Gas-Transport Properties through Various Cations Exchanged Sulfonated Poly(ether imide) Membranes

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Abstract : The surface of poly(ether imide) (PEI) membranes has been sulfonated using $ClSO_3H$. The resulting membranes were characterized through the analysis of ESCA and contact angle measurements. The sulfonated PEI membranes were exposed to gases of O_2, N_2, and CO_2 to measure the permeation rates and ideal separation factors. In addition, the diffusivities and solubilities of individual gases were measured. The diffusivity effect is more dominant than the solubility one on gas transports.

Keywords :

1. Introduction

The membrane-based gas separation processes have been investigated during the past decades and numerous advancements have been made, leading to industrial applications. Membrane-based gas separations seem to have a tremendous potential as energy-efficient alternatives to cryogenic separations [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 Martin[10] investigated the gas transport properties of sulfonated polystyrene (PSS). They found that permeability coefficients for all the gases studied (O_2, N_2, CO_2, CH_4, H_2) decreased with increasing the extent of sulfonation, and also the separation factor for the Mg^{2+}-form membranes were higher than that for

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the Na^+-form membranes. They concluded that the introduction of metal ions remarkably improved the separation efficiency due to electrostatic cross-linking. Chiou and Paul [11] studied the gas transport properties of Nafion[TM], a perfluorosolfonic acid polymer. They found that an incorporation of sulfonate groups and metal counterions improved gas transport selectivity. Liu and Martin [12] prepared defect free composite membranes using highly ionic polymers exchanged with sodium salt (SO_3-Na^+) PSS membranes and this material enhanced the selectivity, 8.0-8.2, for O_2 and N_2. Bikson et al. [13] coated a lithium form of sulfonated poly(phenylene oxide) (SPPO-Li) onto polysulfone hollow fiber substrate membranes. They obtained the separation factor of 5.7 for oxygen and nitrogen with a permeation rate of 22 GPU for oxygen. Moreover, lithiated sulfonated hexafluoro Bis A polysulfone (F6 SPS-Li) membrane showed O_2/N_2 separation factor of 7.1. Sakai et al. [14] examined gas transport properties of O_2 and N_2 gases for Nafion 117 and 225 membranes with free acid and K^+ forms. They

observed that diffusivity values of K^+ form membrane were smaller than those of acid form one, while solubilities of K^+ were greater than those of acid form one, for both gases. As a result, K^+ form membrane led to increase the selectivity of O_2/N_2 from 2.2 to 7.4.

Recently, Rhim et al. [15,16] investigated the effects of various metal ions, such as Li^+, Na^+, and K^+ for monovalents, Mg^{2+}, Ba^{2+}, and Ca^{2+} for divalents, and Al^{3+} for trivalent, exchanged in both sulfonated poly(phenylene oxide) (SPPO) and sulfonated polysulfone (SPS) membranes on the permeability for several gases. All metal ion exchanged SPPO and SPS membranes enhanced the selectivities while the permeation rates decreased.

The current research is focused on the development of membranes based on poly(ether imide) (PEI) and investigated the effect of the introduction of counterions into ionic polymers on gas transport properties. Particularly, the effect of exchange with metal ion including monovalent (Li^+, Na^+, K^+), divalent (Mg^{2+}, Ba^{2+}, Ca^{2+}), and trivalent (Al^{3+}), was investigated in terms of permeation rate and permeation ratios of O_2, N_2, and CO_2 gases. In addition, the diffusivities and solubilities were measured for all the gases to realize which factor, either diffusivity or solubility, was dominant.

Experimental

Preparation of SPEI Membranes

The commercial poly(ether imide) Ultem was dissolved in N-methyl-2-pyrrolidone (NMP, Aldrich Chemical Co., Milwaukee, WI, U.S.A.) and left overnight to be dissolved completely with mechanical stirring at room temperature. After a 10 wt% PEI solution was filtered with Fluoropore (Millipore, FSLW 04700, pore size=3 μm) membrane, the purified solution was cast onto glass plate using the Gardner knife and then dried completely in vacuum oven at 60°C. The dry membranes having a thickness of 15-18 μm were cut into the size of the permeation cell (14.7 cm^2) and then put into carbon tetrachloride (CCl_4)

solution as the sulfonation medium. Then, a stochiometric quantity of chlorosulfonic acid was added to the CCl_4 solution with vigorous stirring. The sulfonation reaction was carried out at 30 °C for 1 hr. The sulfonated PEI membranes were then washed several times with distilled water.

