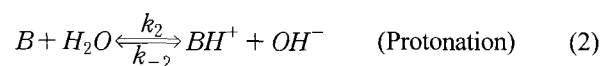
(b) Reaction scheme for Hofmann elimination



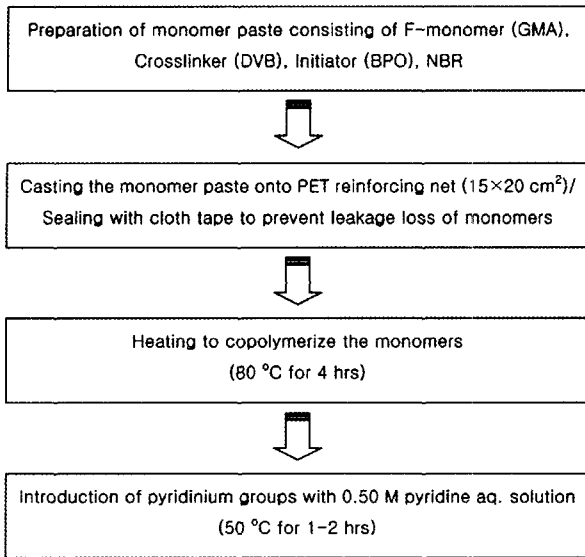
(c) Water splitting mechanism: Protonation of the tertiary amine group

Fig. 2. Chemical degradation of quaternary ammonium groups into tertiary amines and catalytic water splitting mechanism.

OH<sup>-</sup> ions (mol dm<sup>-3</sup>) in the solution of the same volume) of cation-(CM-1) and anion-(AM-1) exchange membranes are compared in Fig. 1. The difference between the two membranes cannot be explained by the classical electric field enhanced model (*i.e.* the Second Wien effect). To explain the enhancement of water splitting in the anion-exchange membranes, Simons suggested a catalytic proton transfer reaction of weakly basic groups, *i.e.* tertiary amines, as follows [14,18]:



where  $B$  is a neutral base group such as tertiary/secondary amines generated by the degradation of quaternary ammonium groups. The mechanism of the chemical change in the quaternary ammonium groups is illustrated in Fig. 2: The degradation of quaternary ammonium groups into tertiary amine



**Fig. 3.** Procedures for preparing pyridinium anion-exchange membranes (paste method).

groups occurs on the cathode side of the membrane surface under the strong electric field (a). Initially, 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 (E2-type elimination, (b)) possibly takes place on the surface [19] because the previously generated hydroxyl ions can attack the aliphatic alkyl chain of quaternary ammonium groups with the help of 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 (c). Namely, the unshared electron pairs attract the hydrogen atoms of pre-polarized water molecules (Protonation) and then catalytic water dissociation is activated under a strong electric field. Moreover, the pre-polarization of water molecules can be accelerated because the tertiary amine is a H-affinity group while the quaternary ammonium group is an OH-affinity group[13].

Since the water splitting in anion-exchange membrane depends predominantly upon the characteristics of fixed charge groups, the introduction of alternative anion-exchange groups has been challenged.

For example, Rubinstein *et al.* reported that water dissociation was indeed determined by the characteristics of the charged groups in the anion-exchange membrane[20]. They examined anion-exchange membranes containing crown ether complexed with alkali metals instead of classical quaternary ammonium groups and the results showed the significant reduction in water splitting. 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. It can be also expected that aromatic pyridinium groups are more stable than aliphatic ammonium groups under the high electric field since they exhibit the aromatic resonance behavior. Recently, the preparation of anion-exchange membranes having pyridinium derivatives as anion-exchangeable groups has been investigated. Sata *et al.* prepared anion-exchange membranes containing pyridinium derivative groups and characterized them [2]. 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 study was to develop novel anion-exchange membranes having very weak water-splitting property by introducing pyridinium groups into a base membrane. A poly((glycidyl methacrylate) (GMA)-divinyl benzene (DVB)) base membrane reinforced with poly(ethylene terephthalate) (PET) net was prepared via a traditional paste method and then pyridine was 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. In addition, the electrodynamic properties of the pyridinium membranes were evaluated in a semi-pilot scale.

