

# Novel Anion Exchange Membranes Having Fluorocarbon Backbone: Preparation and Stability

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## Synopsis

Anion exchange membranes with excellent durability were prepared by chemical modification of Nafion. The modification was achieved by transformation of the sulfonic acid group into quaternary ammonium group. Namely, Nafion membrane was first converted into an amide-type membrane. Reduction of the carbonyl group to methylene followed by quaternarization with alkyl iodide resulted in the formation of an anion exchange membrane. The electric resistance of the resulting membranes depends on the equivalent weight of the starting membranes (4.4–6.0  $\Omega$  cm<sup>2</sup> in 0.5N NaCl). The characteristics of the membranes are the excellent stability toward chemical substances such as organic solvents, oxidizing agents, acids, etc. For example, the membranes are stable in aqueous saturated chlorine solution at 60°C for 1000 hr.

## INTRODUCTION

Anion exchange membranes have widely been used in electro dialysis and diffusion dialysis as well as separators for secondary batteries.<sup>1–4</sup> In order to extend or diversify the use of anion exchange membranes, the membranes should overcome several limitations. For example, new membranes should have high thermal stability, high stability to various solvents, and high stability under oxidizing, acidic, or basic conditions. No conventional anion exchange membranes are stable against chlorine, and thus a membrane stable to chlorine is highly desirable.<sup>5</sup> Moreover, for construction of module-type apparatus, it is desirable to use tubular-type membrane.

The objective of this paper is to demonstrate novel fluorocarbon-type anion exchange membranes, which can overcome most of the above limitations. The Nafion membrane and its analogs are chemically stable and have good mechanical strength and desirable functionality.<sup>6</sup> Thus, the transformation of the cation exchange functionality into anion exchange functionality was studied.

As anion exchange groups, quaternary ammonium salts are generally more stable than sulfonium salts or phosphonium salts.<sup>7</sup> Among various quaternary ammonium salts, aliphatic ones are reported to be more stable than benzylic ones toward Hoffmann degradation or nucleophilic substitutions.<sup>8</sup> The strong electron-withdrawing effect of the perfluoroalkyl group

and the instability of intermediate fluoroalkylamine<sup>9</sup> would resist the direct attachment of the ammonium group to the Nafion skeleton.

In this investigation the trialkylammonium group was used as the anion exchange function, and one methylene group was placed between the Nafion skeleton and the ammonium function based on the stability test of model compounds such as 1H,1H-pentadecafluoro-octyltrimethylammonium chloride. The stabilities of the resultant membranes were also measured.

## EXPERIMENTAL

### Materials

The membranes used in our studies were Nafion 117, Nafion 415, and Nafion 125 membranes. These membranes are composed of the perfluoroethylene backbone and contain perfluoroalkyl ether side chain having sulfonic acid end group. Equivalent weight (EW) of these membranes are 1100, 1100, and 1200, respectively. Nafion 415 is reinforced with a Teflon mesh. The dyeing test was conducted by using 0.05% MeOH solution of crystal violet, cresol red, or bromocresol purple. The membranes used as references in the chlorine stability test were Selemion AMV (Asahi Glass Co., Ltd.) and Neocepta ACH-45T (Tokuyama Soda Co., Ltd.).

### MEMBRANE PREPARATION

**Amidation.** The Nafion membranes were treated with 2 N hydrochloric acid and then converted to sulfonyl chloride form, which was further subjected to hydroiodic acid treatment and then washed with alkali. These membranes were treated with a mixture of 8 N hydrochloric acid/MeOH (1:1) and then heated in a mixture of  $\text{PCl}_5/\text{POCl}_3$  (1:1.6) at 120°C for 24 hr. The membranes were immersed in dry ether, and dimethylamine gas was introduced (1.3 M) under cooling with ice, whereupon the membranes were allowed to react for 6 hr under cooling and 18 hr at room temperature. The infrared (IR) absorption of the obtained membranes were observed at 2950, 2800, 1500–1410  $\text{cm}^{-1}$  (C—H), and around 1700  $\text{cm}^{-1}$  (C=O). The membranes were not dyed by crystal violet or cresol red.

