

Preparation of supported carbon molecular sieve membrane from novolac phenol–formaldehyde resin

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Abstract

An asymmetric carbon membrane was prepared by coating alcohol solution of novolac phenol–formaldehyde resin containing a little hexamine on a porous resin support from the same material. After drying in air for two days at room temperature, the coated support was heated at 150 °C for 1 h in air (heating rate: 0.5 °C/min) and then carbonized at 800 °C (heating rate: 0.5 °C/min) in Ar atmosphere. The support and the membrane layer were carbonized simultaneously. The coating–pyrolysis cycle only needed one time. SEM photographs showed the carbon membrane had an asymmetric structure formed by a dense skin layer with a thickness of around 35 μm and a porous substrate. Pure gases of different molecular size (H₂, CO₂, O₂, N₂ and CH₄) were used to test the carbon membrane permeance property. The membrane has a good selectivity for H₂/N₂ and H₂/CH₄ with H₂ permeance of $4.05 \times 10^{-6} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$. The permeance is independent of pressure. The results indicate that the gases transport through the membrane according to molecular sieve mechanism.

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1. Introduction

Carbon molecular sieve membranes are very promising candidates for gas separation, both in terms of separation property and stability. But it has proven difficult to prepare this membrane in a defect-free, continuous form. Carbon membranes can be classified as two types: unsupported membrane and supported membrane. Only supported membrane can be used in large-scale industrial application. Generally, supported carbon membranes for gas separation are prepared by coating a suitable polymeric solution on porous carbon, ceramic or metal supports and subsequent carbonization under controlled conditions. One limit to incorporating carbon membranes into actual application is the preparation process. In order to obtain a defect-free carbon membrane the coating–pyrolysis cycle must be repeated several times

which needs time and special care. Some researchers are making great efforts to prepare carbon membrane in one casting step [1]. The factors which determine microstructure and gas permeance properties of carbon membrane include polymeric precursor, membrane formation method and pyrolysis conditions.

Nowadays, a lot of researchers have used different polymeric precursors to prepare carbon membrane. The polymeric precursor needs to have thermosetting property in order to avoid melting when heated and thus retain structure shape during heating and pyrolysis. Damle et al. [2] obtained carbon membranes by coating porous carbon tube with several thermosetting polymer solutions. These polymers include polyacrylonitrile, polyfuryl acid, thermosetting phenol–formaldehyde resin, cellulose, and furfuryl alcohol–phenolic resin. The carbonization was carried out at temperature between 500 and 750 °C under nitrogen atmosphere. The coating–pyrolysis procedure was repeated several times.

Rao et al. [3] coated a macroporous graphite sheet with thin layers of polyvinylidene chloride latex. The membrane was carbonized at 1000 °C under nitrogen atmosphere. The coating–pyrolysis procedure was repeated five times. The

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effective pore diameter of skin layer is about 5–6 Å. The membrane can be used to separate hydrogen–hydrocarbon mixtures by the surface diffusion mechanism.

Kusakabe et al. [4] prepared carbon membrane by coating condensed polynuclear aromatic (COPNA) compounds solution, synthesized from pyrene, phenanthrene, and 1,4-benzenedimethanol, on the outer surface of a porous alumina support. The coated support was carbonized at 400–1000 °C.

Carbon membranes by pyrolysis of various types of polyimide have been developed and a considerable body of data has been collected. Koros and co-workers reported a series of works about polyimide membranes [5–12], mixed matrix membranes [13,14] and carbon membranes [15–18] for gas separation. Both the synthesis and application of polymeric and carbon membranes were studied. It has been investigated how the proceeding conditions and raw materials affect the membrane characteristics. Hayashi et al. [19] coated a poly(amic acid) solution from 3,3',4,4'-biphenyltetracarboxylic dianhydride (BPDA) and 4,4'-oxydianiline (ODA) on the outer surface of a porous alumina tube. The poly(amic acid) film was imidized to a polyimide membrane in nitrogen atmosphere. Fuertes et al. [20] used BPDA-pPDA as precursor to make flat carbon molecular sieve membranes supported on a macroporous carbon substrate. Furthermore, they also used two other commercially available polyimide-type polymers, Matrimicel and Kapton to prepare supported carbon composite membranes in a single casting step [1].

