

전자선 가속기에 의해 방사선 처리한 양이온교환막을 이용한 전해-전기투석에 의한 HIx용액으로부터 HI의 농축

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Electro-electrodialysis Using the Radiation-treated Cation Exchange Membrane by Accelerated Electron Radiation to Concentrate HI from HIx Solution

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요약: HI몰랄리티가 9.5 mol/kg-H₂O인 HI의 전해-전기투석을 시판의 양이온교환막(CMB)을 이용하여 요오드의 존재 하에 실험을 진행하였다. 수소이온 투과의 선택성을 증가시키기 위해, 막은 전자선 가속기를 이용하여 방사선 처리하였다. 방사선 처리한 막의 막특성(막 저항, 이온교환용량, 함수율)을 측정하였다. 각각의 방사선량에서 처리한 막의 2 mol/dm³의 KCl 용액에서의 막저항, 이온교환용량과 함수율은 처리하지 않은 막과 거의 동등의 값을 가졌다. HI몰랄리티가 9.5 mol/kg-H₂O인 HI의 전해-전기투석을 75°C, 9.6 A/dm²에서 진행하였다. 전자선 가속기에 의해 방사선 처리한 양이온교환막은 처리하지 않은 막과 비교하여 고분자의 가교구조와 함께 수소이온투과의 높은 선택성을 가졌다.

Abstract: Electro-electrodialysis of hydriodic acid with HI molality of ca. 9.5 mol/kg-H₂O was examined in the presence of iodine using a commercial cation exchange membrane, CMB, as a separator. For the increase of the selectivity of proton permeation, the membrane was radiation-treated by accelerated electron radiation. The membrane properties (area resistance, ion exchange capacity, water content) of the radiation-treated membranes were measured. The area resistance in 2 mol/dm³ KCl solution, ion exchange capacity and water content of the radiation-treated membranes at each dose rate had almost the same value as that of the non-treated membrane (original of CMB membrane). Electro-electrodialysis of hydriodic acid with HI molality of ca. 9.5 mol/kg-H₂O was examined at 75°C with 9.6 A/dm². The radiation-treated cation exchange membrane by accelerated electron radiation had higher selectivity of the proton permeation by cross-linking structure of polymer than that of the non-treated membrane.

Keywords: electro-electrodialysis, cation exchange membrane, cross-linking, irradiation, thermochemical hydrogen production

1. Introduction

IS (iodine-sulfur) process [1-10] have been investigating for the thermochemical hydrogen production processes using heat energy from nuclear. In KIER

(Korea Institute of Energy Research), IS process is under investigating with KAERI (Korea Atomic Energy Research Institute) [11].

In the IS process, HI is separated form HIx solution (HI-H₂O-I₂ mixture) that was supplied from Bunsen reaction and then decomposed to produce hydrogen. Simple option to realize the chemical change is the dis-

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tillation of HIx solution and the gas phase thermal decomposition of HI. However, because of the presence of azeotropic composition in HI-H₂O mixtures (the molar ratio of HI : H₂O = 1 : 5), the distillation requires a lot of excess thermal burden [6,7].

In the improving the HI processing scheme, JAERI (Japan Atomic Energy Research Institute) are pursuing an application of two types of membrane technologies [3,4]. One is a hydrogen-permselective ceramic membrane to be used in the membrane reactor to enhance one-pass conversion of equilibrium-limited HI decomposition reaction in the gas phase [3-5]. The other concerns utilization of ion exchange membranes for enhancing HI molality of HI-I₂-H₂O mixture (hereafter termed as "HIx solution") in order to facilitate the separation of pure HI.

As for the later one, concentration of hydriodic acid using polymeric membranes at elevated temperature has been studied [6,7]. Therefore, an electro-membrane process using cation exchange membrane was reported in a previous paper [7]. This electro-membrane process had frequently been termed as electro-electrodialysis (EED).

Fig. 1 shows the concept for concentrating HI from HIx solution by EED.

When glassy carbon was used as electrodes in HIx solution (HI-H₂O-I₂ mixture solution), the electrode reaction was the redox reaction of iodine-iodide ions. Consequently, with the help of selective proton permeation through the membrane, it is expected that the aimed "concentration" is possible in the sense that HI molality of catholyte increases while that of anolyte decreases.

For the purpose of applying electro-dialysis process under high temperature and strongly oxidizing conditions, ion exchange membrane should be a more stable and have higher permselectivity.

