TRANSPORT PROPERTIES OF ANION-EXCHANGE MEMBRANE PREPARED FOR PRODUCING HYDROGEN PEROXIDE IN ACIDIC SOLUTIONS BY ELECTRODIALYSIS OF PEROXIDE IONS

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Anion-exchange membranes were prepared by the impregnation method for electrodialysis of peroxide ions generated by electroreduction of oxygen in alkaline solutions. Microporous polyethylene film was soaked with chloromethylstyrene, divinylbenzene and benzoyl peroxide, and polymerized by hotpress. Anion-exchange membranes were obtained by treatment of the resultant polymer film with trimethylamine. The degree of crosslinking (DOC) was varied in the range of 0–30%. The membrane resistivity increased because of the decrease in water content, and the permselectivity of the peroxide ion decreased with increasing DOC. Electroosmotic water increased in volume with decreasing DOC. Transport properties of synthetic membranes were compared with those of commercial membranes including ACLE-5P, AM-1 and SF-17. The synthetic membrane of 5% DOC had the lowest resistivity among all membranes used in this work. The energy consumption to produce unit mole of hydrogen peroxide using synthetic membranes of 5–10% DOC was competitive with that using ACLE-5P.

Introduction

The on-site generation of hydrogen peroxide by electroreduction of oxygen was studied in an electrolyzer of three compartments separated by cation and anion exchange membranes.^{2,9,10} The hydroxide and peroxide ions were transferred by electrodialysis through an anion-exchange membrane from the catholyte to the center electrolyte. As desirable properties of an anion-exchange membrane, the permselectivity of the peroxide ion to hydroxide ion, lower membrane resistivity and durability during electrolysis are postulated. The ACLE-5P membrane described in the previous paper⁹ was found to have durability against the alkaline peroxide but also showed high membrane resistivity.

The thought that it might be possible to decrease the membrane resistivity led to this study, the objectives of which were to prepare anion-exchange membranes by the impregnation method and to

compare transport properties of synthetic membranes with those of commercial membranes.

1. Experimental

1.1 Procedure of membrane synthesis

Microporous polyethylene film Hipore 2200 (Asahi Chem. Ind.) was impregnated with chloromethylstyrene, divinylbenzene and benzoyl peroxide, followed by hotpress polymerization for 1 hour at 373–383 K and for 16 hours at 353 K. Synthetic procedures were determined with reference to those used in the past^{3,4}. The paste method^{5,6} was employed to prepare cation-exchange membrane. Since polyvinyl chloride (PVC) used for preparing the monomer paste in the paste method is known to be less tolerable in concentrated alkaline solution, an impregnation method without PVC powders and with polyethylene film instead of PVC clothes was employed in this work. The resultant polymer film was checked by a leakage of liquid methanol to confirm that the film had no pin-holes. The film was quaternized with a mixed solution of aqueous

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solution of 30% trimethylamine and acetone with a volume ratio of 2:1 for 24 hours at ambient temperature. The resultant membrane was washed in distilled water and stored in 3% NaCl aqueous solution. Membrane properties such as water content, ion-exchange capacity and membrane resistivity were measured using Cl-type membranes according to a commonly used procedure⁵. Commercial membranes of NEOSEPTA AM-1, ACLE-5P (Tokuyama Soda) and TOSFLEX SF-17 (Tosoh) were employed for comparison. AM-1 is a conventional hydrocarbon membrane for demineralization, ACLE-5P is a hydrocarbon membrane tolerable in alkaline solutions, and SF-17 is a perfluorocarbon membrane¹ for special use.

1.2 Electrolysis

The electrolyzer consisted of three compartments separated by anion and cation exchange membranes. A constant current flowed between the DSE anode and the graphite felt cathode. **Figure 1** shows a schematic diagram of reactions and ionic transport in the three compartments. Successive and competitive reactions occur on the cathode as described below⁸

The following reaction occurs on the anode.

The peroxide and hydroxide ions transfer across an anion-exchange membrane from the catholyte to the center, and the hydrogen ion transfers across a cation-exchange membrane from the anolyte to the center. Hydrogen peroxide and water are generated in the center electrolyte.

