

Development of Ion-Exchange Membrane Using an Electron-Beam-Induced Graft Polymerization Method

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Abstract

Cation- and anion- exchange membranes, used for the concentration of sea water, were prepared by an electron-beam-induced graft polymerization method (EB method). After the testing of several different films, an ultra-high-molecular-weight polyethylene (UHMWPE) film, which is a commercially available polymeric film, was selected for use as the base film.

The EB method consists of three main phases, namely, electron beam irradiation, followed by graft polymerization, and then the introduction of an ion-exchange group.

In the electron-beam irradiation phase, the UHMWPE film is irradiated with an electron beam in a nitrogen atmosphere. As a result, radicals are generated in the film. These radicals constitute the starting point of the polymerization.

In the graft polymerization phase, the irradiated film is immersed in a solution of a monomer in xylene, so that the monomer grafts onto the radicals formed in the film. To produce a cation exchange membrane, styrene and chloromethylstyrene are graft-polymerized into the film. On the other hand, to produce an anion-exchange membrane, chloromethylstyrene and divinylbenzene are graft-polymerized into the film.

In the ion-exchange group phase, the grafted film is immersed in a solution to introduce the ion-exchange group. As the cation-exchange group, a sulfonic acid group is introduced using a solution of dichloromethane in chlorosulfonic acid. As the anion exchange group, meanwhile, a trimethylammonium group is introduced using an aqueous solution of trimethylamine.

To evaluate the ability of the ion-exchange membrane to concentrate seawater, an electrodialyzer was used. We found that the performance of the ion-exchange membrane prepared by the electron-beam-induced graft polymerization method was superior to that of a commercially available membrane.

1. Introduction

In Japan, table salt has been manufactured from concentrated seawater since ancient times, given that the country has no deposits of rock salt. Furthermore, salt manufacture by solar evaporation is difficult because Japan is often rainy and the amount of available space is limited.

This situation has led to the development of a salt manufacturing method in which seawater is first concentrated and then subjected to an evaporating crystallization process. This process is unique to Japan¹⁻³. A new innovation in this process, in the form of electro-dialysis seawater concentration, was applied to the concentration process in 1972⁴⁻⁵.

First, the seawater is concentrated, from 3% to 20%, using the electro-dialysis seawater concentration process. Next, the brine from the electro-dialyzer is evaporated and crystallized using multi-effect vacuum-type evaporators. In the electro-dialysis seawater concentration process, the most important measure of performance is the degree of concentration attained by the ion-exchange membrane, which has a low level of membrane resistance. This low resistance promotes energy saving in the electric dialysis process, and this high concentration performance promotes energy saving in the evaporating crystallization process⁵⁻⁷.

Currently, commercially available ion-exchange membranes are manufactured using a heat polymerization method⁵⁻⁷. Any great enhancement in the performance of such membranes is unlikely, because the method was developed more than 50 years ago and has probably evolved as far as it can.

In the present study, we set out to develop an electron-beam-graft-polymerization method (EB method) as a next-generation manufacturing process for ion-exchange membranes. The EB method can produce graft-polymers in a polymer film by using radicals as a starting point. Radicals are generated in a film that has been irradiated with an electron beam. An advantage of this method is that a wide range of polymer films and monomers can be used.

The goal of the present study was to establish a process for manufacturing an ion-exchange membrane for the concentration of seawater by using an electron-beam-graft polymerization method. After the testing of several different films, an ultra-high-molecular-weight polyethylene (UHMWPE) film, which is a commercially available polymeric film, was selected for use as the base film. An UHMWPE film has a high mechanical strength and high chemical resistance.

2. Experimental

2.1 Materials

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Cation- and anion-exchange membranes, used for the concentration of seawater, were prepared by an electron-beam-induced graft polymerization method (EB method). An ultra-high-molecular-weight polyethylene (UHMWPE) film, which is a commercially available polymeric film, was selected for use as the base film.

Ultra-high-molecular-weight polyethylene (UHMWPE) films were purchased from SAXIN CORPORATION. Commercially available ion-exchange membranes were purchased from AGC ENGINEERING CO., Ltd.