**Reduction.** The amide-type membranes obtained were immersed in a tetrahydrofuran (THF) solution of  $\text{NaBH}_4$  (0.53 M). The THF solution of  $\text{BF}_3 \cdot \text{Et}_2\text{O}$  (0.62 molar eq. to  $\text{NaBH}_4$ ) was added dropwise under ice cooling. The reaction was conducted for 5 hr under cooling and 18 hr under reflux, whereby the IR absorption around 1700  $\text{cm}^{-1}$  disappeared. The IR absorption was observed at 2970–2800  $\text{cm}^{-1}$  (C—H). The membranes were not dyed by crystal violet or cresol red.

**Quaternization.** The amine-type membranes obtained were immersed in a MeOH solution of MeI and the whole was heated at 60°C for 48 hr. The membranes were washed with MeOH and then treated with LiCl in MeOH. The resultant membranes were not dyed by crystal violet, but dyed red with bromocresol purple and yellowish orange with cresol red. The IR absorption was observed at 3050, 2950, 2800  $\text{cm}^{-1}$  (C—H). The degree of conversion of sulfonic acid group in the starting Nafion to the nitrogen-containing

membranes was determined based on the elemental analyses upon amine-type membranes. The determination upon the ammonium-type membranes led to erroneous results owing to high hygroscopicity.

### MEASUREMENT OF ELECTRIC RESISTANCE AND TRANSPORT NUMBER

The electric resistance of the membranes were measured in 0.5 N NaCl at 1000 Hz at 25°C under stirring. The transport numbers were calculated from the membrane potentials generated between 0.5 N NaCl and 2 N NaCl according to the Nernst equation.

### ELECTROLYSIS OF HYDROCHLORIC ACID

Electrolysis was conducted using a cell having two chambers separated by a membrane under the following conditions: Membrane surface area = 9.6 cm<sup>2</sup>; electrodes = Pt; electrolytes = 6 N hydrochloric acid; temp. = room temperature. Stirring the electrolytes in both chambers was continued during the electrolysis to prevent concentration polarization at the membrane surfaces.

## RESULTS AND DISCUSSION

### Preparation and Properties

A typical procedure for the conversion of the carboxylic acid group to the trimethylammonium group is summarized in Figure 1. The starting carboxylic acid-type membranes were prepared from Nafion membranes according to the known procedure.<sup>10</sup>

The membranes were first converted to methyl ester-type membranes and then converted into amide-type membranes by treatment with dimethylamine. The resulting membranes were transformed into amine-type membranes by reduction with diborane generated *in situ* from sodium borohydride and boron trifluoride-ether complex. Ammonium chloride-type membranes were finally prepared by successive treatments with methyl iodide and lithium chloride in methanol.

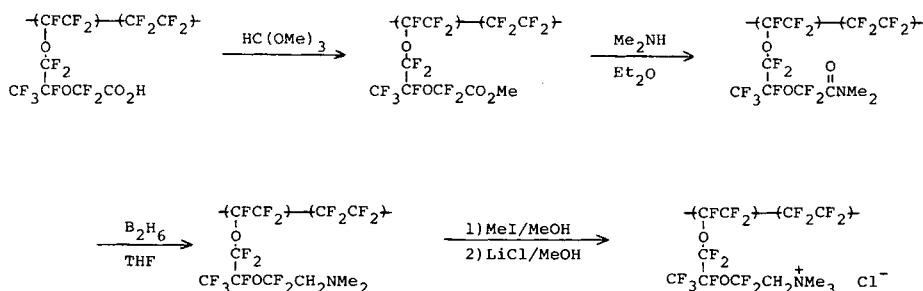


Fig. 1. Typical procedure for preparation of trimethylammonium-type anion exchange membrane from Nafion membrane.

