Preparation of Bipolar Membrane for Acid/Base Production and Studies on the Water Splitting Characteristics

Moon-Sung Kang, Yong Soo Kang, and Seung-Hyeon Moon*

Center for Facilitated Transport Membranes, Korea Institute of Science and Technology (KIST)
Department of Environmental Science and Engineering, Kwangju Institute of Science and Technology (K-JIST)*

산/염기 생산을 위한 바이폴라막의 제조 및 물분해 특성 연구

강문성, 강용수, 문승현*
한국과학기술연구원 촉진수송분리막 연구단
광주과학기술원 환경공학과*

1. Introduction

Electro-membrane processes using ion-exchange membranes (IEMs) have gained increased industrial importance since about 30 years ago when polymeric membranes with a high permselectivity became commercially available. There are many examples of applications, such as electrodialysis (ED) for the desalination of brackish water or the production of salts from seawater [1] and electrodeionization (EDI) for the production of ultra-pure water used for semi-conductor production or nuclear power coolants [2] etc. The electro-membrane processes are considered to be environment-friendly, as well as energy efficient, since the generation of salt wastes can be minimized in these processes [3]. As the government regulation to prevent water pollution becomes more stringent, the role of electro-membrane processes for the separation of ionic substances is becoming more important in the various chemical

and food industries.

Bipolar membranes in which the anion- and cation-exchangeable layers (AEL/CEL) are adjoined together in series easily split water molecules into protons and hydroxyl ions under a reverse bias condition. Recent developments in high performance bipolar membranes enable us to further expand the potential uses of electrodialysis in the chemical industries [4]. It is expected that water-splitting electrodialysis using bipolar membrane can make zero-emission possible and be applied as a clean technology without the production of undesirable by-products. Since water dissociation occurs at the bipolar junction, the water-splitting capability significantly depends on the interface characteristics [4]. Therefore, a clear understanding of the interrelation between the bipolar junction and water splitting is required when preparing high performance bipolar membranes. Many studies have progressed from this. Strathmann *et al.* proposed novel method for preparing a high-performance bipolar membrane by inserting a very thin polyelectrolyte complex layer at the bipolar junction [5]. Their investigation demonstrated that catalytic water dissociation could be promoted by introducing an intermediate layer at the bipolar junction. Tanioka *et al.* investigated the effect of polymer materials on water splitting in the bipolar membranes. Their results showed that the chemical composition of the anion-exchange layer plays an important role in water splitting in bipolar membrane [6]. From these previous researches, it can be concluded that the nature of fixed charge groups and the charge density at the bipolar junction are very important parameters dominating the water splitting characteristics.

Introduction of inorganic substances into the bipolar membrane is also known to be an effective technique for enhancing the water splitting performance [4]. Simons reported a method for preparing novel bipolar membranes using an alkaline solution of a metal salt (*e.g.* $CrCl_3$) as the binder [7]. Moreover, commercial Neosepta BPM (BP-1, Tokuyama Corp., Japan) was treated with an iron (III) chloride solution [4,8]. As described previously, however, the mechanism brought on by metallic compounds leading to a decrease in the water-splitting voltage is still unclear and a deeper investigation is needed. Additionally, the development of a more effective catalyst and immobilization method is of interest.

Since the water splitting properties are dependent predominantly upon the fixed charge density at the bipolar junction and the ionic permselectivity of the ion permeable layers, the performance optimization of a BPM can be achieved by controlling these two factors.

In this study, bipolar membranes with composite anion-exchange layers (AELs) were prepared to investigate the effect of the AEL composition on the water splitting characteristics of a BPM. Moreover, understanding of the water-dissociation mechanism induced by inorganic species is also very essential when preparing high performance bipolar membranes. Therefore, the role of inorganic substances (i.e., $Fe(OH)_3$ and silica groups) in the water splitting phenomena was investigated in the hope of furthering the understanding of the water splitting mechanism in ion-exchange membranes. Additionally, the immobilization of inorganic substances on the bipolar membrane junction was studied and the amount of inorganic catalysts that should be deposited to give optimum results was evaluated.