Styrene (St), divinylbenzene (DVB), xylene, dichloromethane, chlorosulfonic acid, and an aqueous solution of trimethylamine were purchased from Wako Pure Chemical Industries Ltd. Chloromethylstyrene (CMS) was purchased from AGC SEIMI CHEMICAL CO., LTD.

2.2 Electron-beam-induced graft polymerization method

The preparation scheme of the ion-exchange membrane using the EB method is shown in **Figure 1**.

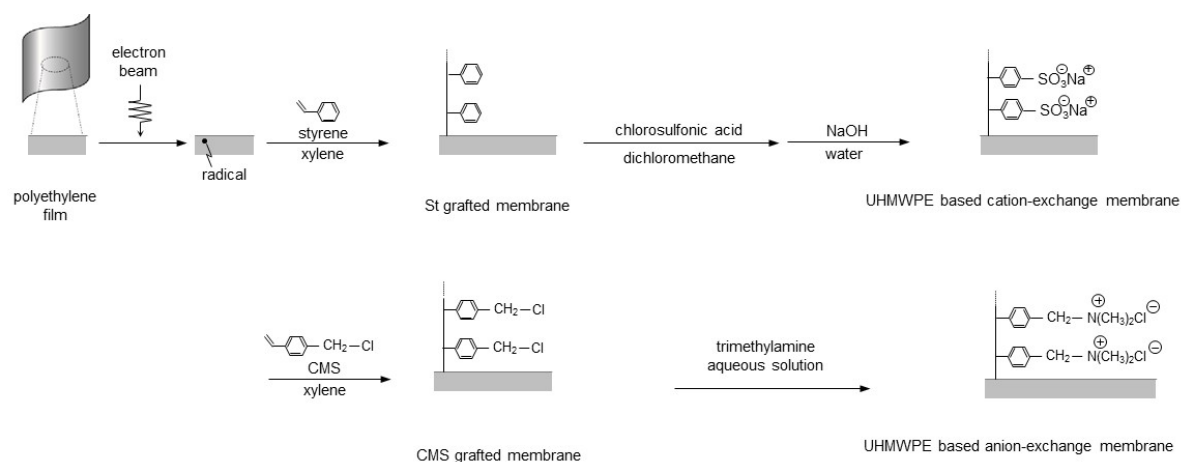


Figure 1: Preparation scheme of ion-exchange membrane using EB method

The EB method consists of three main phases. The preparation conditions for the respective processes are listed in **Tables 1** and **2**. These processes are explained in detail below. (1) Electron beam irradiation. (2) Graft polymerization. (3) Introduction of an ion-exchange group.

(1) Electron-beam irradiation	200 keV N ₂ atmosphere room temperature
(2) Graft polymerization of St	50 wt% St / Xy crosslinking agent: CMS 30 °C
(3) Introduction of trimethylammonium group	5 wt% chlorosulfonic acid / EDC room temperature 24 h

St; styrene, Xy; xylene, CMS; chloromethylstyrene, EDC; dichloromethane

Table 1: Preparation conditions for cation-exchange membrane

(1) Electron-beam irradiation	200 keV N ₂ atmosphere room temperature
(2) Graft polymerization of St	50 wt% CMS / Xy crosslinking agent: CMS 40 °C
(3) Introduction of trimethylammonium group	30 wt% aqueous solution of trimethylamine room temperature 48 h

CMS; chloromethylstyrene, Xy; xylene, DVB; divinylbenzene

Table 2: Preparation conditions for anion-exchange membrane

(1) In the electron-beam irradiation phase, the UHMWPE film is irradiated with an electron beam in a nitrogen atmosphere. As a result, radicals are generated in the film. These radicals constitute the starting point of the polymerization. The irradiation voltage was set to 200 keV and the radiation dose was adjusted to attain 20 –100 kGy.

