

Gas-Transport Properties Through Cation-Exchanged Sulfonated Polysulfone Membranes

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ABSTRACT: Sulfonated polysulfone (SPS) membranes were prepared, and the gas-transport properties of the resulting ionic polymers were examined. Gas-transport measurements were made on dense films of these polymers with a continuous flow technique. The sulfonation of polysulfone and the metal-cation exchange of SPS were confirmed with Fourier transform infrared spectroscopy and electron spectroscopy for chemical analysis. The SPS membranes exchanged with the monovalent metal ions showed higher permeability coefficients than the SPS membranes exchanged with the multivalent metal ions, whereas the selec-

tivities of all the metal-cation-exchanged sulfonated polysulfone (MeSPS) membranes for O₂/N₂ and CO₂/N₂ gas pairs were higher than those of SPS membranes. When the MeSPS membranes with metal cations of similar ionic radii were compared, the ideal selectivities of O₂/N₂ and CO₂/N₂ through MeSPS with divalent cations were higher than those through MeSPS with monovalent cations. © 2002 Wiley Periodicals, Inc. *J Appl Polym Sci* 86: 2611–2617, 2002

Key words: diffusion; gas permeation; ionomers; membranes

INTRODUCTION

Membrane-based gas separations are of particular interest and importance. In this field, polymer membranes are used commercially to separate air, to remove carbon dioxide from natural gas, and to remove hydrogen from mixtures with nitrogen or hydrocarbons in petrochemical processing applications.¹ Considerable effort has been made to identify new classes of polymer membranes that show high permselectivity^{2–4} and to investigate the effect of membrane chemistry on gas-transport properties.^{5–9}

Chen and Martin¹⁰ investigated the gas-transport properties of sulfonated polystyrenes. They found that permeability coefficients for all the investigated gases (O₂, N₂, CO₂, CH₄, H₂) decreased with the increasing extent of sulfonation, and they also found that the separation factor for Mg²⁺-form polymers were higher than that for the Na⁺-form polymers. They concluded that the introduction of metal ions remarkably improved separation efficiency due to the effect of electrostatic crosslinking. Chiou and Paul¹¹ studied the gas-transport properties of Nafion, a sulfonated perfluorocarbon ionomer. They found that an incor-

poration of sulfonate groups and metal counterions improved gas-transport selectivity. Liu and Martin¹² prepared defect-free composite membranes using highly ionic polymers exchanged with sodium salt (—SO₃Na⁺) poly(styrene sulfonic acid) (PSS) membranes, and this material enhanced the selectivity (8.0–8.2) for O₂ to N₂. Sakai et al.¹³ examined the gas-transport properties of O₂ and N₂ for Nafion 117 and 225 membranes with free acid and K⁺ forms. They observed that the diffusivity values of the K⁺-form membrane were smaller than those of acid-form one, whereas solubilities of K⁺-form membrane were greater than those of acid-form one for both gases. As a result, the K⁺-form membrane led to an increase in the selectivity of O₂/N₂ from 2.2 to 7.4.

Recently, Rhim et al.¹⁴ investigated the effects of various metal ions, such as Li⁺, Na⁺, and K⁺ for monovalents, Mg²⁺, Ba²⁺, and Ca²⁺ for divalents, and Al³⁺ for trivalents, exchanged in sulfonated poly(phenylene oxide) (SPPO) membranes on the permselectivity of CO₂ and CH₄. All metal-ion-exchanged SPPO membranes enhanced the selectivities, whereas the permeation rates decreased.

