Preparation of Thin Cation-Exchange Membranes Using Glow Discharge Plasma Polymerization and Its Reactions

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Thin cation-exchange films with fixed sulfonic acid groups were prepared by plasma polymerization followed by hydrolysis of sulfonyl halide groups using benzenesulfonyl fluoride and benzenesulfonyl chloride as starting materials. For benzenesulfonyl fluoride, sulfonyl fluoride groups were introduced into the plasma-formed polymers, whereas benzenesulfonyl chloride tended to decompose during plasma polymerization. The difference between the reaction in the glow discharge plasma of benzenesulfonyl fluoride and that of benzenesulfonyl chloride is discussed based on results obtained by *in situ* mass spectrometry and molecular orbital calculations. For benzenesulfonyl fluoride, the parent ion ($[C_6H_5SO_2F]^{+\bullet}$) is the major species which introduces the sulfonic fluoride groups into the plasma polymer because S–F bond cleavage is difficult. However, the parent ion of benzenesulfonyl chloride is unstable in the glow discharge plasma, and cleavage of the S–Cl bond is facile and produces Cl radicals. The plasma polymer formed at 3.5 W using benzenesulfonyl fluoride exhibits a cation-exchange capacity of 1.3 mequiv g^{-1} after hydrolysis, which is comparable to the capacities of commercially available cation-exchange membranes.
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Ion-exchange films have been used in a variety of electrochemical applications including fuel cells,[1-6] electrolyzers,[7,8] batteries,[9,10] and sensors.[11] To use them in these electrochemical devices, it is desirable to reduce the ohmic resistance of the ion-exchange films, while maintaining high ion-exchange capacity. One way of solving this problem is to prepare thin ion-exchange films.

Plasma polymerization is expected to become a novel and unique preparation method for organic thin films because uniform, pinhole-free, and chemically and thermally stable thin films with cross-linked structures can be obtained by this technique.[12,13] However, it is not easy to introduce functional groups such as ion-exchange moieties into the polymers because the functional groups are easily decomposed by active species in the glow discharge plasma.[12]

We studied the introduction of sulfonic acid groups into polymers and prepared thin plasma-polymerized ion-exchange films. We showed that the selection of the starting material and plasma parameters are important for introducing functional groups into the polymer.[14-17] To improve the performance of these plasma-formed polymers, knowledge of the reaction which introduces functional groups into the polymer is necessary for proper selection of starting materials. The reactions during plasma polymerization, however, are not well understood due to their complexity.[13]

The direct detection of species in the glow discharge plasma provides key information about the reactions. In the field of dry etching and plasma chemical vapor deposition (CVD) for a-Si:C deposition, plasma species have been investigated by emission spectroscopy,[18,19] absorption spectroscopy,[20,21] and mass spectrometry.[22-24] Emission and absorption spectroscopies detect only specific chemical species because the assignment of emission or absorption is very difficult without spectroscopic data. Investigation by *in situ* mass spectrometry is considered to be the most useful method to detect complex chemical species and investigate the reactions taking place in glow discharge plasmas containing large organic molecules.

In a previous paper[15] we reported the preparation of thin films with fixed sulfonic acid groups by hydrolysis of sulfonyl halide

groups by plasma polymerization using benzenesulfonyl halides, *e.g.*, benzenesulfonyl fluoride and benzenesulfonyl chloride, as starting materials. For benzenesulfonyl chloride, however, the sulfonyl chloride groups decomposed and were not fixed to the plasma-formed polymers. The reactions of benzenesulfonyl halides in the glow discharge plasma are key processes for introducing sulfonyl halide groups into the polymers. In this paper the species and reactions in the glow discharge plasma, including sulfonyl halide molecules, are analyzed and discussed based on *in situ* mass spectroscopy analysis supported by molecular orbital calculations. To our knowledge, there is no literature example of a mass spectrometric study of glow discharge plasmas for the preparation of functional plasma-polymerized thin films from such large organic molecules.

Experimental

Materials.—Benzenesulfonyl chloride (Wako Pure Chemical Industries, extra pure grade) and benzenesulfonyl fluoride (Aldrich Chemical Company, Inc., extra pure grade) were used without further purification. Water was purified using a Barnstead Nanopure water purifying system and had a resistivity higher than 18.5 MΩ cm.

Plasma polymerization.—The apparatus used in this study is shown in Fig. 1. The reactor, which was made of 304 stainless steel, was equipped with two capacitively coupled inner electrodes to which an alternating voltage was applied at a frequency of 10 kHz. The reactor was incorporated into a vacuum system consisting of a mechanical booster pump, a rotary pump, and a cold trap. Glass plates deposited with gold and 304 SUS plates were utilized as substrates. These substrates were placed on a glass substrate holder mounted on the grounded electrode. Argon gas [30 cm^3 at standard temperature, pressure (STP) min^{-1}] and benzenesulfonyl chloride or benzenesulfonyl fluoride vapor [5 cm^3 (STP) min^{-1}] were introduced into the reactor through the showerhead AF electrode, and the pressure was maintained at desired values. Benzenesulfonyl fluoride and benzenesulfonyl chloride were maintained at 50 and 75°C, respectively, during plasma polymerization to enhance their vapor pressures. Metering valves controlled the monomer flow rates.

The pressure in the reactor was monitored using a Pirani vacuum gauge and fixed at 0.2 Torr. The plasma polymerization was carried out at various levels of discharge power.

Mass spectrometry.—The plasma reactor was connected with a quadrupole mass spectrometer (QMS, ULVAC MSQ400) housed in a separate vacuum chamber pumped by a turbomolecular pump. The pressure difference of the plasma reactor and the mass spectrometer

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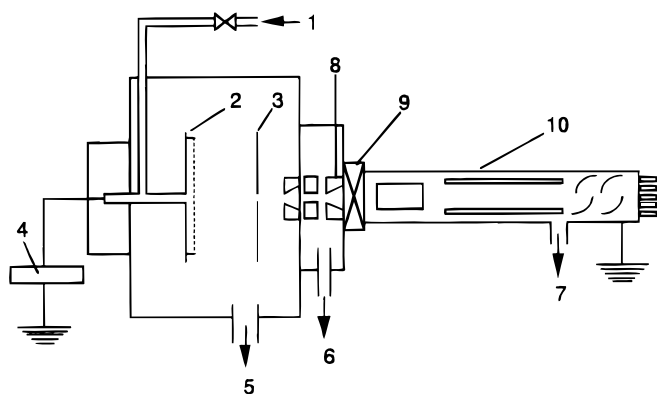
Figure 1. Schematic diagram of an apparatus for plasma polymerization. (1) Monomer inlet, (2) AF electrode, (3) ground electrode, (4) 10 kHz AF power generator, (5-7) pumping system, (8) magnet (ion repeller), (9) valve, and (10) QMS.

was maintained by a 0.1 mm diam orifice in an aperture with a 35 mm diam Con Flat flange. This electrically isolated aperture was placed behind a 5 mm diam hole in the grounded electrode; the distance between the grounded electrode and the aperture was about 1 mm. Species were sampled from the glow discharge plasma through a hole in the grounded electrode and the orifice and were detected and mass-analyzed using the QMS.