(2) In the graft polymerization phase, the irradiated film is immersed in a solution of a monomer in xylene so that the monomer grafts onto the radicals formed in the film. To produce a cation exchange membrane, styrene is graft-polymerized into the film. On the other hand, to produce an anion-exchange membrane, chloromethylstyrene is graft-polymerized into the film. The degree of grafting is defined as follows:

$$\text{Degree of grafting (\%)} = 100 (W_1 - W_0) / W_0 \quad (1)$$

where W_0 and W_1 are the weights of the base film and grafted film, respectively.

To produce a cation exchange membrane, CMS is used as a cross-linking agent. On the other hand, to produce an anion-exchange membrane, DVB is used as the cross-linking agent.

(3) In the ion-exchange group phase, the grafted film was immersed in a solution to introduce the ion-exchange group. As the cation-exchange group, a sulfonic acid group was introduced using a solution of dichloromethane in chlorosulfonic acid. As the anion exchange group, meanwhile, a trimethylammonium group was introduced using an aqueous solution of trimethylamine.

2.3 Evaluation of resistance of membrane

The membrane resistance was measured using a membrane resistance measuring cell. After the ion-exchange membrane was mounted on the cell (given an effective membrane area of 1.77 cm^2), the alternating-current resistance at 1 kHz in a 0.5 mol/L NaCl aqueous solution was measured using an impedance meter (Agilent Technologies Japan, Ltd.) After measuring the total AC resistance of the film and 0.5 mol/L NaCl aqueous solution, the film was removed and the AC resistance of the solution alone was measured. The AC resistance of the film R_m [Ω] was calculated as the difference between the two measured values. The membrane resistance was defined as

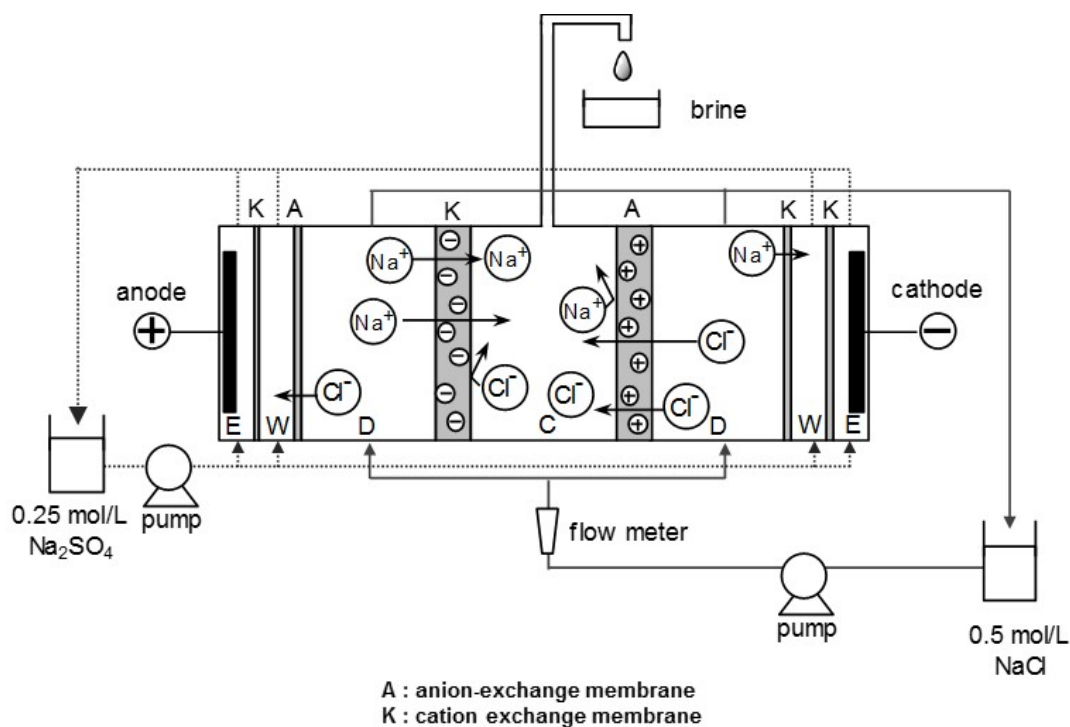
$$\text{Membrane resistance } [\Omega\text{cm}^2] = R_m \times S \quad (2)$$

where S is the effective film area (1.77 cm^2).