Preparation of SPEI Membranes in Metal Cation Form

The metal counterions used in this study were Li^+, Na^+, and K^+ for monovalents, Mg^{2+}, Ba^{2+}, and Ca^{2+} for divalents, and Al^{3+} for trivalent. The SPEI membrane in proton form was immersed in a solution of alkali metal hydroxide or alkaline earth metal hydroxide of 0.1 to 1 N, depending on the solubility of hydroxide in water. When the solubility was low, the solution saturated with hydroxide was used. The membrane was kept immersed for 48 hr at room temperature to complete the exchange of the proton to metal ions. The exceptions were Mg^{2+} and Al^{3+}, 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.

Contact Angle Measurements

The water contact angle, an indicator of the wettability of surfaces, was measured at room temperature using a contact angle goniometer (Model 100-0, Rame-Hart, Inc., U.S.A.). More than three different specimens for modified PSf samples were prepared at several different parts for each specimen. For each part, 3 μL of a drop of purified water was deposited onto the surface. 5~10 times were measures for each specimen and then averaged.

ESCA Analysis

The compositional change in the surface of sulfonated PEI membrane by the exchange of metal ions was investigated by Electron Spectroscopy for Chemical Analysis (ESCA). The ESCA (ESCALAB MK II, V. G. Scientific Co., U.K.) was equiped with Al K α radiation source
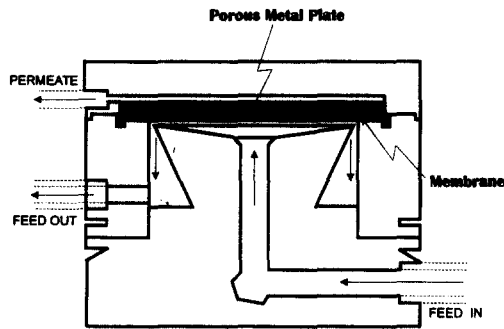
Fig. 1. Configuration of the membrane cell for the measurement of pure water and gas permeability in this study.

at 1487 eV and 300 W at the mode. Survey scans and carbon 1 s core level scan spectra were taken to analyze the surface of SPEI and SPEI membranes exchanged with metal ions.

Gas Permeability Measurement

The permeation apparatus which had been built for liquid permeation was modified to be suitable for the measurement of gas flux transients to solve the problems associated with the drawbacks in the existing continuous-flow technique. A schematic diagram of membrane cell is illustrated in Figure 1. The membrane cell was placed in

the heating oven to maintain at a desired temperature. The effective membrane area in the membrane cell was 14.7 cm^2. After mounting the membrane in the membrane cell, both the upstream and downstream sides in the cell were degassed simultaneously until the pressure reached below 0.05 torr. Then permeation transients were measured by introducing the permeant gas in the upstream side and taking the mass flow readings with time. Gases were measured in the sequence N_2, O_2, CO_2 to avoid any plasticization of the membrane occurring when exposed to CO_2. The measurements were carried out at feed pressures to about 1 MPa.

