Preparation of a Cation-Exchange Membrane from Fluorocarbons by Means of Plasma Multiphase Polymerization

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In order to prepare a cation-exchange membrane, trifluoromethanesulfonic acid (TFMS) and octafluorocyclobutane (OFCB) were plasma-polymerized. Addition of water vapor to the plasma reactor was more effective in preserving the sulfonic acid group in the polymer matrix than was the addition of argon (Ar). Addition of hexafluoropropene (HFP), known as a polymerization promoter, scarcely improved the deposition rate. However, plasma multiphase polymerization, which we called the plasma polymerization process when reactant monomer materials existed in different phases, was effective in accelerating the rate. This technique also increased the ionic conductivity of the resultant plasma polymer. It was found that the polymer film grew uniformly over a 50 cm² area. A very high ion-exchange capacity of the polymer was obtained using a method that yielded an approximate value.

Key words: Cation-Exchange Membrane, Plasma Polymerization with Water Vapor Addition, Plasma Multiphase Polymerization, Deposition Conditions and Electrochemical Properties of the Plasma Polymer

1. Introduction

An efficient cation-exchange membrane is one of the electrochemical and functional materials which are highly sought after. Perfluorosulfonic acids have been utilized as cation-exchange membranes because of their chemical and thermal stabilities [1-5]. One application for these membranes is a solid polymer electrolyte for fuel cells. This application has attracted attention in recent years especially from the viewpoint of environmental protection. However, additional cost reduction and improvement of efficiency are needed before putting these materials to practical use.

Plasma polymerization is a promising technique for synthesizing ion-exchange membranes because it introduces a high concentration of crosslinks,

film thickness can be easily controlled and plasma polymers generally adhere well to substrates. We previously published on plasma copolymerization of hexafluoropropene (HFP) and trifluoromethanesulfonic acid (TFMS) and the electrochemical properties of the resultant polymer [6,7]. The polymer had a higher cationic permselectivity and an ion-exchange capacity comparable to commercial perfluorosulfonate membranes but a lower ionic conductivity, perhaps resulting from its high degree of crosslinking. On the basis of these results, we copolymerized octafluorocyclobutane (OFCB) with TFMS taking aim at the suppression of some crosslinking [8]. It was found that the addition of argon (Ar) to the reaction system was effective in suppressing the decomposition of the -SO₃H functional group, although it did not bring

about a higher ion conductivity than the currently available perfluorosulfonate membranes. Therefore, experiments in which the addition of HFP and water vapor instead of Ar along with refrigeration of the substrate upon which the polymer was deposited were carried out. The objective of these experiments was to improve both the rate of deposition and the electrochemical properties of the resultant polymer [9].

In this paper, we describe the differences between Ar and water vapor during copolymerization of TFMS-OFCB. The effect of plasma multiphase polymerization which was carried out by refrigeration of the substrate, the deposition conditions and the electrochemical properties of plasma-polymerized TFMS-OFCB-HFP (PPTOH) are also reported.

2. Method

2.1. Materials and Apparatus

The monomers shown in Fig. 1 and the substrates used in these experiments were obtained

Fig. 1. Chemical structures of fluorocarbon monomers.

through the same routes as described in our last report [9]. Reagents used for the evaluation of PPTOH were also described previously [9]. The plasma reactor system illustrated in Fig. 2 and the polymerization procedure were also identical to those in our previous report [9]. The polymerization was carried out with a radio frequency (RF) power source of 13.56 MHz and sccm (cm^3/min under STP) was used as a unit of the monomer flow rate.

2.2. Evaluation of the Plasma Polymer

The plasma polymers were evaluated in respect to the deposition rate, X-ray photoelectron spectroscopy (XPS) spectra, relative ratios of atom numbers, and ionic conductivity. All the data were obtained using the same methods as described earlier [9].

The PPTOH film on the substrate was viewed with a microscope image display system consisting of a microscope (Examet System MVS-11SA, Union Optical Instruments Inc., Tokyo), a camera (Microscope Color Monitor CCD-X2, Shimadzu Physicochemical Instruments Ltd., Tokyo), a television monitor (Color Video Monitor TMA14S, Victor Company of Japan, Ltd., Ibaragi), and a printer (Color Video Printer UP-2300, Sony Corp., Tokyo). Optical micrographs exhibiting a process of the deposition were obtained from some Si wafers coated with PPTOH films having different thicknesses.

Ion-exchange capacity of the PPTOH polymer was estimated by a simplified acid-base titration.

Fig. 2. Schematic diagram of plasma reactor system.
MFC: mass flow controller.