Cations, radicals, and excited species may exist in the glow discharge plasma.[13] The cationic species in the plasma reactor were analyzed by introduction to the QMS without electron impact. To detect radicals and excited species, it was necessary to avoid any influence of cationic species. Cationic species were rejected from the QMS by its magnetic field. Thus, only neutral species, radicals, excited species, and monomers were introduced into the QMS. An electron impact of 10-15 eV was applied to these neutral species. To remove the influence of monomer fragments, spectra of radicals and excited species were obtained by subtracting the QMS spectra at plasma-off conditions from QMS spectra at plasma-on conditions.

Measurement techniques.—The chemical structures of the plasma-formed polymers were analyzed by X-ray photoelectron spectroscopy (XPS, Shimadzu model ESCA-850) and Fourier transform infrared (FTIR spectroscopy, Shimadzu model FTIR-4100) using the reflection method. A reflecting gold layer was deposited onto the glass substrate by evaporation prior to plasma polymerization.

The ion-exchange capacity of the plasma-formed polymer was measured by acid-base titration. As-deposited polymers in proton form were soaked in 30 mL of 0.5 M NaCl solution for 1 h at 25°C. Then the solution was titrated with 10^{-3} mol dm^{-3} sodium hydroxide, using a Horiba model F7 pH-meter.

Method of calculation.—*Ab initio* molecular orbital calculations were carried out with the GAUSSIAN 90 program.[25] All structures were optimized by the Hartree-Fock method with a 6-31G basis set level.[25] The restricted Hartree-Fock (RHF)[26] procedure for calculation of closed-shell species and the restricted open-shell Hartree-Fock (ROHF)[26,27] procedure for calculation of open-shell species were used.

Results and Discussion

Characterization of plasma polymerization.—The chemical structures of plasma-polymerized films formed from benzenesulfonyl chloride and benzenesulfonyl fluoride were first investigated by XPS and FTIR spectroscopy. XPS S_{2p} spectra were examined to investigate the chemical state of sulfur in the plasma-formed polymers. Figures 2 and 3 illustrate XPS S_{2p} spectra for the polymers formed from benzenesulfonyl fluoride and benzenesulfonyl chloride, respectively, at various levels of applied discharge power. Figure 2 shows that the S_{2p} spectra for the polymers formed from benzenesulfonyl fluoride consist of three component peaks. The peaks