In the permeation apparatus as shown in Figure 2, the major measuring system of permeation properties which is connected with the permeate side of the membrane cell is mass flow meter (MFM). The permeate pressure is controlled by the back pressure regulator. A solenoid valve is installed between the membrane cell and MFM, and cut off the permeate line to protect the measuring system. A MFM (Brooks, Japan) used in this study has a capacity 1000 $cm^3(STP)/min$. When permeation happens, a voltage is produced in MFM correspondingly and transformed to mass flow rate using the linear relationship
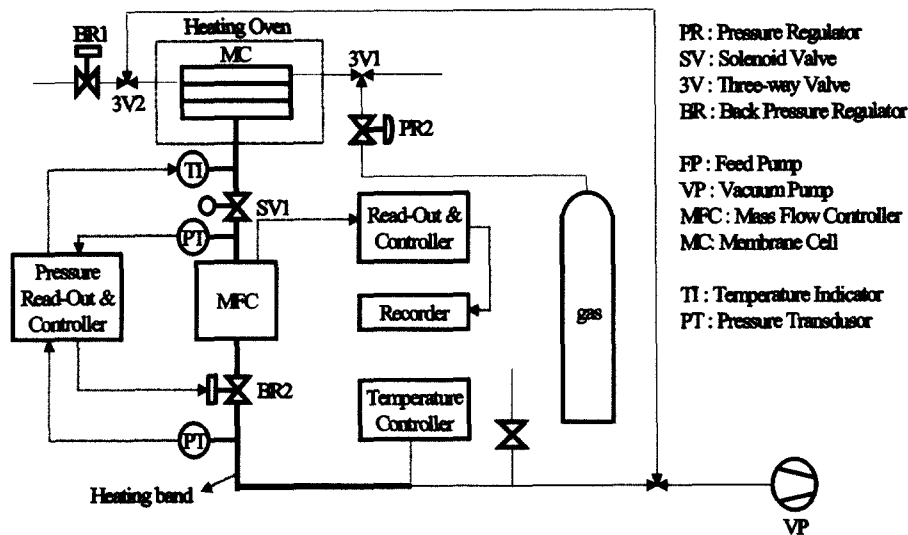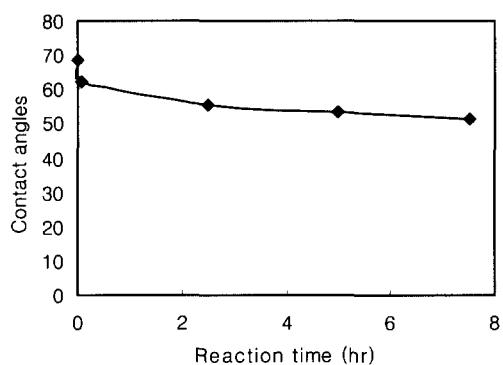

Fig. 2. Schematic representation of gas permeation apparatus.

Fig. 3. Effect of the reaction time on the contact angles at 25℃.

between the produced voltage and mass flow rate. The digital values of mass flow rates can be monitored on computer screen so that diffusivities can be calculated. For more details, one can refer the following references [17,18].

Results and Discussion

Contact Angle Measurement

The water contact angle is explained as an indicator of the wettability of film surfaces. It is well known that the increase of the contact angles means the reduction of the hydrophilic properties of surfaces whereas the decrease indicates the increase of that properties.

Figure 3 illustrates the contact angles with different reaction time. As expected, the contact angles decrease with increasing the reaction time. Once the reaction started, the contact angle decreased from 68.75 ° to 62.1 °. Then, as the

time increased, the contact angle value decreased to 51 ° after 7.5 hr passed. This result showed indirectly that the surface was changed due to the sulfonation.

ESCA Analysis

ESCA is sensitive to the chemical composition in the surface region extending several monolayers (100 Å) below the actual surface. The elemental composition data determined by ESCA for the surface of metal-ion exchanged SPEI membranes are shown in Table I. which illustrates the quantitative metal ion changes for SPEI films reacted with ClSO₃H at 45℃ for 5 hr.

For monovalents, the exchanged quantity of lithium is larger than that of sodium since the lithium ions could penetrate easier than the sodium ions because of the molecular sizes shown in Table 2. However, for divalents, even if the molecular sizes are smaller than those of monovalents, the exchanged quantities are smaller. Since divalents have two branches which need two sulfonic acid groups to react, so-called, electrostatic cross-linking, the reaction chances are less than the case of monovalents. As the molecular size becomes larger, Table 2 shows that the exchanged degree gets smaller which is same as the case of monovalents.

Effect of Metal Cations on the Permeability and Selectivity Coefficients

In this study, protons of the sulfonic acid group in SPEI were exchanged with various metal ions in order to investigate the effects of

Table 1. ESCA Results for PEI Tilms Reacted with ClSO₃H at 45℃.

Monovalent	Area %	Divalent	Area %	Trivalent	Area %
SPEI-Li	0.618	SPEI-Mg	0.413	SPEI-Al	0.356
SPEI-Na	0.373	SPEI-Ba	0.290	–	–
SPEI-K	N/A	SPEI-Ca	0.175	–	–

