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Adsorption of carbon dioxide in plasma polymers prepared from silicon compounds and carbon dioxide separation membrane

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Summary

Three silicon compounds, dimethyldimethoxysilane (DMDMOS), decamethylcyclopentasiloxane (DMCPS), and 1,1,3,3-tetramethyldisiloxane (TMDSO), were plasma-polymerized, and the solubility coefficient and the permeation coefficient of carbon dioxide and nitrogen gas were determined. The permeation properties of the deposited films were discussed. The plasma polymers formed from DMDMOS, DMCPS, and TMDSO showed preferential solubility for carbon dioxide. The solubility coefficient of carbon dioxide was closely related to the concentration of Si-(O-)$_4$ moieties in the plasma polymers. However, these plasma polymers showed no selective permeation of carbon dioxide. The diffusion process rather than the solution process controlled the permeation of carbon dioxide across the plasma polymers. Plasma polymers formed from silicon compounds, if the polymers are less cross-linked, are expected to be a good material for CO_2-selective membrane.

Introduction

Plasma polymerization is a good manner of thin film formation without fabrication. From the viewpoint of thin film fabrication, many investigators have applied plasma polymers for materials of separation membrane in oxygen/nitrogen mixture (1) and of pervaporation membrane in ethanol/water mixture (2). Carbon dioxide separation from waste gases (carbon dioxide/nitrogen mixture) of automobiles and heat plants with membrane is an important technology to solve the environmental pollution and the global warming.

Preferential separation of carbon dioxide from carbon dioxide/nitrogen mixture using polymer membranes shows two difficulties: (i) plasticization by carbon dioxide molecules dissolved in the polymer membranes and (ii) smaller diffusion coefficient of carbon dioxide molecule in the permeation process across the polymer membranes than that of nitrogen molecules. Plasma polymer is a solution of the problem (i) because crosslinked chains in plasma polymers suppress the plasticization. Essentially, there is no solution of the problem (ii) because the diffusion coefficient is a function of the size of the permeants. Preferential dissolution of carbon dioxide molecules in the polymer membrane is a useful approach to compensate the problem (ii) (3).

This study focused on plasma polymers formed from silicon compounds as a raw material for carbon dioxide separation membranes. The solubility coefficient of carbon dioxide and nitrogen gas in the plasma polymers was estimated by the quartz crystal micro balance method (4). The advantage and the disadvantage of the plasma polymers in using them as a raw material for carbon dioxide separation membrane were discussed.

Experimental

Materials

Dimethyldimethoxysilane (DMDMOS), decamethylcyclopentasiloxane (DMCPS), and 1,1,3,3-tetramethyldisiloxane (TMDSO) the purity of which was higher than 99% were purchased from Petrach System Inc., U.S.A. and were used as starting compounds for plasma polymerization without further purification. Millipore filters (VSWP 04700, pore size 25 nm) were used as porous substrates for plasma polymer deposition.

Plasma polymerization:

Plasma polymerization was carried out using a capacitively coupled system at a 20 kHz frequency. The system was consisted of a reaction chamber of a Pyrex glass bell-jar (400 mm diameter, 470 mm high), which contained a pair of aluminum electrodes (150 mm x 150 mm) with a gap of 100 mm, a substrate stage (340 mm diameter) which lay midway between the electrodes and which was rotated at 60 rpm during the plasma polymerization by an electric motor drive to accomplish deposition of plasma polymers of homogeneous thickness, a pressure gauge, a thickness monitor, a monomer inlet, and a vacuum system consisting of a diffusion and a rotary pump. The silicon compound gases were introduced into the reaction chamber through a metering valve from a reservoir which was temperature-controlled by an electric heater. The details of the reaction system was reported elsewhere (5).

The plasma polymerization of the silicon compounds were carried out at two levels of W/FM parameter, 156 - 160, and 445 - 455 MJ/kg. The W/FM parameter in Joule/kg means apparent input electric energy per a mass of silicon compound for plasma polymerization. W, F, and M are the input electric power, the flow rate of the silicon compound, and the molecular weight of the silicon compound, respectively. The plasma polymers deposited on Millipore filter at a 400 nm thickness.

IR and XPS spectra:

IR spectra of the deposited plasma polymers were recorded on a Horiba Fourier transform spectrometer FT300 with an MCT detector. The spectral resolution was 4 cm^{-1}. XPS (C_{1s}, O_{1s}, Si_{2p}) spectra of the deposited plasma polymers were obtained on a Shimadzu ESCA 750 with a non-monochromatic MgK_{α} photon source. The anode voltage was 8 kV and the current 30 mA. The spectra were referenced with respect to the 285.0 eV carbon 1s level observed for hydrocarbon. The C_{1s} and Si_{2p} spectra were deconvoluted by fitting Gaussian functions to an experimental curve using an ESCAPAC program supplied by Shimadzu.