## 2. Experimental

### 2.1. Materials

Glycidyl methacrylate (GMA, Tokyo Kasei Co.,

Japan) and divinyl benzene (DVB, Aldrich, USA) were used without further purification to prepare the base membrane, with benzoyl peroxide (BPO, Fluka, Switzerland) as an initiator, which was purified by re-crystallizing in a methanol/water mixture at  $-5^{\circ}\text{C}$ . Analytical grade pyridine (Py, Aldrich, USA) was used without further purification to introduce quaternary pyridinium groups into the base membrane. Acrylonitrile butadiene rubber (NBR) was added to monomer paste (NBR/paste=1/6 as weight ratio) and poly(ethylene terephthalate) (PET) net (thickness = 45-180  $\mu\text{m}$ , SEFAR PETEX<sup>®</sup>, Sefar Inc., Switzerland) was utilized as a reinforcing material.

## 2.2. Membrane Preparation

The pyridinium membranes were prepared by a traditional paste method. The procedures for preparing poly(GMA-DVB-Py) membranes are diagrammatized in Fig. 3. Initially, the monomer paste, consisting of GMA, DVB, NBR and BPO, was prepared and then the paste was cast on the PET reinforcing net ( $15 \times 20 \text{ cm}^2$ ). The selected composition of the monomer paste was: GMA/DVB (99.5/0.5 wt.%); NBR (NBR/paste=1/6 as weight ratio); BPO (0.04 part). After casting, it 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. Polymerization was carried out at  $80^{\circ}\text{C}$  for 3-4 hrs. After co-polymerization, the base membrane was dried under atmospheric conditions at room temperature for 24 hrs to remove the non-reacted monomers. The base membranes were treated with  $0.5 \text{ mol dm}^{-3}$  Py aqueous solution to introduce quaternary pyridinium anion-exchange group for 1-2 hrs at  $50^{\circ}\text{C}$ . The membranes were treated with  $1 \text{ mol dm}^{-3}$  HCl for 2 hrs and then alternately washed in  $0.5 \text{ mol dm}^{-3}$   $\text{NH}_4\text{Cl}$  and  $1 \text{ mol dm}^{-3}$  HCl several times. The reaction scheme for the pyridinium anion-exchange membrane is shown in Fig. 4.

## 2.3. Membrane Characterization

The membrane electrical resistances (MER) were

measured using a clip cell and a LCZ meter (NF electronic instruments, Japan) with a frequency of 100 kHz. Prior to the measurement, the samples were equilibrated in  $0.5 \text{ mol dm}^{-3}$  NaCl at  $25^{\circ}\text{C}$  more than a day. The magnitude of impedance ( $|Z|$ ) and the phase angle of impedance ( $\theta$ ) of the membranes were measured and converted into MER ( $\Omega\text{cm}^2$ ) using the following equation:

$$MER = (|Z|_{\text{sample}} \cdot \cos \theta_{\text{sample}} - |Z|_{\text{blank}} \cdot \cos \theta_{\text{blank}}) \times \text{area} \quad (4)$$

