Modification of an Ion-Exchange Membrane Surface by Plasma Process Part 3: Interfacial Resistance of Monovalent Cation Perm-Selective Membrane from Nafion®

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The monovalent cation perm-selectivity of Nafion® 117, perfluoro-sulfonate cation-exchange membrane, was enhanced by depositing on its surface an ultrathin anion-exchange layer prepared by plasma polymerization. The anion exchanger was deposited from a 4-vinylpyridine monomer vapor followed by quaternarization with 1-bromopropane. The resulting anion-exchange layers were found to be pinhole-free and of uniform thickness. The monovalent cation perm-selectivity of the plasmamodified Nafion membrane was determined by measuring the Fe $^{2+}$ ion transference number, t_{Fe}, in a Li^+-Fe^{2+} system. The influence of the thickness of the plasma layers on the t_{Fe} and the membrane resistance was investigated. The t_{Fe} decreased with increasing thickness of the plasma polymer layer, but at the cost of enhanced membrane resistance. The resistance of treated Nafion was separated into bulk resistance and interfacial resistance. A large interfacial resistance was observed between Nafion and the plasma polymer layer, and was ascribed to the implantation of cation species.

On account of their relatively high ionic selectivity, ion-exchange membranes have recently received considerable attention as materials for use in water electrolyzers,[1,2] sensors,[3,4] redox-flow batteries,[5,6] and organic electrolyzers.[7,8] Ion-exchange membranes have a high selectivity of counter ions over co-ions. However, their ion selectivity among different counter ions is generally low. If these ion-exchange membranes had a higher selectivity among counter ions of different valency, the performance of such systems as redox flow batteries and brine electrolysis would be improved and membranes might find new fields of application. In previous reports[9-11] we reported that the perm-selectivity of the monovalent ion of a perfluorinated ion-exchange membrane, Nafion®, in the systems containing monovalent ion/divalent ions was enhanced by depositing on its surface an ultrathin anion-exchange membrane layer. The thin layer of the anion exchanger was prepared by the plasma polymerization of 4-vinylpyridine.

The principle of enhanced perm-selectivity of a monovalent ion is shown in Fig. 1. A thin plasma polymer layer of an anion exchanger is deposited on the surface of a cation-exchange membrane. On account of the electrostatic repulsion from the fixed anionic groups in the cation-exchange membrane, the anion can not be transported through the membrane. Similarly, the transport of monovalent ions and the divalent cation is also suppressed by an electrostatic repulsion from the fixed cationic groups in the thin cationic plasma polymer layer on the surface of the cation-exchange membrane. However, since the repulsion of monovalent ions from the fixed cations in the plasma polymer layer is weaker than that of divalent ions, monovalent ions can be transported through the plasma polymer layer much more easily than can divalent ions.

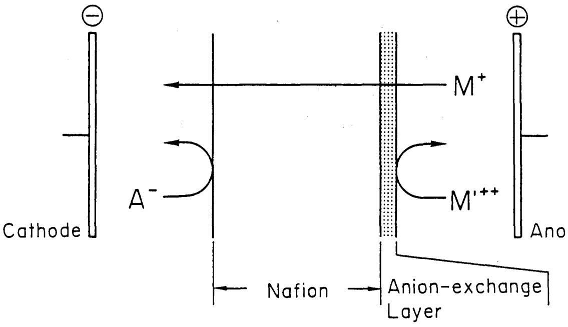

Fig. 1. Principle of the enhancement of monovalent ion perm-selectivity through a cation-exchange membrane.

In a previous study,[11] the lithium ion perm-selectivity of Nafion was enhanced by depositing on its surface an ultrathin anion-exchange layer by the plasma polymerization of 4-vinylpyridine, followed by quaternarization with 1-bromopropane in the Li^+-Fe^{2+} system. This, however, was at the cost of membrane ionic conductivity. In the present paper, we discuss the high membrane resistance, and, in particular, how the membrane resistance was enhanced during plasma polymerization.

Experimental

Plasma Polymerization. The apparatus used to carry out plasma polymerization, which was described in detail in a previous report,[11] consisted of a glass reactor equipped with capacitively coupled inner disk electrodes to which an alternating voltage was applied at a frequency of 13.56 MHz. This reactor was introduced into a vacuum system comprising of a mechanical booster pump, a rotary pump, and a

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"Nafion" is a registered trade mark of the Du Pont de Nemous and Co., Inc.

