

GAS SEPARATION PROPERTIES OF FREE-STANDING FILM OF POLYANILINE

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ABSTRACT

The gas separation properties of free-standing film of polyaniline (PANI) for gas pairs of He/N_2 , H_2/N_2 , CO_2/N_2 and CO_2/CH_4 at room temperature were measured as a function of the protonation state. Variation of the gas permeabilities coefficient of PANI with an insulator to metal transition upon the protonation processes was observed, which might be due to a change in both gas solubility coefficient and diffusion coefficient with the protonation state.

INTRODUCTION

The gas separation by membrane is of particularly interesting because it is not only the most recently and rapidly growing segment of the industry, but also one of the most technically challenging in many ways. Recently, Anderson et al.^[1] reported the properties of gas separation of polyaniline (PANI) in the emeraldine oxidation state for all gas pairs of He/N_2 , H_2/N_2 , CO_2/N_2 , CO_2/CH_4 . Moreover, Liu et al.^[2] have studied the effect of dopant properties and temperature on the properties of gas separation of PANI. These results suggested that dopable conjugated polymers may be used as gas separation membranes which will open a new application for these materials. However, the mechanism of gas separation for these materials is not understood yet.

MacDiarmid et al.^[3] have first reported that an insulator to metal transition for PANI by protonic acid doping was observed and their chemical and physical properties were controlled by both the oxidation state and the protonation state. We have found that the optic, conductive and magnetic properties as well as the infrared emissivity in $8 \sim 20 \mu\text{m}$ varied with this transition^[4-5]. These results suggest that the electronic states of PANI at insulating, semiconducting and metallic regime are quite different. Therefore, it is necessary to study the properties of gas separation of PANI at above-described different states to understand the mechanism of the gas separation of PANI.

In this paper, the dependence of the protonation state of free standing film in the emeraldine oxidation state on their properties of gas separation for all gas pairs of He/N_2 , H_2/N_2 , CO_2/N_2 and CO_2/CH_4 was reported and its mechanism of gas separation was discussed.

EXPERIMENTAL

The emeraldine base powder was synthesized by MacDiarmid's method^[6]. The emeraldine base form of free-standing films of PANI was prepared by solution

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casting method at 60—70 °C described elsewhere^[7]. The thickness of the PANI films was controlled by the quantity and the concentration of solution of PANI in NMP. The emeraldine salt form of PANI films with different protonation state was obtained by the treatment of its base form of film with aqueous acid solution of different acidity. The doping level of the protonation state was controlled by the value of pH in aqueous acid solution and was measured by pH meter (10A-ST model). The conductivities of PANI films at room temperature were measured by four-probe method. The gas permeabilities coefficient of PANI film with different protonation state at room temperature were measured by Gas Permeabilities Rate Measurement Device with low vacuum method (K-315-N-01 model).

RESULTS AND DISCUSSION

A typical gas permeability coefficients (P) and separation factor (α) of PANI film with different protonation state are shown in Table 1 and Table 2, respectively. As shown in Table 1, an order of $P_{He} > P_{H_2} > P_{CO_2} > P_{O_2} > P_{N_2} > P_{CH_4}$ for gas permeability coefficient of PANI at the same protonation state was observed. This obeys common law of gas separation of general polymers. For uncondensed gases, the gas permeability coefficient of PANI is controlled by

Table 1 Dependence of the protonation state on the gas permeability coefficient of PANI films

	pH	P·He	P·H ₂	P·CO ₂	P·O ₂	P·N ₂	P·CH ₄
1	7.00	1.397	1.058	.2340	.047	.006	.0076
2	3.87	1.342	1.152	.2300	.048	.008	.0063
3	2.91	1.877	1.361	.2260	.032	.007	.0056
4	1.87	.845	.533	.0220	.008	.001	.0002
5	1.17	.317	.159	.0033	.001	.001	.0009

Unit of P as Barrers (1 barrer = 10⁻¹⁰ Cm³ · Cm/Cm² · s · CmHg)

Table 2 Dependence of the protonation state on the gas separation factors of PANI films

	pH	α·He/N ₂	α·H ₂ /N ₂	α·CO ₂ /CH ₄	α·O ₂ /N ₂
1	7.00	233.40	176.75	30.76	7.88
2	3.87	175.69	150.77	36.36	6.28
3	2.91	272.67	197.74	40.35	4.66
4	1.87	727.94	459.46	113.79	6.59
5	1.17	322.28	161.96	3.54	1.14

diffusion processes. As shown in Table 2, moreover, an order of $\alpha_{He/H_2} > \alpha_{H_2/N_2} > \alpha_{CO_2/CH_4} > \alpha_{O_2/N_2}$ for protonated PANI film (1 ≤ pH ≤ 7) was observed. In order to understand the mechanism of gas separation of PANI film, the conductivity of PANI film with different protonation state at room temperature was measured by four probe method and its results are shown in Fig. 1. It showed that the curve of logσ ~ pH can be divided into three parts: at lower protonation state (4 ≤ pH ≤ 7), conductivity is independent of the protonation state and its magnitude shows insulator behavior. At middle protonation state (2 ≤ pH ≤ 4), conductivity increases with the increase of the protonation state (decrease of pH) and its magnitude is in semiconducting regime. At high protonation state (pH ≤ 2), the conductivity at room temperature is independent of the protonation state, and its magnitude exhibits a metallic behavior Thus, these results suggest that an insulator