To measure the water content, after the membrane samples were soaked in  $0.5 \text{ mol dm}^{-3}$  NaCl for more than a day, they were wiped with a filter paper and immediately weighed. The samples were then dried at  $60^{\circ}\text{C}$  under vacuum until a constant weight was obtained. The water contents were determined from the weight difference between the wet and dry membranes (g water/ g dry membrane). The apparent transport number for the counter ion through the membranes was determined by the emf method using a two-compartment cell and a pair of Ag/AgCl electrodes [21]. To ignore the change in the electrolyte's activity coefficient, dilute solutions ( $0.001 \text{ mol dm}^{-3}$  and  $0.005 \text{ mol dm}^{-3}$  of NaCl) were used. Current-Resistance (I-R) curves were obtained via a two-compartment cell experiment using  $0.025 \text{ mol dm}^{-3}$  NaCl as an electrolyte[21]. The water-splitting capabilities were evaluated using the six-compartment cell illustrated in Fig. 5. The each compartment was separated by a Neosepta<sup>®</sup> ACM anion exchange membrane (Tokuyama Co., Japan), which is known as a proton blocking membrane, and a Neosepta<sup>®</sup> CMX cation exchange membrane (Tokuyama Co., Japan). Sodium sulfate solution ( $\text{Na}_2\text{SO}_4$ ,  $0.25 \text{ mol dm}^{-3}$ ) was used as an electrolyte solution and a constant current was supplied for 30 min. The pH values of the acid/base compartments were measured as a function of time.

## 2.4. Desalting Electrodialysis

The electro-dialytic properties of the pyridinium membranes prepared were evaluated by using a semi-

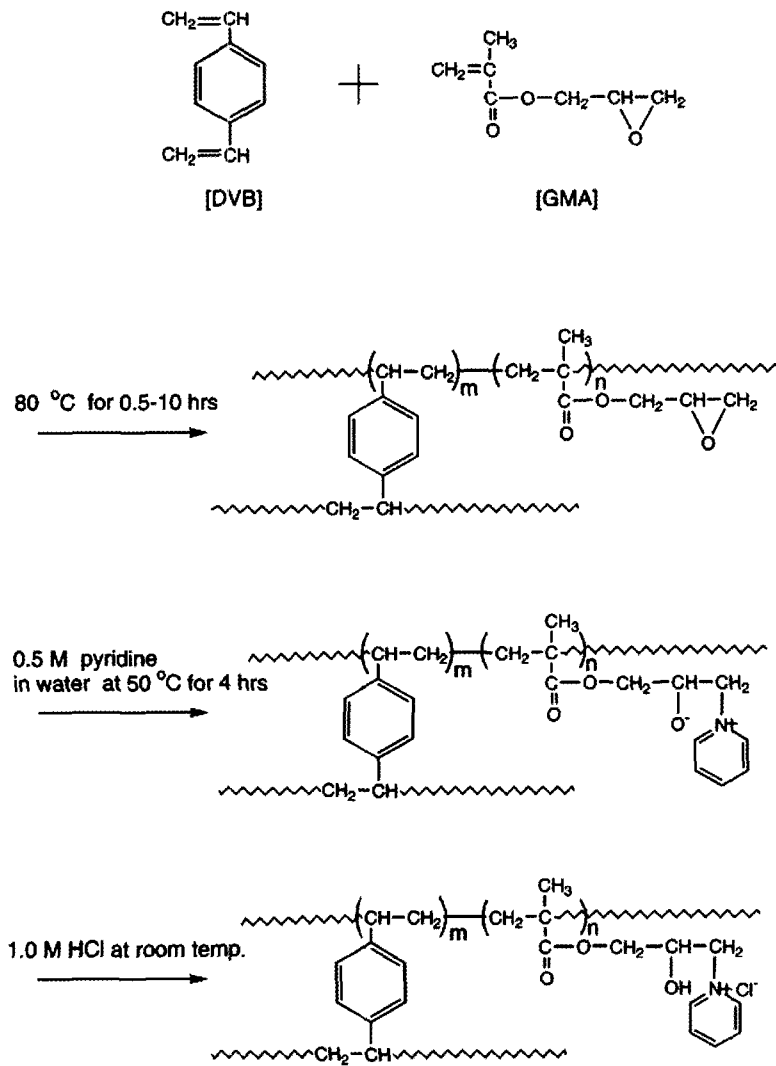


Fig. 4. Reaction scheme for the pyridinium anion-exchange membrane.

