Ion-Exchange Membrane for the Chlor-Alkali Process

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Monolayer perfluorocarboxylic acid membrane has high current efficiency in chlor-alkali electrolysis, but rather high electric resistance. We have developed unique multilayer membrane of perfluorocarboxylic and perfluorosulfonic acid which has both a current efficiency of about 95% and a low electric resistance by forming a carboxylic acid layer on one surface of the perfluorosulfonic acid membrane through chemical reaction. The performance of this type of membrane is influenced by the chemical structure of the monomer from which the starting material is prepared. New perfluoro monomers containing sulfonic acid or its precursors were synthesized and utilized for the preparation of the multilayer membrane. The resulting membrane has high current efficiency in a wide range of caustic soda concentrations and excellent service life.

1 Introduction

In our research on chlor-alkali electrolysis utilizing ion-exchange membrane of fluorocarbon polymer since the early 1970's, we have discovered that the perfluorocarboxylic acid membrane provides the only possible means of obtaining a high current efficiency in the electrolysis of concentrated caustic soda solution¹⁻⁹⁾.

The world's first membrane chlor-alkali plant was started in April 1975 at a capacity of 40,000 metric tons per year of caustic soda. This plant was expanded to a capacity of 120,000 metric tons per year of caustic soda.

Since the announcement of this plant operation⁹⁾ it has become the consensus of expert opinion that membrane electrolysis will be the predominant process for chlor-alkali production in the future. This is based on the following advantages.

1. Reduced energy consumption in the membrane chlor-alkali process through the utilization of perfluorocarboxylic acid membrane
2. Lower investment cost due to high current density
3. Ease of operation
4. Lower operating cost
5. High product purity

We have licensed around the world the entire package of technology including membrane, electrolysis system, electrolyzer, and heat recovery

evaporator system¹⁰⁻¹³⁾. In 1982, the total worldwide capacity of caustic soda production utilizing our technology will be 520,000 metric tons per year.

This report describes some of the features of our perfluorocarboxylic acid membrane, including the basic design concept and the synthesis, structure, and performance of the membrane.

2 Membrane Containing Carboxylic Acid

Perfluorocarboxylic acid membrane is the most desirable for chlor-alkali production, as it is the only fluorocarbon membrane to exhibit both a high chlorine resistance and a high current efficiency in highly concentrated caustic soda.

The high current efficiency is possible because perfluorocarboxylic acid membrane has a low water content and thus effectively prevents back migration of hydroxide ion. Perfluorosulfonic acid membrane, by contrast, is unable to prevent such back migration due to its low pKa value and its high water content¹⁴⁾. Figure 1 shows the relation between water content of membrane and caustic soda concentration. Figure 2 shows the relation between electric resistance and caustic soda concentration.

The general methods for preparation of perfluorocarboxylic acid membranes are indicated in Table 1. Membrane may be prepared by copolymerization of tetrafluoroethylene with perfluorovinyl ether monomer containing carboxylic acid, its ester or precursor convertible to carboxylic acid^{1,5,7)}, or by the introduction of carboxylic acid group through chemical reaction

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Fig. 1 Water content, equivalent weight and concentration of NaOH, for perfluorocarboxylic and perfluorosulfonic acid membranes

Fig. 2 Electric resistance, ion exchange capacity (meq/gram dry resin) and concentration of NaOH, for perfluorocarboxylic and perfluorosulfonic acid membranes

causing the scission of C-S bond contained in the pendant of the perfluorosulfonic acid polymer¹⁵⁻²⁰). Another method involves the coating of perfluorocarboxylic acid polymer on perfluoro-

Table 1 Process for the preparation of perfluorocarboxylic acid membrane

sulfonic acid membrane or the lamination of two different films of perfluoro polymer, one containing carboxylic acid group and the other containing sulfonic acid group^{2-4, 6, 8, 21, 22}).