Phenol–formaldehyde resin (PF) was used as precursor to prepare carbon membrane due to its high carbon yield and low cost. Kita et al. [21] made carbon membrane using thermosetting phenolic resin as polymeric precursor and porous alumina tubes as support. The coating–carbonization cycle was repeated several times to obtain carbon membranes, which have good separation properties for H₂/N₂, H₂/CH₄ and O₂/N₂. Fuertes et al. prepared a carbon membrane by carbonization of a thin film of novolac phenolic resin deposited on the inner face of a porous alumina tube [22]. The coating–carbonization cycle only needs one time. The membrane has high selectivity for O₂/N₂. Kishore et al. used phenol–formaldehyde resin to prepare carbon membrane for nanofiltration [23].

Although a great deal of effective practical and fundamental studies have been reported, the development of new methods is still needed to simplify the fabrication process and improve the reproducibility of carbon membranes. In this study, one novel energy-saving, simple and reproducible one-step method is reported. The alcohol solution of novolac phenol–formaldehyde resin containing a little hexamine was coated on a porous resin support from the same material. The membrane layer and support were carbonized simultaneously which saves energy. Furthermore, the crack was dramatically reduced because the top layer and support had similar constriction during carbonization. This resin will partially melt when heated which can eliminate the pinhole in the separation layer effectively. Using this method, defect-free supported carbon membranes have been prepared successfully and reproducibly. The coating–pyrolysis cycle only needs one time. The permeation rates of different gases through the support and the overall membrane as well as the separation

selectivity are also reported. The obtained carbon membrane has good separation properties for H₂/N₂ and H₂/CH₄.

2. Experimental

The resin support was prepared by blending fine novolac resin particles with additives. The blend was pressed in tube-shaped support of 15 mm in diameter and 2 mm in thickness. The preparation procedure was described elsewhere [24]. The resin support was dipped in 60 wt.% alcohol solution of novolac resin with a little hexamine. The coated support was dried at air for two days at room temperature, then was heated following the sequence (a) drying at 150 °C for 1 h in air (heating rate: 0.5 °C/min); (b) carbonization at 850 °C for 1 h (heating rate: 0.5 °C/min) in Ar atmosphere. The resulted carbon membrane was slowly cooled down to room temperature. The coating–carbonization cycle just needs one time.

In order to investigate the characteristics of support, the resin support was carbonized to 850 °C in Ar atmosphere lonely. The pore size distribution of carbon support was tested by the bubble point method. Isopropanol–nitrogen was used as a wetting–permeating system [25].

A system was designed to determine the gas permeation rate through the carbon membrane. In contact with the inner surface of the tube membrane, high purity gases supplied from compressed gas cylinders were introduced at high-pressure side. The permeation rate of pure gases was estimated at the low-pressure side of the membrane by a soap film flow meter. All pure-component permeance experiments were conducted at approximately 20 °C. Permeance was measured for H₂, N₂, CH₄, CO₂ and O₂. Permeation of the *i*-component gas through a membrane is described as follows: $q(i) = P(i)[p_H(i) - p_L(i)]$ where $q(i)$ and $P(i)$ are the flux and permeance of the *i*-component respectively, $p_H(i)$ and $p_L(i)$ are the partial pressure of the *i*-component at the feed and permeate sides, respectively. The ideal selectivity of the *i*-component relative to the *j*-component is calculated from $\alpha(i/j) = P(i)/P(j)$.

3. Results and discussion

3.1. Characteristics of supports

Support is important for preparation of gas separation carbon membrane because the defects of substrate will be translated to the top separation layer. Fig. 1 shows the pore size distribution of carbon support. The mean and maximum pore diameters are 0.1 and 0.3 μm, respectively. Table 1 is the permeance of several gases and ideal selectivity through carbon support. The data showed a high gas permeance and low selectivity. The gas permeance through the membrane decreased with molecular weight of gas molecules increasing. The selectivity of different gas pairs was lower than that predicted from Knudsen transport mechanism, which indicated that gas transport through the carbon support occurred according to Knudsen mechanism and Poiseuille flow.