Forty ml of 0.5 mol/L NaCl aqueous solution was placed in a 100-ml beaker and a silicone rubber stopper was put on the beaker. After the solution was degassed by purging with Ar for 1 h, the pH of the solution was measured using a pH meter (Model D-13, Horiba Inc., Kyoto). A porous polymer membrane, either Celgard® 2500 (made from polypropylene and polyethylene resins, and with an average pore size of $0.19 \times 0.05 \mu\text{m}^2$; CG) or Duragard® 3401 (a polypropylene membrane treated for hydrophilicity, and with an average pore size of $0.20 \times 0.03 \mu\text{m}^2$; DG), was coated with PPTOH and the mass of the copolymer deposited was measured with a microbalance. The rubber stopper of the beaker was taken off and the weighed membrane was quickly soaked in the NaCl solution. The beaker was again stoppered and allowed to stand for 1 h while it was purged with Ar. The solution was then titrated with a 0.01 mol/L aqueous NaOH solution until the value of pH was returned to the initial value. The ion-exchange capacity was calculated from the mass of PPTOH and the titer.

3. Results and Discussion

3.1. Effect of Gas Additives

Previously we reported that the addition of Ar to the plasma polymerization reactor had effects

on improvement of the deposition rate of the plasma copolymer derived from TFMS-OFCB and suppression of dissociation of oxygen atoms from $-\text{SO}_3\text{H}$ [8]. However, it was desirable that the deposition rate and the ionic conductivity of the polymer be much higher than was found. The addition of water vapor was therefore attempted based on the following thoughts. (1) The H radicals dissociated from water vapor would deactivate F and fluorocarbon radicals both of which were derived from TFMS and exhibited strong ablation functions. (2) The addition of water vapor during plasma polymerization was expected to have a similar preservation effect on S, which might have some analogy with halogens, as oxygen on halogens. (3) It was found that plasma polymerization of organic compounds in the presence of water vapor added oxygen in the forms of $-\text{OH}$, $-\text{O}-$ and others to the resultant plasma polymer [10, 11]. Therefore, addition of oxygen atoms in the molecular structure of the plasma polymer and less reduction of $-\text{SO}_3\text{H}$ during the plasma deposition process were anticipated for these experiments. Consequently, the method was thought to be advantageous in obtaining a higher ionic conductivity and higher ion-exchange capacity plasma polymer film.

The result is shown in Fig. 3. As compared

Fig. 3. Effect of a gas additive on XPS spectra in plasma copolymer from TFMS-OFCB. TFMS: 2.8 sccm, OFCB: 5.0 sccm, gas additive (Ar or H_2O): 5.0 sccm; electrode gap: 2.5 cm; pressure: 23-24 Pa; RF power: 2.0 W (Ar), 5.0 W (H_2O); substrate: Celgard 2500®. Spectra: C_{1s} (left, upper), F_{1s} (right, upper), S_{2p} (left, lower), O_{1s} (right, lower).

with Ar addition, water vapor addition did not significantly improve the deposition rate of about 3 Å/min, contrary to our expectations. However, water vapor did significantly suppress the decomposition of $-\text{SO}_3\text{H}$. An S_{2p} peak in the XPS spectrum appears in the binding energy range of 166.4-171.1 eV in the case of an oxidized form ($\text{R}-\text{SO}_2-\text{R}'$, $-\text{SO}_3$, $\text{RO}-\text{SO}_2-\text{OR}'$, $-\text{SO}_4$), while it appears in the range of 160.1-164.0 eV in the case of a reduced form (S , $\text{R}-\text{S}-\text{R}'$, $\text{R}-\text{SH}$). Although a reduced form of S existed within the plasma polymer with Ar addition to the reactants, an oxidized form was preserved, not only on the surface but also in the polymer matrix, with water vapor addition.

The ratios of atom numbers in the two polymers are shown in Fig. 4. This data clearly shows the difference in effects between Ar and water vapor. With regard to Ar, every ratio of F, S and O to C within the polymer matrix decreased to about a half of that on the surface. It was postulated that these elements were lost from the surface as formation of the polymer structure proceeded. The water vapor addition brought

about different changes in the atom ratios among these elements. In the case of Ar, the F/C value from inside of the polymer matrix was much lower than that on the surface when compared with the same F/C values for water vapor. In other words, in the case of water vapor the surface composition based on the F/C ratio is closer to the F/C value in the polymer matrix. The difference of F/C between Ar and water vapor was more noticeable on the surface than in the matrix. The results suggested that the H radicals derived from water vapor abstracted F atoms from the monomer while the numbers of F atoms which remained in the polymer matrix were close to each other in the cases of both Ar and water vapor. Water vapor addition did not increase the S/C in comparison with the Ar addition, contrary to our expectation, but equalized the value between the surface and inside of the polymer matrix. The results shown in both Figs. 3 and 4 indicated that water vapor addition was effective in keeping S in an oxidized forms and with ion-exchange functionality uniformly throughout the polymer, including the surface. The O/C of the inside was about 40%

Fig. 4. Effect of a gas additive on elemental composition of plasma copolymer from TFMS-OFCB. TFMS: 2.8 sccm, OFCB: 5.0 sccm, gas additive (Ar or H₂O): 5.0 sccm; electrode gap: 2.5 cm; pressure: 23-24 Pa; RF power: 2.0 W (Ar), 5.0 W (H₂O); substrate: Celgard 2500®. Surface: before Ar ion etching; inside: after 120 s of Ar ion etching.