In this study, we focused on the development of membranes based on sulfonated polysulfone (SPS) and investigated the effect of the introduction of counterions into ionic polymers on the gas-transport properties. Particularly, the effect of exchange with metal ions, including monovalent (Li⁺, Na⁺, K⁺), divalent (Mg²⁺, Ba²⁺, Ca²⁺), and trivalent (Al³⁺) ions, was

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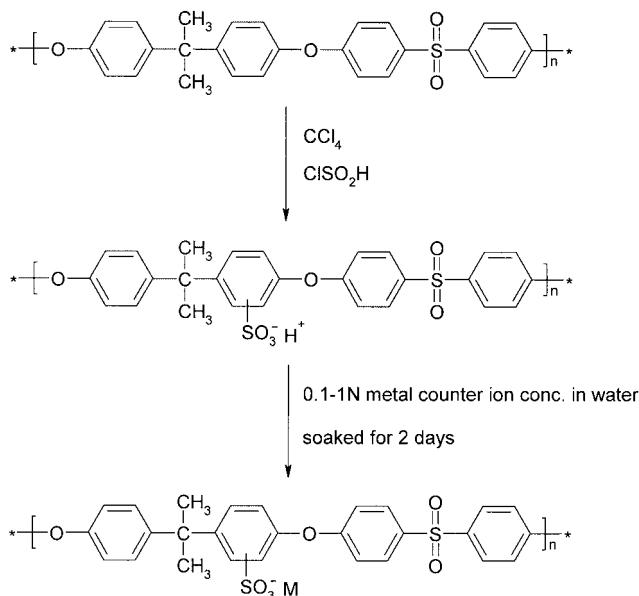


Figure 1 Postulated sulfonation mechanism of PS.

investigated in terms of the permeation rate and permeation ratios of O₂, N₂, and CO₂ gases.

EXPERIMENTAL

Preparation of SPS membranes

The commercial polysulfone (PS) Udel (Amoco, Augusta, GA) was dissolved in *N*-methyl-2-pyrrolidone (Aldrich Chemical Co., Milwaukee, WI) and left overnight to dissolve completely with mechanical stirring at room temperature. After a 10 wt % PS solution was filtered with a Fluoropore membrane (Millipore, Bedford, MA; FSLW 04700; pore size = 3 μm), the purified solution was cast onto a glass plate with a Gardner knife and then dried completely in vacuum oven at 60°C. The dry membranes, with thicknesses of 15–20 μm were cut to the size of the permeation cell (13.8 cm²) and then put into carbon tetrachloride (CCl₄) solution as the sulfonation medium. Then, a stoichiometric quantity of chlorosulfonic acid was added dropwise to the CCl₄ solution with vigorous stirring. The sulfonation reaction was carried out at 30°C for 1 h. We then washed the SPS membranes several times with purified water obtained by passing house-distilled water through a Milli-Q (Millipore) water-purification system. The postulated reaction mechanism is illustrated in Figure 1.

Ion exchange capacity (IEC) measurement

We treated preweighed samples of the SPS membrane in the free sulfonic acid form with 1M HCl for at least 10 h at 60°C to obtain the acid form of the SPS membrane. The hydrated samples were suspended in

deionized water and titrated with 0.1N aqueous NaOH with phenolphthalein as an indicator. IEC was recorded as an average value of five separate samples in units of milliequivalents of NaOH per gram of polymer.

In addition, a Carlo Erba CHNS—O analyzer (model EA 1110) was used for elemental analysis (EA) of the SPS membrane. EA data were used to evaluate the sulfonation degree and the theoretical IEC value. Table I summarizes the sulfonation degree and IEC value of the SPS membrane. The sulfonation degree of the SPS used in this study was 54 ± 1%.

Preparation of SPS membranes in metal cation form

The metal counterions used in this study were Li⁺, Na⁺, and K⁺ for monovalents; Mg²⁺, Ba²⁺, and Ca²⁺ for divalents; and Al³⁺ for the trivalent. The SPS membrane in proton form was immersed in a solution of alkali metal hydroxide or alkaline earth metal hydroxide of 0.1–1N, depending on the solubility of hydroxide in water. When the solubility was low, the solution saturated with hydroxide was used. We kept the membrane immersed for 48 h at room temperature to complete the exchange of the proton to metal cations. The exceptions were Mg²⁺ and Al³⁺, for which magnesium nitrate and aluminum chloride were used, respectively. The membranes after ion exchange were dried in air and then stored in a vacuum oven for at least 5 days before use.

