

Preparation of anion exchange membrane using polyvinyl chloride (PVC) for alkaline water electrolysis

Gab-Jin Hwang*, Soo-Gon Lim**, Soo-Yeon Bong*, Cheol-Hwi Ryu*, and Ho-Sang Choi***,†

*Grad. School, Department Green Energy, Hoseo University, Asan City, Chungnam 336-795, Korea

**Energy & Machinery Korea Co., Ltd., Changwon 642-090, Korea

***Department Chemical Engineering, Kyungil University, Gyeongsan 712-701, Korea

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Abstract—An anion exchange membrane was prepared by the chloromethylation and the amination of polyvinyl chloride (PVC), as the base polymer. The membrane properties of the prepared anion exchange membrane, including ionic conductivity, ion exchange capacity, and water content were measured. The ionic conductivity of the prepared anion exchange membrane was in the range of 0.098×10^{-2} – 7.0×10^{-2} S cm^{-1} . The ranges of ion exchange capacity and water content were 1.9–3.7 meq./g-dry-membrane and 35.1–63.1%, respectively. The chemical stability of the prepared anion exchange membrane was tested by soaking in 30 wt% KOH solution to determine its availability as a separator in the alkaline water electrolysis. The ionic conductivity during the chemical stability test largely did not change.

Keywords: Hydrogen Production, Water Electrolysis, Alkaline Water Electrolysis, Separator, Anion Exchange Membrane

INTRODUCTION

Hydrogen is an attractive fuel because it is a renewable energy resource and is also flexible as an energy carrier. Water electrolysis produces hydrogen from water as an extremely abundant resource. There are three main kinds of water electrolysis: alkaline water electrolysis (AWE), polymer electrolyte membrane water electrolysis (PEMWE), and high temperature steam electrolysis (HTSE) [1,2].

Alkaline water electrolysis is a well known method for hydrogen production. Typically, 20–30 wt% of KOH or 15–20 wt% of NaOH is used as an electrolyte. Alkaline water electrolysis cells employ a separator that is selectively permeable OH^- anions, and the anode and cathode generate oxygen and hydrogen gas, respectively. AWE is operated in the range of 40–80 °C [3,4].

In AWE, an anion exchange membrane should have a high hydroxide ion conductivity and stability in alkaline environment to increase the electrolyzer efficiency and to avoid the mixing of anodic and cathodic electrolytes.

Qiao et al. [5] reported that an anion exchange membrane prepared from poly(vinyl alcohol)/poly(vinylpyrrolidone) (PVA/PVP) by blending and chemical cross-linking, followed by doping in aqueous KOH solution, had a maximum conductivity of up to 0.53 S cm^{-1} and stability in a 10 M (mol L^{-1}) KOH solution. Cao et al. [6] reported that an anion exchange membrane prepared from methylated melamine grafted poly vinyl benzyl chloride (mm-qPVBz/Cl⁻) had a conductivity of 1.6×10^{-2} – 2.7×10^{-2} S cm^{-1} . Wu and Scott [7] reported that an anion exchange membrane prepared from a quaternary OH^- conductive ionomer binder based on polymeth-

acrylate, by copolymerization of a three kinds of methacrylate monomers followed by quaternization, had a conductivity of 0.059 S cm^{-1} at 50 °C. Hung et al. [8] reported that a prepared bipolar membrane prepared from polyvinylidene fluoride-grafted 2-methacrylic acid 3-(bis-carboxymethylamino)-2-hydroxyl-propyl ester (PVDF-g-G-IBM), improved the hydrogen production efficiency in alkaline water electrolysis using 0.5 M NaOH.

Several researchers [9–15] have reported the preparation of anion exchange membranes from poly(phthalazinone ether sulfone ketone), poly(ether imide), quaternary-ammonium-functionalized radiation-grafted ETFE (ethylene tetrafluoroethylene), quaternized polybenzimidazoles, and polyepichlorohydrin matrices for alkaline fuel cells and Donnan dialysis.

In this study, an anion exchange membrane was prepared by the chloromethylation and the amination using polyvinyl chloride as the base polymer. The properties of the prepared membrane were determined including ionic conductivity, ion exchange capacity, and chemical stability in a solution of 30 wt% KOH.