*Calculated from peak areas of XPS spectra (C_{1s} , F_{1s} , S_{2p} , O_{1s}).

less than that of the surface, but the ratios in the case of water vapor were more significant than those in the case of Ar. The data indicated that the O content of the plasma polymer could be increased by the addition of water vapor to the reactant gas mixture, as we had anticipated.

Since the O atom involved in the molecular structure takes part in a free rotation site, the ionic conductivity of the polymer should be improved. The ion-exchange capacity should also be increased because of the uniform distribution of $-\text{SO}_3\text{H}$ in the polymer. In another investigation carried out with a different plasma polymerization system (Model PD-105, Samco International Inc., Kyoto), we studied the effect of water vapor addition on similar polymerizations [12]. Without water vapor addition the plasma polymer (TFMS:OFCB:Ar = 1:5:5 sccm, 20 Pa, 2 W) had atomic ratios of 1.30, 0.05 and 0.30 for F/C, S/C and O/C, respectively, and its ionic conductivity was 6.6×10^{-5} S/cm. However, the polymer with water vapor addition (TFMS:OFCB:Ar:H₂O = 2:5:3:1 sccm, 20 Pa, 2 W) had atomic ratios of 0.70 in F/C, 0.05 in S/C and 0.50 in O/C, and an ionic conductivity of 1.0×10^{-4} S/cm. Even a small addition of water vapor to the TFMS-OFCB-Ar system gave rise to a decrease in F/C, an increase in O/C, and an increase in ionic conductivity. In this case we concluded that the improvement in conductivity was caused by reduced decomposition of $-\text{SO}_3\text{H}$ and the existence of hydrophilic functional groups such as R-O-R' or -OH. These differences in molecular structure between the two polymers were confirmed in the XPS spectra.

3.2. Effect of Substrate Refrigeration

Refrigeration of the substrate to be coated was effective in improving the rate of deposition when monomers that cause polymer ablation coexist in the plasma phase [9]. We have already proposed utilization of the difference in phases between coexisting monomers, which was brought about by refrigeration. This technique, which we named "plasma multiphase polymerization" to distinguish it from plasma polymerization of a monomer in a liquid or solid phase [13-16]. The technique enabled the control of the molecular structure of functional groups within the plasma polymer [9]. In practice, the polymerization was carried out with the lower electrode temperature ranging from 250 to 270 K depending on the thermal properties of the monomers being studied as shown in Fig. 5.

Fig. 5. Thermal properties of monomers.

The electrode temperature was shifted between the two values during the reaction by spontaneous increase in temperature entailed by supplying the RF power without refrigerating (ca. 27 min) and successive quick refrigeration (ca. 5 min). As a polymerization-promoter, HFP was replaced in part by OFCB.

The deposition rate of PPTOH increased slightly by the addition of HFP but increased significantly by refrigeration, namely 7 Å/min and 220 Å/min, respectively. In comparison between the temperatures 250-270 K and 300-310 K, the F/C obtained at the lower temperature was 0.6-1.1 on both the surface and inside of the polymer matrix while the value at the higher temperature changed from 0.5-0.8 on the surface to 0.2-0.7 in the matrix. The significant difference in F/C was attributed to the irregular vaporization of TFMS that occurred, even though the monomer introduction line was heated. The S/C and the O/C were 0.01-0.2 and 0.1-0.6, respectively, being independent of both temperature and the observed site. The ionic conductivity nearly doubled by using refrigeration. It was generally in the range of 4.3×10^{-7} - 3.3×10^{-5} S/cm and with a maximum conductivity of 2.6×10^{-4} S/cm.

It was thought that the above improvements brought about by refrigeration were due to improved activation of all of the monomers brought about by the different phases. An image of

Fig. 6. Imaginable illustration of plasma multiphase polymerization.

plasma multiphase polymerization is illustrated in Fig. 6. The reactions thought to occur in the different phases are the: (1) formation and reaction of plasma active species derived from HFP and OFCB in the gas phase; (2) excitation, adsorption and reaction caused by the species in the liquid and solid phases; (3) transport of TFMS and advancement of affinity between TFMS and PPTOH both induced by OFCB in the liquid phase; (4) protection of TFMS by water in the liquid and/or solid phase.