3 Ion-Exchange Groups and Membrane Structure

Perfluorocarboxylic acid membrane is prepared in monolayer or multilayer form. Table 2 shows a comparison of the properties of perfluorosulfonic acid membrane, perfluorocarboxylic acid membrane and multilayer perfluorocarboxylic and perfluorosulfonic acid membrane in which the carboxylic acid layer faces the catholyte.

Table 2 Membrane properties classified by ion-exchange group and membrane structure

Ion-exchange group	R _f SO ₃ H	R _f COOH	R _f COOH/ R _f SO ₃ H
pKa	<1	2-3	2-3/1
Hydrophilicity	high	low	low/high
Water content	high	low	low/high
Current efficiency % (8N NaOH)	75	96	96
Electric resistance	low	high	low
Chemical stability	very high	high	high
Handling condition (pH)	>1	>3	>3
pH of anolyte	>1	>3	>1
Neutralization of OH ⁻ by HCl	applicable	impossible	applicable
O ₂ in product Cl ₂	<0.5%	>2%	<0.5%
Life of anode	long	short	long
Current density	high	low	high

As shown in Table 2, the multilayer membrane of perfluorocarboxylic acid and perfluorosulfonic acid has a current efficiency of about 95% or more and the lowest electric resistance, and is therefore the most desirable for use in electrolysis. With this membrane, hydrochloric acid can be injected into the brine stream in order to neutralize hydroxide ion migrating from catholyte, thus reducing the generation of oxygen and the formation of chlorate to very low levels. Consequently, chlorine of high purity

containing less than 0.5% oxygen can be readily obtained with this membrane, and the anode life can be greatly extended over that obtained with other membranes²³. The low electric resistance and high current density of this membrane allow significant reductions in the number of cells required and in electrolyzer investment cost.

Membrane of 100% perfluorocarboxylic acid has high electric resistance and does not dissociate in lower pH, thus making it difficult to neutralize hydroxide ion migrating from catholyte by injecting hydrochloric acid. Consequently, the oxygen content of the chlorine is high and the anode life is reduced. Perfluorosulfonic acid membrane have relatively low current efficiencies, and thus cannot be utilized economically.

4 Multilayer Membrane Prepared by Chemical Treatment

Multilayer membrane of perfluorocarboxylic and perfluorosulfonic acid can be prepared either by coating perfluorocarboxylic acid polymer on perfluorosulfonic acid membrane or lamination of two different polymer films containing carboxylic and sulfonic acid^{2~4, 6, 8, 21, 22} or by chemical conversion of perfluorosulfonic acid to perfluorocarboxylic acid^{15~20}. A comparison of these membranes is shown in Table 3.

Table 3 Comparison of monolayer and multilayer perfluoro ionomer membranes

Type of membrane	Monolayer perfluorocarboxylic acid membrane (COOH)	Multilayer membrane of perfluorocarboxylic and sulfonic acid by lamination or coating (COOH/SO ₃ H)	Multilayer membrane of perfluorocarboxylic and sulfonic acid by chemical treatment (COOH/SO ₃ H)
Thickness of COOH layer (micron)	>125	25~50	<10
Current efficiency % (8N NaOH)	96	96	96
Electric resistance	high	medium	low
Necessary number of functional monomers	1	2	1
Membrane fabrication	extrusion	extrusion and lamination or coating	extrusion and chemical treatment

In the coating of perfluorocarboxylic acid polymer and the lamination of two polymer films, the minimum thickness of the carboxylic acid layer which can be obtained is about 25~50 microns. This limits the degree to which the electric resistance can be lowered. A further disadvantage of this process is the necessity of separately preparing both sulfonic acid and carboxylic acid polymers.

Chemical treatment is considered to be the best method for preparation of membrane for

chlor-alkali process. With this method, the thickness of the carboxylic acid layer which forms on the surface of perfluorosulfonic acid membrane can be easily reduced to less than 10 microns, resulting in a corresponding reduction in the electric resistance of the membrane. In this process, moreover, only perfluorosulfonic acid polymer need be prepared beforehand to obtain the multilayer membrane of sulfonic acid and carboxylic acid.