Oxygen was sparged at a flow rate of $3.3 \times 10^{-5} \text{ m}^3 \cdot \text{s}^{-1}$ into the packed-bed cathode flowing $1 \text{ kmol} \cdot \text{m}^{-3}$ KOH aqueous solution. A cation-exchange membrane CM-2 (Tokuyama Soda) was employed as a separator between the center electrolyte and the anolyte, which were both $1 \text{ kmol} \cdot \text{m}^{-3}$ H_2SO_4 aqueous solutions. Initial volumes of catholyte, center electrolyte and anolyte were $1\text{--}1.5 \times 10^{-4} \text{ m}^3$, $8.0 \times 10^{-5} \text{ m}^3$ and $1.0 \times 10^{-4} \text{ m}^3$ respectively, and were recycled from respective reservoirs to the electrolyzer at a flow rate of $2.0 \times 10^{-7} \text{ m}^3 \cdot \text{s}^{-1}$. The effective area where the current flowed was 50 cm^2 . Bed depths of felt cathode, center and anolyte compartments were 10 mm, 7.9 mm and 5 mm respectively. Concentrations of HO_2^- in alkaline catholyte and H_2O_2 in acidic center electrolyte were determined by sampling aliquots. The terminal voltage and electrolyte volumes

Fig. 1. Schematic diagram of transport of ions and water by electrodialysis

Table 1. Membrane properties

Membrane	W	Q_m	R_a	α	β
SYN-2	1.40	1.03	0.314	11.0	3.3
SYN-5	0.773	1.34	0.902	10.0	2.1
SYN-10	0.410	1.45	1.03	6.0	0.9
SYN-20	0.338	1.57	2.22	5.7	1.3
SYN-30	0.274	1.52	2.50	5.5	1.7
ACLE-5P	0.219	0.897	14.7	6.1	0.34
SF-17	0.180	1.20	2.15	6.1	0.34
AM-1	0.249	1.54	1.62	—	—

W : $\text{kg} \cdot \text{H}_2\text{O} \cdot \text{kg}^{-1} \cdot \text{dry mem}$; Q_m : $\text{kmol} \cdot \text{m}^{-3} \cdot \text{wet mem}$; R_a : $\Omega \cdot \text{cm}^2$

were measured at specified amounts of electricity. Partial potential differences in the electrolyzer were estimated by the potential profile as measured by using Pt probes.⁹ Details of the electrolyzer and the electrolysis procedure were described in previous papers⁷⁻⁹.

2. Results and Discussion

2.1 Membrane properties

The degree of crosslinking was varied within the range from 0% to 30%. The membrane thickness ranged from $100 \mu\text{m}$ to $150 \mu\text{m}$. **Table 1** shows membrane properties of the Cl-type membranes. The synthetic membrane is abbreviated, as SYN-2 for example, where the numeral refers to the degree of crosslinking (DOC). The synthetic membrane with 2% DOC had extremely high water content and became swollen in aqueous solutions. The Cl^- ion associating with fixed charge was stripped by KNO_3 solution and the concentration of Cl^- ion was determined by Mohr's titration. The ion exchange capacity Q_m based on the volume of wet membrane increased because of shrinkage of the membrane with increasing DOC.

2.2 Transport number of peroxide ion

Figure 2 shows the number of peroxide moles in the catholyte and the center electrolyte with increasing amount of electricity Q . The number of peroxide moles, m_{BP} , in the center electrolyte at a certain value of Q became lower in the order ACLE-5P, SYN-10, SF-17. The lines depicted in Fig. 2 are calculated ones according to the model analysis reported previously⁹.

Fig. 2. Change in peroxide moles in catholyte and center electrolyte with increasing amount of electricity

The number of peroxide moles, m_{AP} , in the catholyte increased and approached saturated value with increasing amount of electricity because the generation of peroxide ions by electrolysis became balanced with the transport of peroxide ions across the membrane. The top of the figure shows the change of overall current efficiency Ce with Q . The Ce became lower in the order ACLE-5P, SYN-10, SF-17.