Table 2. Kinetic Sizes of Metal Ions Used in This Study

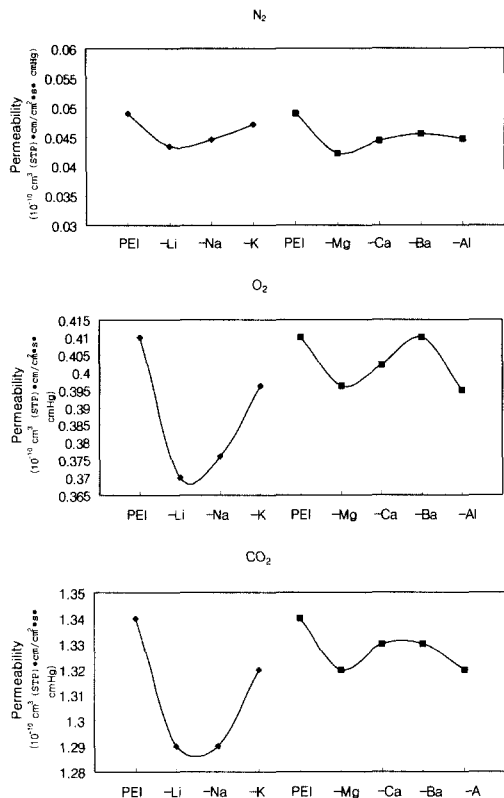| Cations	Li$^+$	Na$^+$	K$^+$	Mg^{2+}	Ca^{2+}	Ba^{2+}	Al^{3+}
Ionic radii*	0.059	0.102	0.138	0.072	0.100	0.136	0.053

* unit=nm

Fig. 4. Permeabilities of N_2, O_2 and CO_2 for the SPEI membranes exchanged with various metal cations at 25℃.

counterion on permeability and selectivity coefficient. The permeability coefficients data and the selectivity of O_2/N_2 and CO_2/N_2 obtained are illustrated in Figures. 4 and 5, respectively. Note that the permeability coefficients for all of the gases through metal cations exchanged SPEI membrane (MeSPEI) are lower than those of non-exchanged SPEI membrane. It is well-known from literatures that an incorporation of ionic groups into a polymer chain causes electrostatic cross-linking and a concomitant decrease in free volume [19]. Since the molecular size of lithium is the smallest, it could penetrate easily inside the membrane so that the free volume reduces. And as a result, the permeation rate is the lowest among monovalent ions. However, for divalents and trivalent, SPEI-Mg and SPEI-Al membranes show the lowest permeation rates due to the
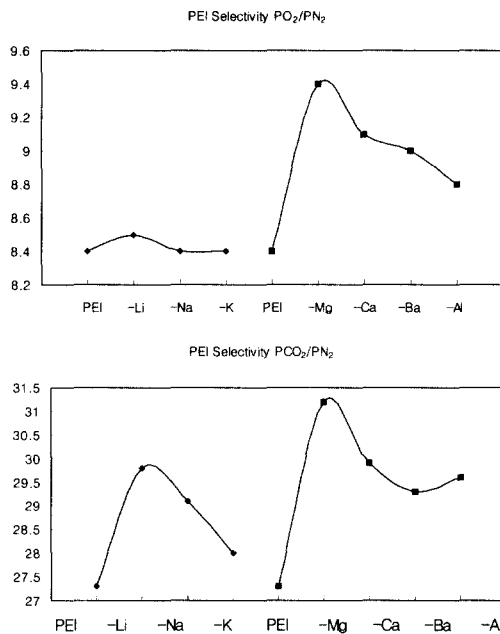

Fig. 5. Ideal separation factors of O_2/N_2 and CO_2/N_2 for the SPEI membranes exchanged with various metal cations at 25℃.

electrostatic cross-linking. When the permeation rates of MeSPEI membranes for all gases are compared one another, it could be apparently considered that the effect of free volume is more dominant than that of electrostatic cross-linking.