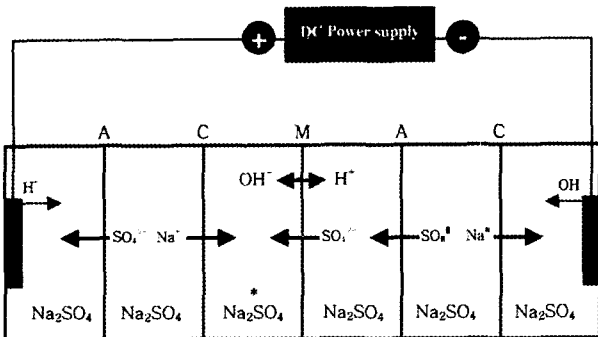


Fig. 5. Schematic drawing of electrodiolytic cell configuration for evaluating water splitting capability (\* pH measurement compartment).

pilot scale ED stack (TS-1-10, Tokuyama Corp.,

Japan). The stack configuration is illustrated in Fig. 6 and the detailed specifications for desalting experiments are as follows:

- Stack: TS-1-10 (equipped with auto-data acquisition system)
- Membrane effective area: 100 cm<sup>2</sup>
- Cell pair: 2 cell pair
- Cell configuration: + | C | A | C | A | C | C | -
- Electrolyte: 0.10 mol dm<sup>-3</sup> NaCl
- Constant current operation: 130 A m<sup>-2</sup>
- AEM: AMX (Tokuyama Corp., Japan), poly (GMA-DVB-Py) membrane
- CEM: CMX (Tokuyama Corp., Japan).

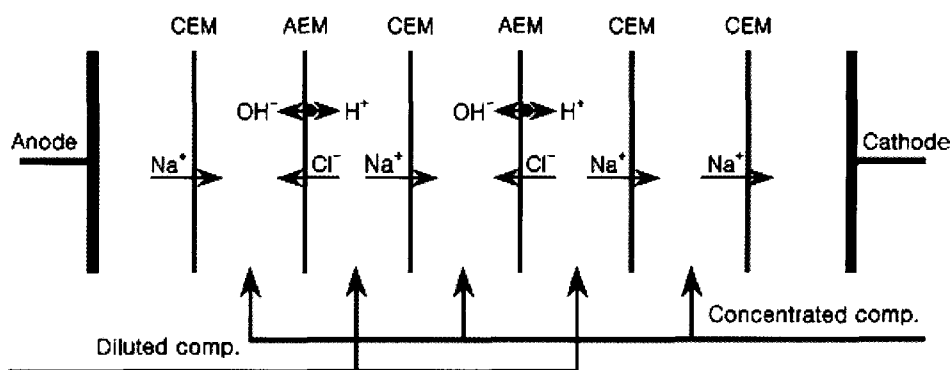
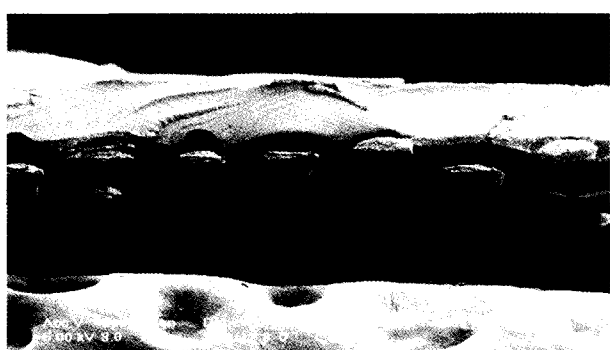
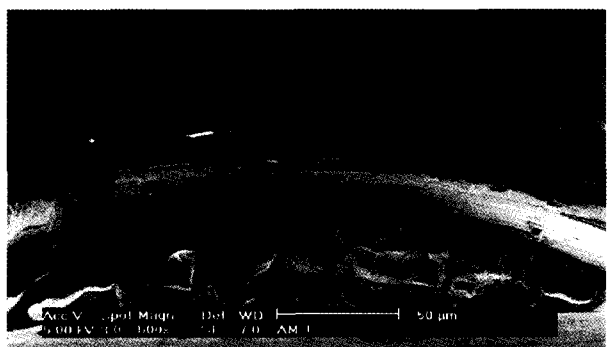


Fig. 6. Stack configuration (TS-1-10) for desalting experiments.



