ASYMMETRIC CARBON MOLECULAR SIEVE MEMBRANES BASED ON POLY(PHENYLENE OXIDE) FOR GAS SEPARATION

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Introduction

Carbon molecular sieve (CMS) membranes have recently emerged as a promising gas separation processes especially for the production of oxygen enriched air, recovery of CO_2 from natural gas, purification of H_2, and separation of olefin/paraffin mixtures. In earlier studies, a variety of precursors such as polyimide, polyacrylonitrile, phenolic resin, poly(furfuryl alcohol) and others have been applied to carbon molecular sieve membranes. The most popular precursor of reported carbon membranes is related to polyimide due to their high thermal stabilities and excellent gas separation performances, however, the greater material cost constrains their commercial availabilities [1].

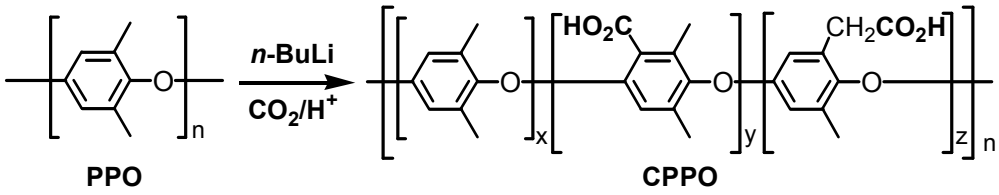
We have been investigating the carbon molecular sieve membranes for gas separation using poly(phenylene oxide) (PPO) as one of the alternative precursors instead of conventional ones such as polyimide. PPO offers a lot of advantages such as cost performance, high thermal stability, widespread availability and easy modification with functional groups. In our previous study, we synthesized PPO derivatives with various functional groups in one-step reaction. We found that the resulting PPO based carbon membranes provided excellent O_2/N_2 separation performances comparable to the polyimide based carbon membranes [2,3]. To develop these membranes for commercial application, we fabricated asymmetric hollow fiber carbon membrane using carboxylated PPO (CPPO) and its gas transport property was investigated in this study.

Experimental

Poly(2,6-dimethyl-1,4-phenylene oxide) (PPO) was purchased from Aldrich Chemicals. All the solvents and 1.6 mol l^{-1} *n*-butyllithium hexane solution were obtained from Wako Pure Chemical Industries. Carboxylated PPO (CPPO) was synthesized by a simple one-step reaction according to the literature by lithiation of PPO followed by treatment with dry ice, as illustrated in Scheme 1 [4].

The hollow fiber membranes were prepared by using the well-known dry/wet spinning process. A 20–25 wt.% CPPO solution in DMAc was extruded through the spinneret into a water bath as a coagulating agent. After drying in air at room temperature, the CPPO asymmetric precursor membranes were obtained. CPPO carbon membranes were obtained through the pyrolysis of CPPO precursor membranes at 823–1023 K for 2 hours under vacuum by a heating rate of 10 K min^{-1}. Prior to carbonization process, the membranes were preoxidized in air at 553 K for 45 min. The resulting CPPO hollow fiber membranes were characterized with IR, TG analysis and SEM observation.

Gas permeance (He, H_2, CO_2, O_2, N_2 and CH_4) was measured at 298–363 K with a high-vacuum time-lag system under the pressure difference of 76 cmHg. Both the feed and permeate sides of the membrane cell were evacuated ($<10^{-5}$ Torr) prior to each measurement. In this study, the selectivities were determined as the ideal separation factors by considering the ratio of the permeabilities for the selected gas pairs.



Scheme 1. Synthesis of carboxylated poly(phenylene oxide) (CPPO)

Results and discussions

The cross-sectional morphology of the hollow fiber CPPO carbon membrane fabricated from 25 wt.% DMAc solution was shown in Fig. 1. Many finger-like voids were observed in the polymeric precursor membrane, this asymmetric structure remained even after the pyrolysis. The thickness of the CPPO carbon membrane was decreased by shrinkage from 68 μm to 25 μm.

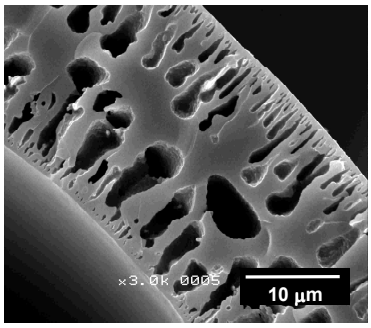


Fig. 1. SEM image of asymmetric CPPO carbon membrane.

Fig. 2 gives the single gas permeance against the kinetic diameter of the gas molecule for CPPO carbon membranes pyrolyzed at 923 K. The permeance dropped sharply for gases with a molecular size in the range of 0.3–0.4 nm, clearly indicating that the gas molecules penetrate through the CPPO carbon membranes by a molecular sieve transport mechanism. In case of CPPO carbon membrane fabricated from 20 wt.% DMAc solution, the gas selectivities such as H_2/CH_4, CO_2/CH_4 and O_2/N_2 were lower than that from 25 wt.% DMAc solution, suggesting that there might be small defects on the surface of the membrane. On the other hand, CPPO carbon membrane fabricated from 25 wt.% DMAc solution showed excellent gas transport properties, of which H_2 permeance was 9.4×10^{-5} $cm^3(STP)\ cm^{-2}\ s^{-1}\ cmHg^{-1}$ and H_2/CH_4 selectivity was over 1000. Furthermore, the permeance of O_2 was 2.3×10^{-6} $cm^3(STP)\ cm^{-2}\ s^{-1}\ cmHg^{-1}$ and the O_2/N_2 selectivity was attained to 10. The asymmetric hollow fiber CPPO carbon membranes prepared in this study achieve a performance comparable to that of polyimide-based carbon membranes with regard to the separation of gas pairs such as H_2/CH_4 and O_2/N_2 [5].

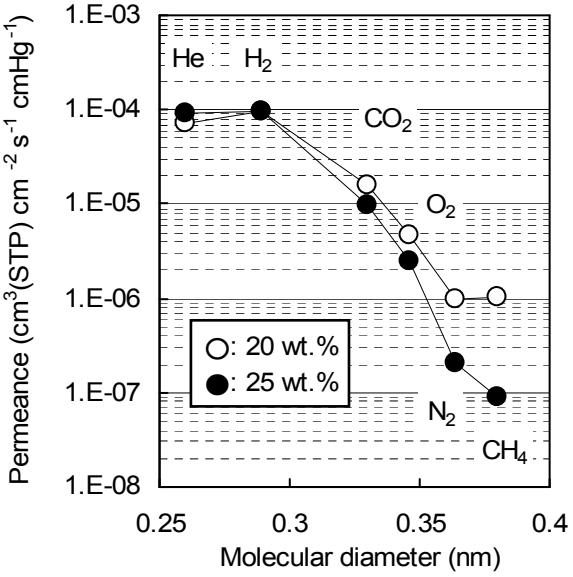


Fig. 2. Gas transport properties of CPPO carbon membranes measured at 298K.

References

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