Characterization of membranes

Fourier transform infrared (FTIR) spectroscopy analysis

IR spectra were measured with a PerkinElmer 1725X FTIR spectrometer (Shelton, CT). The thickness of specimens ranged from 0.01 to 0.02 mm.

Electron spectroscopy for chemical analysis (ESCA)

The compositional change in the surface of the SPS membranes by the exchange of metal ions was investigated by ESCA. The ESCA analyzer (ESCALAB MK II, V. G. Scientific Co., West Sussex, UK) was equipped with a AlK α radiation source at 1487 eV and 300 W at the anode. We took survey scans and carbon 1s core-

TABLE I
Characteristics of the SPS Membrane

	Thickness (μm)	Sulfonation by EA (%)	IEC by EA (meq/g)	IEC by titration (meq/g)
SPS	20	54%	1.08	1.12

level scan spectra to analyze the surface of SPS and SPS membranes exchanged with metal ions.

Gas permeation measurements

Most diffusion coefficients are measured with the high vacuum technique, the so-called time-lag method, developed by Barrer.¹⁵ This involves measuring the cumulative amount of gas that has passed through the membrane. However, the time-lag technique is not without difficulties,^{16,17} and these experimental and analytical problems have led to the development of a number of flow techniques. The flow techniques differ from the time-lag methods in that they do not involve measuring the cumulative amount of gas, $Q(t)$, which has crossed the membrane. Instead, the actual flux of gas, $J(t)$, is measured where $Q(t) = \int_0^t J(t) dt$. Analytically, this corresponds to an alternate solution to Fick's second law of diffusion equation that was given by Daynes¹⁸ as

$$\frac{J}{J_s} = 1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-n^2 \pi^2 D t}{l^2}\right) \quad (1)$$

where J and J_s are the fluxes in transient state and in steady state, respectively; l is the membrane thickness; D is the diffusion coefficient; and t is the permeation time. Equation (1) is valid only for flat-sheet membranes. The two diffusion coefficients derived from the flux transient are given by the expressions

$$D_{1/2} = \frac{l^2}{7.2 t_{1/2}} \quad (2)$$

$$D_{\text{slope}} = \frac{l^2}{5.91 t_{\text{slope}}} \quad (3)$$

In this study, D_{slope} was taken as the diffusion coefficient of a gas. In a steady-state permeation, the total amount of permeating substance, $Q(t)$, that has passed through the membrane in time t is given by the simplified eq. (2):

$$Q(t) = \frac{DC_1}{l} \left(1 - \frac{l^2}{6D}\right) \quad (4)$$

where C_1 is a permeant concentration interface of the membrane at the feed side, which is usually assumed to be in equilibrium with feed. Thus C_1 is interpreted as the solubility of the permeant in the membrane. Also in eq. (4), the slope of the equation is equivalent to the flux, J_s' in a steady state:

$$J_s = \left[\frac{dQ(t)}{dt} \right]_{t \rightarrow \infty} = \frac{DC_1}{l} \quad (5)$$

Therefore, eq. (1) can be rewritten as

$$J = \frac{dQ(t)}{dt} = \frac{DC_1}{l} \left[1 + 2 \sum_{n=1}^{\infty} (-1)^n \exp\left(\frac{-Dn^2 \pi^2 t}{l^2}\right) \right] \quad (6)$$

The previous equation describes the flux with permeation time, that is, the flux transient. Thus, diffusion coefficients were calculated from the response times with eqs. (2) and (3). When the diffusion coefficient and flux are known, the solubility of the permeant in the membrane can be determined from eq. (5). The solubility coefficient (S) and the permeability (P) can be expressed by their definitions:

$$S = \frac{C_1}{\Delta p} \quad (7)$$

$$P = \frac{J_s l}{\Delta p} \quad (8)$$

where Δp is the pressure difference between the feed and permeate sides.