Generally, polymers with high selectivities of the given gas pairs show low permeabilities while polymers with high permeabilities typically show low selectivities [20,21]. As expected, the selectivities of all the MeSPEI membranes for O_2/N_2 and CO_2/N_2 gas pairs are higher than those of SPEI membranes before metal ions-exchange. According to Sakai et al.[14] who investigated the effect of cation form of Nafion[TM] membranes on the gas permeability of O_2 and CO_2 gases, the change in cation forms could influence the cluster size, resulting in the reduction on the gas permeability. Namely, metal cations exchanged to hydrogen of Nafion[TM] membrane hinder the gas diffusion through the interchain of polymer. Likely, metal cation exchanged to SPEI membranes investigated in this study would act as a barrier for the diffusion of pene
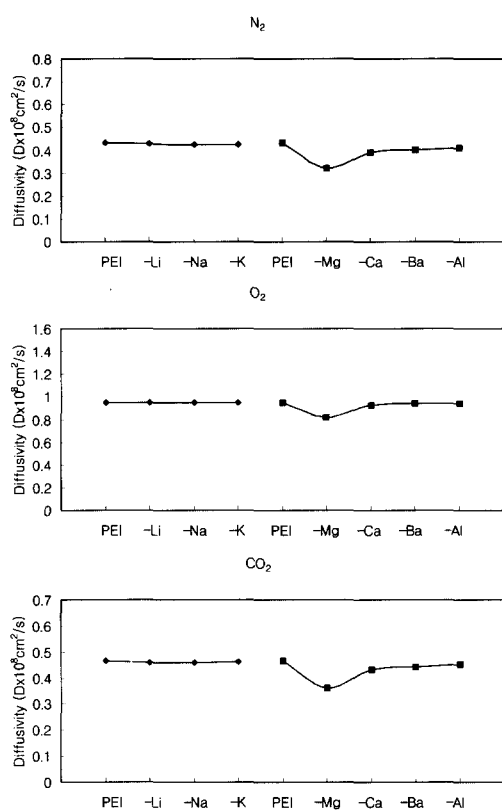
Fig. 6. Diffusivities of N_2, O_2 and CO_2 for the SPEI membranes exchanged with various metal cations at 25℃.

Fig. 7. Solubilities of N_2, O_2 and CO_2 for the SPEI membranes exchanged with various metal carions at 25℃.

trating gas molecules, resulting in a decrease of the permeabilities but in the enhancement of the selectivities. For both P_{O_2}/P_{N_2} and P_{CO_2}/P_{N_2}, SPEI-Li and SPEI-Mg membranes showed the highest results.

Effects of Metal Cations on Diffusion and Solubility Coefficients

The diffusion and solubility coefficients are illustrated in Figures. 6 and 7, respectively. The diffusion coefficients for all the gases look constant when the SPEI membranes are exchanged with metal cations. The SPEI membranes exchanged with the monovalent-metal ions show a little higher diffusion coefficients than the SPEI membranes exchanged with the divalent-and trivalent-metal ions, particularly Mg^{2+}. This might be due to the reduction of distance between polymer
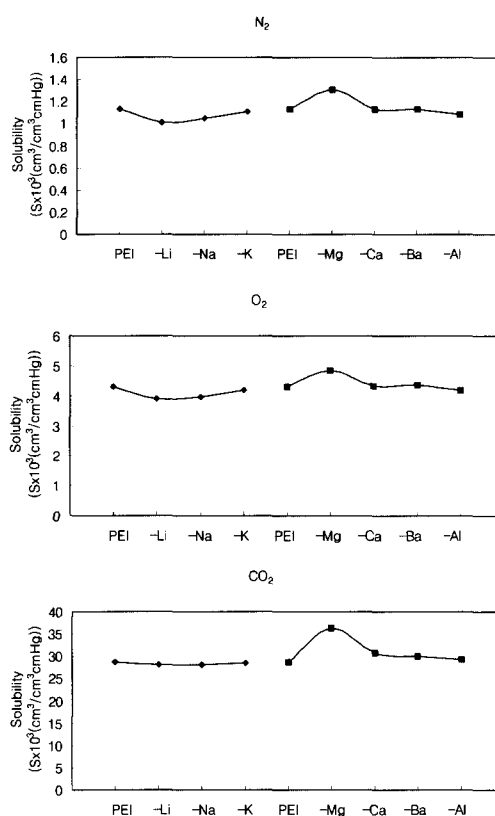
interchains by electrostatic cross-linking. Typically, the magnitude of the diffusion coefficient of a gas through a polymer matrix decreases with decreases with the size of gas molecule and with a reduction of d-spacing in polymer interchain. For all MeSPS membranes, the diffusion coefficients for various gases decreased in the order $O_2 > CO_2 > N_2$. This trend follows the effective molecular diameters for these gas molecules ($N_2 > CO_2 > O_2$) instead of the order of kinetic diameters of each gas molecule (CO_2 (3.3Å) $<O_2$ (3.46Å) $<N_2$ (3.64Å)) [22].