2. Experimental

Neosepta CM-1 (Tokuyama Corp., Japan) and Nafion117 (DuPont, USA) were utilized as the cation-exchange layer in the preparation of bipolar membranes. A traditional paste method was employed to prepare the anion-exchange layer. Vinylbenzyl chloride (VBC, Aldrich, USA) was selected as the F-monomer to introduce quaternary ammonium (QA) groups while styrene (Sty, Kanto Chem., Japan) was used for co-polymerizing. Divinylbenzene (DVB, Aldrich, USA) was used as the crosslinker and benzoyl peroxide (BPO, Fluka, Switzerland) as the initiator. In the monomer mixture, the weigh ratios of VBC/St were 3:1, 2:1, or 1:1 and while DVB was added to a concentration of 3 wt.%, 6 wt.%, or 10 wt.%. Acrylonitrile butadiene rubber (NBR) was added to the monomer mixture to enhance the mechanical properties of the membrane and the weight fraction of NBR to monomer mixture (VBC/Sty/DVB) was fixed at 1/6. As the active junction material, polyacrylonitrile (PAN, Mw.=168,000 Daltons, Hanil Synthetic Fiber Corp., Korea) was used without further purifications. To prepare another type of anion-exchange layer, glycidyl methacrylate (GMA, Tokyo Kasei Co., Japan) and divinyl benzene (DVB, Aldrich, USA) were used without further purification. Analytical grade pyridine (Py, Aldrich, USA) was used without further purification to introduce quaternary pyridinium groups into the base membrane. To prepare the multi-layered BPMs, a thin poly(Sty-DVB-VBC-QA) junction layer of different compositions was introduced before casting the AEL on cation-exchange membrane. In addition, very thin PAN layer was introduced at the bipolar (BP) junction by the spin coating method (spin

coater, KW-4A, Chemat Tech., INC., USA). The PAN-coated cation-exchange membranes were chemically modified using a 2 N NaOH solution and at 45 °C for 0.5-5.0 hrs. To immobilize the inorganic substances at the BP junction, Iron(III) chloride (Aldrich, USA) and tetraethoxylsilane (TEOS, $Si(OC_2H_5)_2$, Aldrich, USA) were employed as the precursors. The prepared membranes were washed with D.W. and then stored in 0.5 mol dm^3 NaCl for more than a day.

Water-splitting experiments were carried out in a cell with six compartments, separated by a Neosepta CMX cation exchange membranes (Tokuyama Corp.). Sodium sulfate solution (Na_2SO_4, 0.25 mol dm^3) was used as the electrolyte solution and a constant voltage (10 V) was supplied through the membrane cell with a power supply (HP 34410, HP, USA) through the membrane cell.

3. Results and Discussion

Variations in the water splitting fluxes of the BPMs according to their degrees of cross-linking are shown in Fig. 1. The results show that the water splitting fluxes mainly increased with increases in the degree of crosslinking in the AEL, as well as the fixed charge density at the junction. With a high degree of cross-linking (i.e., DVB 6-10 wt.%), however, there were no significant differences in the ion-permselectivities of the AELs (transport no. > 0.975), and, in these cases, the water splitting capabilities depended upon the water swelling property. It is known that when more hydrophilic polymers are used for the membrane matrix, there is an increase in the water-splitting capacity [9]. It seems that the enhanced hydrophilicity promotes the diffusion of water molecules into the junction layer and the transport of protons and hydroxyl ions. From the results, it was found that the water splitting performances of the BPMs could be optimized by controlling the fixed charge densities and the degrees of crosslinking in the AEL.
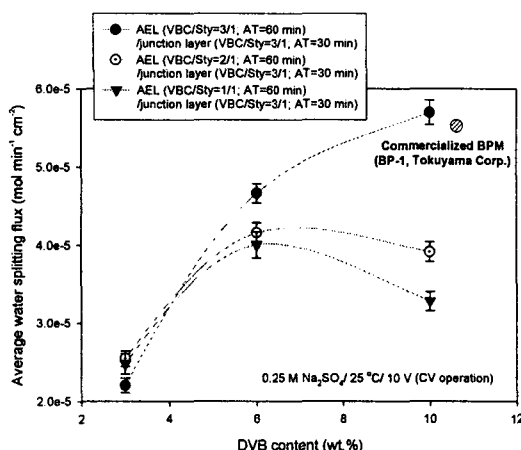
Fig. 1. Water splitting fluxes of prepared bipolar membranes containing different active junction layers according to the DVB contents of AEL.

Another method for enhancing the water splitting property of BPMs is the introduction of water splitting catalysts at the BP junction [4]. The catalysts for water dissociation can be classified as both organic functional groups and inorganic substances. The organic functional groups are generally weakly basic or acidic groups, such as tertiary/secondary amines (NR_2/NRH, R=alkyl groups) and carboxylic acids (COOH). In this study, alkali-treated polyacrylonitrile (PAN) was investigated as a possible active junction layer (AJL) within the BPM, and a very thin PAN layer was introduced by the spin coating method. As well known, the CN groups of PAN can be partially transformed into COOH and $CONH_2$ during the alkali-treatment [10] and these groups (CN, COOH and $CONH_2$) are classified as H-affinity groups [11]. Therefore, it was expected that the modified PAN layers adjoined with the AEL at the BP junction may function as an effective catalyst.