at 170, 168, and 163 eV are assigned as sulfonyl fluoride (-SO_2F), sulfone (-SO_2-), and sulfur groups of lower oxidation state such as sulfide, respectively.[28,29] By decomposition of the starting sulfonyl fluoride groups during plasma polymerization through collisions with highly energetic species, sulfone and sulfur of a lower oxidation state were introduced into the polymer. At low applied power levels, the content of sulfonyl fluoride groups is high in the polymers and the content of sulfur of lower oxidation number is low, whereas in the polymers formed at high applied power levels the content of sulfur at a low oxidation state is high.
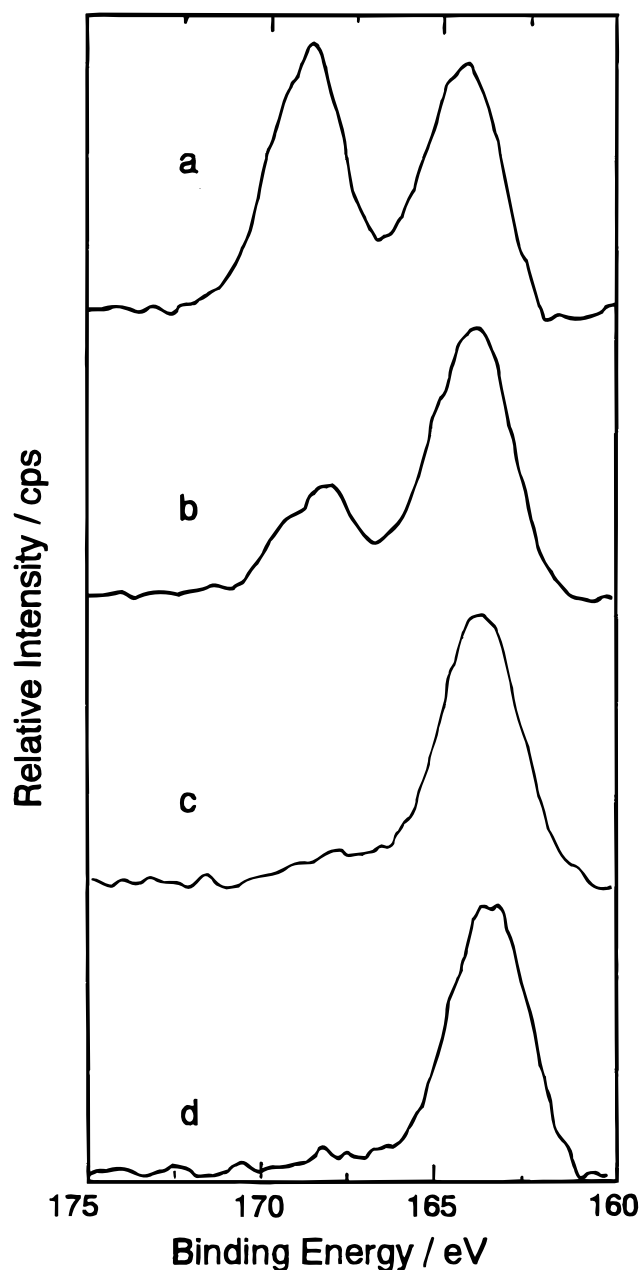
The decomposition of sulfonyl chloride groups during plasma polymerization proceeds more extensively. The spectra of Fig. 3 exhibit no peaks assigned to sulfonyl chloride groups. The polymers formed at low discharge power consist of two component peaks, assigned to sulfone and sulfur of a low oxidation state. The polymers
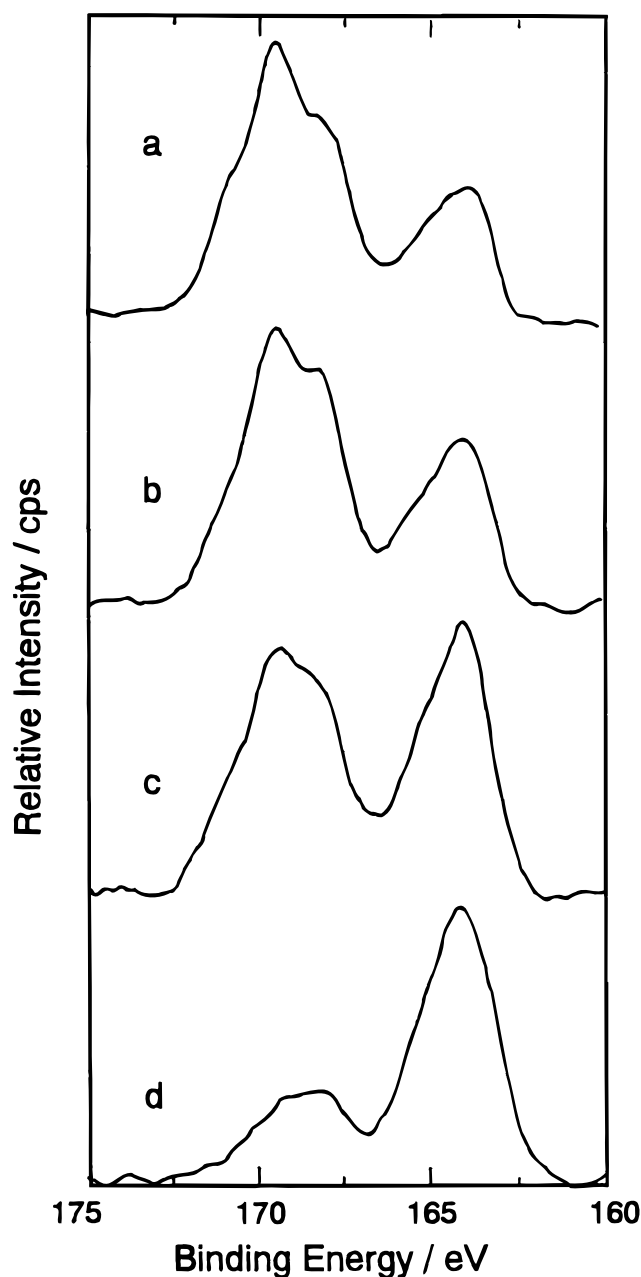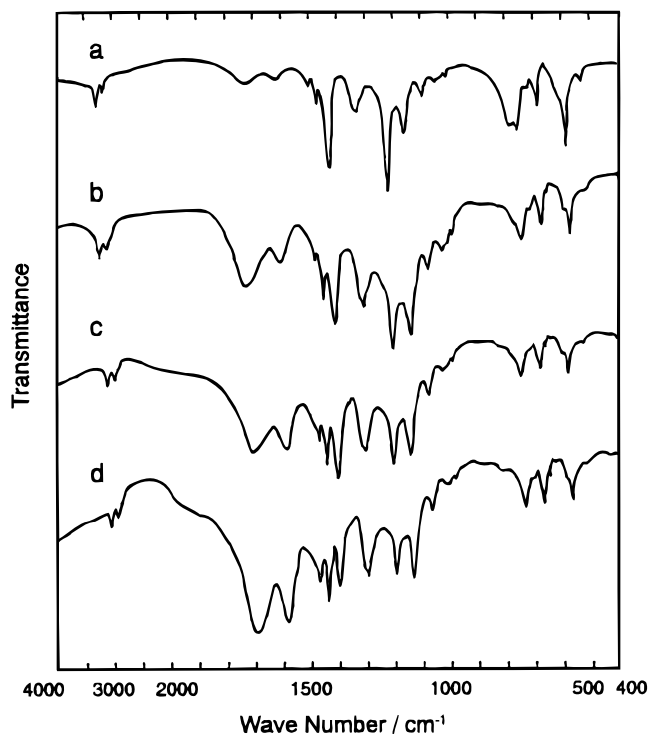

Figure 2. XPS S_{2p} spectra of plasma polymers formed from benzenesulfonyl fluoride. (a) 3.5, (b) 12.0, (c) 20.3, and (d) 28.8 W. (Flow rate of benzenesulfonyl fluoride = 5 cm^3 (STP) min^{-1}, flow rate of Ar = 30 cm^3 (STP) min^{-1}, and polymerization pressure = 0.2 Torr.)

prepared at high power levels contain neither sulfonyl chloride groups nor sulfone groups.

FTIR spectra of the polymers formed from benzenesulfonyl fluoride and benzenesulfonyl chloride are shown in Fig. 4 and 5, respectively. In Fig. 4, the main absorption peaks are: C–H vibration of the benzene ring at 3050 cm^{-1}; C=O stretching at about 1720 cm^{-1}; benzene ring at 1590, 1490, 1450, 760, and 700 cm^{-1}; sulfonyl fluoride asymmetrical and symmetrical stretching at 1410 and 1210 cm^{-1}; and sulfone asymmetrical and symmetrical stretching at 1260 cm^{-1} and 1150 cm^{-1}.[30] These results indicate that the polymers formed from benzenesulfonyl fluoride contain sulfonyl fluoride and sulfone. The sulfur of lower oxidation state as seen in XPS S$_{2p}$ spectra was not detected because it gives only weak peaks in the infrared region. At the low applied discharge power of 3.5 W the intensity of the absorption peak assigned to sulfone was small.

