

Enhancement of Monovalent Cation Perm-Selectivity of Nafion
by Plasma-Induced Surface Modification¹⁾

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Novel monovalent cation perm-selective membranes were prepared by the surface modification of perfluorosulfonate cation exchange membranes, Nafion. Nafion was sputtered with oxygen plasma in order to produce radical sites on its surface. Ultra-thin cationic layers was produced on the Nafion surface by reactions between the radical sites and 4-vinylpyridine vapor. The resultant membranes showed high monovalent cation perm-selectivity (transference number of divalent cation = 2×10^{-2}) and low membrane resistance of $2 \Omega \text{ cm}^2$.

Ion-exchange membranes have been used in a variety of electrochemical applications, including electrolyzers,²⁾ sensors,³⁾ redox-flow batteries,⁴⁾ and fuel cells.⁵⁾ Although ion-exchange membranes have high perm-selectivities for counter-ions over co-ions, their perm-selectivities among different counter-ions are generally low. The enhancement of perm-selectivities for monovalent ions over multivalent ions would extend the application of ion-exchange membranes. The authors have been reported on the surface modification of cation-exchange membranes by using a plasma polymerization method aiming the preparation of monovalent cation perm-selective membranes.⁶⁻⁹⁾ The monovalent cation perm-selectivity of perfluorosulfonate cation exchange membranes, Nafion,¹⁰⁾ was enhanced by depositing on its surface an ultra-thin anion-exchanger layer containing quaternarized pyridyl and/or amino groups. The surface modified Nafion membranes exhibited very high monovalent ion perm-selectivities at the cost of high membrane resistance. The membrane resistance was separated into the bulk resistance and the interfacial resistance between Nafion and plasma polymer layer. The latter was inferred to be caused by an implantation of cationic species containing nitrogen which were formed during plasma polymerization process.⁹⁾ This paper reports on the enhancement of monovalent cation perm-selectivity of Nafion without significant increase of membrane resistance by a novel method of plasma-induced surface modification.

The principle of the enhancement of monovalent cation perm-selectivity was described previously.^{6,7)} A thin layer of anion exchanger is deposited on the surface of Nafion. The transport of both monovalent and multivalent cations is suppressed by the electrostatic repulsion

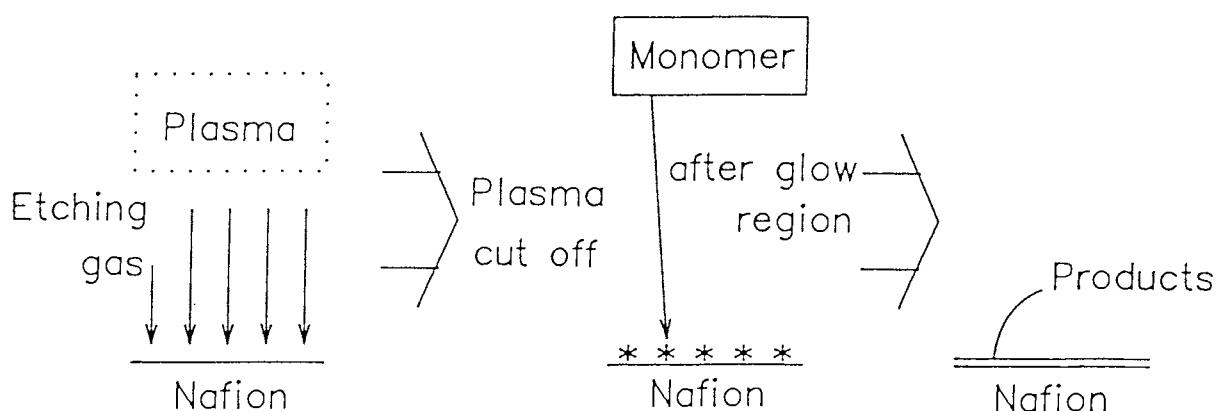


Fig. 1. Schematic diagram of process for plasma-induced modification of Nafion surface.

from the fixed cationic groups in the anion-exchanger layer. However, since the repulsion of monovalent cations from the fixed cationic groups is weaker than that of multivalent cations, monovalent cations can be transported through the anion-exchanger layer much more easily than can be multivalent cations. Anions can not permeate through the cation exchange membrane, Nafion.