EXPERIMENTAL

1. Preparation of Anion Exchange Membrane

1-1. Chloromethylation

The used reagents in the chloromethylation were similar to those of Hwang et al. [16,17] and Sata et al. [18].

The chloromethylation was performed in the following way. PVC (polyvinyl chloride, Wako Co.) powder (20 g) was dissolved in TCE (1,1,2,2-tetrachloroethane), after which 7 g of SnCl_4 and 10 ml of CME (chloromethyl methyl ether) were added. The mixture was placed in a round-bottomed flask, as shown in Fig. 1, and was then allowed to react at 90–100 °C for 4 h. The product was washed with deionized water and methanol, and was then precipitated with meth-

†To whom correspondence should be addressed.

E-mail: choihs@kiu.kr

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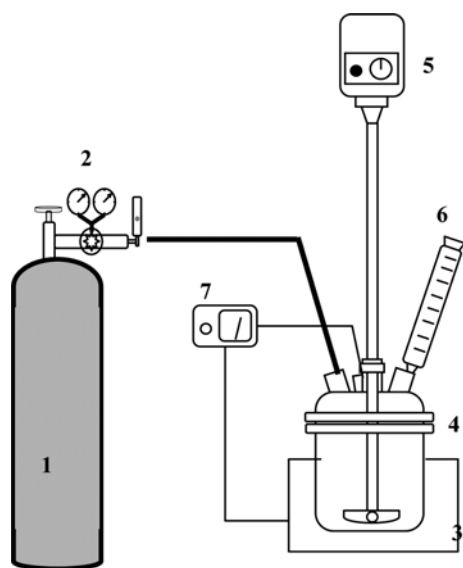
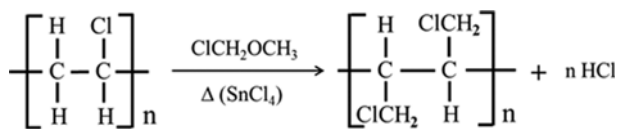


Fig. 1. Schematic diagram of chloromethylation apparatus.

- | | |
|-----------------------|---------------------------|
| 1. Nitrogen bombe | 5. Mechanical stirrer |
| 2. Regulator | 6. Additional funnel |
| 3. Heating mantle | 7. Temperature controller |
| 4. 4-Neck round flask | |



Scheme 1.

anol for about 20 h to obtain a chloromethylated polymer (Scheme 1).
1-2. Amination and Membrane Preparation

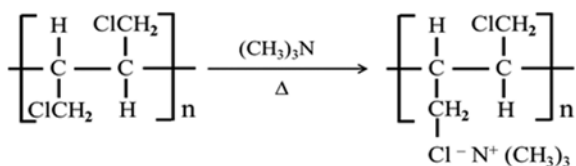
The chloromethylated polymer was dissolved in DMF (N,N-dimethylformamide). Then, 0.1-0.6 g of TMA (30% trimethylamine solution, supplied by Wako Co.) was added for each 1 g of chloromethylated polymer, with stirring at 110 °C for 1 h to obtain the aminated polymer solution.

This solution was cast on a glass plate, and was dried at 110 °C for about 30 min in a drying oven. The product was then released from the glass plate to obtain an anion exchange membrane; the chemical structure is shown in Scheme 2.

2. Membrane Properties of the Prepared Anion Exchange Membrane

2-1. Ionic Conductivity in 1 M (mol L⁻¹) KOH Aqueous Solution

The measurement method and experimental apparatus for membrane resistance in 1 M KOH aqueous solution were the same as reported in a previous paper [16,17]. The electric resistance of the



Scheme 2.