2.4 Evaluation of concentration performance

To evaluate the concentration performance of the ion-exchange membrane, an electro-dialyzer was used. The experimental apparatus is shown in **Figure 2**. This device is basically the same as an industrial electro-dialyzer. The effective membrane area was 8cm^2 . The feed solution was a 0.5 mol/L NaCl aqueous solution, the concentration of which was approximately equal to that of seawater. The electrode solution was a 0.25 mol/L Na_2SO_4 aqueous solution. The linear velocity of the feed solution and the electrode solution was 6cm/s. This is similar to that in an industrial electro-dialyzer. The temperature of the feed solution was 25°C . The temperature of the seawater used in industrial processes varies from $25 - 30^\circ\text{C}$.

The current density was 0.03 A/cm^2 . In an industrial process, the current density is varied depending on the temperature of the seawater, between $0.02 - 0.03 \text{ A/cm}^2$. After electrical dialysis was performed for 2 h and the Cl^- concentration in the brine had stabilized, the brine was sampled. The Cl^- concentration in the brine was determined using Mohr's method.



	width [mm]	cross-sectional area [cm]
C : concentration chamber	1.5	8.0 (2.0 × 4.0 cm)
D : desalination chamber	6.5	8.0 (2.0 × 4.0 cm)
E : electrode chamber	6.5	8.0 (2.0 × 4.0 cm)
W : wash chamber	6.5	8.0 (2.0 × 4.0 cm)

Figure 2: Salt enrichment of seawater using electrodialyzer

3. Results and discussion

3.1 Graft polymerization

The effects of the radiation dose on the degree of grafting are shown in **Figure 3**. The degree of St grafting increased linearly as the radiation dose reached 0 – 50 kGy, but the rate of increase decreased above 50 kGy.

The degree of CMS grafting increased linearly with the radiation dose from 0 – 40 kGy, but

the rate of increase decreased above 40 kGy.

The time courses of the degree of grafting are shown in **Figure 4**. The degree of St grafting increased linearly with the reaction time. On the other hand, the degree of CMS grafting increased with the reaction time, but the rate of increase decreased.

As a result, it was possible to adjust the radiation dose and reaction time to attain the desired degree of St and CMS grafting.