The apparatus used to carry out the plasma-induced surface modification consisted of a glass reactor equipped with capacitively coupled inner parallel disk electrodes to which an alternating voltage was applied at a frequency of 13.56 MHz. Nafion 117 sheets were placed on an RF electrode. A schematic diagram of the process for the plasma-induced surface treatment is shown in Fig. 1. Oxygen gas was introduced into the reactor at a flow rate of $10 \text{ cm}^3(\text{STP}) \text{ min}^{-1}$ and the pressure was maintained at 0.05 Torr. Sputtering of the Nafion sheets was carried out under these conditions at various levels of RF power for 1 min in order to produce radical sites on its surface. After sputtering, 4-vinylpyridine vapor was introduced into the

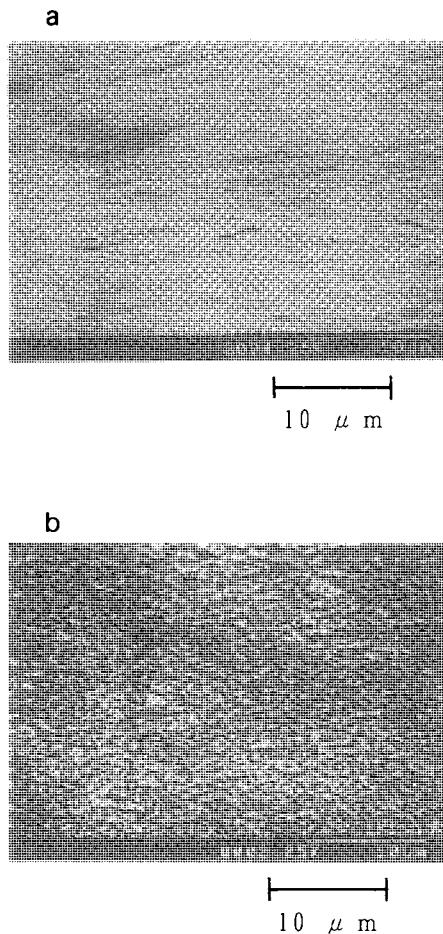


Fig. 2. Scanning electron micrographs of Nafion surface after sputtering for 30 min. (a) RF power = 10 W, (b) RF power = 50 W

reactor to react with the radical sites. A thin layer formed from 4-vinylpyridine was quaternarized by treatment with 1-bromopropane.¹¹⁾

Figure 2 shows scanning electron micrographs of the Nafion surface after sputtering for 30 min. These figures show that its surface roughness increased by an attack of highly energetic species accelerated in an ion sheath under large input energy conditions. The Nafion surface before sputtering was flat and no observable contrast was detected. ESCA S_{2p} peaks for Nafion after oxygen sputtering indicate that a small amount of sulfonic acid group on its surface was decomposed to sulfoxide. Transference number of Fe²⁺, t_{Fe} , and membrane resistance of untreated Nafion 117 were 0.32 and 0.5 Ωcm^2 , respectively.¹²⁾ On the other hand, t_{Fe} and membrane resistance of Nafion after oxygen sputtering at 10 W were 0.17 and 0.9 Ωcm^2 , respectively. These results indicate that the density of anionic groups on Nafion decreased as a result of decomposition of its surface sulfonic acid groups.