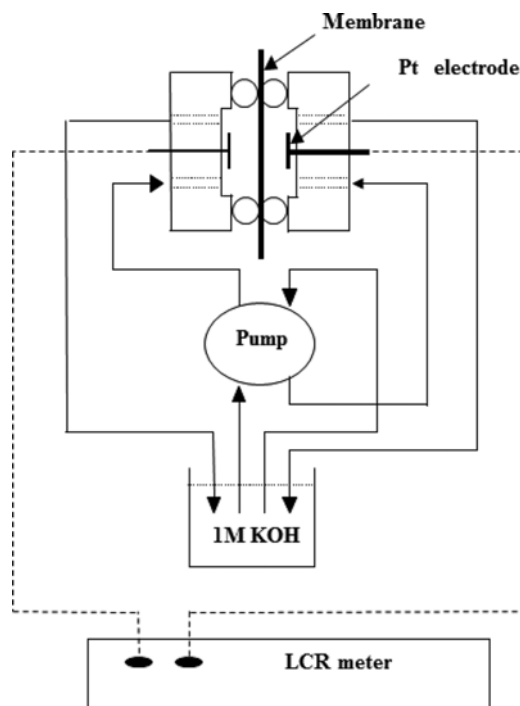


Fig. 2. Schematic of device used to measure electrical resistance in 1 M (mol L⁻¹) KOH aq. solution.

conductivity cell shown in Fig. 2 with membrane (R_1) and without membrane (R_2) was measured at room temperature using an LCR meter (Furuka Co., PM-6304). Each compartment of the cell was filled with 1 M KOH aqueous solution by circulation. The effective membrane area (S) of the cell was 0.79 cm². The membrane resistance, R (in $\Omega \text{ cm}^2$) was calculated by Eq. (1):

$$R = (R_1 - R_2) \times S \quad (1)$$

The ionic conductivity, C (in S cm^{-1}) was calculated by Eq. (2):

$$C = 1/R \times t \quad (2)$$

where, t was the thickness of the prepared anion exchange membrane.

2-2. Ion Exchange Capacity (IEC)

The measurement method for ion exchange capacity (IEC) was the same as reported in a previous paper [16]. After being dipped in pure water for one day, a membrane sample was immersed for two days in a large volume of 1 M NaOH aq. solution to convert the membrane to the OH⁻ form. The membrane sample was then washed free of excess NaOH with distilled water, and further equilibrated with distilled water for 4 h with frequent changes in the distilled water to remove the last traces of alkali. The membrane sample was then equilibrated with 30 ml of 0.01 M HCl aq. solution for 24 h, and the anion exchange capacity was determined by back titration. The IEC of the prepared anion exchange membrane was calculated from the following equation:

$$\text{IEC} = (M_{\text{O,HCl}} - M_{\text{E,HCl}}) / W \quad (3)$$

2-3. Water Content

The membrane was immersed in distilled water for 24 h at the

ambient temperature, after which its surface moisture was wiped with tissue paper, and the wet membrane was then weighed. Then, this weighed wet membrane was dried at a fixed temperature of 60 °C until a constant weight of dry membrane was achieved.

The water content was calculated from Eq. (4):

$$W_c = (W_w - W) / W_w \times 100 \quad (4)$$

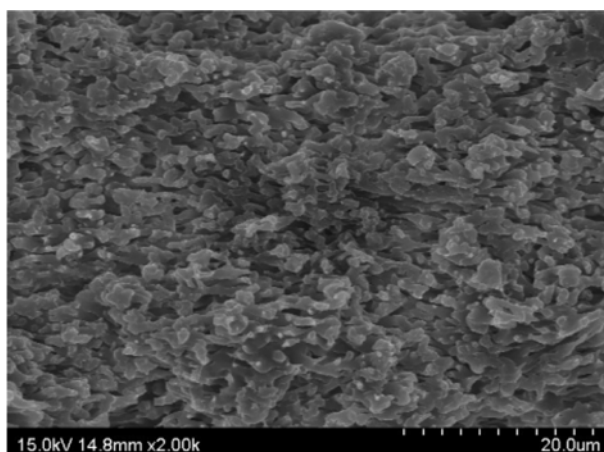
3. Chemical Stability in 30 wt% KOH Solution

A chemical stability test was carried out by soaking in 30 wt% KOH solution at the ambient temperature. The chemical stability of the prepared anion exchange membrane was determined based on the change of the surface state and the membrane resistance in 1 M KOH solution induced by alkali degradation during storage in 30 wt% KOH solution.