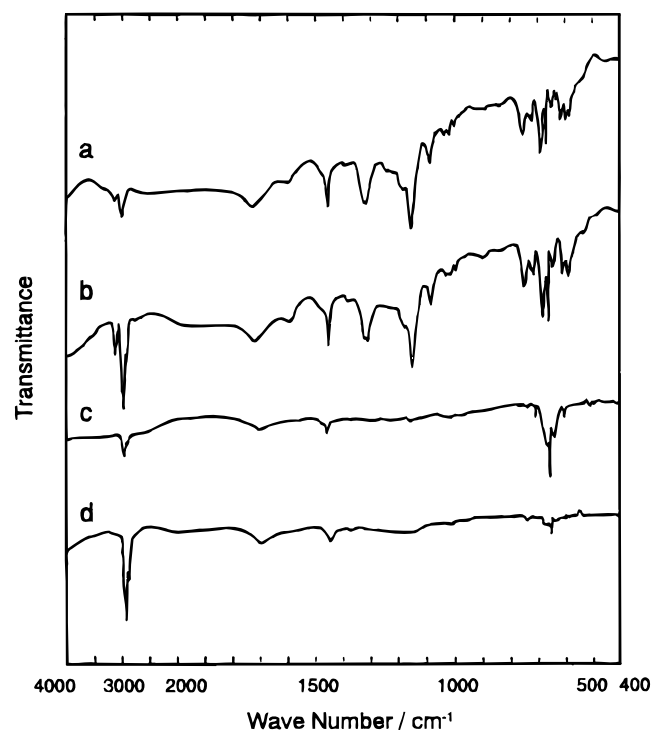**Figure 4.** FTIR spectra of plasma polymers formed from benzenesulfonyl fluoride. (a) 3.5, (b) 12.0, (c) 20.3, and (d) 28.8 W. (Gas conditions as in Fig. 2.)

With increasing discharge power, the intensity of the sulfone peaks relative to the sulfonyl fluoride peaks increased, and the intensity of the aromatic C–H peak at 3050 cm^{-1} relative to the aliphatic C–H peak at 2920 cm^{-1} decreased.

Figure 3. XPS S$_{2p}$ spectra of plasma polymers formed from benzenesulfonyl chloride. (a) 3.0, (b) 12.4, (c) 21.7, and (d) 30.6 W. (Flow rate of benzenesulfonyl chloride = 5 cm^3 (STP) min^{-1}, flow rate of Ar = 30 cm^3 (STP) min^{-1}, and polymerization pressure = 0.2 Torr.)

Figure 5. FTIR spectra of plasma polymers formed from benzenesulfonyl chloride. (a) 3.0, (b) 12.4, (c) 21.7, and (d) 30.6 W. (Gas conditions as in Fig. 3.)

In contrast to the spectra of the polymers formed from benzenesulfonyl fluoride, the spectra of those from benzenesulfonyl chloride (Fig. 5) showed very weak peaks assigned to the sulfonyl chloride asymmetrical and symmetrical stretching absorption peaks at 1380 and 1180 cm^{-1} and strong peaks assigned to sulfone groups at 1150 cm^{-1} at applied power below 12.4 W. These results indicate that the polymers formed from benzenesulfonyl chloride contain sulfone groups and a small amount of sulfonyl chloride groups at low applied discharge power. With increasing applied discharge power the aromatic character decreased and the peaks corresponding to sulfone groups disappeared above 12.4 W.

From these XPS and FTIR results, it is clear that sulfonyl fluoride groups were introduced into the polymer by use of benzenesulfonyl fluoride, whereas for benzenesulfonyl chloride, sulfonyl chloride groups decomposed during exposure to the plasma and were not introduced into the polymer.

The difference between the chemical structure of the polymer formed from benzenesulfonyl fluoride and that from benzenesulfonyl chloride is believed to result from the difference of reactivity of these starting materials in the plasma.

Cationic species detected by in situ mass spectrometry.—To clarify the gas-phase reactions of the starting materials, chemical species in the glow discharge plasma were detected by *in situ* mass spectrometry. Cationic species in the glow discharge plasma were observed directly without an ionization process in the QMS.

Cationic species incident and passing through the orifice were sampled and detected using QMS with its ionizer switched off. Therefore, all detected ions were not formed in the mass spectrometer but were formed in the glow discharge plasma and survived until they reached the detector. As the sampling orifice is electrically floating as are the substrates, all cationic species adjacent to the substrates are expected to be detected by the mass-analyzing system.

Various cationic species were detected such as benzene cation ($m/e = 77$), its fragment ions ($m/e = 50, 51$), species containing sulfur-oxygen, and other species expected to be generated by reaction with the starting molecule or active species. To investigate the decomposition of sulfonyl halide groups, the relative intensities of sulfur-containing species were calculated from their net intensity. Figures 6 and 7 show the effects of discharge power on the relative ion currents. Because the relative sensitivities of the detector decrease with increasing mass, the intensities were corrected with a normalization curve obtained using a noble gas with the same vapor pressure. Although S$^+$ ($m/e = 32$) may exist, this ion was not taken into consideration because its distinction from O$_2^+$ is difficult.

Figure 6 shows the discharge-power dependence of the relative peak intensity of S-containing species in a benzenesulfonyl fluoride-Ar discharge plasma. The relative intensity of the parent ion peak ([C$_6$H$_5$SO$_2$F]$^{+\bullet}$) was large, especially under low applied power conditions. This result shows that the parent ion is relatively stable and is the main cation in the glow discharge plasma. An increase of the discharge power decreases the parent ion current and raises the amounts of SO$_2^+$ and SO$^+$. These results show that decomposition of sulfonyl fluoride groups is enhanced with increasing applied power.
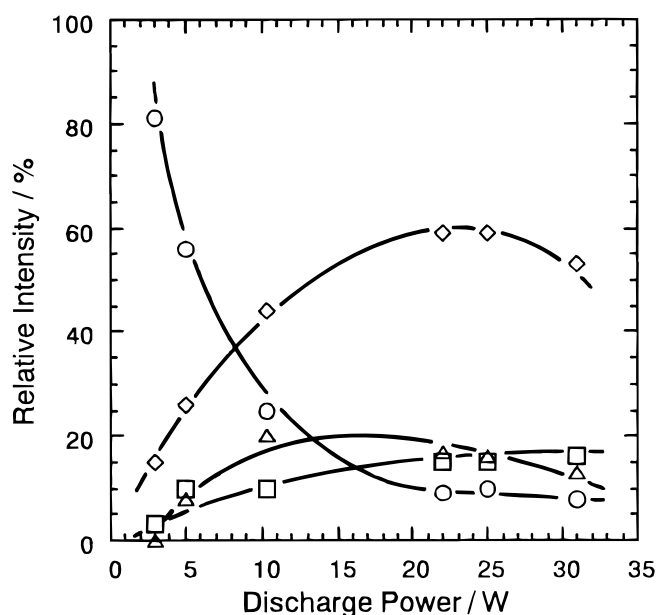
Figure 7 shows discharge-power dependencies of the relative intensities of cationic species for benzenesulfonyl chloride. Note that the relative intensity of the observed parent ion differs strongly from that observed for benzenesulfonyl fluoride. The relative intensity of the parent ion is small; however, the relative intensity of the cation [C$_6$H$_5$SO$_2$]$^+$ is large, especially at low discharge power. These results indicate that the parent ion of benzenesulfonyl chloride is unstable in the glow discharge plasma and that cleavage of the S–Cl bond is facile. The increase of SO$_2^+$ and SO$^+$ amounts with applied power is similar to the benzenesulfonyl fluoride results.