RESULTS AND DISCUSSION

IR spectroscopy

Figure 2 shows the FTIR spectra of PS and SPS membranes, indicating the appearance of the absorption peaks of sulfonic acid groups on the membrane surface. It is known that the symmetrical and asymmetrical stretching vibrations of sulfonic acid groups appear at 1028 and 1180 cm^{-1} , respectively. Another characteristic absorption peak is usually observed at 950 cm^{-1} . However, we observed the sulfonic acid group only at 1028 and 950 cm^{-1} . Thus, we inferred that the sulfonation of PS by chlorosulfonic acid was appropriately performed in the carbon tetrachloride medium.

ESCA analysis

ESCA is sensitive to the chemical composition in the surface region extending several monolayers ($\approx 100 \text{ \AA}$) below the actual surface. The elemental composition data determined by ESCA for the surface of metal-ion-exchanged SPS membranes are shown in Table II. As shown in Table II, an increase of the compositions of O and S elements in SPS indicated the successful progress of sulfonation in comparison with PS. Furthermore, the similar composition of each metal coun-

TABLE III
Gas Permeability and Selectivity of MeSPS Membranes

Membrane	N ₂	O ₂	CO ₂	P _{O₂} /P _{N₂} (Barrer) ^a	P _{CO₂} /P _{N₂}
PS	0.28	1.60	5.80	5.71	20.71
SPS	0.21	1.26	5.40	6.00	25.70
Li-SPS	0.17	1.25	5.19	7.38	30.54
Na-SPS	0.19	1.35	5.45	7.13	28.67
K-SPS	0.20	1.36	5.35	6.80	26.73
Mg-SPS	0.08	0.46	2.16	5.80	27.06
Ca-SPS	0.09	0.53	2.38	5.90	26.44
Ba-SPS	0.09	0.56	2.45	6.20	27.19
Al-SPS	0.07	0.42	2.00	6.01	28.59

Operating temperature = 25°C.

^a 1 Barrer = 10⁻¹⁰ × cm³(STP)cm/cm²sec cmHg

sion through the interchain of the polymer. Likely, the metal cations exchanged to SPS membranes investigated in this study would have acted as a barrier for the diffusion of penetrating gas molecules, resulting in a decrease of the permeabilities but in the enhancement of the selectivities.

Effects of metal cations on diffusion and solubility coefficients

Equation (3) was used to obtain diffusion coefficients for N₂, O₂, and CO₂ in the various polymers we studied. Figure 3 illustrates typical experimental plot obtained in a continuous flow technique for measuring diffusion coefficients. The diffusion coefficients data obtained by this experimental plot are shown in Table IV. The diffusion coefficients for all the gases decreased as the SPS membranes were exchanged with metal cations. As expected, the SPS membranes exchanged with the monovalent metal ions showed higher diffusion coefficients than the SPS membranes exchanged with the divalent metal ions and the trivalent metal ions. That is, the diffusion coefficients of all of the gases decreased in the following order: mono-

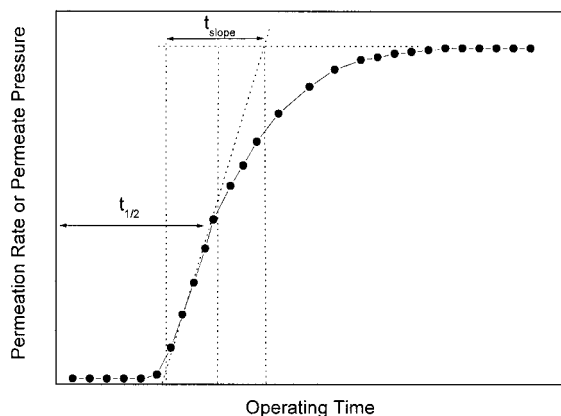


Figure 3 Typical experimental plot of continuous flow technique.