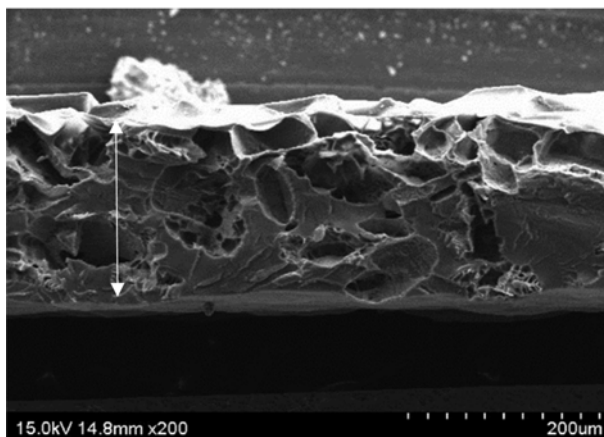
RESULTS AND DISCUSSION

1. Morphology of the Prepared Anion Exchange Membrane

Fig. 3 shows the morphologies of the surface and cross-section of the prepared anion exchange membrane obtained with a scan-



(a) surface



(b) cross-section

Fig. 3. Morphologies of the surface and cross-section of the prepared anion exchange membrane obtained with a scanning electron microscope (SEM).

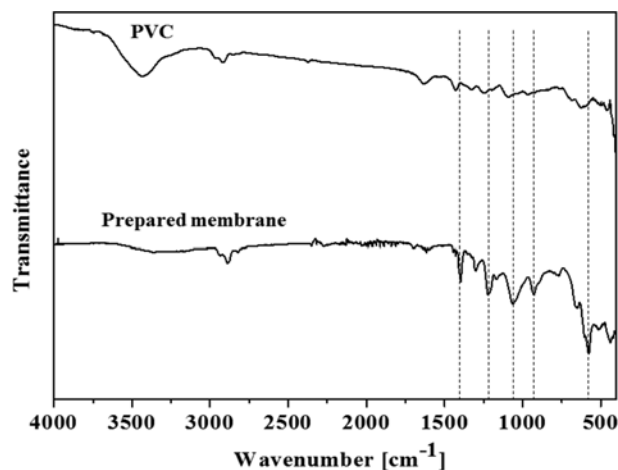


Fig. 4. IR spectra of the prepared anion exchange membrane obtained using a Fourier transform infrared spectrometer (FT-IR).

ning electron microscope (SEM).

The surface of the prepared anion exchange membrane had macropores and a thickness of over 120 μm measured by a micrometer caliper. The reason of the macro-pore presence was not clear, yet. But, it was guessed as the follows: In the amination, the chloromethylated polymer completely did not dissolve, and the solvent (DMF) which was used to dissolve copolymer was locally remained on the internal copolymers. And then the solvent was removed from the copolymers; therefore the macro-pore remained at the location of the removed solvents like to the macroreticular preparation behavior [16]. The gases such as hydrogen and oxygen did not path through this macro-pore because the channel was closed as shown in Fig. 3(b).

Fig. 4 shows the IR spectra of the prepared anion exchange membrane obtained using a Fourier transform infrared spectrometer (FT-IR).

As shown in Fig. 4, the peak of the prepared anion exchange membrane was different with PVC as a base polymer.

The transmittance values for the prepared anion exchange membrane were as follows: wagging vibration of cis C-H, 605.7 cm^{-1} ; vibration of C-Cl, 680.3 cm^{-1} ; wagging vibration of trans C-H, 956.7 cm^{-1} ; stretching vibration of C-H, 1,252.7 cm^{-1} ; and stretching vibration of $\text{CH}_3\text{-NH-}$, 1,425.5 cm^{-1} . From the IR spectrums of Fig. 4 it was confirmed that the prepared membrane showed the vibration of amine as an anion exchange group.

Fig. 5 shows an energy dispersive X-ray spectroscopy (EDXS) analysis of the prepared anion exchange membrane with 20 keV.

As shown in Fig. 5, the Sn which was used as a catalyst in the chloromethylation remained in the anion exchange membrane. It seems that the remaining Sn was due to insufficient washing. However, the remaining Sn did not affect the properties of the anion exchange membrane because of its non-reactivity with KOH. From the result of EDXS, it was confirmed that an anion exchange group was reasonably formed in the PVC chemical matrix.