Permeability coefficientt

Plasma polymers (about 500 nm thick) deposited on Millipore membranes were served as specimens for the measurement of permeability coefficient. The carbon dioxide, oxygen, and nitrogen permeation rates were measured according to ASTM D143V. From data of the permeation rate and the thickness of the deposited plasma polymers, the carbon dioxide (P_{CO_2}) and nitrogen permeability coefficients (P_{N_2}) were estimated.

Solubility coefficient:

The mass of gas dissolved into the plasma polymers was measured by a quartz crystal micro balance method. In the quartz crystal micro balance method, the weight change of the piezoelectric quartz crystal, ΔM, is directly related to change in the oscillating frequency of the crystal, Δf, according to the equation 1 (4)

$$\frac{\Delta f}{f} = \frac{\Delta M}{\rho A t} \qquad (1)$$

where f is an inherent oscillating frequency of the quartz crystal, and ρ, A, and t are the density, the surface area, and the thickness of the quartz crystal, respectively. Weight change of few nanograms is determined with the quartz crystal micro balance. Plasma polymers (400 nm thick) deposited on a piezoelectric quartz crystal (12.5 mm diameter, 0.2 mm thick) were used as specimens for the measurement of gas solubility. The specimens of which the temperature was controlled by circulating water at 20°C were exposed to carbon dioxide or nitrogen gas at a given pressure of 9.86×10^4 to 19.72×10^4 Pa, and the oscillating frequency shift caused by the dissolution of the gas into the plasma polymers was recorded on an Ulvac oscillator CRTM-1000.

Results and Discussion

Plasma Polymers prepared from Silicon Compounds

The plasma polymerization of three silicon compounds, DMDMOS, DMCPS, and TMDSO, was carried out at two levels of the W/FM factor and gave the deposition of transparent films. These plasma polymers showed essentially same ir spectra, regardless of the kind of the silicon compounds and the level of the W/FM parameter. Characteristic ir absorption peaks appeared at 2958 (ν_{C-H} in CH_3), 2925, 2857 (ν_{C-H} in CH_2), 1730 ($\nu_{C=O}$), 1457, 1380 (δ_{C-H} in CH_3 and CH_2), 1270 (δ_{CH_3} in $Si-CH_3$), 1200 - 1000 (ν_{Si-O} and ν_{C-O}), 850, and 796 cm^{-1} (δ_{C-H} and δ_{Si-C} in $Si-CH_3$). A strong and broad absorption peak at 1200 - 1000 cm^{-1} indicates that the plasma polymers contain siloxane units.

The XPS (C_{1s} and Si_{2p}) spectra showed details of the carbon and silicon moieties constructing the plasma polymers (Table 1 and 2).

Table 1 XPS (C_{1s}) Spectra of Plasma Polymers

Plasma polymerization conditions		C_{1s} components (mol%)		
Monomer	W/FM factor (MJ/kg)	CH, C-Si	C-O	C=O
DMDMOS	156	74	19	7
	445	83	12	5
DMCPSO	159	84	11	5
	455	83	11	6
TMDSO	160	81	14	5
	447	85	10	5

Table 2 XPS (Si_{2p}) Spectra of Plasma Polymers

Plasma polymerization conditions		Si_{2p} components (mol%)		
Monomer	W/FM factor (MJ/kg)	Si-O	$Si-(O-)_2$ and 3	$Si-(O-)_4$
DMDMOS	156	3	80	17
	445	4	37	59
DMCPSO	159	1	88	11
	455	2	87	11
TMDSO	160	32	62	6
	447	28	65	7

The carbon components in the plasma polymers, as shown in Table 1, were CH and C-Si, C-O, and C=O moieties which appeared at a binding energy of 285.0, 286.8 - 287.0, and 289.1 - 289.4 eV, respectively. The silicon components contained at least three Si moieties, Si-O, Si-(O-)$_2$ and 3, and Si-(O-)$_4$ groups which appeared at a binding energy of 101.3 - 101.5, 102.2 - 102.6, and 103.7 - 104.0 eV, respectively (Table 2) (6). The subscript x in Si-(O-)$_x$ means the number of oxygne atoms bonded directrly with silicon atom. Comparison of Table 1 and 2 indicates that there is less differences among the three polymers in the content of the carbon component but in the content of the silicon component. The plasma polymers formed from DMD MOS, especially formed at a W/FM value of 445 MJ/kg, are rich in Si-(O-)$_4$ component. The content of the Si-(O-)$_4$ component for the plasma polymer formed from DMDMOS at a W/FM value of 445 MJ/kg was 59 mol% of the Si components. On the other hand, the plasma polymers formed from TMDSO are poor in Si-(O-)$_4$ component but rich in Si-O component. The Si-(O-)$_4$ content was 6 and 7 mol% for the plasma polymers formed from TMDSO at a W/FM value of 160 and 447 MJ/kg, respectively. The plasma polymers formed from DMCPS are in the middle between the plasma polymers formed from DMDMOS and TMDSO from the viewpoint of the Si-(O-)$_4$ content. The Si-(O-)$_4$ content was 11 mol%. Therefore, the three plasma polymers are characterized by the chemical composition of the Si-(O-)$_4$ group.