Table 1 shows the average water splitting fluxes and the increase rates (R_{WS}) of BPMs w/ or w/o active junction layer (alkali-treated PAN). The results obviously exhibit that the water splitting capabilities are dependent upon the components at the BP junction. The BPM containing quaternary ammonium groups (reacted with TMA) exhibited higher water splitting fluxes than the BPM in which pyridinium groups were introduced. In addition, the modified PAN junction layer significantly enhanced the water splitting flux of the BPM. The average water splitting fluxes increased with increases in the alkali-treatment time, indicating that the chemical transformation of PAN enhanced the

water splitting property of the membrane.

Table 1 Average water splitting fluxes and increase rates (Rws) of
BPMs w/ or w/o active junction layer (alkali-treated PAN)

Membranes	Average water splitting flux ($\times 10^5$, mol min^{-1}cm^{-2})	R_{ws} (%)
BP-1 (Tokuyama Corp., Japan)	5.58 ± 0.18	–
CM1-GMA-DVB-Py	2.92 ± 0.12	–
CM1-GMA-DVB-QA	3.16 ± 0.15	8.0
CM1 PNA-treated with NaOH for 30 min GMA-DVB-Py	4.01 ± 0.19	37.2
CM1 PNA-treated with NaOH for 1 hr GMA-DVB-Py	4.44 ± 0.12	52.0
CM1 PNA-treated with NaOH for 3 hr GMA-DVB-Py	4.56 ± 0.15	56.0
CM1 PNA-treated with NaOH for 5 hr GMA-DVB-Py	4.78 ± 0.17	63.5
CM1 PNA-treated with NaOH for 5 hr GMA-DVB-QA	5.54 ± 0.19	89.5

Fig. 2 (a) shows the variations in the water splitting fluxes
according to metal contents at the BP junction. The water splitting
fluxes increased with increases in the metal contents (~2.5 mg
Fe/cm^2). The result indicates that the iron hydroxides provide
alternative reaction paths for water dissociation by forming very
reactive, activated complexes [7]. However, the water splitting flux
decreased and then was leveled off at metal concentrations higher than
3.0 mg Fe/cm^2. It is believed that the excessive metal hydroxides
interfered with the polarization of the water molecules, occurring
between the sulfonic acid and quaternary ammonium groups, indicating
that an optimum metal concentration exists for water splitting. As
another inorganic substance for catalytic water dissociation, silica
groups were investigated. Fig. 2 (b) shows that the increase rate of
water splitting (Rwd) is enhanced with an increase in the
silica-treatment time. The maximum Rwd was found to be about 42 %
under the optimal condition. The results imply that the inorganic
substance provides alternative paths for water dissociation, but on the
other hand they can reduce the polarization effects between the sulfonic
acid and quaternary ammonium groups when present at high
concentrations. From the results, it can be concluded that the
concentration of the catalyst should be considered when optimizing the
water splitting properties of the bipolar membrane. Moreover, it was
revealed that the silica group (i.e. ≡Si-OH), as well as the metal

hydroxides, could be utilized as effective water splitting catalysts.
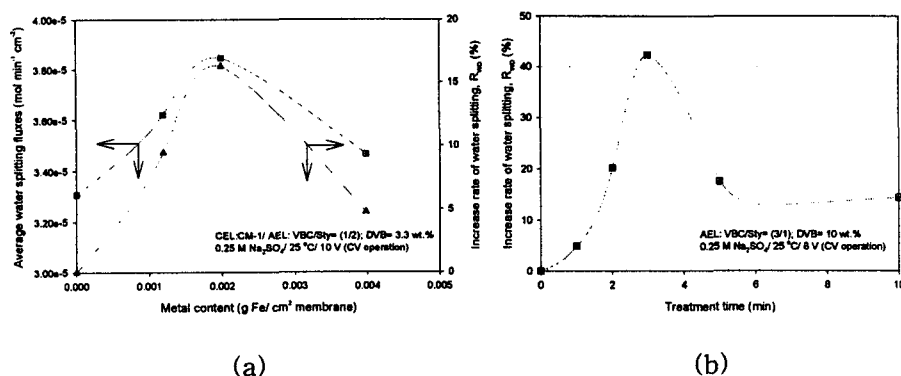

(a)   (b)

Fig. 2. Variations in water splitting fluxes and flux increase rates according to metal (Fe) contents at the BP junction (electrodeposition) (a) and silica-treatment time (b).

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