Table 1. Compositions of the Electrolyte Used for Perm-Selectivity Measurement

Catholyte	Anolyte
0.2M CH_3COOH	0.2M CH_3COOH
0.2M CH_3COOLi	0.2M CH_3COOLi
0.8M LiCl	0.7M LiCl
	0.05M $FeCl_2$

cold trap. The pressure in the reactor was monitored by using a Pirani gauge. Nafion 117 sheets were utilized as a substrates. The pretreatment of Nafion was described previously.[10] In order to obtain a tight adhesion of the plasma layer onto Nafion, the Nafion surface was pretreated by an oxygen plasma preceding plasma polymerization. A Nafion sheet was fixed on an RF electrode and sputtered with an oxygen plasma at a flow rate of 10 cm^3 (STP) min^{-1}, 6.6 Pa pressure, and 50 W RF power. The substrate was placed in a nominal "after-glow" region, 2 cm downstream from the edge of the electrodes. 4-vinylpyridine vapor at a flow rate of 10 cm^3 (STP) min^{-1} was introduced into the reactor and the pressure was maintained at a constant value of 67 Pa. Plasma polymerization was carried out at an RF power of 5W. The thickness of the plasma polymer film was changed by controlling the plasma polymerization time.

Quaternarization of Plasma-Polymerized 4-Vinylpyridine. A thin layer of plasma-polymerized 4-vinylpyridine was quaternarized by treatment with a 1 vol% 1-bromopropane/propylene carbonate solution at 50 °C for 48 h.[12] After soaking, each film was washed with propylene carbonate in order to remove any excess 1-bromopropane. These films treated were then dried under reduced pressure (10^{-1} Pa) in order to evaporate the propylene carbonate.

Properties of the Plasma Polymer. The measuring technique of the ohmic resistance of the plasma-modified Nafion was described previously.[10] The membrane resistance was measured in an aqueous 1.0 M HCl solution (1 M=1 mol dm^{-3}).

The monovalent ion perm-selectivity of the plasma-modified Nafion was evaluated from the transference number of the Fe^{2+} ion (t_{Fe}) in the Li^+-Fe^{2+} system. A total charge of 100 C was passed at a constant current of 10 mA (12.8 mA cm^{-2}) through the system:

anolyte of Table 1	plasma-modified Nafion (plasma layer contacting the anolyte)	catholyte of Table 1

Each compartment was filled with an electrolyte solution (listed in Table 1), respectively. After electrolysis, the total amount of Fe^{2+} in the catholyte was measured by absorption spectrometry using 1,10-phenanthroline[13] to evaluate the amount of Fe^{2+} transported through the plasma-modified Nafion. The values of t_{Fe} were calculated from the amount of Fe^{2+} transported and the total charge passed during electrolysis.

Results and Discussion

Influence of Thickness of Plasma Polymer Layer on Membrane Resistance of Plasma-Modified Nafion®. The IR spectrum of the plasma polymer layer showed absorption peaks of N–H and C≡N vibration, which indicated a cleavage of the pyridine ring of 4-vinylpyridine. On the scale of the scanning electron micrograph, the plasma polymer layer was found to be free from pinholes and uniform in thickness. The membrane resistances of the plasma-modified Nafion are shown in Fig. 2 as a function of the thickness of the plasma polymer layer. Also indicated in Fig. 2 is the transference number of Fe^{2+} through plasma-modified Nafion. The transference number of Fe^{2+} decreased with increasing thickness of the plasma polymer layer. This fact indicates that the ion-exchange capacity of the plasma polymer layer is low because of a decomposition of the monomer of 4-vinylpyridine in glow region, as described above.

The membrane resistance of the plasma-modified Nafion is in direct proportion to the thickness of the membrane. However, the resistance obtained by extrapolating to zero membrane thickness is not zero but, rather, 7.6 Ω cm^2. In this case, the resistance of the oxygen-sputtered Nafion used as a substrate is only 1.5 Ω cm^2. These facts indicate that the membrane resistance consists of two different components; viz, the bulk resistance of the plasma polymer layer and interfacial resistance between the plasma polymer layer and the Nafion membrane, which is 6.1 Ω cm^2 (different between 7.6 and 1.5 Ω cm^2).

Interfacial Resistance between Plasma Polymer Layer and Nafion®. The interfacial resistance might be ascribed to neutral layers containing no or few ion-exchange groups, or caused by stable ion pairing between the sulfo group of the Nafion membrane and the quaternarized amino or pyridyl group. The former layer is formed by a decomposition of the sulfo group in the Nafion membrane by the attack of a highly energetic species in the glow region. The