3.3. Deposition Conditions and Electrochemical Properties

Uniform deposition or thickness of polymer thin films is one of the general requirements for a functional coating. Therefore, uniformity was studied with respect to plasma multiphase polymerization. Observations with the optical microscope confirmed that PPTOH deposited by plasma multiphase polymerization had a smooth surface. When the substrate was a porous polymer such as DG, PPTOH covered the microscopic roughness on the surface of the substrate. Growth of PPTOH on a smooth surface, such as a Si wafer, significantly differed from the deposition processes of a large majority of other plasma-polymers in which the polymer was prepared as a

thin film uniformly grown on a substrate from the early stage of polymerization in a gas phase. It was observed that nuclei of PPTOH increased in width and in depth which eventually resulted in the coalescing and development of a continuous polymer film. This process was similar to that of a plasma polymerization of an organic compound containing a metal [16].

The uniformity of the deposition rate of the PPTOH film was also measured. The results are tabulated in Table 1. As the measurement point on a piece of Si wafer was more distant from the center of the electrode, the deposition rate decreased while its relative standard deviation increased. But the relative standard deviation calculated from all the points was $\pm 5\%$ within the distance of 4.0 cm, that is to say, over an area more than 50 cm². Therefore, the PPTOH film thickness was almost uniform enough for practical use.

The electrochemical properties of the PPTOH films prepared by the plasma multiphase polymerization technique are presented in Table 2. The difference in the mass deposition rate on CG versus DG was attributed to the higher hydrophobicity of CG versus DG. However, the ionic conductivities and the ion-exchange capacities of PPTOH on both substrates were similar. The

Table 1. Distribution of PPTOH^{a)} Deposition

Distance from center of electrode : r (cm)	Area of circle having radius of r (cm^2)	Deposition rate ^{b)}		
		Mean ($\text{\AA}/\text{min}$)	Standard deviation ($\text{\AA}/\text{min}$)	Relative standard deviation (%)
1.0	3.14	200	4.1	2.1
2.5	19.63	190	2.7	1.4
4.0	50.24	180	8.0	4.5

a) TFMS: 2.0 sccm, OFCB: 3.5 sccm, HFP: 2.0 sccm, H_2O : 5.0 sccm ; pressure: 20-23 Pa ; RF power: 5.0 W ; temperature of sample stage: 250-270 K. b) Number of measurements: 4. Substrate: Si wafer.

Table 2. Electrochemical Properties of PPTOH^{a)}

Substrate ^{b)}	Area of Membrane (cm^2)	Mass deposition rate ($\text{mg}/\text{cm}^2/\text{hr}$)	Ionic conductivity ^{c)} (S/cm)	Ion-exchange capacity ^{d)} (meq/g)
Celgard 2500	57.285	0.21	1.5×10^{-6}	5.2
Duragard 3401	58.440	0.27	2.0×10^{-6}	4.3

a) TFMS: 2.0 sccm, OFCB: 3.5 sccm, HFP: 2.0 sccm, H_2O : 5.0 sccm ; pressure: 20-23 Pa ; RF power: 5.0 W ; temperature of sample stage: 250-270 K. b) Trade name. c) Measured in 0.5 mol/L H_2SO_4 aq. d) Obtained by simplified test.

electrochemical data shown in Table 2 does not reflect the substrate properties but rather the properties of the PPTOH film itself. The extremely high ion-exchange capacities, although the measurement yielded an approximate value, would be able to supplement the lower conductivities and at the same time to reduce the film thickness in practical use.

4. Conclusion

This report describes the preparation of a cation-exchange membrane derived from TFMS, OFCB and HFP by means of plasma multiphase polymerization. The following conclusions can be drawn from this work: (1) The addition of water vapor to the plasma copolymerization system of TFMS-OFCB was effective in preserving the $-\text{SO}_3\text{H}$ functional group derived from TFMS. (2) Refrigeration of the substrate enabled plasma multiphase polymerization and improved the

deposition rate, the ionic conductivity and the ion-exchange capacity of PPTOH. (3) The PPTOH film was deposited uniformly within an area of about 50 cm^2 .

Problems left for future research are better control of supplying TFMS vapor to the plasma, optimizing plasma deposition conditions, improving reproducibility, and investigating the use of PPTOH in an actual fuel cell.

Acknowledgments

This work was funded by the Creative and Fundamental R&D Program for Small and Medium Enterprises in Japan (Project No. 8-22). The authors are grateful to the Japan Small Business Corporation (JSBC) and the New Energy and Industrial Technology Development Organization (NEDO) of Japan for their support. The authors also wish to thank Showa Denko Co., Ltd. for donating the HFP.

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