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Gas permeation property of organic-inorganic hybrid membrane made by ion-beam irradiation

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Abstract

In this study, we have reported an organic-inorganic hybrid membrane, which exhibits an asymmetric structure consisted of a carbonized skin layer and a polyimide porous substructure, to synthesize a novel gas separation membrane combining high gas permeability and selectivity. Both the gas permeability and selectivity of the carbonized layer significantly enhanced when compared with those determined in the control polyimide.

Introduction

The gas separation process using polymer membranes has received much attention, however, many studies for the structure/permeability relationships of polymer membranes have led to the trade-off correlations between the gas permeability and selectivity, which have become a major problem in realizing a gas separation process using polymer materials. Recently, a great interest can be seen in the syntheses of inorganic membranes for gas separation. One of the candidates is a carbon molecular sieve (CMS) membrane, which is synthesized by the pyrolysis of a polymer. However, it is very difficult to prepare a thin CMS membrane because of its poor mechanical property, therefore, the gas permeances of CMS membranes were not so high.

On the other hand, we reported the gas permeability through an asymmetric polyimide membrane with a ultrathin (10 nm) and defect-free skin layer prepared by a dry-wet phase inversion process.[1-5] Additionally, we reported that the gas selectivities of an asymmetric polyimide membrane with a defect-free skin surface orientated by shear stress without a coating process increased with an increase in the molecular orientation of the polyimide.[4,5] This result indicates that an asymmetric membrane with a modified ultrathin and defect-free skin layer would enhance both the gas permeability and selectivity.

In this study, we have reported an organic-inorganic hybrid membrane, which exhibits an asymmetric structure consisted of a carbonized skin layer and a polymeric porous substructure, used to synthesize a novel gas separation membrane combining high gas permeability and selectivity. It is well known that ion-beam irradiation can directly modify the surface of a membrane and that the polymer surface irradiated with high ion fluence is carbonized. We prepared an asymmetric polyimide membrane with a thin skin layer carbonized by the ion-beam irradiation. The gas permeances of the asymmetric polyimide membranes irradiated with 50keV He^+ at fluences less than $3x10^{15}$ ions/cm^2 have been measured using a high vacuum apparatus with a Baratron absolute pressure gauge at 76cmHg.

Experimental Section

Polyimide, 6FDA-6FAP, was synthesized by chemical imidization of the poly(amic acid) precursors as reported in the literature.[1,2] The synthesized 6FDA-6FAP had an Mw of $3.2x10^5$ with a polydispersity index of 2.1. The membranes with the different skin layer, approximately 80nm and 4μm, were prepared by a dry/wet phase inversion process.[1,2]

Ion-beam irradiation is a physico-chemical surface-modification process resulting from the impingement of a high-energy ion beam (Riken ion implanter, Riken, Saitama, Japan). In this study, ion irradiation was performed on polyimide membranes and He^+ was used. Ion irradiation was carried out on the a 2 x 2 cm^2 surface area at an energy of 50keV with a fluence range from 1 x 10^{12} to 3 x 10^{15} ions/cm^2.

Gas permeances of oxygen and nitrogen were measured with a high vacuum apparatus (Rika Seiki, Inc., K-315-H, Tokyo, Japan). The gas permeation measurements of the membranes were carried out at 35°C and 76cmHg.

Results and Discussio n

The results of gas permeance and selectivity of the asymmetric polyimide membranes for O_2 and N_2 at 35°C and 76cmHg are shown in Figure 1. The control asymmetric membrane indicated an O_2 permeance of 8.0 x 10^{-5} [cm^3(STP)/(cm^2 sec cmHg)], and the apparent skin layer thickness calculated from the oxygen permeability coefficient was 80nm. The depth profiles of energy loss for He^+ irradiation at 50keV in the asymmetric polyimide membrane were estimated using a well-established Monte Carlo simulation method (TRIM code). The mean projected range of the He^+ ions in the membrane was 975nm, and the energy loss was relatively flat over a large portion of the depth range. That is, He^+ ions are considered to have completely penetrated through the skin layer in the asymmetric polyimide membrane, because the apparent skin layer thickness was approximately 80nm.

Both the gas permeance and selectivity of the asymmetric polyimide membranes strongly depended on the He^+ fluence, and the O_2 permeances of the asymmetric membranes irradiated at the fluence of less than 1x10^{13} (ions/cm^2) increased when compared with the asymmetric membrane before the ion irradiation. In contrast, the permeances of the asymmetric membranes irradiated at the fluence of more than 1x10^{14} (ions/cm^2) decreased with an increase in the He^+ fluence. On the other hand, the (O_2/N_2) selectivities in the irradiated asymmetric membrane increased with an increase in the He^+ fluence.

In addition, the effects of the ion-irradiated skin layer thickness on the gas permeation properties are also discussed in this study.

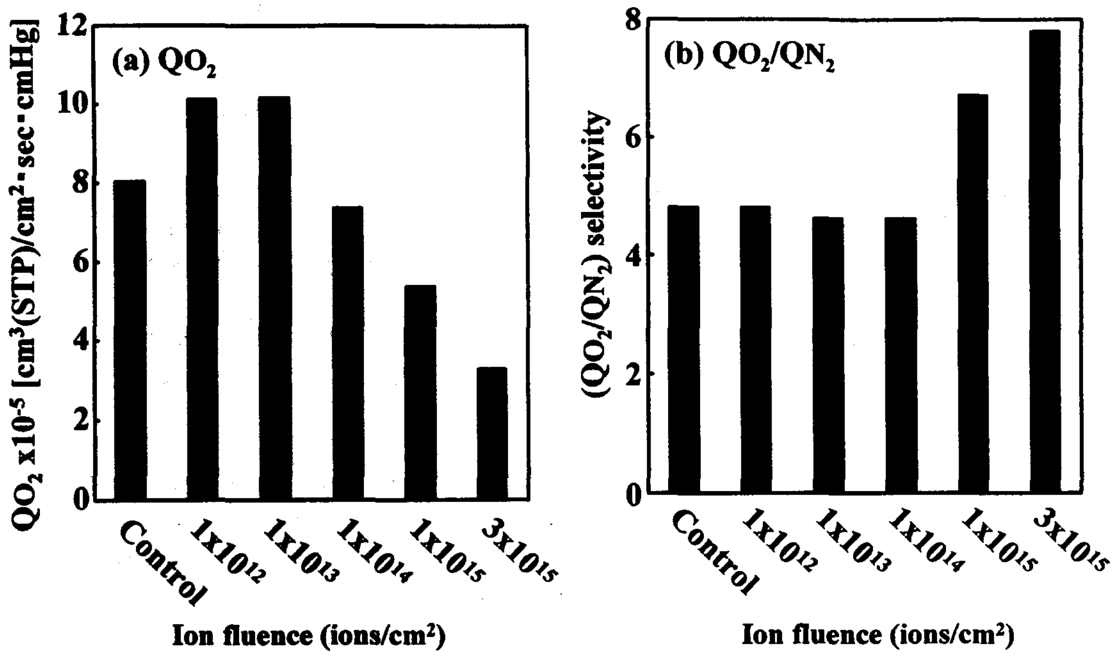

Fig.1 Effect of ion fluence in the (a) gas permeance and (b) selectivity for the asymmetric polyimide membranes at 35°C and 76cmHg.

References

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