TABLE IV
Diffusion Coefficients for Various Gases in the MeSPS Membranes

	N ₂	O ₂	CO ₂	D _{O₂} /D _{N₂}	D _{CO₂} /D _{N₂}
Li-SPS	1.80	4.68	2.20	2.60	1.22
Na-SPS	1.60	3.73	1.79	2.33	1.12
K-SPS	1.61	4.66	2.19	2.91	1.37
Mg-SPS	0.92	2.87	1.29	3.12	1.40
Ca-SPS	0.88	2.83	1.27	3.33	1.45
Ba-SPS	0.91	2.86	1.38	3.14	1.52
Al-SPS	0.73	2.50	0.98	3.42	1.34

Unit = 10⁻⁸ cm²/s.

valent > divalent > trivalent cation-exchanged SPS membranes. This might have been due to the reduction of distance between polymer interchains by electrostatic crosslinking. Typically, the magnitude of the diffusion coefficient of a gas through a polymer matrix decreases with the size of gas molecule and with a reduction of *d* spacing in polymer interchain. For all MeSPS membranes, the diffusion coefficients for various gases decreased in the order O₂ > CO₂ > N₂. This trend followed the effective molecular diameters for these gas molecules (N₂ > CO₂ > O₂) instead of the order of kinetic diameters of each gas molecule [CO₂ (3.3 Å) < O₂ (3.46 Å) < N₂ (3.64 Å)].²²

The solubility coefficients for N₂, O₂, and CO₂ in the MeSPS membranes are shown in Table V. In all cases, the solubility coefficients increased in the order N₂ < O₂ < CO₂, which was in agreement with the order of condensability of gases.²³ Chen and Martin¹⁰ explained that dipole-induced dipole interactions contributed to the solubilization process of the gases for the sulfonated polymers and metal-ion-exchanged polymers. A polar —SO₃⁻M⁺ (monovalent metal ion) in the MeSPS membranes could have induced a dipole in a nonpolar gas molecule. That is, the induced dipole interacted with the permanent dipole of the first molecule, and two dipoles were attracted together so that the solubility coefficients increased with the addition of monovalent metal ions. However, divalent ions in MeSPS membranes would exist mainly in the form of —SO₃⁻ ··· M²⁺ ··· ⁻OS— so that this symmetrical

TABLE V
Solubility Coefficients for Various Gases in the MeSPS Membranes

	N ₂	O ₂	CO ₂	S _{O₂} /S _{N₂}	S _{CO₂} /S _{N₂}
Li-SPS	1.39	2.99	25.5	2.15	18.36
Na-SPS	1.06	3.37	29.0	3.17	27.27
K-SPS	1.19	2.91	24.9	2.45	20.93
Mg-SPS	2.17	4.74	41.5	2.18	19.09
Ca-SPS	0.91	1.58	17.0	1.74	18.66
Ba-SPS	0.99	1.86	17.2	1.88	17.39
Al-SPS	1.23	2.24	25.0	1.81	20.29

Unit = 10⁻³ cm³(STP)/cm³cmHg

TABLE VI
Ionic Radii of Metal Cations Used in This Study

	Metal cation						
	Li ⁺	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Ba ²⁺	Al ³⁺
Ionic radius (nm)	0.059	0.102	0.138	0.072	0.100	0.136	0.053

nature might not lead to a dipole-induced dipole interaction. Therefore, the solubility coefficients for all the gases in the divalent metal ions exchanged SPS membranes were lower than those in the monovalent metal-ion-exchanged SPS membranes.

Generally, the selectivity of a polymer for gas A over gas B ($\alpha_{A/B}$) is given by a product of a diffusion selectivity term (D_A/D_B) and a solubility selectivity term (S_A/S_B):

$$\alpha_{A/B} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \times \frac{S_A}{S_B} \quad (9)$$

As shown in Tables V and VI, the diffusion selectivity of MeSPS membranes decreased in the order monovalent > divalent > trivalent ion, whereas the solubility selectivity of MeSPS increased in the order monovalent < divalent < trivalent ions. Apparently, multivalent metal ions in the polymer rather than monovalent metal ions contributed to an increase in the solubility selectivity of gas pairs.

