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# Gas permeation properties for the post-oxidized polyphenylene oxide (PPO) derived carbon membranes: Effect of the oxidation temperature

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## Abstract

Of thermosetting polymers, polyphenylene oxide (PPO) is considered as one of the alternative promising polymeric precursors for carbon-based membranes. The post-oxidized PPO derived carbon membranes were prepared by carbonization, followed by air-oxidation as post-treatment method in this study. It was observed that air-oxidation increased the pore characteristic values (pore volume, pore size and its distribution) of carbon materials. It was shown that the post-oxidation increased gas permeance due to change in the pore properties. The permeation results for the post-oxidized carbon membranes showed that the extent of the permeation modification is strongly dependent on the oxidation temperature. Also, it was observed that the post-oxidation at higher temperature changed permeation mechanism from the molecular sieving to Knudsen-like diffusion especially for larger gas species.

*Keywords:* Carbon membrane; Pyrolysis; Post-oxidation; Polyphenylene oxide

## 1. Introduction

Membrane processes have become competitive in a wide variety of large-scale industrial applications because of low capital costs and high energy efficiency compared with conventional separation methods [1]. Interests on inorganic membranes have increased for the potentials in gas separation processes due to good thermal and chemical stabilities than polymeric membranes. Attractive opportunities for gas separation are found in the various areas of natural gas processing, landfill gas recovery, olefin/paraffin separation, air separation and hydrogen recovery [2–5].

Gas transport mechanisms in inorganic membranes are primarily varied depending on the pore size distribution and chemical interaction between the diffusing gas species and the membrane material [6–8]. The transport mechanism through inorganic membranes can be divided into four mechanisms, i.e., the Knudsen diffusion, the molecular sieving, the surface diffusion, and the capillary condensation mechanisms. The transport of the adsorbing gas species in the surface diffusion mechanism increases because of the preferential adsorption on the membrane pore surface. Therefore, the adsorbing gas species show a higher permeability than predicted from the Knudsen diffusion since the preferential adsorption reduces open porosity and limits the diffusion of the less adsorbing gases into the micropores [9,10]. In addition, gas separation can occur by the molecular sieving when the pore dimensions approach those of the diffusing gas species, where nearly infinite separation factors are theoretically attainable. The capillary condensation can occur in the mesoporous membrane structure in the presence of condensable gas species such as water vapor and butane. The high permeance and high selectivity for condensable gas species in this mechanism can be observed due to their pore filling effect in the membrane pore structure.

Of inorganic membranes, carbon membranes are considered to be one of the promising materials for membrane-based gas separation because of their excellent permeation and separation properties and thermal and chemical stability even under high

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pressure and temperature [11,12]. Selection of the polymeric precursor is one of the important considerations for making carbon membranes [13]. So far, different polymeric materials were considered such as polyimides, phenolic resins, polyfurfuryl alcohol, and phenol formaldehyde, polyacrylonitrile, cellulose and others. Of polymers, polyphenylene oxide (PPO) is considered as one of the alternative promising polymeric materials since it has a linear structure assigned to the rotational motion of its phenyl ring, giving excellent mechanical properties [14–16]. The preparation of carbon membranes involves the consecutive following steps: polymer precursor selection, polymeric membrane preparation, pretreatment, pyrolysis/carbonization, and post-treatment [13]. A distinctive feature of carbon membranes is that pyrolysis conditions of a polymeric precursor can yield a series of membranes having micropores of desired molecular dimensions. Until now, the preparation of carbon membranes derived from PPO polymer and the permeation results have been reported only in limited sources [17–19].

Of post-treatment methods, the post-oxidation in the air circumstance is considered to increase the pores size and the pore volume for carbon membranes. It is known that the permeation performance is affected by the post-oxidation conditions, such as oxidation temperature and oxidation time for the carbon membranes derived from polyimides [20,21] and phenolic resins [22,23]. Suda and Haraya reported that mild oxidation slightly enlarged micropore of carbon molecular sieve membranes and the post-oxidized membranes exhibited excellent performance in the alkane/alkene permselectivity [24]. Yamamoto et al. also showed that the values of the permeability and the selectivity in the presence of the adsorbing gas species (e.g., $C_2H_6$, $C_3H_6$, $C_3H_8$) increased after carbonization (700 °C) of polyimide polymeric precursor, followed by air-oxidation (300–400 °C) [20]. In the previous results, the permeating gas species was transported by the molecular sieving effect in the carbon membrane derived from a phenolic resin film at 700 °C. And, it was reported that gas transport was affected by the surface diffusion mechanism for the post-oxidized carbon membranes prepared at temperatures between 100 and 450 °C [22,23]. The oxidation effect on the membrane pore properties was not clearly discussed in the previous results. Also, it is expected that the influence of the oxidation on the gas permeation performance show different aspects according to different polymeric precursors.