5 Thickness of Carboxylic Acid Layer, Current Efficiency and Membrane Resistance

The current efficiency and the electric resistance are shown in Fig. 3 for the multilayer membrane prepared by chemical treatment. As shown in this figure, the electric resistance increases linearly with the thickness of carboxylic acid layer. The current efficiency increases greatly until the thickness of the carboxylic acid layer reaches 7 microns, where saturation tends to occur. From the point of view of power consumption, the optimum thickness of the carboxylic acid layer is in the range of 2~10 microns. Thus chemical treatment is the most appropriate method for preparation of carboxylic acid membrane, because the highest current efficiency can be obtained with a minimum increase in electric resistance.

Fig. 3 The thickness of COOH layer, current efficiency, and electric resistance of a multilayer perfluorocarboxylic and sulfonic acid membrane prepared by chemical treatment (COOH/SO₃H)

Figure 4 shows the relation between the current efficiency, caustic soda concentration and ion exchange capacity of multilayer membrane prepared by chemical treatment of perfluorosul-

Fig. 4 Current efficiency, ion exchange capacity (meq/gram dry resin) and concentration of NaOH, for multilayer perfluorocarboxylic and sulfonic acid membrane prepared by chemical treatment (COOH/SO₃H)

fonic acid membrane. Each membrane shows maximum current efficiency at a certain caustic soda concentration. This is because with increasing concentration of the external caustic solution up to a certain value, the membrane tends to shrink and the COO⁻ fixed ion concentration in the membrane tends to increase. However, if the concentration of the caustic soda increases beyond this value, hydroxide ion diffusion tends to increase due to increased electrolyte sorption, thus tending to decrease current efficiency.

Increasing the ion exchange capacity of the membrane results in the occurrence of the maximum current efficiency at a higher caustic soda concentration. Therefore in order to obtain high concentration of catholyte, the membrane should have carboxylic acid groups of high exchange capacity.

6 Carboxylic Acid Formation

Table 4 shows the most appropriate method of chemical treatment to convert perfluorosulfonic acid membrane or its precursor to perfluorocarboxylic acid membrane^{15,16}. In this process sulfonyl halide group in the membrane is con-

Table 4 Chemical treatment to prepare perfluorocarboxylic acid membrane from perfluorosulfonic acid membrane or its precursor

verted to sulfinic acid which is then converted to perfluorocarboxylic acid group through desulfonylation reaction. The perfluorocarboxylic acid pendant has one CF₂ less than the original chain of perfluorosulfonic acid. The extremely high selectivity of this reaction effectively prevents the formation of impure products, which would be impossible to remove from the membrane.

The following alternative reactions for conversion of perfluorosulfonic acid to perfluorocarboxylic acid have been reported^{17-20,24}, but have not been found practical or appropriate.

1. Conversion through CF₃I
2. Direct preparation of carboxylic acid group from SO₂Cl or SO₃H group
3. Addition reaction of the pendant having CF₃I or SO₂Cl group

7 Monomer Structure

Perfluorosulfonic acid membrane is utilized as a raw material for preparing multilayer membrane by chemical treatment. Table 5 shows the conventional method of du Pont de Nemours and Co. to prepare perfluorosulfonic acid membrane which utilizes perfluorosulfonyl fluoride monomer copolymerized with tetrafluoroethylene^{25,26}. However, short chain sulfonyl fluoride monomer of $m=0$ cannot be synthesized with this method, since its production is made impossible by ring formation²⁷. It is therefore necessary to utilize long chain sulfonyl fluoride monomer of $m=1$. With this monomer, however, it is impossible to obtain the ion exchange capacity of more than 0.9 meq per gram dry resin which is essential for electrolysis involving high concentrations of caustic soda. Moreover, the current efficiency of multilayer membrane prepared from this perfluorosulfonic acid membrane tends to decline during long term electrolytic operation.