The tensile strength of the prepared anion exchange membrane, which was measured by a tensile testing machine (TO-101, TEST ONE Co.), was about 0.87 $\text{kg}_f\text{-mm}^{-2}$. That of Nafion 117 was about

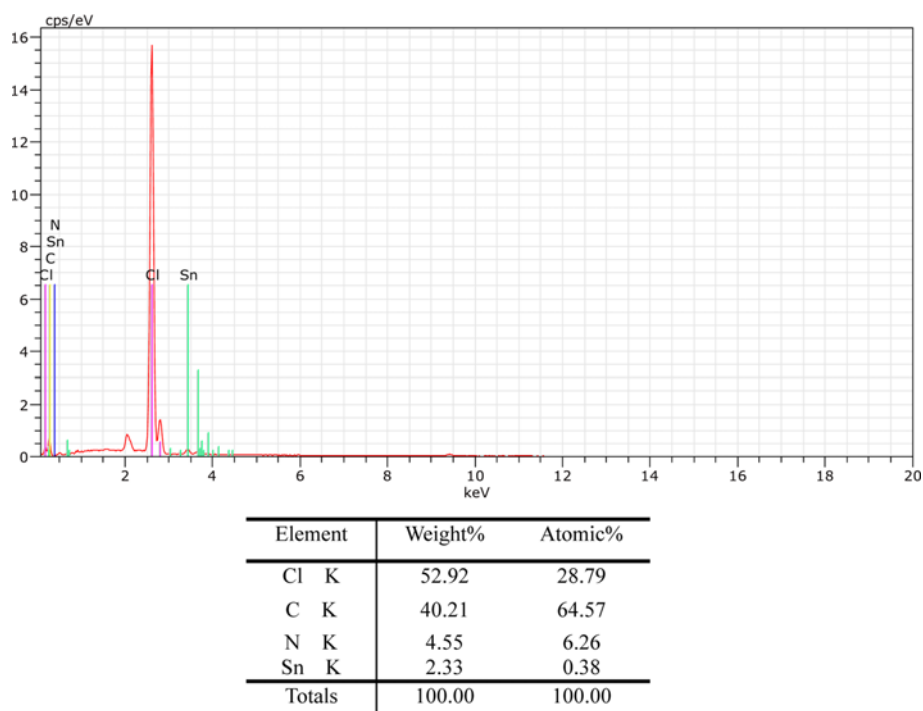


Fig. 5. Energy dispersive X-ray spectroscopy (EDXS) analysis of the prepared anion exchange membrane.

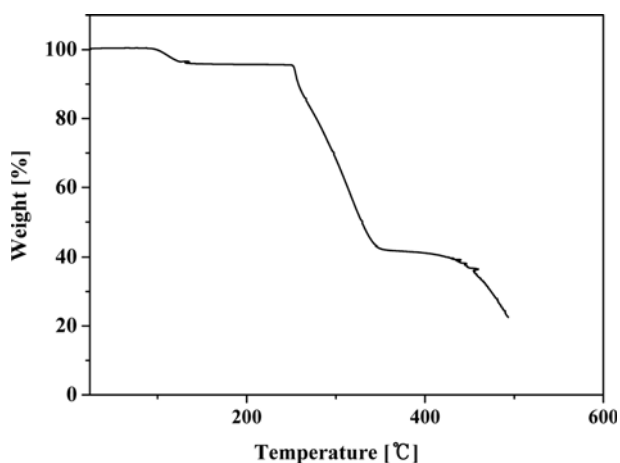


Fig. 6. TGA thermograms of the prepared anion exchange membrane.

$3.0 \text{ kg} \cdot \text{mm}^{-2}$. The mechanical strength of the prepared membrane was lower than Nafion117. From this result, further research for the improvement of the mechanical strength is needed.

2. Thermal Stability of the Prepared Anion Exchange Membrane

Fig. 6 shows the thermal stability of the prepared anion exchange membrane analyzed by thermogravimetric analyzer (TGA).