Figure 3 shows the effect of degree of crosslinking of synthetic membrane on production of peroxide. The m_{BP} and Ce values became lower with increasing degree of crosslinking. The higher the permselectivity of the membrane, the higher was value of Ce . Since the concentration of peroxide ion decreases by chemical reaction in alkaline solutions ($2HO_2^- \rightarrow 2OH^- + O_2$), higher permselectivity of peroxide ions might lead to higher current efficiency. Detailed factors affecting the overall current efficiency will be the focus of future study.

Transport number t_p of the peroxide ion, defined as the ratio of the flux of peroxide ion to the total flux transferred across the anion-exchange membrane, was calculated from the increment in moles of peroxide in the center compartment with respect to the incremental amount of electricity.

Figure 4 shows the changes in t_p of synthetic membranes of different DOC's with increasing amount of electricity. The t_p gradually increased to saturation with increasing amount of electricity Q . The saturation value of t_p maximized for SYN-10.

Fig. 3. Effect of degree of crosslinking of synthetic membrane on production of peroxide moles

Fig. 4. Change in transport number of peroxide ion with increasing amount of electricity

Since the intramembrane structure of high-DOC membrane became more dense, as was evidenced by the results⁵⁾ for a cation-exchange membrane, peroxide ion with larger ion radius than that of the hydroxide ion might be controlled to the transport across the membrane.

2.3 Electroosmotic water

Electrolyte volumes of the three compartments were varied with electrolysis period. It is necessary to clarify the effects of electroosmotic water related to the transporting ion, generation and consumption of water by the reaction, evaporation and pressure-driven transport on the total volume change. The α number of water moles hydrates on HO_2^- mole and the β number of water moles hydrated on unit OH^- mole.

The hydrogen ion is accompanied by water as the hydronium ion. The change in electrolyte volume was estimated from the mass balance in each compartment.

Mass change in anolyte was affected by anode reaction, transporting hydrogen ion and hydrating water.

$$\rho_C \Delta V_C = -\left\{\left(\frac{1}{4}\right) \cdot 32 + 1 + 18\right\} \frac{Q}{F} = -27 \frac{Q}{F} \quad (5)$$

Mass change in center electrolyte was affected by the input HO_2^- , the hydrating water of HO_2^- , the input OH^- , the hydrating water of OH^- , pressure-driven transport from catholyte, the input H^+ , and the hydrating water of H^+ .

$$\begin{aligned} \rho_B \Delta V_B = & (33 + 18\alpha)m_{BP} + (17 + 18\beta)\left(\frac{Q}{F} - m_{BP}\right) \\ & + v_p t \rho_w + \frac{19Q}{F} \end{aligned} \quad (6)$$

Mass change in the catholyte was affected by the transporting HO_2^- , the hydrating water of HO_2^- , the transporting OH^- , the hydrating water of OH^- , pressure-driven water, evaporation, and the cathode reaction.

$$\begin{aligned} \rho_A \Delta V_A = & -(33 + 18\alpha)m_{BP} - (17 + 18\beta)\left(\frac{Q}{F} - m_{BP}\right) \\ & - (v_p + v_e)t\rho_w + \frac{16Q}{F} \end{aligned} \quad (7)$$

Figure 5 shows changes in electrolyte volumes with increase in Q . From preliminary experiments, v_e was obtained as $1.4 \times 10^{-10} \text{ m}^3 \cdot \text{s}^{-1}$, and v_p ranged from 1.7 – $2.8 \times 10^{-10} \text{ m}^3 \cdot \text{s}^{-1}$ for different membranes and the average value of $2.2 \times 10^{-10} \text{ m}^3 \cdot \text{s}^{-1}$ was adopted for calculation. The pressure difference between the catholyte and the center electrolyte was caused by sparging oxygen into the packed-bed cathode. The following values were used as electrolyte densities: $\rho_A = 1045 \text{ kg} \cdot \text{m}^{-3}$, $\rho_B = \rho_C = 1070 \text{ kg} \cdot \text{m}^{-3}$. The change in anolyte volume is well expressed by the relationship of Eq. (5). The assumption of the hydronium ion was ascertained to be true. The α and β values were determined by the least-squares method to fit the data of the catholyte and the center electrolyte. The α values were larger than β , as shown in Table 1. The hydration numbers α and β of SYN-2 and SYN-5 were higher than the others. The membrane of high t_p had large values of α and β . The objectives of preparing a membrane having both high t_p and less transport of osmotic water seem to be contradictory.