Ab initio molecular orbital calculations.—Electron impact ionization is most important in sustaining glow discharge, and electron collisions are dominant in determining the behavior of a glow discharge plasma.[31] As the parent molecule is predominant in the glow discharge plasma, it is expected that reactions are initiated by electron
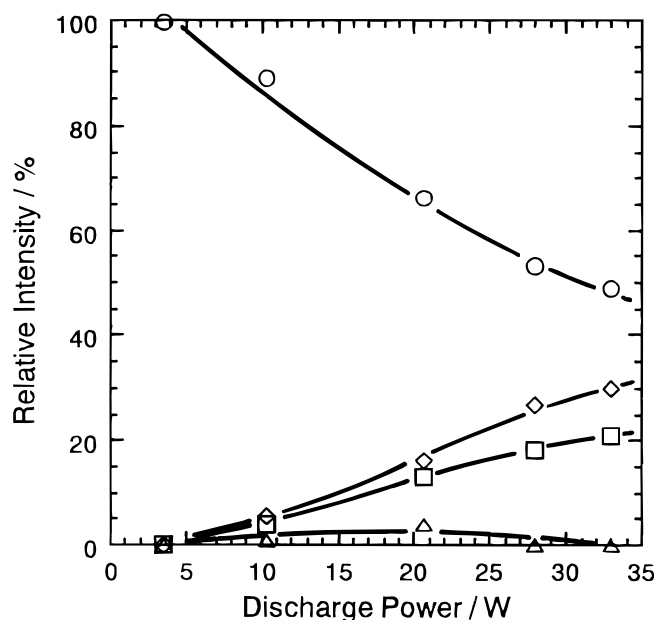

Figure 6. Discharge-power dependence of the relative peak intensity of S-containing species in benzenesulfonyl fluoride-Ar discharge plasma. ○: [C$_6$H$_5$SO$_2$F]$^{+\bullet}$; ◇: SO$^+$; □: SO$_2^+$; △: [C$_6$H$_5$SO$_2$]$^+$. (Gas conditions as in Fig. 2.)

collisions with the parent molecule. To account for the generation of cations described above by electron collisions with the parent molecule of the starting material, *ab initio* molecular orbital calculations were carried out for the reactants and products. A calculation was applied to study the dissociation reaction in the glow discharge plasma. Following the collision of an electron with benzenesulfonyl halides, four fragmentation reactions (Reactions A-D) via the parent molecular cation shown in Fig. 8 should be considered from prior studies of one-electron impact mass spectrometry of aromatic sulfonyl halides.[15,32] Reactions A and B in this figure are bond cleavages of sulfur and benzene ring. Reactions C and D are bond cleavages

Figure 7. Discharge-power dependence of the relative peak intensity of S-containing species in benzenesulfonyl chloride-Ar discharge plasma. ○: [C$_6$H$_5$SO$_2$]$^+$; ◇: SO$^+$; □: [C$_6$H$_5$SO$_2$Cl]$^{+\bullet}$; △: SO$_2^+$. (Gas conditions as in Fig. 3.)
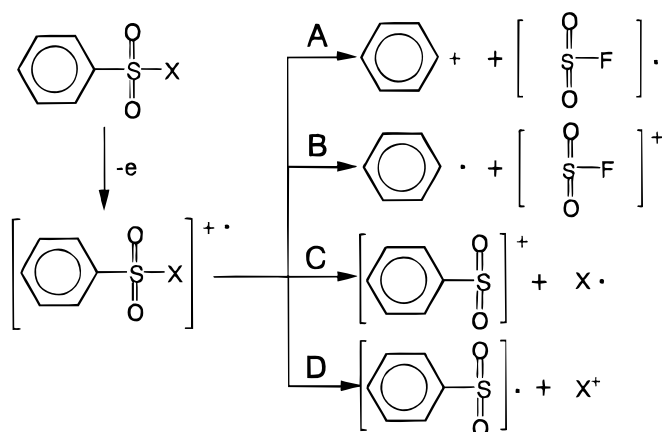
Figure 8. Typical reaction schemes of benzenesulfonyl halides in glow discharge plasma.

between sulfur and halogen. The energy obtained for each relevant species is listed in Table I. The energy of the $C_6H_5SO_2$ radical was estimated from the energy of $C_6H_5SO_2^-$ using Koopman's theoem.[33] The total energy of $C_6H_5SO_2^-$ anion was calculated, then one electron was removed from the highest occupied molecular orbitals (HOMOs) of the $C_6H_5SO_2^-$ anion to estimate the ionization potential. The total energy differences between the starting molecules and the products, *i.e.*, the reaction enthalpies, are shown in Fig. 9 and 10. A relative comparison of dissociation energies can be made from these results by assuming that the activation energy corresponds to the reaction enthalpy qualitatively, although these reactions are not reversible.[34] Because the values of total energy difference between the reactants and the products for Reactions B and D were much larger than those for Reactions A and C, bond cleavage was examined by comparison of Reactions A and C. Although the ionization energy estimated by Koopman's theory tends to be small, the results show that Reaction D involving the $C_6H_5SO_2$ radical was the most sluggish. The results in Fig. 9 reveal that reaction A, where S–C bond cleavage occurs, is energetically more favorable than Reaction C, *i.e.*, S–F bond cleavage, by 0.0203 Hartree (0.556 eV) for benzenesulfonyl fluoride. However, the results in Fig. 10 imply that Reaction C, *i.e.*, S–Cl bond cleavage, is energetically more favorable than Reaction A by 0.0552 Hartree (1.51 eV) for benzenesulfonyl chloride.