The TGA traces of the prepared anion exchange membrane exhibit the typical three-step weight loss at temperatures of approximately 100°C , 230°C and 410°C . The first weight loss (at 100°C) is due to removal of the impurities. The second weight loss (at 230°C) is due to splitting-off of an anion exchange group (trimethylamine). The third thermal degradation, which occurred at 410°C , arises from decomposition of the main chain. It suggests from the results

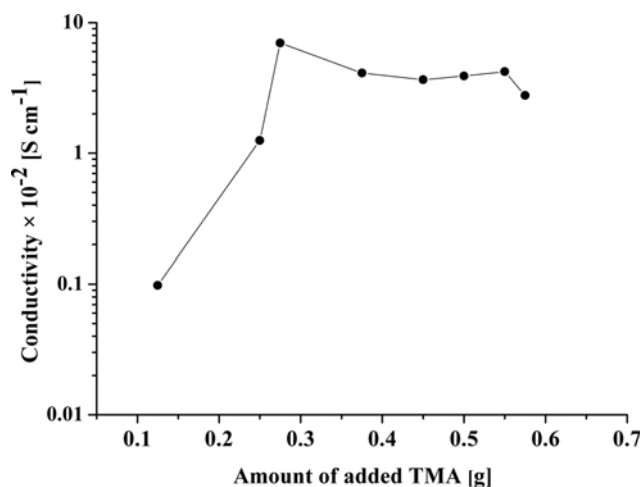


Fig. 7. Relationship between the ionic conductivity measured in 1 M KOH solution and the amount of added TMA (g) in the copolymer for the amination.

that the prepared anion exchange membrane could be used in alkaline water electrolysis operation condition with the high thermal stability.

3. Ionic Conductivity in 1 M KOH Solution

Fig. 7 shows the relationship between the ionic conductivity measured in 1 M KOH solution and the amount of added TMA (g) in the copolymer for the amination.

With an increase of amount of added TMA, the ionic conductivity was increased from $0.098 \times 10^{-2} \text{ S cm}^{-1}$ to $6.95 \times 10^{-2} \text{ S cm}^{-1}$ at 0.28 g of TMA, and decreased to $4.11 \times 10^{-2} \text{ S cm}^{-1}$ at 0.38 g of TMA, and then maintained almost the same value until 0.55 g of

Table 1. Characteristics of the prepared anion exchange membrane

Name	Amount of added TMA (g)	Thickness (μm)	Membrane resistance ($\Omega \text{ cm}^2$)	Ionic conductivity ($\times 10^{-2} \text{ S cm}^{-1}$)
A-1	0.13	130	132.0	0.098
A-2	0.25	130	10.4	1.25
A-3	0.28	140	2.0	7.0
A-4	0.38	140	3.4	4.11
A-5	0.45	140	3.84	3.65
A-6	0.50	130	3.33	3.9
A-7	0.55	140	3.32	4.22
A-8	0.58	130	4.7	2.77

TMA, finally reaching to $2.77 \times 10^{-2} \text{ S cm}^{-1}$.

With an increase of the amount of added TMA, the ionic conductivity of the prepared anion exchange membrane had a maximum value at 0.28 g, and the ionic conductivity was largely unchanged in the region of 0.38–0.55 g. This suggests that the amount of added TMA in the preparation of anion exchange membrane using PVC as a base polymer is suitable from 0.28 g to 0.55 g from the view point of the ionic conductivity.