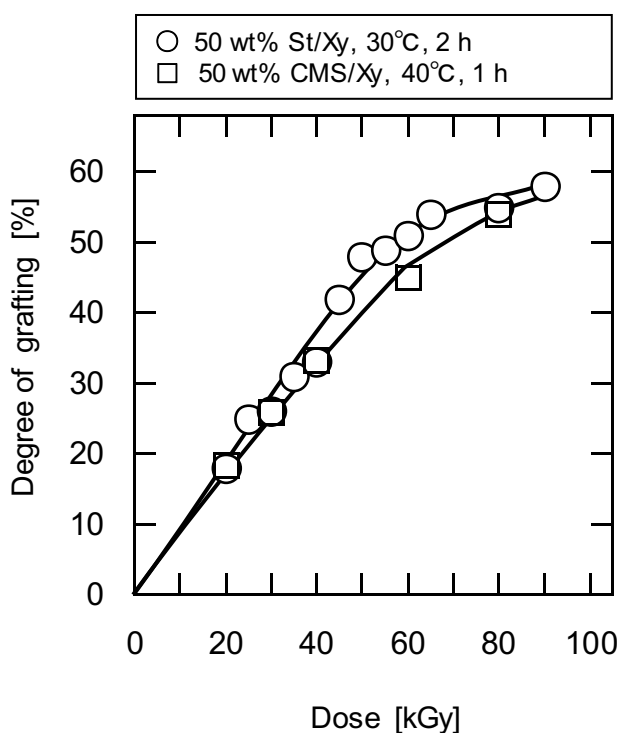


Figure 3: Degree of grafting as a function of dose

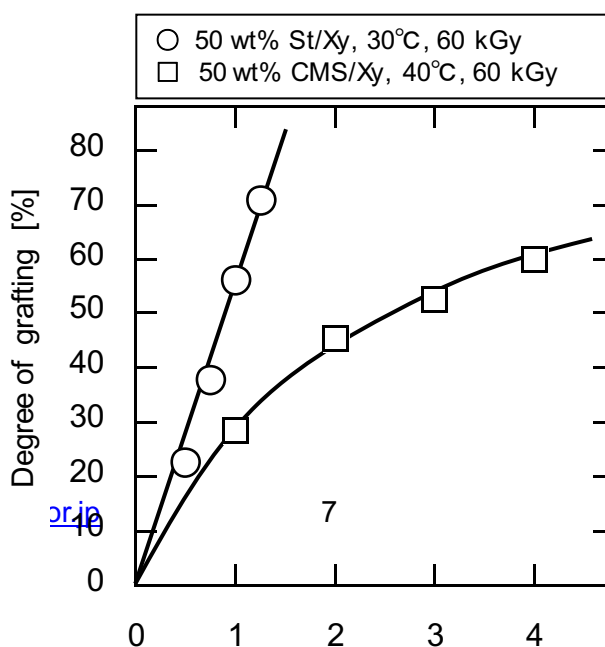


Figure 4: Degree of grafting vs. reaction time

3.2 Concentration performance

3.2.1 Membrane resistance

The relationship between the degree of grafting and the resistance of the ion-exchange membrane prepared by the EB method is shown in **Figure 5**. In the figure, the resistances of the commercially available ion-exchange membranes are indicated for comparison. The resistance of the ion-exchange membranes prepared by the EB method decreased with an increase in the degree of grafting. When the degree of grafting was the same, the resistance of the cation-exchange membrane was lower than that of the anion-exchange membrane. As a result, it was possible to adjust the degree of grafting to attain an ion-exchange membrane with the desired degree of resistance when using the EB method. The resistances of commercially available cation- and anion-exchange membranes (Selemion® CSO and ASA) are 2.4 and 2.2 Ωcm^2 , respectively. For the electro-dialysis seawater concentration process, one of important performance indicators is a low resistance.

When the degree of grafting was more than 30%, the resistance of the ion-exchange membrane prepared by the EB method was lower than that of commercially available ion-exchange membranes.

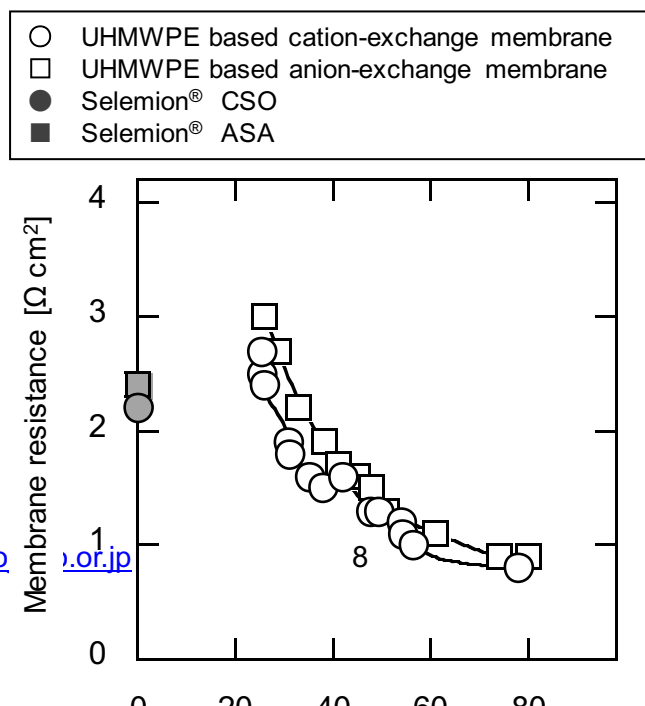


Figure 5: Membrane resistance as function of degree of grafting

3.2.2 Electro-dialysis concentration process

The concentration performance of the ion-exchange membrane prepared by the EB method is shown in **Figure 6**. The black line in the figure shows the relationship between the membrane resistance and the Cl^- concentration in the brine and indicates that both the concentration performance and energy cost are superior to those of commercially available cation- and anion-exchange membranes⁸. Therefore, upper plot, more than the black line, indicates that the concentration performance is superior to that of commercially available membranes.