Effect of valence and ionic radii of metal cations on gas-transport properties

The gas selectivities were considered for given gas pairs through the SPS membranes exchanged by the metal cations of a similar ionic radius. The ionic radii for metal ions used in this study are shown in Table VI.²⁴ When we compared MeSPS membranes with

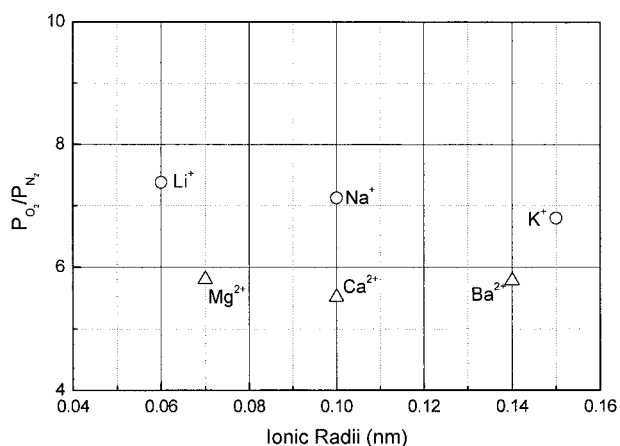


Figure 4 Effect of ionic radii of metal cations on O₂/N₂ selectivity.

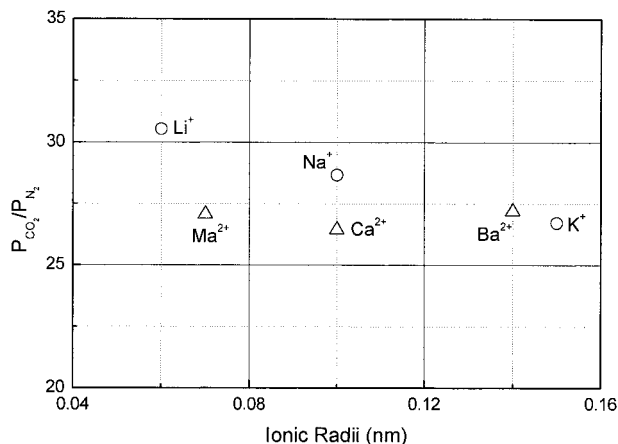


Figure 5 Effect of ionic radii of metal cations on CO₂/N₂ selectivity.

similar ionic radii, the ideal selectivities of O₂/N₂ and CO₂/N₂ for divalent cations were higher than those for monovalent cations. For example, when Li⁺ and Mg²⁺, which had ionic radii of 0.059 and 0.072 nm, respectively, were compared, the ideal selectivity of Li-SPS was greater than that for Mg-SPS. Similarly, when Na⁺ and Ca²⁺, which had ionic radii of 0.102 and 0.100 nm, respectively, were compared, the ideal selectivity for Na-SPS was also greater than that for Ca-SPS.

Figures 4 and 5 show the effect of the ionic radii of metal cations on the ideal selectivities of O₂/N₂ and CO₂/N₂, respectively. The ideal selectivity of MeSPS membranes was in the order Li-SPS > Na-SPS > K-SPS for the monovalent-cation-exchanged SPS membranes, whereas divalent-metal-cation-exchanged SPS membranes showed similar ideal selectivity values.

CONCLUSIONS

The SPS membranes exchanged with the monovalent metal ions showed higher permeability coefficients than the SPS membranes exchanged with the multivalent metal ions, whereas the selectivities of all the metal-ion-exchanged SPS membranes for O₂/N₂ and CO₂/N₂ gas pairs were higher than those of SPS membranes before metal ion exchange. When metal cations with similar ionic radii exchanged to SPS membranes were compared, the ideal selectivities of O₂/N₂ and CO₂/N₂ for divalent cations were higher than those for monovalent cations.

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