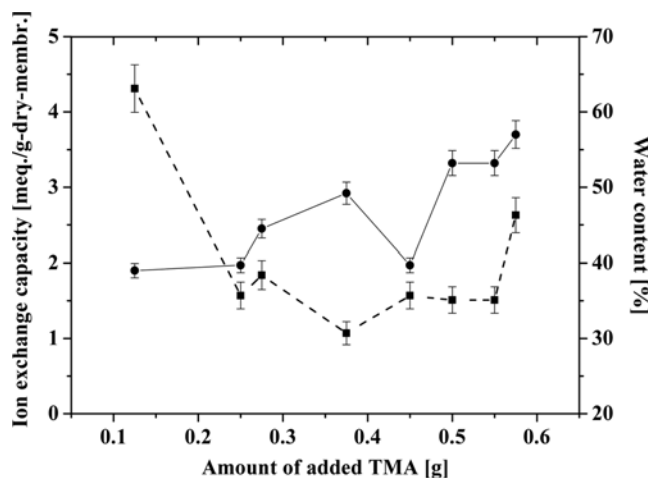
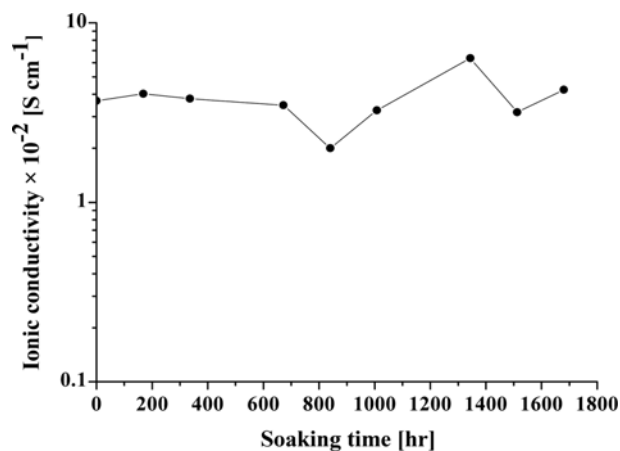
Table 1 shows the characteristics of the prepared anion exchange membranes.

The thickness of the prepared anion exchange membranes, which was measured by a micrometer caliper, was 120–140 μm .

4. Ion Exchange Capacity and Water Content of the Prepared Anion Exchange Membrane

Fig. 8 shows the influence of amount of added TMA in the membrane on the water content and ion exchange capacity.

With an increase of amount of added TMA, the ion exchange capacity (IEC) increased from 1.90 meq./g-dry-membrane to 2.92 meq./g-dry-membrane at 0.38 g of TMA, and decreased to 1.97 meq./g-dry-membrane at 0.45 g of TMA, then increasing to 3.7 meq./g-dry-membrane. As shown in Fig. 8, the ion exchange capacity

**Fig. 8. Influence of amount of added TMA in the membrane on the water content and ion exchange capacity.****Fig. 9. Change of ionic conductivity in A-5 membrane before and after soaking in 30 wt% KOH solution.**

ity showed the increasing tendency with an increase of amount of added TMA.

The water content decreased from 63.1% to 30.7% at 0.38 g of TMA, and increased to 35.1% at 0.55 g of TMA, and rapidly increased to 46.3% at 0.58 g of TMA.

The membrane, having a maximum ionic conductivity of $6.95 \times 10^{-2} \text{ S cm}^{-1}$, had IEC and water content values of 2.45 meq./g-dry-membrane and 38.4%.

The prepared anion exchange membranes with a water content of 30–35% exhibited ionic conductivity values of 3.65×10^{-2} – $6.95 \times 10^{-2} \text{ S cm}^{-1}$ and IEC values of 1.97–3.32 meq./g-dry-membrane.

In general, the optimal water content is that which allows the best ion exchange capacity-ionic conductivity combination [12]. From this viewpoint, the results suggest that the optimal water content of the prepared anion exchange membrane for a good ionic conductivity and ion exchange capacity is in the range of 30–35%.

5. Chemical Stability in 30 wt% KOH Solution

Fig. 9 shows the change of ionic conductivity in A-5 membrane before and after the chemical stability test, which was carried out by soaking in 30 wt% KOH solution.

With an increase of soaking time in the 30 wt% KOH solution, the ionic conductivity had almost the same value between 0 h and 672 h, and decreased a little at 840 h, then increasing a little again at 1,344 h, and finally, had almost the same value at 1,680 h compared to that at 0 h.

The surface change of the membrane was not altered during the chemical stability test.

As shown in Fig. 9, the ionic conductivity after 1,680 h of chemical stability test in 30 wt% KOH solution had almost the same value as that before the chemical stability test. It suggests that the anion exchange membrane, which was prepared using PVC as a base polymer, had good chemical stability with largely unchanged ionic conductivity in 30 wt.% KOH solution.

It is expected that the prepared anion exchange membrane can be used as a separator in alkaline water electrolysis with a high ionic conductivity, ion exchange capacity, good chemical stability with a long lifetime in 30 wt% KOH solution, and thermal stability until 100 °C.