Table I. Calculated energy of benzenesulfonyl halides and their decomposed species.

Species	Calculated energy (Hartee)
	RHF (6-31G)
$C_6H_5SO_2F$	−876.3441
$C_6H_5SO_2Cl$	−1236.3985
$C_6H_5^+$	−229.6729
SO_2F^+	−645.8152
SO_2Cl^+	−1005.9108
$C_6H_5SO_2^+$	−776.6213
F^+	−98.6289
Cl^+	−458.4428
	ROHF (6-31G)
$SO_2F•$	−646.3289
$SO_2Cl•$	−1006.3360
$C_6H_5•$	−229.9724
$F•$	−99.3602
$Cl•$	−459.4428
$C_6H_5SO_2•$ [a]	−776.9072

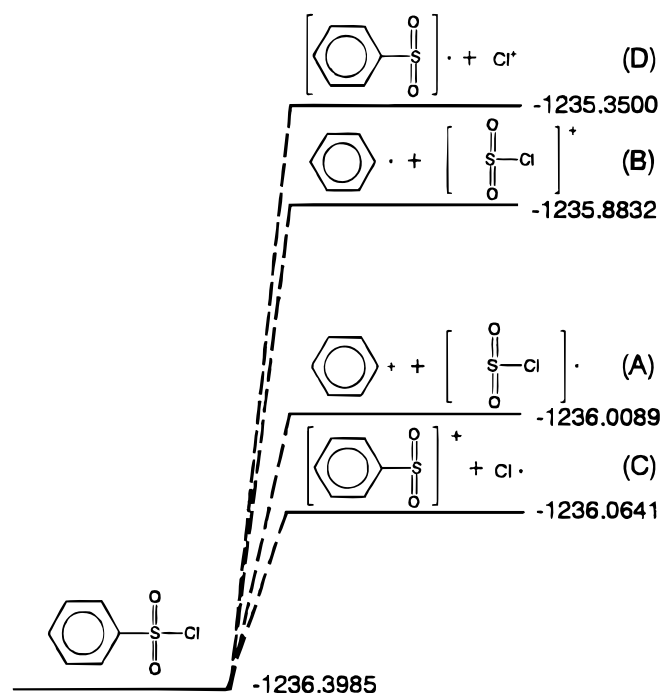[a] Estimated from $C_6H_5SO_2^-$ by Koopman's theorem.
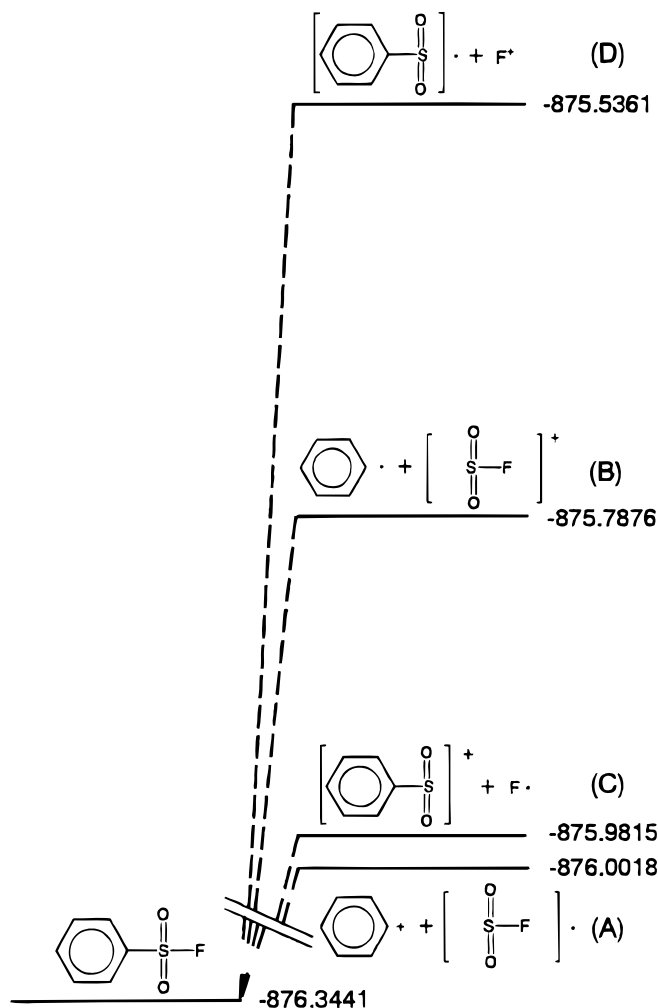
Figure 9. Energy diagram of the reaction of benzenesulfonyl fluoride from *ab initio* molecular orbital calculation. (Energies in Hartree.)
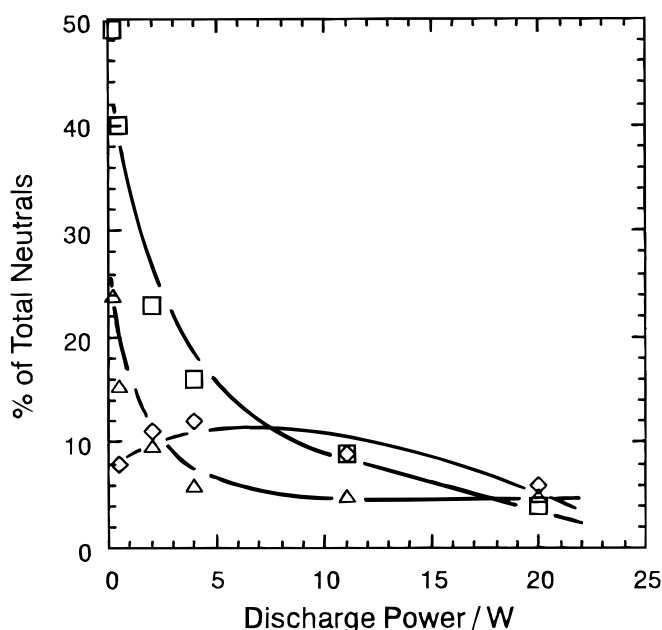
In situ mass spectrometry to detect radical and excited species.— Figure 11 shows the discharge-power dependence of the relative peak intensities of three major neutral species in the benzenesulfonyl fluoride-Ar discharge plasma. Because the relative sensitivities of the detector decrease with increasing mass, the intensities were corrected with a calibration curve obtained using a noble gas with the same vapor pressure. The relative intensity of the C_6H_5 radical was large, especially under low applied power conditions, however the content of C_6H_5F species was small. This means that concentration of the F radical in the plasma was low. These results indicate that the S–F bond cleavage is difficult. Neutral species that contain sulfonyl fluoride groups were not detected. Figure 12 shows the discharge power dependence of the relative peak intensities of three major neutral species in benzenesulfonyl chloride-Ar discharge plasma. Large amounts of C_6H_5 radical and C_6H_5Cl species are detected. C_6H_5Cl species were apparently formed by a reaction between the C_6H_5 radical and the Cl radical. These results indicate that the S–Cl bond cleavage easily produces Cl radicals.