Table 5 Synthesis of CF₂=CFO(CF₂CF₂CF₂SO₂F)_m Where : $m=0$ or 1

Table 6 Synthesis of $\text{CF}_2=\text{CFO}(\text{CF}_2\text{CFO})_m$
 $(\text{CF}_2)_n\text{-SO}_2\text{F}$ Where: $m=0$ or 1 ,
 $n=3\sim5$

In order to avoid these disadvantages of the conventional perfluorosulfonic acid membrane, we developed new perfluorovinyl ether monomers, which are synthesized as indicated in Table 6^{1,6, 28~35}. These monomers are unique in the number of CF_2 groups bonded to the functional group. This effectively prevents cyclization and thus allows the synthesis of monomer with $m=0$.

Figure 5 illustrates copolymer composition curves for the perfluorovinyl ether monomer with $n=3$ and $m=0$ or 1 when it is copolymerized with tetrafluoroethylene. Polymer can be obtained in a wide range of ion exchange capacities by adjusting the initial composition.

Fig. 5 Copolymer composition curves
 $n=3$, $m=0$ (○) or 1 (×)

Figure 6 shows the relation between the electric conductivity and the ion exchange capacity of perfluorosulfonic acid membrane prepared from the monomer. The membrane of monomer with $m=0$ has an ion exchange capacity of more than 1 meq per gram dry resin, and high physical strength. The membrane of monomer with $m=1$ has a lower ion exchange capacity but is still highly flexible. These properties are different from those of conventional per-

Fig. 6 Electric conductivity in 0.1 M NaOH at 25°C and ion exchange capacity for perfluorosulfonic acid

fluorosulfonic acid membranes.

In our process, membrane can be prepared by utilizing combinations of monomers with $m=1$ and $m=0$ in any given composition. Therefore membrane can be tailored for any specific concentration of caustic soda from 5 to 40% in electrolysis. Because of the structure of the perfluorosulfonic acid pendant, which differs from that in conventional membranes, our multilayer membrane retains a stable, high current efficiency regardless the length of electrolytic operation.

8 Hydrogen Gas Adhesion on the Surface of the Membrane

In the electrolysis conditions, a certain amount of hydrogen gas bubbles tends to adhere to the surface of the membrane. The bubbles can not be removed easily when the distance between the electrodes is below 1 mm resulting in an increase of cell voltage in this region with decreasing the electrode distance, as shown in

Fig. 7 Cell voltage versus electrode distance
 — : Conventional membrane
 --- : Surface treated membrane

Fig. 7. To overcome this disadvantage, we developed a unique surface treatment preventing the adhesion of hydrogen gas bubbles to the membrane. With the surface treated membrane, cell voltage decreases with the electrode distance even when it is below 1 mm as the dotted line in Fig. 7 shows, which allows a further reduction in electrolytic energy consumption.

9 Typical Membrane Structure

Table 7 shows a typical example of the structure of our multilayer membrane of perfluorocarboxylic acid and perfluorosulfonic acid made by chemical treatment which has a carboxylic acid layer of about 2 to 10 microns thickness. This membrane exhibits high current efficiency and low electric resistance and can be tailored to any concentration of caustic soda. It yields high performance and especially long service life.

Table 7 Structure of Asahi Chemical's membrane

Table 8 shows typical examples of electrolysis performance in small laboratory cells. These membranes are designed for use with caustic soda in concentrations of 21% and 30%.

Table 8 Performance of Asahi Chemical's membrane

membrane	current efficiency	electric resistance 25°C in 0.1N NaOH	cell voltage*
membrane for 21% NaOH	96%	4.2 ohm	2.98V
membrane for 30% NaOH	96%	3.9 ohm	3.12V

* in laboratory cell at 40 Amperes/dm² and 90°C

10 Power Consumption of our Membrane Chlor-Alkali Process

Figure 8 shows the improved performance obtained in our commercial cells incorporating recent improvements. We have conducted extensive work in improving the characteristics

and performance of anode and cathode. The high level of performance of commercial cell indicated in Fig. 8 is the result of development of high performance anode and catalytic cathode for industrial cells.

Fig. 8 Power consumption vs. current density

Figure 9 shows the view of our electrolyzer.

Fig. 9 Asahi Chemical electrolyzer

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