CONCLUSIONS

An anion exchange membrane was prepared by the chloromethylation and amination of polyvinyl chloride (PVC), used as a base polymer. The FT-IR and EDXS analysis confirmed that the anion exchange group was reasonably formed in the PVC chemical matrix. The thickness of the prepared anion exchange membrane was 120-140 μm . The maximum conductivity of the prepared anion exchange membrane was $6.95 \times 10^{-2} \text{ S cm}^{-1}$. The membrane having a water content of 30-35% exhibited ionic conductivity values of 3.65×10^{-2} - $6.95 \times 10^{-2} \text{ S cm}^{-1}$ and IEC values of 1.97-3.32 meq./g-dry-membrane. The prepared anion exchange membrane had a good stability during 1,680 h in 30 wt% KOH solution. Finally, it was expected that the prepared anion exchange membrane can be used as a separator in the alkaline water electrolysis with a high ionic conductivity, ion exchange capacity, good chemical stability with a long lifetime in 30 wt% KOH solution and thermal stability until 100 °C.

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NOMENCLATURE

R : membrane resistance in 1 M KOH aqueous solution [$\Omega \cdot \text{cm}^2$]
 R_1, R_2 : electric resistance of the conductivity cell with and without membrane, respectively [Ω]
 S : effective membrane area [cm^2]
 C : conductivity [S cm^{-1}]
 t : thickness of the membrane [μm]
 IEC : ion exchange capacity, meq./g-dry-membrane
 $M_{O,HCl}$: moles of HCl in the flask at the start of titration
 $M_{E,HCl}$: moles of HCl after equilibration

W_C : water content [%]
 W : weight of dry membrane [g]
 W_W : weight of wet membrane [g]

REFERENCES

1. G.-J. Hwang, K.-S. Kang, H.-J. Han and J.-W. Kim, *Trans. of the Korean Hydrogen and New Energy Society*, **18**, 95 (2007).
2. H.-S. Choi, C.-H. Ryu, S.-G. Lee, C.-S. Byun and G.-J. Hwang, *Trans. of the Korean Hydrogen and New Energy Society*, **22**, 184 (2011).
3. J. Hnat, M. Paider, J. Schauer, J. Zitka and K. Bouzek, *J. Appl. Electrochem.*, **41**, 1043 (2011).
4. K. Zeng and D. Zhang, *Progress in Energy and Combustion Sci.*, **36**, 307 (2010).
5. J. Qiao, J. Fu, R. Lin, J. Ma and J. Liu, *Polymer*, **51**, 4850 (2010).
6. Y.-C. Cao, X. Wu and K. Scott, *Int. J. Hydrogen Energy*, **37**, 9524 (2012).
7. X. Wu and K. Scott, *J. Power Sources*, **214**, 124 (2012).
8. C. Y. Hung, S.-D. Li, C.-C. Wang and C.-Y. Chen, *J. Membr. Sci.*, **389**, 197 (2012).
9. J. Fang and P. K. Shen, *J. Membr. Sci.*, **285**, 317 (2006).
10. G. Wang, Y. Weng, D. Chu, D. Xie and R. Chen, *J. Membr. Sci.*, **326**, 4 (2009).
11. J. R. Varcoe and R. C. T. Slade, *Electrochem. Commun.*, **5**, 662 (2003).
12. L. Jheng, S. L. Hsu, B. Lin and Y. Hsu, *J. Membr. Sci.*, **460**, 160 (2014).
13. D. Stoica, L. Ogier, L. Akrou, F. Alloin and J.-F. Fauvarque, *Electrochim. Acta*, **53**, 1596 (2007).
14. J. Chattopadhyay, R. Srivastava and P. K. Srivastava, *Korean J. Chem. Eng.*, **30**, 1571 (2013).
15. A. Boubakri, N. Helali, M. Tlili and M. B. Amor, *Korean J. Chem. Eng.*, **31**, 461 (2014).
16. G.-J. Hwang and H. Ohya, *J. Membr. Sci.*, **149**, 163 (1998).
17. G.-J. Hwang and H. Ohya, *J. Membr. Sci.*, **140**, 195 (1998).
18. T. Sata, M. Tsujimoto, T. Yamaguchi and K. Matsusaki, *J. Membr. Sci.*, **112**, 161 (1996).