Explanation of introduction of sulfonyl halide groups.—From the results described above, the following mechanism is postulated to account for the difference between the chemical structure of the polymer formed from benzenesulfonyl fluoride and that from benzenesulfonyl chloride. For benzenesulfonyl fluoride, *in situ* mass spectrometry showed that the parent ion ($[C_6H_5SO_2F]^{+•}$) is stable and the F radical concentration in the plasma is low. These results are consistent with *ab initio* molecular orbital calculations, which indicate that S–F bond cleavage is difficult. From these results, it is
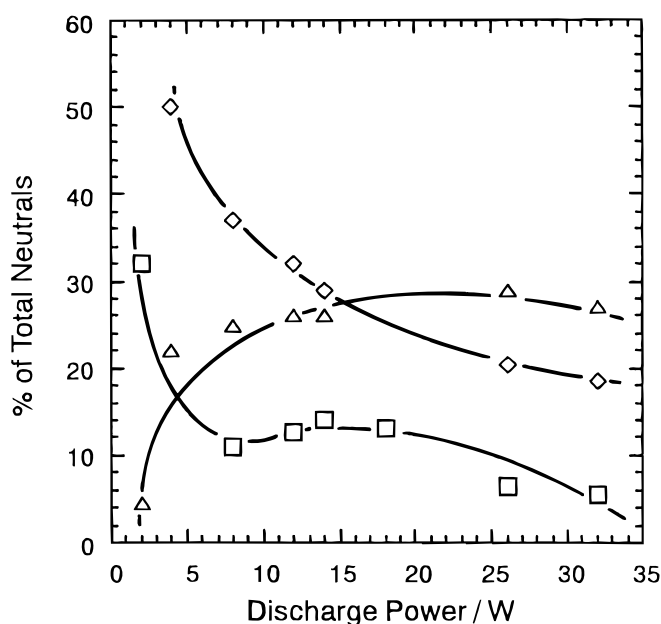
Figure 10. Energy diagram of the reaction of benzenesulfonyl chloride from *ab initio* molecular orbital calculation. (Energies in Hartree.)

Figure 12. Discharge-power dependence of the relative peak intensity of typical neutral species in benzenesulfonyl chloride-Ar discharge plasma. □: $C_6H_5SO_2$; ◇: C_6H_5Cl; △: C_6H_5. (Gas conditions as in Fig. 3.)

fonyl fluoride and benzene rings is deposited at high applied discharge power (Fig. 13).

The concentration of cationic species in the glow discharge plasma is generally smaller than that of radicals and excited species. According to ambipolar diffusion theory,[37] in a nonequilibrium plas-

believed that the parent ion ($[C_6H_5SO_2F]^{+\bullet}$) is the major species to introduce the sulfonic fluoride groups into the plasma-formed polymer. The contribution of the parent ion to polymer formation gives a polymer with minimal decomposition of sulfonyl fluoride and an aromatic structure. Because both electron temperature and concentration in the glow discharge plasma increase with applied discharge power,[35,36] decomposition reactions proceed, and small species generated by further fragmentation of the parent ion or other secondary decomposition reactions increase as shown by *in situ* mass spectrometry. Therefore a polymer with significant decomposition of sul-
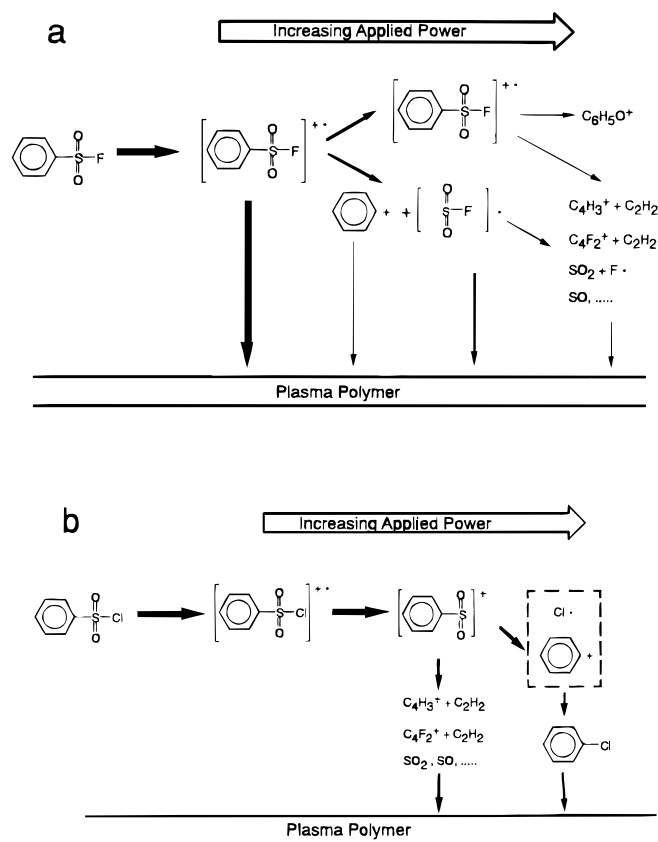

Figure 11. Discharge-power dependence of the relative peak intensity of typical neutral species in benzenesulfonyl fluoride-Ar discharge plasma. □: C_6H_5O; ◇: C_6H_5F; △: C_6H_5. (Gas conditions as in Fig. 2.)

Figure 13. Possible reaction schemes of (a) benzenesulfonyl fluoride and (b) benzenesulfonyl chloride in plasma polymerization.