The solubility coefficients for N_2, O_2 and CO_2 in the MeSPEI membranes are shown in Figure 7. In all cases, the solubility coefficients increase in the order $N_2 < O_2 < CO_2$, which is in agreement with the order of condensability of gases [23]. Chen et al. [10] explained that dipole-induced
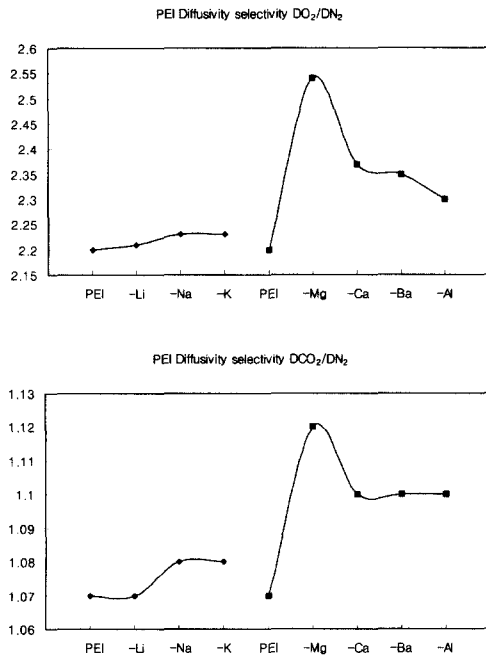
PEI Diffusivity selectivity DO₂/DN₂

PEI Solubility selectivity SO₂/SN₂

PEI Diffusivity selectivity DCO₂/DN₂

PEI Solubility selectivity SCO₂/SN₂

Fig. 8. Diffusivity selectivity of O_2/N_2 and CO_2/N_2 for the SPEI membranes exchanged with various metal cations at 25°C.
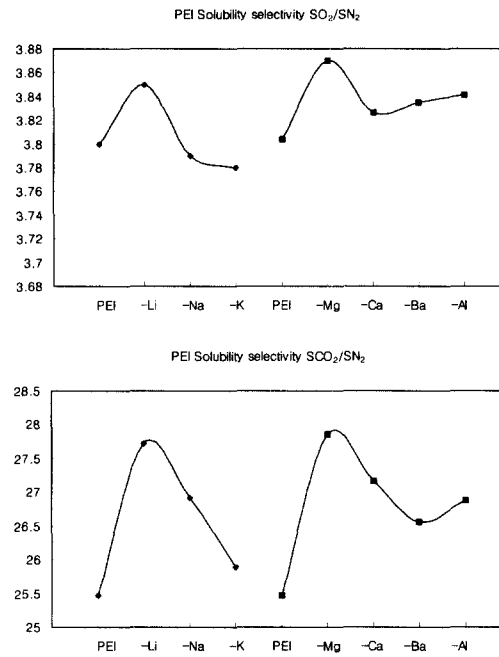
Fig. 9. Solubility selectivity of O_2/N_2 and CO_2/N_2 for the SPEI membranes exchanged with various metal cations at 25°C.

dipole interactions contributed to the solubilization process of the gases for the sulfonated polymers and metal-ion exchanged polymers.

Generally, the selectivity of a polymer for gas A over gas B, 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):

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

The diffusion and solubility selectivity shown in the above equation, (D_A/D_B) and (S_A/S_B), are illustrated in Figures. 8 and 9. The diffusion selectivity of MeSPEI membranes decreases in the order divalent>trivalent>monovalent ion, while the solubility selectivities for monovalent and divalent and trivalent can not be differentiated which one is superior. Therefore, it seems that the diffusivity factor is more dominant than the solubility one.

Conclusion

The surface of PEI membranes has been sulfonated. SPEI membranes were characterized through ESCA analysis and contact angle measurement, and exposed to measure the permeabilities and separation factors for O_2, N_2, and CO_2 gases. From this investigations, the following conclusion can be drawn :

(1) For contact angle measurement, the contact angles decrease as the reaction time increases.

(2) For ESCA analysis, metal ion contents decrease with increasing the molecular weight of metal ions.

(3) In all cases, the permeabilities for SPEI membranes decreased more than those for unreacted PEI films. Particularly, for N_2 and O_2 gases, the decrease degree of permeabilities is not severe when comparing with that for CO_2 gas. The selectivities of SPEI films for two gas mixtures are larger than those of unreacted PEI membranes. From

the diffusivity and solubility measurements, the diffusivity effect is more dominant than the solubility one on gas transports.

Acknowledgement

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