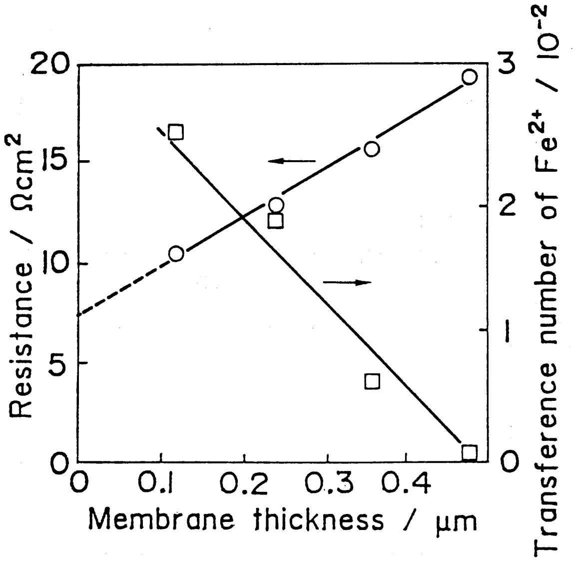

Fig. 2. Variation of Fe^{2+} ion transference number and membrane resistance with membrane thickness of plasma polymer layer. Flow rate of 4-vinylpyridine: 10 cm^3 (STP) min^{-1}. RF power: 5 W. Polymerization pressure: 67 Pa.

latter layer is formed by the penetration of nitrogen-containing species into the Nafion membrane.

Nafion membranes sputtered by oxygen showed a membrane resistance value of 1.5Ω cm^2, despite the fact that the sputtering conditions were harder than those for plasma polymerization. This fact does not indicate that the decomposition of the sulfo group of Nafion during plasma polymerization extended very remarkably. Therefore, the interfacial layer is composed of a tightly bound ion pair. The penetration of a nitrogen-containing species into the Nafion would occur through a process like the implantation of cationic species containing nitrogen, which were accelerated by an electric field between the plasma bulk and the substrate. However, the electric field was not as high as in a conventional ion-implantation method.

The cationic species containing nitrogen is of interest. Since various kinds of reactive species exist in the glow region, it is difficult to identify the nitrogen-containing cation. The cationic species in the glow region can, however, probably be inferred from the mass spectra of the 4-vinylpyridine used as a monomer. The mass spectra of 4-vinylpyridine are shown in Fig. 3. The ionization was affected by electron bombardment at 30 (Fig. 3A), 20 (Fig. 3B), and 10 (Fig. 3C) eV, respectively. The average electron temperature under the glow discharge used in this study was less than 10 eV.[14] Therefore, the fragmentation at 10 eV should approximate more closely what occurs under the plasma polymerization conditions. The mass spectrum of 4-vinylpyridine at 10 eV had a major peak at m/z=105 (a parent peak) and at m/z=78. A similar spectrum was obtained at 20 and 30 eV, except for the appearance of peaks of m/z=51, 52, and so on, since fragmentation proceeded more extensively than at the lower energy levels. The probable major species of the mass spectra are shown in Fig. 4. Among these cationic species in Fig. 4, only the species at m/z 105, which is a parent peak, contains nitrogen. Since higher-energy particles exist in significant amount under the conditions of plasma polymerization, the other cationic species may be capable of appearing in the mass analysis at a high fragmentation energy. Further, since the cationic species collide more than two times in the glow region, cationic species containing nitrogen (other than that of m/z=150) can be formed. However, the species of m/z=105 is inferred to be the main, important species for the production of an ion-exchange layer.

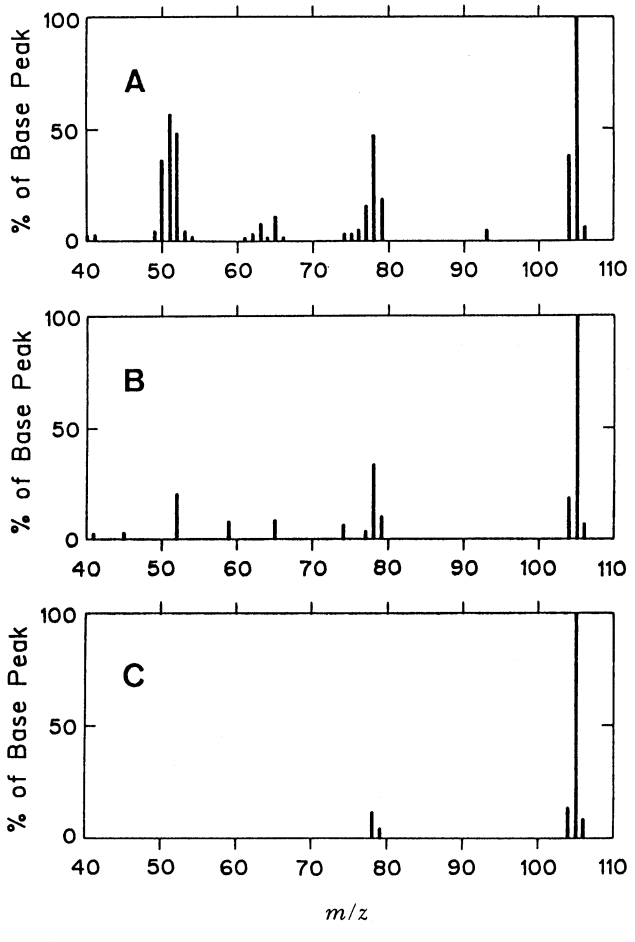

Fig. 3. Mass spectra of 4-vinylpyridine: (A) electron temperature=30 eV, (B) 20 eV, and (C) 10 eV.