(a) Poly(GMA-DVB-Py) membrane reinforced with PET Net;



(b) Commercial AM-1 membrane

Fig. 7. Cross-sectional FE-SEM images of pyridinium membrane (a) and commercial membrane (b).

### 3. Results and Discussion

#### 3.1. FE-SEM Image

The morphology of the membranes prepared was investigated by a FE-SEM (XL30, Philips, USA) analysis. Fig. 7 shows the cross-sectional FE-SEM images of pyridinium AEM (Py-AEM, (a)) and commercial AEM (AM-1, (b)). The thickness of the

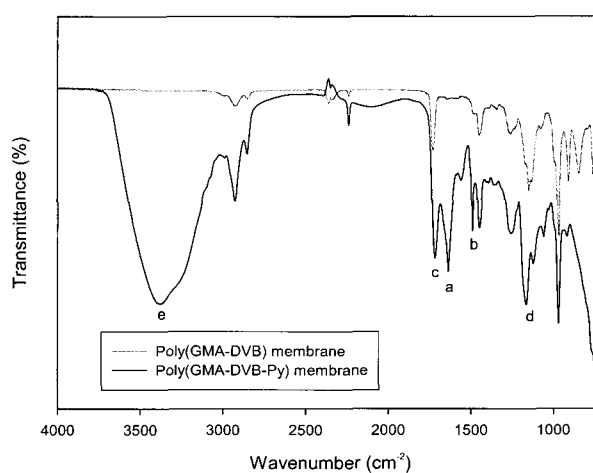


Fig. 8. ATR spectrum of poly(GMA-DVB-Py) membrane reinforced with PET net.

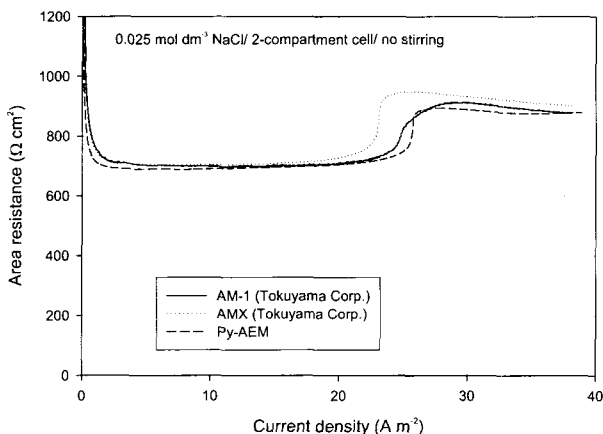
prepared Py-AEM (100-200  $\mu\text{m}$ ) was somewhat thicker than that of the commercial membrane (120-160  $\mu\text{m}$ ) as observed in this figure. The thickness could be controlled using the PET nets of different thickness. The membrane was found to be defect-free in surface and cross-sectional observations and phase separation was not observed in the membrane.

#### 3.2. ATR Analysis

The ATR/ FT-IR spectrum of poly(GMA-DVB-Py) membrane is shown in Fig. 8. In the spectrum, the absorption band corresponding to aromatic (pyridinium) groups was observed near  $1625\text{ cm}^{-1}$  (peak a) and the C-N stretching band near  $1490\text{ cm}^{-1}$  (peak b)[22]. Also, the absorption band (C=O) for carboxylic groups was observed at  $1710\text{ cm}^{-1}$  (peak c) indicating that