Hwang and Ohya [12,13] reported that the cross-linked ion exchange membrane having a base polymer such as polyethylene and polysulfone by accelerated electron radiation showed good chemical stability in 4

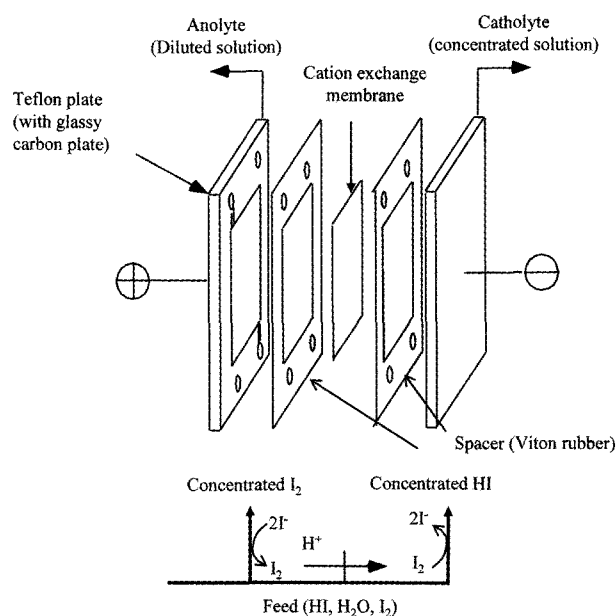


Fig. 1. Concept of an electro-electrodialysis for concentrating HI from HIx solution (HI-H₂O-I₂ mixture solution).

mol/dm³ H₂SO₄ solution and increased a permselectivity as a separator for the all-vanadium redox flow battery.

The aim of this paper is to increase a permselectivity of commercially available cation exchange membrane (CMB). In general, it is well known that the base polymer of CMB, polystyrene, could be cross-linked by accelerated electron radiation [14].

In this study, it was carried out the radiation-treatment of CMB cation exchange membrane by accelerated electron radiation, and evaluated the permselectivity by the EED process for the concentration of HI from the HIx solution.

2. Experimental

2.1. Chemicals and Membrane

Hydriodic acid (56 wt.%) and iodine of reagent grade were purchased from Kanto Chemical Co. and used without further purification. The commercial cation exchange membrane, CMB (TokuyamaCo.), was employed in the experiments.

2.2. Radiation-treat of the Membrane

CMB was radiation-treated by accelerated electron radiation. A high-energy accelerator was used as the accelerated electron radiation source. The accelerated electron radiation was irradiated with a 2 MeV and current of 20 mA (25 kGy or 2.5 Mrad/pass). Radiation-treatment of the membrane was conducted under doses of 25, 50, 75, 100, 150, 200 and 250 kGy.

2.3. Membrane Properties

(Membrane area resistance in 2 mol/dm³ KCl aqueous solution, Ion Exchange Capacity and water content)

The measurement methods and experimental apparatus for membrane area resistance, ion exchange capacity (IEC) and water content were same as reported earlier by Hwang *et al.* [12,15].

2.4. Experimental Set Up for EED

Experimental apparatus was composed of a cell, two reservoirs, and two peristaltic pumps, and, was same as reported earlier by Onuki *et al.* [7]. Considering the corrosive nature of HIx solution, the end plate and the spacer were made of Teflon, the gasket was made of Viton, and the electrode was made of glassy carbon (GC-20, Tokai Carbon). Effective membrane size was 12 × 80 mm (9.6 cm²). Thermocouples were set in glass sheaths just at the outlet of the cell to monitor the temperature of test solution. Reservoir was made of glass and dipped in an oil bath for heating solution. Vapor pressure of HIx solution is known to increase steeply with increasing HI molality in the range higher than ca. 10 mol/kg-H₂O. So, in order to avoid the pressure increase in the glass reservoir and also to minimize the dissipation of HI vapor, the reservoir was equipped with a long and narrow neck connected to a vent line of draft chamber.

2.4.1. Concentration by EED

Experiments were carried out under constant D.C. current. Amounts of HIx solution fed to the anolyte and the catholyte reservoir were 200 and 120 mL, respec-

tively. Flow rates of the solution were 100 cm³/min, which corresponded to a linear velocity of ca. 2 cm/s in the cell. Preliminary experiments showed that the cell voltage was proportional to current in the examined range, i.e. up to 9.6 A/dm². The experiment was carried out at 75°C for 4 hours. In the course of EED, compositions of anolyte and catholyte were measured periodically by titration with a sample of 0.1 mL.