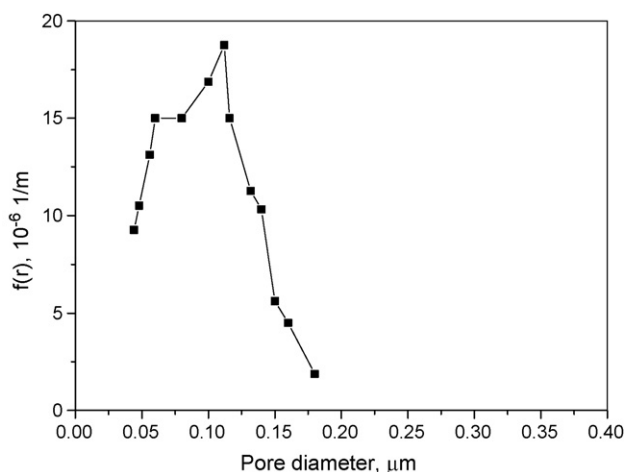


Fig. 1. Pore size distribution of carbon support.

Table 1
Gas permeance and separation property of carbon support

Permeance ($\times 10^{-3} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$)	
H ₂	4.12
CH ₄	2.53
CO ₂	1.70
N ₂	1.68
O ₂	1.48
Ideal selectivity	
H ₂ /N ₂	2.45
H ₂ /CH ₄	1.63
O ₂ /N ₂	0.88
CO ₂ /CH ₄	0.67

3.2. Polymeric precursor and membrane property

The typical chemical structure of novolac phenol–formaldehyde resin was shown in Fig. 2. The novolac resin is a linear chain condensation product, which is favor to prepare a nonporous dense layer. Such resin has plastic property, which will melt when heated and eliminate the pinhole in dense layer effectively. However, such property also results in deforming the support and the membrane cannot retain its structure shape during pyrolysis. Therefore, novolac resin cannot be used as precursor lonely. A little hexamine was added in novolac resin, thus the novolac resin became thermosetting resin during heat-treatment. When the resin solution concentration is high, the coating–pyrolysis cycle

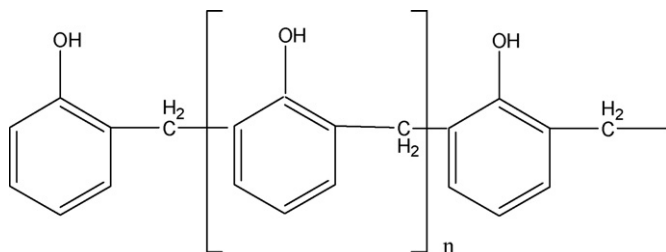


Fig. 2. Chemical structure of novolac phenol–formaldehyde resin.

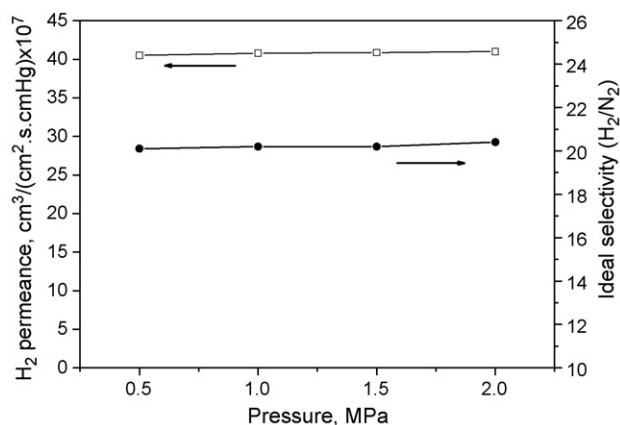
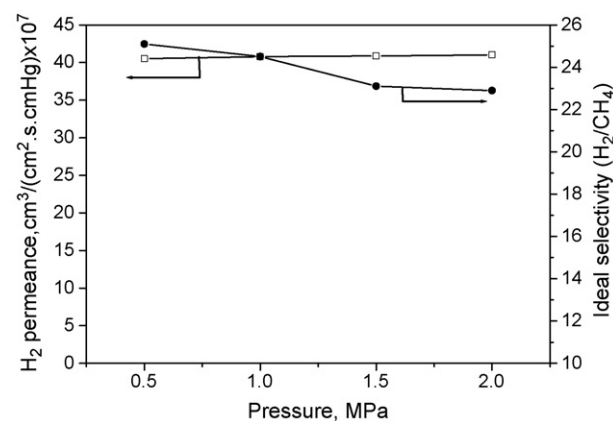
Table 2