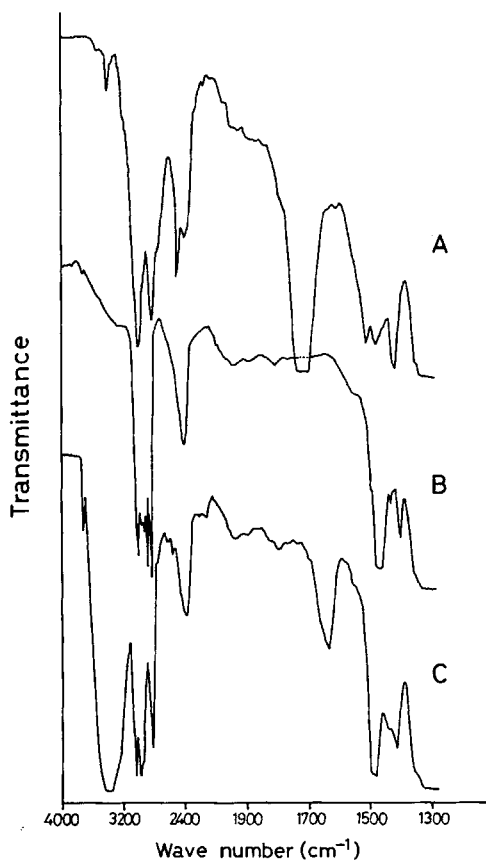


Fig. 2. IR spectra of transformed membranes (starting membrane = Nafion 125): (A) *N,N*-dimethylamide-type membrane; (B) *N,N*-dimethylamine-type membrane; (C) trimethylammonium-type membrane.

In these transformations, it is important to achieve complete reaction. Otherwise, ions cannot permeate through the membranes and/or transport properties of the resulting membranes were impaired. The completion of each reaction step was checked by dyeing and IR absorption. Dyeing with crystal violet shows the presence of anionic groups such as the sulfonic acid group or the carboxylic acid group; dyeing with cresol red or bromocresol purple indicates the formation of quaternary ammonium groups. In IR absorption, amide-type membranes show strong absorption around  $1700\text{ cm}^{-1}$  which diminishes as reduction of the amide group to amine group proceeds as shown in Figure 2. Absorption at  $2900\text{--}2850\text{ cm}^{-1}$  shifts to higher wave number size up to  $3025\text{ cm}^{-1}$  by quaternization. The degree of conversion was checked with elemental analysis of the amine-type membranes. The results are shown in Table I, which also shows electric resistances and transport numbers of the ammonium-type membranes. The electric resistances are comparable or slightly higher than those of conventional anion exchange membranes. The transport numbers of the present membranes were also comparable to those of conventional membranes.

TABLE I  
Anion Exchange Membranes Having Trimethylammonium Group

Membrane	Starting Nafion	Conversion <sup>a</sup> (%)	Electric resistance ( $\Omega \cdot \text{cm}^2$ )	Transport number
1	117	88	4.4	0.86
2	125	87	5.4	0.88
3	415	—	6.0	0.90

<sup>a</sup> The conversion was calculated based on the elemental analysis.

Membranes having other types of quaternary ammonium groups were also prepared by using various amines instead of dimethylamine according to the above procedure. Table II shows typical results of conversion of Nafion 125 into corresponding quaternary ammonium-type membranes. In the case of monoalkylamine, the resulting quaternary ammonium group has the alkyltrimethylammonium structure ( $-\text{N}^+(\text{Me})_2\text{R Cl}^-$ ). Steric hindrance of the amines would account for the observed low degree of conversion, which resulted in high electric resistances of the resulting membranes. The use of ethyl iodide instead of methyl iodide, yielded a membrane which has ethyltrimethylammonium group ( $-\text{N}^+(\text{Me})_2\text{Et Cl}^-$ ). On the other hand, quaternization with butyl iodide hardly proceeded, presumably owing to the low nucleophilicity of the amine group attached to the electron-withdrawing fluoroalkyl group.

