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A Study on water-splitting characteristics of bipolar membranes for acid/base generation

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산/염기 제조를 위한 바이폴라막의 물분해 특성 연구

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1. Introduction

The clean technology using ion exchange membranes have drawn attention increasingly with advancement of the membrane synthesis. Ion exchange membranes have been used for diffusion dialysis, electrodialysis, electrodialytic water splitting and electrodeionization. Bipolar membranes(BPM), consisting of a cation exchange layer and an anion exchange layer, can convert a salt to an acid and a base without chemical addition. Using the bipolar membrane, a large quantity of industrial wastes containing salts can be reprocessed to generate acids and bases. Recent development of high performance bipolar membranes enables to further expand the potential use of electrodialysis in the chemical industry[1]. The water-splitting mechanism in the bipolar membrane, however, is a controversial subject yet[1,2]. In this study bipolar membranes were prepared 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 water splitting mechanism by a metal catalyst was discussed.

2. Experimental

Bipolar membranes were prepared by binding a cation exchange membrane, CM-1 or CMS (Tokuyama Co.) and an anion exchage membrane, AM-1 or ACS (Tokuyama Co.) in conjunction with a metal catalyst, a binding agent, and a crosslinking agent. Of many metal catalysts reported in the literatures $FeCl_3$ and $Fe(OH)_3$ were used in this study[1]. Prior to binding, the membranes were immersed in 1 or 2 wt.% HEMA/MPD(2-hydroxyethyl metacrylate/m-phenylenediamine) monomer solution for 6 hrs. Then the membranes were bonded with a cross-linking agent, 1 wt.% TMC(trimesoyl chloride), using a hydraulic press at 4000 psi. The polymerization mechanims of PolyHEMA\MPD was shown in Figure 1. The prepared membranes were characterized in a WSED(water splitting electrodialysis) cell. HEMA, iron(Ⅲ) chloride hexahydrate, iron(Ⅲ) sulfate pentahydrate were obtained from Aldrich, MPD from Acros, TMC from TCI, and n-hexane from Merck.

3. Results and discussion

Figure 2 shows the polyHEMA/MPD layer, crosslinked with TMC, formed on the surface of CM-1 and AM-1. The surface roughness was well developed. Also Figure 3 shows the cross-section of the bipolar membrane prepared in this study. Superficial gap was not found between the membrane sheets. The voltage-current relations were presented in Figures 4 and 5. These results show that $Fe(OH)_3$ slurry performs better than $FeCl_3$ solution as catalyst and that the interface hydrophilicity is an important factor to improve the water splitting efficiency of bipolar membranes. The higher water splitting efficiency was observed at the higher metal contents. The water splitting mechanism by metal catalysts has been not clearly understood yet. One explanation for reversible catalytic reactions under basic conditions is following[3].

$$M^{2+} + 4H_2O \Rightarrow M(OH)_2 + 2H_3O^+$$
$$M(OH)_2 \Rightarrow M^{2+} + 2OH^-$$

In this reaction mechanism, the hydrophilic binder may increase the water activity by attracting water from ion exchange membranes. The WSED cell tests were carried out to determine the H^+ and OH^- flux by a metal catalytic reaction. The tested bipolar membranes were prepared using univalent ion exchange membranes(ACS/CMS) and aqueous iron(Ⅲ) sulfate solution as a binder. The concentration of the metal binding solution varied from 2 to 10 g/L and the membrane were tested at the current density upto 400 mA/cm^2. Figures 6 shows the relationship between the hydroxyl ion flux and the applied current densities at various metal contents. The flux of hydroxyl ion increased with the metal content and the applied current. However, at high metal contents the flux of OH^- seems to be inhibited by metal hydroxides that may interfere the contact of the two membrane sheets. The water contents of the prepared membranes were compared in Figure 7. This figure shows that as the contents of the HEMA and metal increase, the water content also increases. This result implies that the water splitting efficiency is enhanced by the wetness of the interface. It is concluded that the metal species immobilized in the membrane may decrease the resistance of a bipolar membrane by enhancing the reversible catalytic reactions and there exists an optimum metal concentration for the water-splitting.

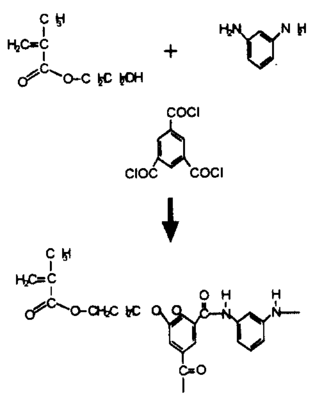
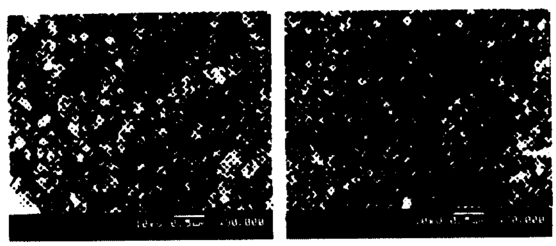


Fig. 1. Crosslinking mechanism of HEMA/MPD with TMC



(a) (b)

Fig. 2. SEM photographs of the pretreted

Fig. 3. SEM photograph of the BPM cross-section prepared in this study

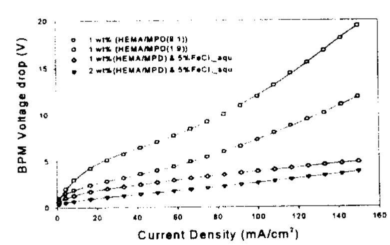


Fig. 4. Voltage-Current relation of the BPMs: Effect of the binder

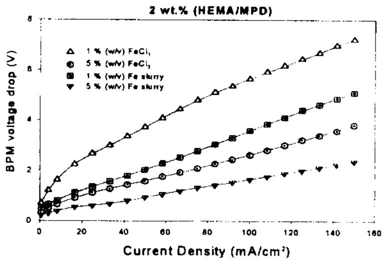


Fig. 5. Voltage-Current relation of the BPMs: Effect of the metal species

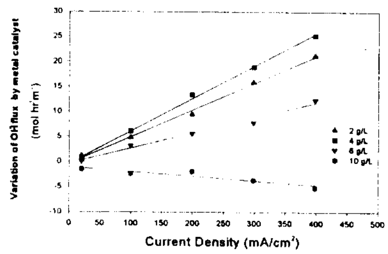


Fig. 6. Enhancement of water-splitting by the metal catalyst

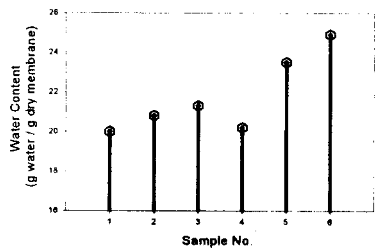


Fig. 7. Water content of the BPMs

(1) (HEMA+MPD) 2 wt%
(2) (HEMA+MPD) 1 wt% Fe (aq., 5 %)
(3) (HEMA+MPD) 2 wt% Fe (aq., 5 %)

4. References

1. R. Simons, *J. Memb. Sci.*, **78**, 13 (1993).
2. H. Strathmann, J. J. Krol, H. J. Rapp, and G. Eigenberger, *J. Memb. Sci.*, **125**, 123 (1997).
3. R. Simons, *Electrochimica Acta*, **30**, 275 (1985).

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