2.4 Membrane resistivity

The resistivity R_a of the membrane soaked in $0.5 \text{ kmol} \cdot \text{m}^{-3}$ NaCl aqueous solution increased because of the decrease in water content with increasing DOC. R_a of ACLE-5P was highest among the

Fig. 5. Changes in electrolyte volumes of three compartments with increasing amount of electricity

Fig. 6. Change in potential difference of components in electrolyzer with amount of electricity

membranes tabulated in Table 1. **Figure 6** shows differences of electric potentials of components in the electrolyzer, which consisted of the felt cathode including the catholyte, the anion-exchange membrane, the membrane supporter, the center electrolyte, the cation-exchange membrane, the anolyte and the anode. The potential difference of the anion-exchange membrane was dominant except those of anode and cathode, and gradually increased with increasing Q . The potential difference of SYN-10 was lower than that of ACLE-5P, 1.56 – 2.22 V , which was reported previously⁹⁾. The membrane resistivity R_a was calculated by use of the potential difference $\Delta\phi_m$ between the opposite sides of the membrane, with and without the current.

$$R_a = \frac{S(\Delta\phi_m - \Delta\phi_{m(I=0)})}{I} \quad (8)$$

Figure 7 shows the relation between R_a and the concentration ratio C_{AP}/C_{AH} for different membranes. R_a was found to increase to its saturation with increasing C_{AP}/C_{AH} . The change in R_a with the concentration ratio C_{AP}/C_{AH} was considered to reflect the change in t_p . The R_a of SYN-5 was lowest among those tested.

The cation-exchange membrane prepared by the paste method had its minimum resistivity at a DOC of 0.02, at which the fraction of polyelectrolyte phase within a membrane maximized.⁶⁾ The low t_p of SYN-2 as shown in Fig. 4 and the high R_a of SYN-2 shown in Fig. 7 might be caused by the low fraction of polyelectrolyte phase within the membrane because of the high water content.

The R_a value of SF-17 membrane was high and was not consistent with the result of Takenaka *et al.*¹⁰⁾ In our work, the anion-exchange membrane was directly attached to the felt cathode and open to oxygen gas. The direct contact of oxygen gas with the membrane might cause the increase in its membrane resistivity. When a dummy compartment, 10 mm in depth, of the alkaline electrolyte without oxygen bubbles was composed between the anolyte and the center compartment, the R_a of SF-17 showed a lower resistivity, as depicted in Figure 8. The SF-17 membrane is a perfluorocarbon-type membrane, and is considered to have sorbed the gas within the membrane. The membrane resistivity of ACLE-5P measured in a three-compartment electrolyzer was consistent with that measured in a four-compartment electrolyzer to prevent oxygen gas from directly contacting the membrane.

2.6 Energy consumption

Figure 9 shows the change in terminal voltage during electrolysis. The terminal voltage V_t increased gradually with increasing amount of electricity because of the increment of membrane resistivity mentioned above. The V_t value for SYN-30 was highest among those for all membranes used in this work. The V_t values for SYN-5 and SYN-10 were lower than those for synthetic membranes, and also for ACLE-5P and SF-17.

Figure 10 shows the change in energy consumption during electrolysis. The energy consumption Ec per unit mole produced in the catholyte and the center electrolyte was defined as follows.

$$Ec = \int_0^Q V_t dQ / (m_{AP} + m_{BP}) \quad (9)$$

The Ec for SYN-5 was lowest among those for all membranes used in this work. The Ec values for SYN-5 and SYN-10 were competitive to that for ACLE-5P, and indicated an almost constant value of $1 \times 10^6 \text{ J} \cdot \text{mol}^{-1}$ ($8.2 \text{ kWh} \cdot \text{kg}^{-1} \cdot \text{H}_2\text{O}_2$) through the electrolysis period at $1 \times 10^5 \text{ C}$. The energy consump-

Fig. 7. Relationship between membrane resistivity and concentration ratio of peroxide ion to hydroxide ion

Fig. 8. Comparison between membrane resistivity measured in three-compartment electrolyzer and that measured in four-compartment electrolyzer to prevent gas from contacting directly with anion-exchange membrane

tion to produce hydrogen peroxide in acidic solution was found to become large than that ($2\text{--}6 \text{ kWh} \cdot \text{kg}^{-1} \cdot \text{H}_2\text{O}_2$) to produce peroxide ions in alkaline solutions, because anion-exchange membrane had larger resistivity than did the cation-exchange membrane used for the latter study.