**Table 1.** Basic Membrane Properties

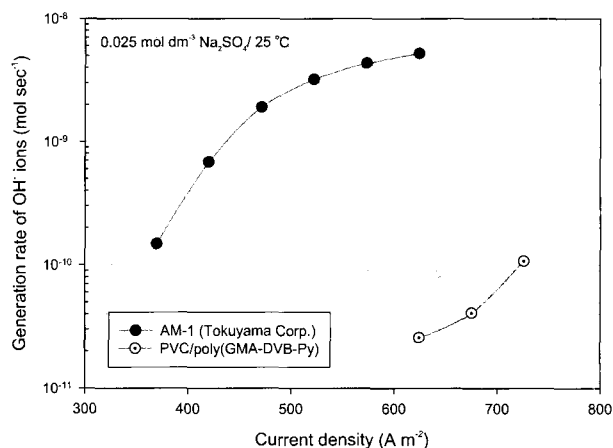
Membranes	AM-1	AMX	Poly(GMA-DVB-Py)
Water swelling ratio(%)	31.0	28.0	48.4
Electrical resistance( $\Omega\text{cm}^2$ )	2.03	2.90	2.72
IEC(meq./g)	2.02	1.58	1.92
Transport No.(-)	0.986	0.983	0.972

**Fig. 9.** Current-resistance (I-R) curves of pyridinium and commercial membranes.

GMA was incorporated into the copolymer. Meanwhile, the C-O stretching vibration assigned to secondary alcohol groups appears at  $1125\text{--}1100\text{ cm}^{-1}$  (peak d). This indicates that the epoxides of GMA were opened and that secondary alcohol groups were formed because the epoxides reacted with the pyridine monomers. Moreover the broad absorption band of hydroxyl group appeared at  $3480\text{ cm}^{-1}$  (peak e) assigned to the hydrogen bonds of water molecules absorbed onto the quaternary pyridinium groups. These results demonstrate that the copolymer (poly(GMA-DVB)) containing pyridinium groups was successfully prepared via the proposed preparation method.

### 3.3. Electrochemical Membrane Properties

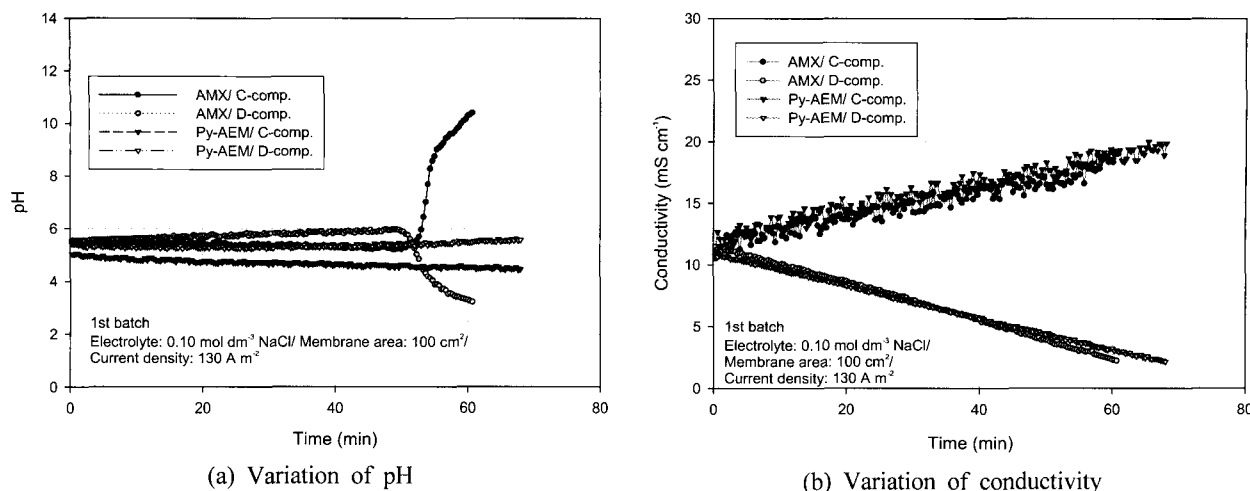
The basic membrane properties are summarized in Table 1. The pyridinium membranes were more swollen than the commercial membranes, which can be explained as follows: alcohol groups were formed in the base membrane during the quaternization through a reaction between pyridine and epoxide groups of GMA. As a result, increasing numbers of alcohol and ion-exchangeable pyridinium groups in the membrane