2.4.2. Transport Properties of Membrane

In the measurements of apparent transport number of proton (t_+) and apparent electro-osmosis coefficient (β), electricity equivalent to ca. 25% of the amount of HI fed to catholyte was supplied and then changes amounts of respective species, HI and H₂O, in catholyte were measured. The transport properties were calculated by the following equations that were derived from the mass balance in catholyte taking the changes due to electrode reaction into account.

$$t_+ = \frac{F\Delta M_{HI}^C(t)}{it} \quad (1)$$

$$\beta = \frac{F\Delta M_{H_2O}^C(t)}{it} \quad (2)$$

3. Results and Discussion

3.1. Membrane Properties

Fig. 2 shows the relationship between the area resistance in 2 mol/dm³ KCl aq. solution and dose.

The area resistances were 1.87 $\Omega \cdot \text{cm}^2$ for the non-treated membrane (original of CMB membrane), and 1.7~1.82 $\Omega \cdot \text{cm}^2$ for the radiation-treated membranes by accelerated electron radiation on the CMB membrane at each dose rate. The area resistance of the radiation-treated membranes had almost the same value as that of the non-treated membrane. It is expected that the radiation-treatment behavior of CMB membrane by accelerated electron radiation do not affect on the area resistance in 2 mol/dm³ KCl aq. solution.

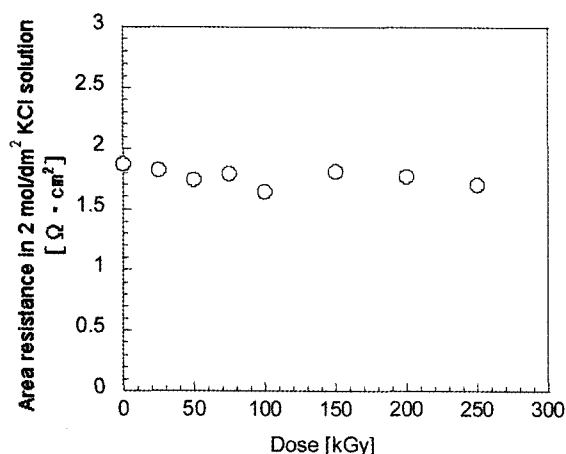


Fig. 2. Relationship between the area resistance in 2 mol/dm³ KCl solution and dose.

Fig. 3 shows the relationship between the ion exchange capacity and water content, and dose.

The ion exchange capacities and water contents were 1.2 meq./g-dry-membrane and 0.145 g-H₂O/g-dry-membrane for the non-treated membrane (original of CMB membrane), respectively, and 1.1~1.3 meq./g-dry-membrane and 0.135~0.153 g-H₂O/g-dry-membrane for the radiation-treated membrane at each dose rate, respectively. The ion exchange capacity and water content of the radiation-treated membranes at each dose had almost the same value as that of the non-treated membrane. It is expected that the radiation-treat behavior of CMB membrane by accelerated electron radiation do not affect the ion exchange capacity and water content.

Those above results cause as follow; the radiation-treat of ion exchange membrane by accelerated electron radiation mainly occurs in polymer chain (here, polystyrene), and a number of the ion exchange groups in the radiation-treated membrane do not change as compared with before the radiation-treatment as confirmed by fluorometric analysis in the previous paper [12].

3.2. Concentration of HIx Solution by EED

Fig. 4 shows an evolution of molalities of HI and I₂ of non-treated membrane and radiation-treated membrane at 50 kGy in a typical experiment at 75°C with 9.6 A/dm². In EED with each membrane, the molality

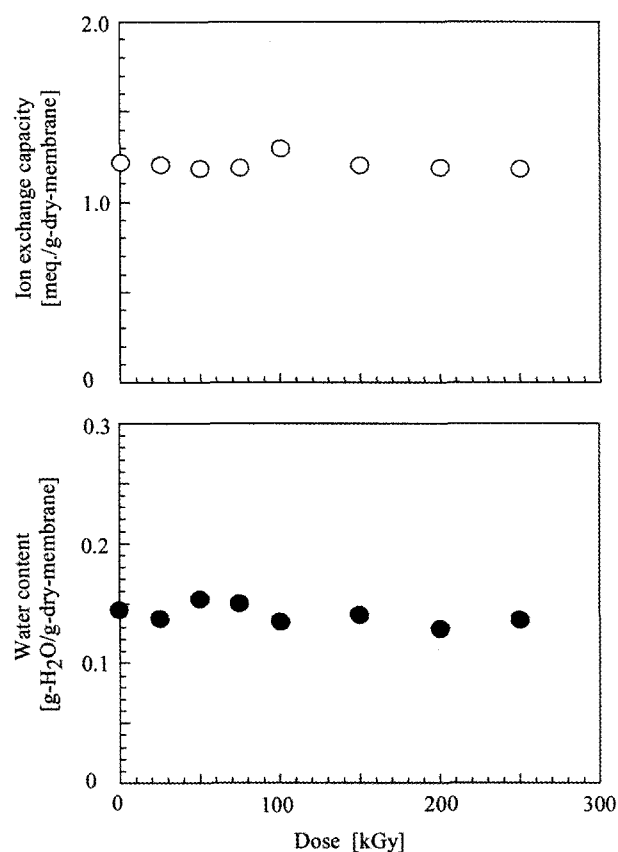


Fig. 3. Relationship between the ion exchange capacity and water content, and dose.