Carbon Dioxide and Nitrogen Solubility Coefficient

The carbon dioxide and nitrogen gas concentration dissolved in the three plasma polymers was measured by the quartz crystal micro balance method. Figure 1 and 2 show typical the dissolved carbon dioxide and nitrogen gas concentration as a function of the gas pressure.

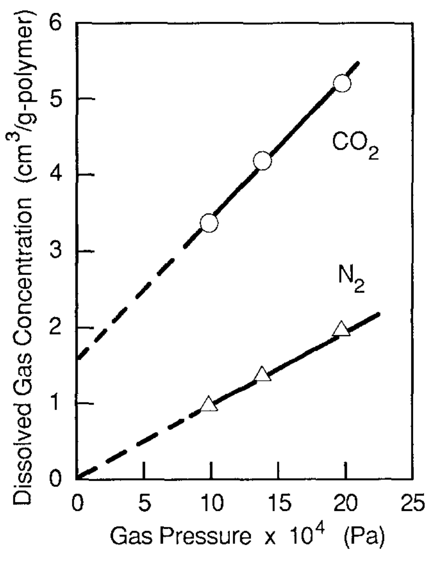

Figure 1 Gas concentration dissolved in plasma polymer formed from DMDMOS (W/FM = 156 MJ/kg) as a function of gas pressure.

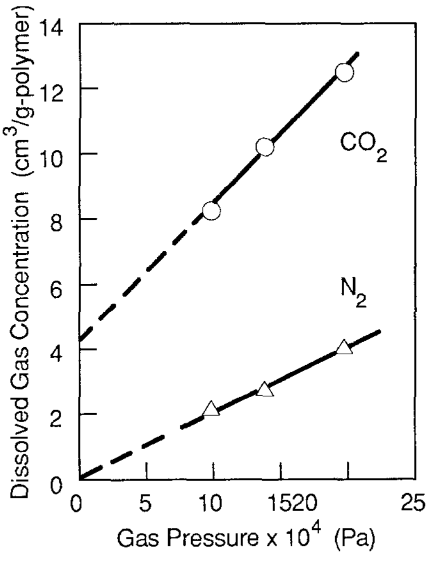

Figure 2 Gas concentration dissolved in plasma polymer formed from DMDMOS (W/FM = 445 MJ/kg) as a function of gas pressure.

The dissolved carbon dioxide and nitrogen gas concentration, as shown in Figure 1 and 2, showed a linear relationship with the gas pressure. The extrapolation of the linear relationship for the nitrogen gas dissolution went through the origin of the ordinate, indicating that the nitrogen gas dissolution into the plasma polymer obeys the Henry rule. However, in the carbon dioxide dissolution a linear relationship between the dissolved carbon dioxide concentration and its pressure did not go through the origin of the ordinate but through an intersection of the ordinate. This means that the carbon dioxide dissolution into the plasma polymers does not obey the Henry rule but obeys the pseudo-Henry rule.

The slope of the linear relationship between the dissolved gas concentration and the gas pressure in Figure 1 and 2 gives the solubility coefficient. The carbon dioxide and nitrogen solubility coefficients at 20°C for the three plasma polymers were calculated from the linear relationship under the assumption that the density of the plasma polymers was 1 g/cm^3. Results of the calculation are shown in Table 3.

Table 3 Solubility Coefficient of Plasma Polymers

Plasma polymerization conditions		Solubility coefficient at 20°C (cm^3/cm^3·Pa)		
Monomer	W/FM factor (MJ/kg)	S_{CO_2}	S_{N_2}	S_{CO_2}/S_{N_2}
DMDMOS	156	1.9×10^{-5}	8.5×10^{-6}	2.2
	445	4.3×10^{-5}	2.0×10^{-5}	2.2
DMCPS	159	1.7×10^{-5}	7.0×10^{-6}	2.4
	455	3.5×10^{-5}	7.9×10^{-6}	4.4
TMDSO	160	1.4×10^{-5}	8.0×10^{-6}	1.7

The nitrogen solubility coefficient for the plasma polymers except that formed from DMDMOS at a W/FM of 445 MJ/kg was almost constant and 7.0 - 8.5 x 10^{-6} cm^3/cm^3·Pa, and the carbon dioxide solubility coefficient was in the range of 1.4 - 4.3 x 10^{-5} cm^3/cm^3·Pa. The nitrogen solubility coefficients is higher than that of silicon rubber (2.0 x 10^{-6} cm^3/cm^3·Pa) (7). The carbon dioxide solubility coefficient is not referred because the carbon dioxide solubility for silicon rubber is not yet reported. The nitrogen dissolution for the plasma polymers, as shown in Table 3, is scarcely influenced by the chemical composition of the plasma polymers. On the other hand, the carbon dioxide solubility coefficient is influenced by the chemical composition of the plasma polymers. Figure 3 shows the carbon dioxide solubility coefficient as a function of the Si-(O-)$_4$ group in the plasma polymers.