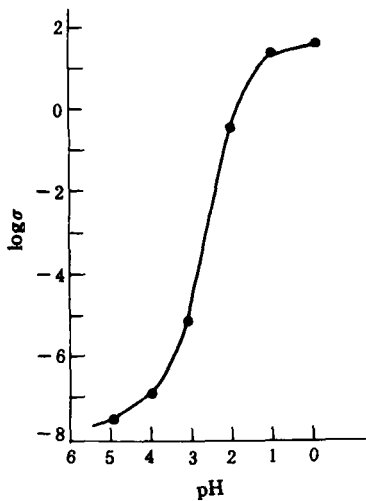


Fig. 1 Dependence of the protonation state on the conductivity of free-standing film at room temperature

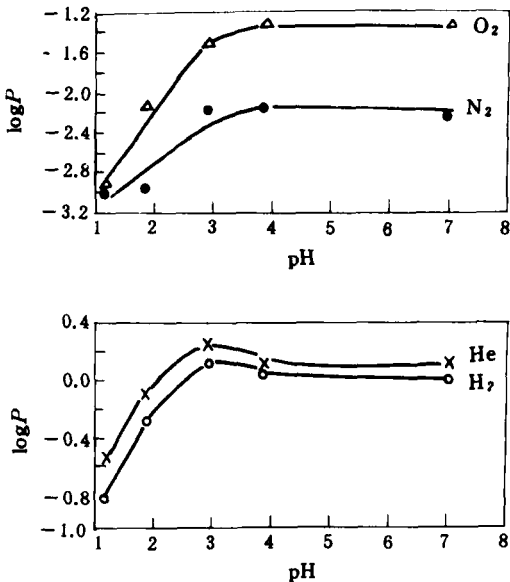


Fig. 2 Relationship between gas permeability coefficient and the protonation state for PANI film at room temperature

to metal transition in conductivity of PANI film was observed when its emeraldine base form of film was protonated by aqueous acid solution. This is consistent with the observations obtained by MacDiarmid^[3].

Based on the results shown in Table 1, the curve of $\log P \sim \text{pH}$ is shown in Fig. 2. It is very interesting to observe the following experimental results: at the insulating regime ($4 \leq \text{pH} \leq 7$), first, the gas permeability coefficients of PANI are constant, which is consistent with the observations from the dependence of the protonation state on its conductivities as shown in Fig. 1. At the semiconducting and metallic regime ($0 \leq \text{pH} \leq 4$), however, it increases with the decrease of the protonation state which is consistent with observations obtained by Kaner^[1]. Based on the results in Table 2, furthermore, a curve of $\log \alpha \sim \text{pH}$ for PANI film is shown in Fig. 3. It showed that the variation in gas separation factors with the protonation state was significant at the insulator to metal transition when PANI film was protonated by aqueous hydrochloride acid solution. As known, the gas permeability coefficient P can be described as^[8]

$$P = S_a \cdot D_a \tag{1}$$

where S_a is the solubility coefficient and D_a is the diffusion coefficient of gas in the polymers. It has been suggested that transport of gas molecule permeating a membrane occurs through the solution of the gas molecule in the membrane

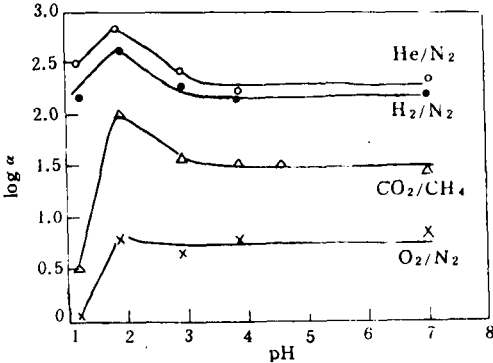
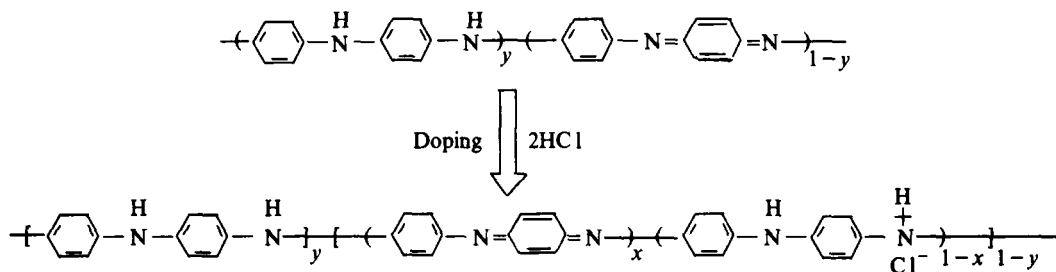


Fig. 3 Relationship between the gas separation factors and the protonation state for PANI film at room temperature

polymer at high-pressure (or high-concentration) surface, the diffusion of the gas molecule in the membrane and the desorption of the gas molecules at the low concentration surface. In addition, the molecular structure of protonated PANI was modified by Wan^[9] shown as



where A^{-1} is counterions, y and x are defined as the degree of the oxidation state and the protonation state of PANI, respectively. This indicates that protonic doping processes will yield a polysemiquinone which has been suggested by Epstein^[10]. Thus, the change in S_a and D_a may be due to the variation of structure of PANI caused by the introduction of both proton and counterions into the polymer chain of PANI. So, it is reasonable to believe that the variations in permeability coefficients with the protonation state are related to the change in the gas solubility coefficient and the diffusion coefficient with the protonation state due to a change in molecular structure of PANI caused by protonic doping processes. This is supported by the evidence that the nature of the counterions affects the properties of gas separation of PANI film reported by Liu et al.^[12].

CONCLUSIONS

The gas permeability coefficient of PANI film mainly depends on its protonation state. It shows that the variation of the gas permeability coefficient of PANI at an insulator to metal transition upon the protonation state is due to a change in the gas solubility coefficient and the diffusion coefficient with the protonation state.

Keywords:

Polyaniline; Gas separation; Membrane; Gas permeability; Separation factor

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