**Fig. 10.** Comparison of water splitting capabilities between the commercial (with quaternary ammonium groups) and lab-made (with quaternary pyridinium groups) anion-exchange membranes.

led to a higher degree of swelling because the alcohol groups readily attract water molecules through a hydrogen bonding. However, there is no significant difference between the poly(GMA-DVB-Py) and commercial membranes in their ion-exchangeable properties. Fig. 9 exhibits the current-resistance (I-R) curves of poly(GMA-DVB-Py) and commercial membranes. All curves show the typical three characteristic regions due to the concentration polarization effect. As shown this figure, the I-R characteristics of the pyridinium membrane were mostly comparable to the commercial anion-exchange membrane, especially AM-1 membrane having excellent electrochemical properties (e.g., low electrical resistance).

### 3.4. Water-Splitting Capability

Fig. 10 presents the trends in water splitting according to the applied current densities. Water splitting (as the generation rate of  $\text{OH}^-$  ion) in the poly(GMA-DVB-Py) membrane were about two or three orders of magnitude lower than that in the



**Fig. 11.** Variation of pH (a) and conductivity (b) values in concentration (C) and dilution (D) compartments during constant current operation.

commercial membrane (AM-1, quaternary ammonium groups) at a same current density. The difference between the commercial and pyridinium membranes was attributed to the different ion-exchangeable groups in each membrane. As mentioned previously, the quaternary ammonium groups are degraded into tertiary or secondary amine forms, and then these weakly basic groups induce a catalytic water splitting by reacting with pre-polarized water molecules when under a strong electric field [13,14,18]. However, in the cases of the pyridinium membranes, these catalytic reactions seem to be negligible and water-splitting mechanism obeys only the Second Wien effect like cation-exchange membranes.

### 3.5. Desalting Performances in Semi-Pilot Scale

Fig. 11 shows the pH and conductivity variations in the concentration (C-) and dilution (D-) compartments during a constant current (CC) operation (130 A m<sup>-2</sup>). Initially, in constant current mode, the system was operated under the LCD. However, the concentration of dilution compartment decrease according to time, and eventually the current reaches at the LCD condition. In the case of AMX membrane, drastic pH increase was observed over the LCD state. The pH of C-compartment varied from 5.6 to 11 during the first batch operation. However, there is no pH change

during the ED operation with the Py-AEM. The conductivity changes in C- and D-compartments at the same condition are shown in Fig. 11 (b). The change rates of conductivity representing a desalting property were almost same in the cases of both membranes.

## 4. Conclusions

Anion-exchange membranes containing pyridinium groups as the ion-exchangeable group were prepared and evaluated in terms of their electrochemical and water-splitting properties. The pyridinium membranes exhibited excellent electrochemical properties mostly comparable to those of the commercial membranes. Moreover, water splitting of the pyridinium membranes was much lower than those of the commercial membranes. For the pyridinium membrane, the resonance stability of the aromatic quaternary pyridinium 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 applicable feasibility of the pyridinium membranes in electrodialysis at the over-LCD condition was considered. The electrodialytic separation properties were evaluated using an electrodialysis system in a semi-pilot scale. The pyridinium membrane showed excellent desalting property



comparable to those of commercial membrane (AMX). In addition, the pH variation was negligible during the operation over the-LCD. From the results, it was revealed that the pyridinium membranes could be effectively utilized in the electro-membrane processes over the-LCD. It is also expected that the pyridinium membranes can be utilized for enhancing the current efficiency in water splitting electro dialysis (WSED). Since the WSED processes are usually operated in high current ranges (over  $1000 \text{ A m}^{-2}$ ), a loss of the current efficiency is possibly caused by the significant water dissociation in anion-exchange membranes during the operation. However, the long-term stability tests should be followed to commercialize the pyridinium membranes. Therefore, the tests for evaluating the long-term stability and researches for improving the membrane properties are in progress.

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