All the ion-exchange membranes prepared by the EB method were found to be superior to commercially available membranes. For a given membrane resistance, the Cl^- concentrations of the brine produced using the EB method membranes were about 20 – 40 % higher than those of commercially available membranes.

Thus, the use of the EB method made it possible to synthesize ion-exchange membranes with a concentration performance that was superior to those of commercially available membranes.

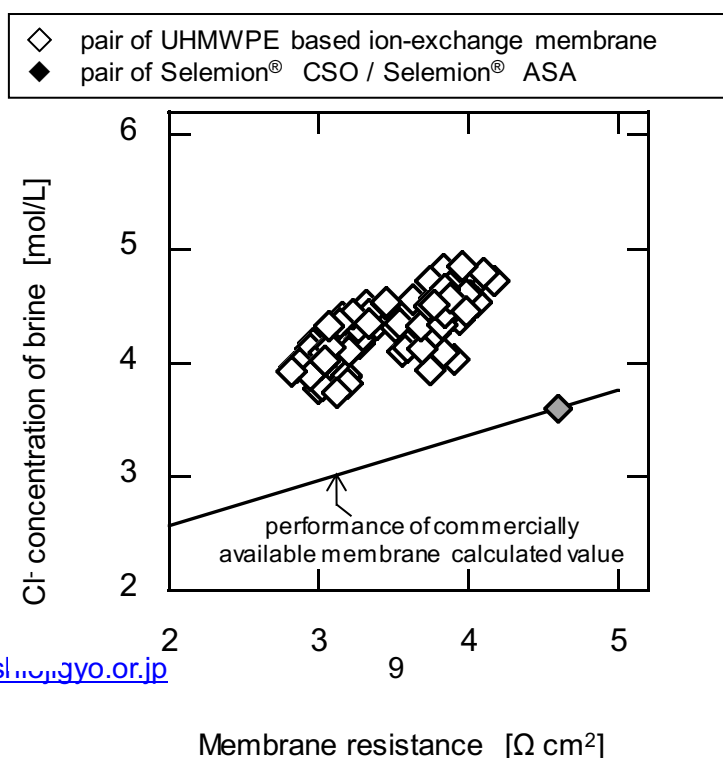


Figure 6: Chloride concentration of brine vs. membrane resistance

4. Conclusions

In the present study, we synthesized cation- and anion-exchange membranes using an EB method. An ultra-high-molecular-weight polyethylene (UHMWPE) film, which is a commercially available polymeric film, was selected for use as the base film.

To produce a cation exchange membrane, styrene and chloromethylstyrene were graft-polymerized into the film. As the cation-exchange group, a sulfonic acid group was introduced using a solution of dichloromethane in chlorosulfonic acid. On the other hand, to produce an anion-exchange membrane, chloromethylstyrene and divinylbenzene were graft-polymerized into the film. As the anion exchange group, a trimethylammonium group was introduced using an aqueous solution of trimethylamine.

In the graft polymerization phase, the degree of St and CMS grafting increased with the radiation dose and reaction time. As a result, it was possible to adjust the radiation dose and reaction time to attain the desired degree of St and CMS grafting.

The resistance of the ion-exchange membranes prepared by the EB method decreased as the degree of grafting increased. As a result, the EB method enabled the adjustment of the degree of grafting to attained an ion-exchange membrane with the desired resistance.

To evaluate the concentration performance of the ion-exchange membrane, an electro dialyzer was used. All the ion-exchange membranes prepared using the EB method were found to be superior to commercially available membranes.

In the next phase of our study, we attempt to scale up our new technique so that it can be applied practically.

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