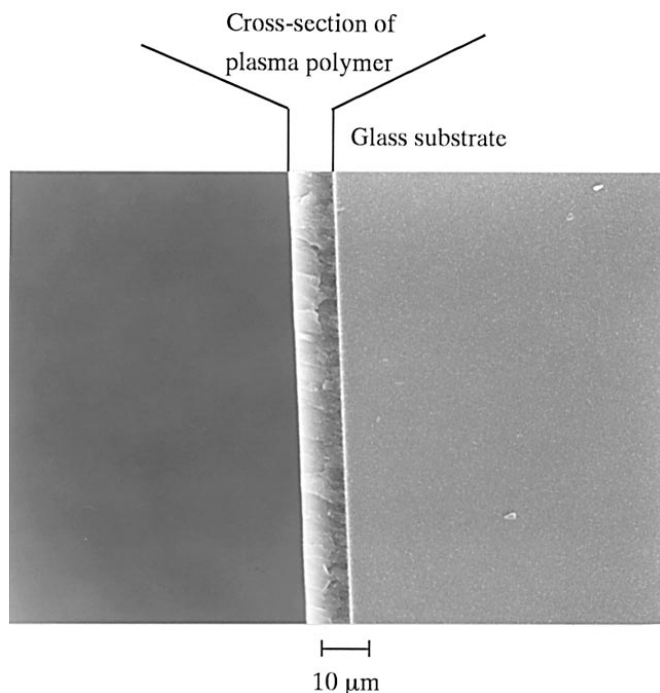**Figure 14.** Scanning electron micrograph of cross section of plasma polymer.

Figure 15. Dependence of ion-exchange capacity of plasma polymers after hydrolysis on AF power. (Gas conditions as in Fig. 2.)

ma, electron mobility of anions is much larger than that of cations and, therefore, electrons diffuse to the reactor wall and collide with it. The result is that a potential difference between the plasma bulk and the reactor wall is established. Cations are accelerated by the potential difference, diffuse to the reactor wall, and collide with it. This phenomenon implies that the flux of cationic species from the bulk plasma to the substrate is similar to that of radicals and excited species, although the bulk plasma concentration of the cationic species is much smaller than that of the radicals and excited species. Furthermore, many parts of the starting material molecules may pass through cationic intermediates, and then the cationic intermediates easily transform to radicals or excited species.[38] Cationic species in the glow region have been reported to be an important active species for plasma polymerization.[39-41] A few workers showed that a reaction facilitated by ions predominates in polymerization at a discharge frequency lower than a few megahertz.[42-44]

For benzenesulfonyl chloride, *in situ* mass spectrometry to detect the cationic species shows that the relative intensity of the parent ion is small. However, the relative intensity of the cation $[C_6H_5SO_2]^+$ is large, especially at low discharge power. Mass spectrometry also showed that the S–Cl bond cleavage easily produces Cl radicals. These results indicate that the parent ion of benzenesulfonyl chloride is unstable in the glow discharge plasma, and cleavage of S–Cl bond is facile, which is consistent with *ab initio* molecular orbital calculations. The sulfonyl chloride groups decompose even at low discharge power. From such gas-phase reactions it is difficult to introduce sulfonyl chloride groups into the polymer by plasma polymerization using benzenesulfonyl chloride.

Characterization of plasma polymer films as ion-exchange membrane.—A typical scanning electron micrograph of a cross section of a plasma-formed polymer film obtained from benzenesulfonyl fluoride on a glass substrate is shown in Fig. 14. The micrograph shows that the plasma polymer film is flat, uniform, and free from pinholes.

The plasma polymers obtained from benzenesulfonyl fluoride were soaked in a solution of 0.5 M NaOH in 1:1 H_2O:methanol at 60°C for more than 24 h in order to hydrolyze sulfonyl fluoride to sulfonic acid. After hydrolysis, the treated films were washed thoroughly with distilled water. The cation-exchange capacities of the treated plasma polymers prepared at various levels of discharge power are shown in Fig. 15. The cation-exchange capacity decreased
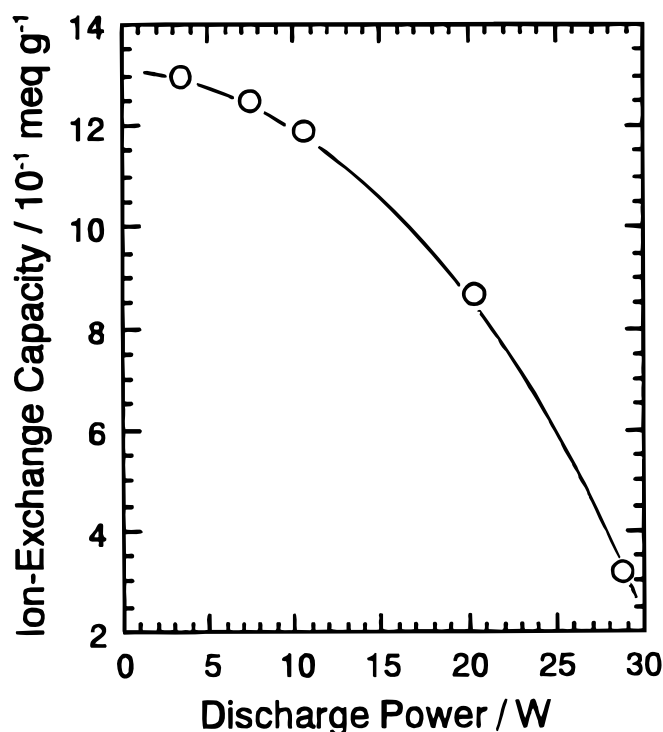
with increasing discharge power. As described earlier, the content of sulfonyl fluoride groups in the plasma polymer formed at high discharge power is low. This decomposition of sulfonyl fluoride groups at high discharge power leads to a decrease in the cation-exchange capacity. The treated polymer formed at 3.5 W exhibits a cation-exchange capacity of 1.3 mequiv g^{-1}, which is higher than that of Nafion 117 (0.9 mequiv g^{-1}). An ion-exchange membrane prepared by RF (13.56 MHz) discharge exhibited a slightly larger cation-exchange capacity of about 1.4 mequiv g^{-1}.[15] Increasing the frequency of the applied voltage, caused positive ions to become immobile. The slight difference of the cation-exchange capacity may be caused by an effect of the positive ions bombardment.

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