Figure 5 schematically shows the process for the formation of the interfacial layer between Nafion and the plasma polymer layer. First, the cationic species contains nitrogen (perhaps the species m/z=105 of Fig. 4) which is accelerated by an electric field caused by a difference between the plasma potential (V_s) and the floating potential on Nafion (V_f) (Fig. 5a). The difference between V_s and V_f under the glow discharge used in this study is expected to be of the order of tens.[15–17] In our preliminary results,[18] the V_s and V_f measured by a single-probe method are 77 and 10 V (vs. ground level) under similar conditions to that of plasma polymerization, except for the absence of 4-vinylpyridine. From these results, the difference

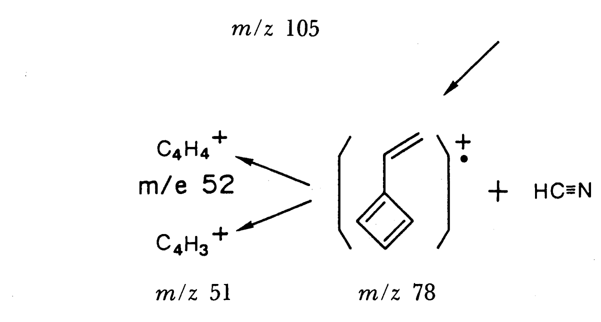

Fig. 4. Probable fragmentation products of 4-vinylpyridine by electron bombardment.

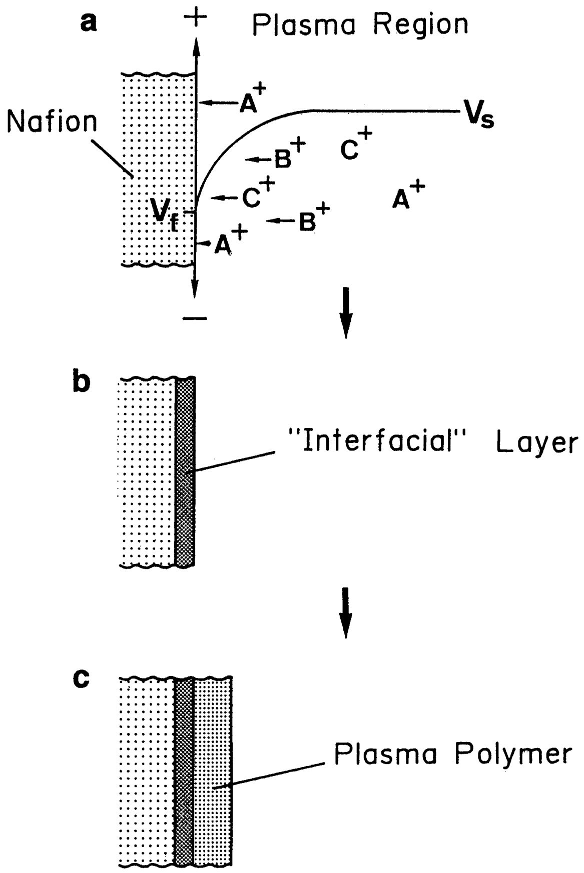

Fig. 5. Schematic diagram of the process for the formation of the interfacial layer between Nafion and the plasma polymer layer. (The thickness ratio is different from practical value.)

between V_s and V_f was approximately estimated to be about 67 V. The cationic species containing nitrogen was implanted by the potential difference between V_s and V_f (Fig. 5a and 5b). In previous studies,[9–11] the membrane resistance increased with increasing RF power, or with decreasing polymerization pressure. The influences of the polymerization pressure, P, and applied RF power, W, are related to each other. It is therefore convenient to consider the RF power-to-pressure ratio (W/P) as being a parameter of the energy given to the plasma. The greater the value of W/P, the higher is the electron temperature in the plasma.[19] The higher electron temperature, the more the extent of decomposition of the monomer becomes, and the larger the potential difference between V_s and V_f. Therefore, in this study, plasma polymerization was carried out at a relatively high pressure of 67 Pa and a low RF power of 5W. The implantation of cationic species having low m/z should not be excluded since these would have a higher kinetic energy, which is favorable to implantation. The plasma polymer layer was deposited on the interfacial layer (Fig. 5c). The penetrating nitrogen-containing species is then quaternarized with 1-bromopropane and forms a tightly bonded ion pair between the sulfo group of the Nafion membrane and the quaternarized amino or the pyridyl group. This bonding causes an increase in the membrane resistance.

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