The carbon dioxide solubility coefficient, as shown in Figure 3, depends strongly on the content of Si-(O-)$_4$ group in the plasma polymers. This relationship indicates some interaction between carbon dioxide molecule and Si-(O-)$_4$ group, while the details of the interaction is not yet clear.

These plasma polymers showed preferential solubility for carbon dioxide rather than nitrogen. The ratio of carbon dioxide solubility coefficient and nitrogen solubility coefficient, S_{CO_2}/S_{N_2}, as shown in Table 3, is more than unity. This indicates that these plasma polymers might be useful materials as carbon dioxide separation membrane. However, the plasma polymers (500 nm thick) deposited on Millipore filter showed no selective permeation toward carbon dioxide. The permeability coefficient ratio (P_{CO_2}/P_{N_2}) was less than unit (0.8 - 0.9). Nevertheless the solubility is perferential for carbon dioxide, the poor selectivity in permeation indicates that the permeation process across the plasma polymers would be controlled by the diffusion process of permeant rather than the dissolution process.

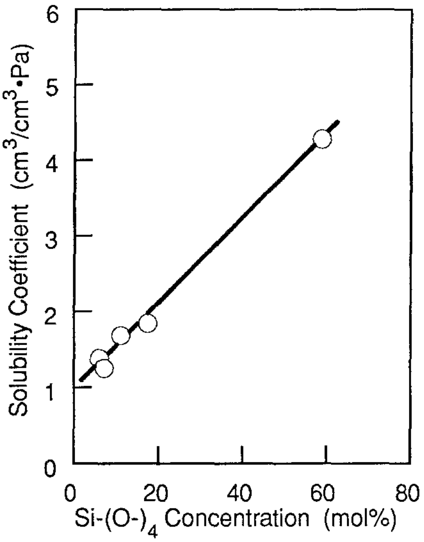

Figure 3 Relationship between solubility coefficient and Si-(O-)$_4$ concentration in plasma polymers.

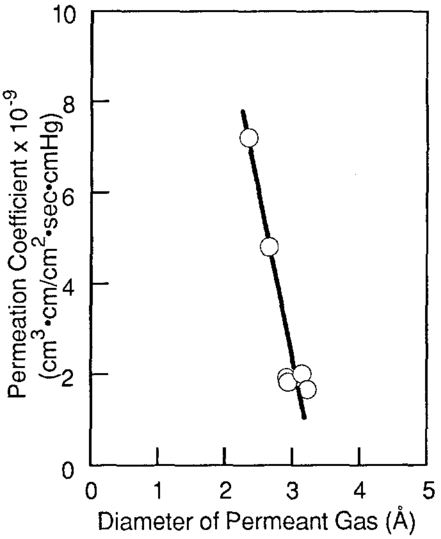

Figure 4 Relationship between permeation coefficient and diameter of permeants (helium, oxygen, argon, nitrogen, and carbon dioxide).

Figure 3 shows the permeation coefficient as a function of the diameter of permeants. The plasma polymer formed from DMDMOS whose solubility coefficients (S_{CO_2} and S_{N_2}) were 4.3 x 10^{-5} and 2.0 x 10^{-5} cm^3/ cm^3·Pa, respectively, was used as a specimen; and helium (molecular diameter 2.65Å), oxygen (2.92Å). argon (2.94Å), nitrogen (3.15Å), and carbon dioxide (3.23Å) were used as permeants. The permeability coefficient, as shown in Figure 4, decreased linearly with increasing the permeant size. This indicates that the permeation process is strongly controlled by the diffusion process. The diffusion coefficient ratio (D_{CO_2}/D_{N_2}) was temporarily estimated from data of the permeability coefficient ratio ($P_{CO_2}/P_{N_2} = 0.82$) and the solubility coefficient ratio ($S_{CO_2}/S_{N_2} = 2.2$) as 0.37. This estimation suggests an importance of the diffusion process rather than the dissolution process in the permeation across the plasma polymers. The small diffusion coefficient may be due to crosslinked networks of the plasma polymer chains.

In conclusion, the plasma polymers formed from DMDMOS, DMCPS, and TMDSO showed preferential solubility for carbon dioxide, while no selective permeation of carbon dioxide. The diffusion process rather than the dissolution process controls the permeation of carbon dioxide across the plasma polymers.

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