Ultra-thin layers containing pyridine ring was formed on the Nafion surface by reaction between the radical sites and 4-vinylpyridine vapor. ESCA N_{1s} peaks after reaction with 4-vinylpyridine indicates that nitrogen was introduced on the Nafion surface. The t_{Fe} and the membrane resistance of the surface-modified Nafion are described in Fig. 3. The t_{Fe} decreased with increasing RF power for oxygen sputtering. The higher the value of RF power, the higher the concentration of radical sites on the Nafion surface. The high concentration of the radical sites leads to the high density of quaternarized pyridine rings on its surface. The t_{Fe} values for surface-modified Nafion were about 2×10^{-2} , which was significantly lower than the value for untreated Nafion membrane. The surface-modified Nafion exhibited a membrane resistance of 2-3 Ωcm^2 , which was considerably lower than the reported value for Nafion surface-modified by a plasma polymerization method,¹³⁾ 12 Ωcm^2 ,⁹⁾ while t_{Fe} was almost unchanged. These results reveal that implantation of cationic species containing nitrogen was suppressed in the present plasma-induced surface modification, and an interfacial layer causing the increase in resistance did not form.

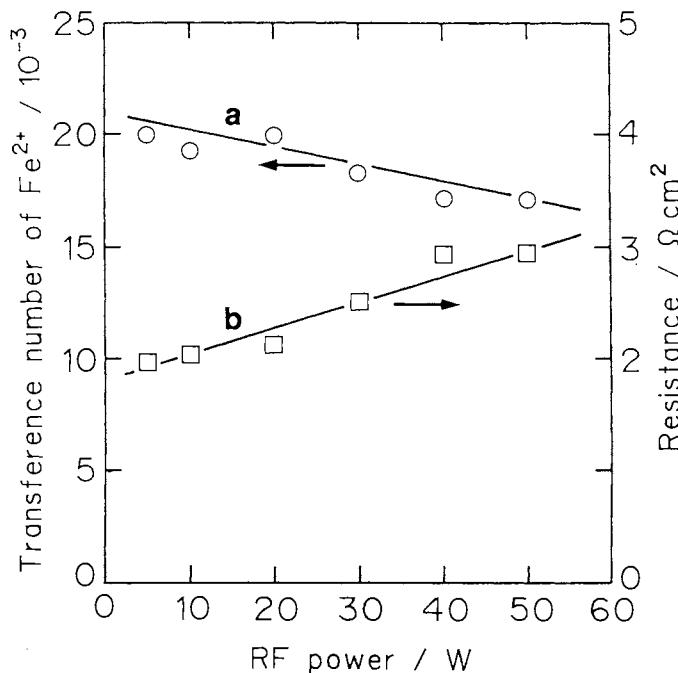


Fig. 3. Variation of Fe²⁺ ion transference numbers and membrane resistance with RF power for oxygen sputtering. Sputtering time: 1 min.

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- 10) "Nafion" is a registered trade mark of the Du Pont de Nemours and Co., Inc.
- 11) A thin layer formed from 4-vinylpyridine was quaternarized by treatment with a 1 vol% 1-bromopropane/propylene carbonate solution at 50 °C for 48 h.¹⁴⁾ 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 in order to evaporate the propylene carbonate.
- 12) The ohmic resistance of the plasma-modified Nafion was measured in 1.0 M HCl solution using a two compartment cell. The perm-selectivity of the plasma-modified Nafion was evaluated from the transference number of Fe^{2+} in a Li^+ - Fe^{2+} system. Since Nafion has the least affinity for Li^+ among the alkali metal cations and $Fe^{2+}/3+$ redox system was used in a variety of practical electrochemical systems such as redox-flow batteries,⁴⁾ Li^+ and Fe^{2+} were selected to elucidate the enhancement of monovalent cation perm-selectivity. The membrane was set as a separator between two compartments of a glass cell. Electrolyte solution filled each compartment was described elsewhere.^{8,9)} After the constant current electrolysis (12.8 mA cm⁻²) by 100 C, the total amount of Fe^{2+} contained in the catholyte was measured by absorption spectrometry using o-phenanthroline.
- 13) Anion-exchanger layer of 0.24 μ m was deposited on Nafion surface from a 4-vinylpyridine monomer vapor using plasma-polymerization technique followed by quaternarization with 1-bromopropane. Plasma polymerization was performed at a monomer flow rate of 10 cm³(STP) min⁻¹, pressure of 0.5 Torr, and RF power of 5 W.
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