2.7 Durability

Table 2 shows the changes in membrane properties before and after electrolysis at $1 \times 10^5 \text{ C}$. The surface of the AM-1 became brown and the surface polymer was peeled off. Since the anolyte was strongly alkaline ($1 \text{ kmol} \cdot \text{m}^{-3} \text{ KOH}$) and oxidizing (HO_2^-), perfluorocarbon and polyethylene were more suitable as

Fig. 9. Change in terminal voltage with increasing amount of electricity

Fig. 10. Change in energy consumption with increasing amount of electricity

Table 2. Changes in membrane properties before and after electrolysis for 1×10^5 C

Property	ACLE-5P		AM-1		SYN-10	
	before	after	before	after	before	after
W	0.219	0.266	0.249	0.376	0.410	0.470
Q_m	0.897	0.808	1.54	1.42	1.45	1.35
R_a (NaCl)	14.7	10.4	1.62	1.17	1.03	1.15

W : kg-H₂O · kg⁻¹-dry mem; Q_m : kmol · m⁻³-wet mem; R_a : Ω · cm²

backing materials rather than polyvinylchloride cloth because of their high stability to chemicals. There were no observational changes in surface polymers of ACLE-5P and SYN-10 membranes. Transport properties of SYN-10 varied less before and after electrolysis than did those of ACLE-5P, as indicated in Table 2. The synthetic membrane prepared by the impregnation method using microporous polyethylene film without PVC powders did show an improvement in chemical stability over a

conventional membrane such as AM-1. Longer testing will be required to confirm the membrane's durability.

Conclusion

The degree of crosslinking of synthetic membranes prepared by the impregnation method affected the permselectivity of the peroxide ion, the osmotic water and the membrane resistivity. The m_{BP} for electrolysis with SYN-10 was lower than that for ACLE-5P but higher than that for SF-17. The osmotic water increased with decreasing degree of crosslinking of the synthetic membrane. The membrane resistivity of SYN-5 was lowest among the membranes used. Energy consumption to produce unit mole of hydrogen peroxide was minimized when using SYN-5 or SYN-10, and was competitive with that for ACLE-5P.

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Nomenclature

C	= concentration	[mol · m ⁻³]
C_e	= current efficiency	[%]
Ec	= energy consumption	[J · mol ⁻¹]
F	= Faraday's constant	[C · mol ⁻¹]
I	= electric current	[A]
m	= number of moles	[mol]
Q	= amount of electricity	[C]
Q_m	= ion-exchange capacity	[mol · m ⁻³]
R_a	= membrane resistivity	[Ω · m ²]
S	= effective area where current flows	[m ²]
T_H^P	= permselectivity of peroxide ion with respect to hydroxide ion	[—]
t	= electrolysis period	[s]
t_P	= transport number of peroxide ion	[—]
V_t	= terminal voltage	[V]
v_e	= evaporation rate	[m ³ · s ⁻¹]
v_p	= pressure-driven transport of water	[m ³ · s ⁻¹]
W	= water content	[kg-water · kg ⁻¹ -dry mem.]
α	= number of water moles hydrated with unit HO ₂ ⁻ mole	[—]
β	= number of water moles hydrated with unit OH ⁻ mole	[—]
ρ	= density	[kg · m ⁻³]
$\Delta\phi$	= potential difference	[V]
$\Delta\phi_m$	= potential difference between opposite sides of membrane	[V]

<Subscripts>

A	= catholyte compartment
B	= center compartment
C	= anolyte compartment
H	= hydroxide ion, OH ⁻
P	= peroxide ion, HO ₂ ⁻
w	= water

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