of HI in catholyte increased from the starting value of 9.5 mol/kg-H₂O to a final one of over 10.5 mol/kg-H₂O, whereas that of anolyte decreased from 9.5 to 9 mol/kg-H₂O. These changes were qualitatively in accord with the expectation that took into account the electrode reaction I/I_2 and the selective proton permeation through the membrane. The molality of HI in catholyte will be more increase with a increase of the EED operation time, whereas that of anolyte will be decrease as shown in earlier reported our paper [7].

Apparent transport number of proton (t_+) and apparent electro-osmosis coefficient (β) were 0.67 and 1.3 mol/Faraday for non-treated membrane, respectively, and 0.73 and 0.8 mol/Faraday for the radiation-treated membranes at 50 kGy, respectively.

The apparent transport number of the radiation-treated membrane at 50 kGy was higher than that of the non-treated membrane. It seems that the apparent transport

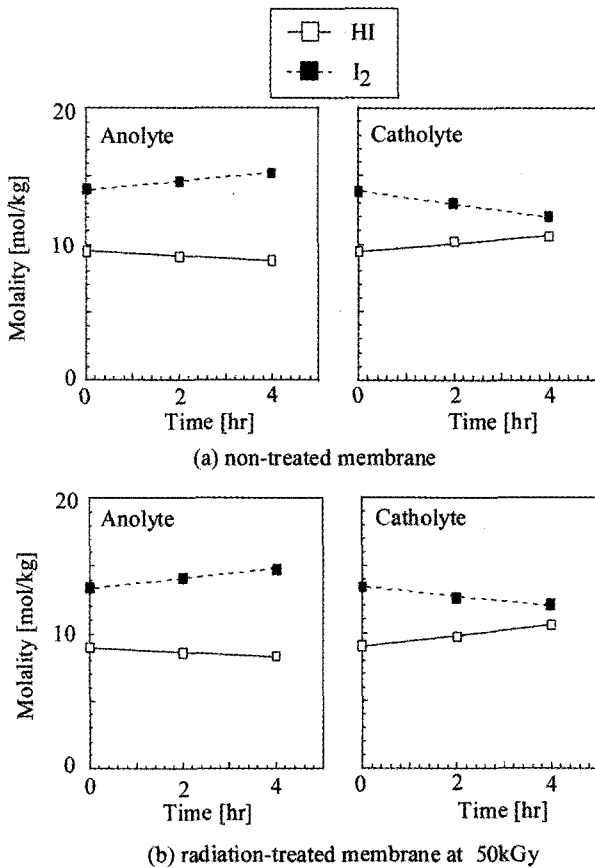


Fig. 4. Evolution of molalities of HI and I₂ in a concentration experiment by EED at 75°C with 9.6 A/dm². Initial composition: [HI] = 9.5 mol/kg-H₂O, [I₂] = 14 mol/kg-H₂O.

number of proton increased with cross-linking structure by accelerated electron radiation.

3.3. Transport Number and Electro-osmosis Coefficient

Fig. 5 shows the relationship between the apparent transport number and the dose after 4 hrs of EED experiment at 75°C with 9.6 A/dm².

With an increase of dose, the apparent transport number increased from 0.67 (0 kGy, original of CMB membrane), and passed through a maximum value of 0.93 at 150 kGy, and then decreased. From this result, the radiation-treatment of CMB membrane was suitable below 150 kGy of dose from the viewpoint of the proton selectivity. When a number of cross-links are formed, the original polystyrene becomes a three-di-

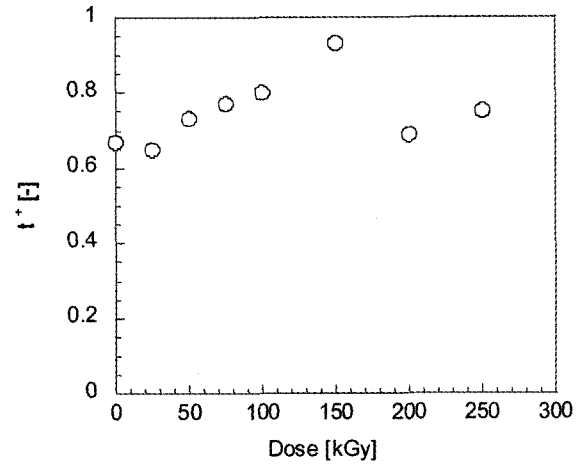


Fig. 5. Relationship between the apparent transport number and dose after 4 hrs of EED experiment at 75°C with 9.6 A/dm². Initial composition: [HI] = 9.5 mol/kg-H₂O, [I₂] = 14 mol/kg-H₂O.