The main aim of this work is to analyze the effect of the extent of oxidation on the permeation properties of carbon membranes derived from PPO as well as the membrane pore properties. The carbon membranes were prepared by coating a thin film of PPO polymer on a macroporous tubular ceramic support, and pyrolysis at 600 °C, followed by post-oxidation of the carbon membranes in air. In this study, the influence of the oxidation temperature on the gas permeation properties was investigated for the post-oxidized carbon membranes.

## 2. Experimental

For making the PPO derived carbon membranes, the PPO polymer (Aldrich, USA) solution in chloroform (Wako, Japan) with 3 wt.% was dip-coated at the speed of 3 cm/min on the surface of the tubular α-alumina ceramic support (NOK, Japan) (average pore size: 100 nm, outer diameter: 2.9 mm, thickness: 330 μm). The polymeric film on the support was dried in the room condition for 1 day. The carbon membranes were prepared by the pyrolysis of the coated PPO polymer on the support surface at 600 °C in the Ar atmosphere (flow rate: 200 ml/min). For the post-oxidized carbon membranes, the oxidation was conducted with different oxidation temperature (between 100 and 400 °C) in the air circumstance. During the pyrolysis and the post-oxidation, the duration time at the maximum heating temperature was set as 1 h with the heating rate of 5 °C/min and the flow rate of 200 ml/min.

Weight change during heat treatment of the polymeric precursor and its carbonized material was measured by means of a thermogravimetric analyzer (TG-DTA 2000SA, Bruker AXS) in the same condition for the pyrolysis and the post-oxidation. The pore properties of carbon materials were characterized by the nitrogen adsorption at −196 °C using an automatic adsorption apparatus (BELSORP-18, BEL Japan Inc.) after the pretreatment at 300 °C during 5 h in the vacuum condition. The surface morphology and the cross-section of a carbon membrane were examined using a scanning electron microscope (SEM), S-2400, Hitachi, Japan.

To investigate the influences of the oxidation temperature on the gas permeation performances, permeance of He (0.26 nm), $CO_2$ (0.33 nm), $N_2$ (0.36 nm) and $CH_4$ (0.38 nm) was measured for the post-oxidized carbon membranes using a permeation apparatus having a film flow meter (STEC, Japan) at a temperature range between 35 and 150 °C. The results were compared with those of the pyrolyzed carbon membrane at 600 °C. Permselectivity of selected gas pairs was estimated as the ratio of the permeance of each permeating gas species.

## 3. Results and discussion

### 3.1. Characterization of non-oxidized and post-oxidized carbonized materials

A SEM microphotograph of the carbon membrane pyrolyzed at 600 °C is shown in Fig. 1. It was shown in the figure that the PPO carbon membrane has layered structure on the macroporous support and is well adhered to the surface. It was observed that the PPO carbon layer on the support surface has a thickness of 3 μm. Fig. 2 shows the thermogravimetric analysis results of the PPO polymeric precursor and its carbonized material. The thermal gravimetric plot for the polymeric precursor in Fig. 2(a) shows that the polymer structure started to degrade and develop the carbonized structure at around 450 °C. The weight loss was measured to 63% around 500 °C, and the remaining weight showed the values within 25 and 28% at higher temperature than 700 °C. The thermal gravimetric plot in the figure shows that the total weight loss was measured to 75% as the heating temperature increased up to 1000 °C. Fig. 2(b) illustrates the thermogravimetric plot during the air-oxidation of the carbonized material pyrolyzed at 600 °C. The weight loss was measured to 0.5% even when the temperature increased up to 400 °C. At higher temperature than 450 °C, a notable decrease