Unconverted end groups of the side chain existing in the present anion exchange membranes are mainly hydroxymethyl group ( $-\text{CH}_2\text{OH}$ ) which are derived from carboxyl group (reduced with diborane).

The above procedure was also extended to the preparation of tubular anion exchange membranes from tubular Nafions. The complete transformation was confirmed by IR absorption and dyeing tests. The degree of conversion was around 90% based on the elemental analysis.

## STABILITY

Chlorine stability tests were conducted by dipping the membranes in water saturated with chlorine at 60°C. Figure 3 shows typical results. Two

TABLE II  
Anion Exchange Membranes Having Various Quaternary Ammonium Groups

Amine	Conversion (%)	Electric resistance ( $\Omega \cdot \text{cm}^2$ )	Transport number
$\begin{array}{c} \text{CH}_2\text{CH}_2 \\   \\ \text{NH} \\   \\ \text{CH}_2\text{CH}_2 \end{array}$	90	5.4	0.88
$\text{Et}_2\text{NH}$	60	33.8	0.91
$n\text{-PrNH}_2$	77	12.5	0.90
$\text{PhNH}_2$	71	26.5	0.91

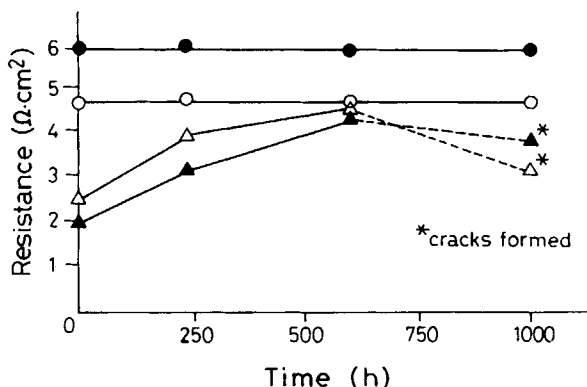


Fig. 3. Stability toward chlorine: (○) membrane 1; (●) membrane 3; (△) Selemion AMV; (▲) Neocepta ACH-45T.

hydrocarbon-type membranes were used as references. The references showed initial increases of the resistance and after about 600 hr cracks were observed. They were completely destroyed after 1000 hr. In contrast to the references, electric resistance of the present membranes hardly changed during the test. Also, no substantial changes in IR absorption were observed after 1000 hr treatment.

These membranes are also stable in 6 N hydrochloric acid, 6 N nitric acid, and peracetic acid at 60°C. However, they were not so stable under basic conditions. These membranes are mechanically superior to typical hydrocarbon-type membranes. For example, presently membranes can be handled in the dry state without any damage even after repeated swelling and drying.

Furthermore, the electrolysis of hydrochloric acid was conducted using membrane 3 in Table I. The relationship between current density and cell voltage is shown in Figure 4. No increase in the membrane resistance and no deterioration of the membranes were observed even when the membranes were subjected to the test for 1000 hr.

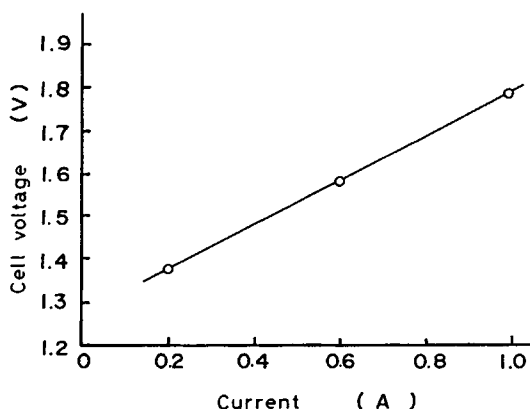


Fig. 4. Relationship between supplied current and cell voltage at electrolysis of 6 N hydrochloric acid.

### CONCLUSION

Novel anion exchange membranes composed of perfluoroethylene backbone and perfluoroalkyl ether side chain having quaternary ammonium end groups were prepared by chemical transformation of Nafion. The resulting membranes have excellent durability and desirable properties. They can be used as diaphragm for electrolysis or dialysis under severe conditions.

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