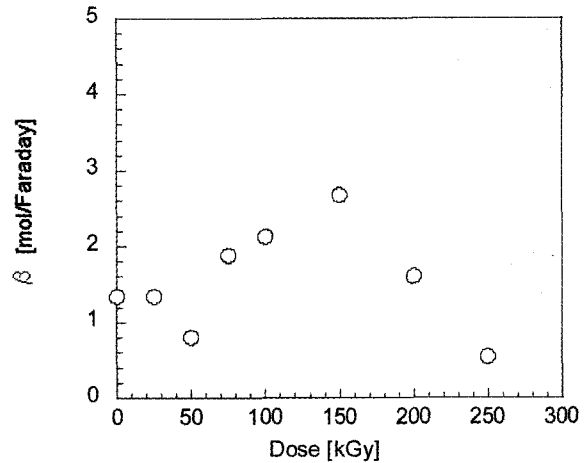


Fig. 6. Relationship between the electro-osmosis coefficient and dose after 4 hrs of EED experiment at 75°C with 9.6 A/dm². Initial composition: [HI] = 9.5 mol/kg-H₂O, [I₂] = 14 mol/kg-H₂O.

mensional network [16]. It seems from this fact that the radiation-treated membrane at each dose rate had higher selectivity of the proton permeation than that of the non-treated membrane due to the formed a three-dimensional network.

Fig. 6 shows the relationship between the electro-osmosis coefficient and the dose after 4 hrs of EED experiment at 75°C with 9.6 A/dm².

With an increase of dose, the electro-osmosis coefficient increased from 1.3 mol/Faraday (0 kGy, origi-

nal of CMB membrane), and passed through a maximum value of 2.7 at 150 kGy, and then decreased. In the cation exchange membrane, the proton passed through the membrane to form H_3O^+ . It seems from this fact that the electro-osmosis coefficient increased due to the increased proton selectivity.

The concentration of HI after 4 hours in EED experiment with the non-treated membrane increased about 11%, and that of the radiation-treated membrane at each dose rate increased about 12%. It seems that this little difference of HI concentration was caused by the increased electro-osmosis coefficient with an increase of the proton selectivity. It is supposed that the almost same concentration of HI after 4 hours in EED experiment with the radiation-treated membrane at each dose rate was also caused by this reason.

For the further study, the effect of radiation-treatment of CMB membrane in EED operation should be studied for the durability in HIx solution.

4. Conclusions

1) For the increase of the selectivity of proton permeation, the membrane was radiation-treated by accelerated electron radiation.

2) The area resistances in 2 mol/dm³ KCl solution were 1.87 $\Omega \cdot \text{cm}^2$ for the non-treated membrane (original of CMB membrane), and 1.7~1.82 $\Omega \cdot \text{cm}^2$ for the radiation-treated membranes by accelerated electron radiation on the CMB membrane at each dose rate. The ion exchange capacities and water contents were 1.2 meq./g-dry-membrane and 0.145 g-H₂O/g-dry-membrane for the non-treated membrane, respectively, and 1.1~1.3 meq./g-dry-membrane and 0.135~0.153 g-H₂O/g-dry-membrane for the radiation-treated membrane at each dose rate, respectively. The membrane properties of radiation-treated membranes at each dose rate had almost the same value as that of non-treated membrane.

3) Electro-electrodialysis of hydriodic acid (HI molality of ca. 9.5 mol/kg-H₂O) with I₂ molality of ca. 14

mol/kg-H₂O was examined for 4 hours at 75°C with 9.6 A/dm².

4) The maximum apparent transport number of radiation-treated membrane was 0.93, which is higher than that of non-treated membrane (0.67, original of CMB membrane). It is expected that the radiation-treatment of the membrane by accelerated electron radiation had higher selectivity of the proton permeation than that of the non-treated membrane.

Nomenclature

F :	Faraday constant
i :	Current density (A/dm ²)
$\Delta M_i^j(t)$:	amount of "i" component in "j" solution at time t (mol)
t :	time (s)
t_+ :	transport number of proton

Greek letters

β :	electroosmosis coefficient (mol/Faraday)
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