Gas permeance and the separation property of one-time coated carbon membrane from novolac resin (six samples from two batches)

Permeance ($\times 10^{-7} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$)	
H ₂	40.1–51.2
CH ₄	0.81–1.76
CO ₂	3.03–5.28
N ₂	1.15–1.68
O ₂	2.52–3.48
Ideal selectivity	
H ₂ /N ₂	24.1–39.5
H ₂ /CH ₄	23.1–45.2
O ₂ /N ₂	1.8–2.8
CO ₂ /CH ₄	1.8–4.8

only needs one time. Table 2 showed the permeance and the ideal selectivity of carbon membrane coated with 60 wt.% novolac resin alcohol solution one time. The permeance of H₂ was $4.01\text{--}5.12 \times 10^{-6} \text{ cm}^3 \text{ cm}^{-2} \text{ s}^{-1} \text{ cmHg}^{-1}$. The membrane exhibited H₂/N₂ selectivity of 24.1–39.5, H₂/CH₄ selectivity of 23.1–45.2 and O₂/N₂ selectivity of 1.8–2.8.

The effects of gas feed pressure on the separation of H₂/N₂, H₂/CH₄ and O₂/N₂ were illustrated in Figs. 3–5. As the feed

Fig. 3. H₂ permeance and ideal selectivity of H₂/N₂ as a function of feed pressure.Fig. 4. H₂ permeance and ideal selectivity of H₂/CH₄ as a function of feed pressure.

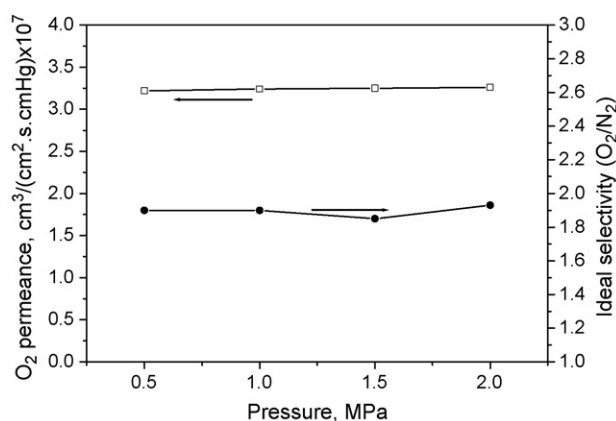


Fig. 5. O₂ permeance and ideal selectivity of O₂/N₂ as a function of feed pressure.

Table 3

Gas permeance and the separation property of two-times coated carbon membrane from thermosetting phenol–formaldehyde resin

Permeance (×10⁻⁷ cm³ cm⁻² s⁻¹ cmHg⁻¹)

H ₂	237.7
CH ₄	75.96
CO ₂	52.67
N ₂	59.41
O ₂	57.86

Ideal selectivity

H ₂ /N ₂	4.00
H ₂ /CH ₄	3.13
O ₂ /N ₂	0.97
CO ₂ /CH ₄	0.69

pressure increased, the H₂ permeance and ideal selectivity of H₂/N₂ did not change while ideal selectivity of H₂/CH₄ decreased a little. The feed pressure has no effect on the O₂ permeance and ideal selectivity of O₂/N₂.

The gas permeance of pure gases with different kinetic dimensions, H₂ (2.83 Å), CO₂ (3.3 Å), O₂ (3.46 Å), N₂ (3.64 Å), CH₄ (4.3 Å), was illustrated in Fig. 6. The gas permeance through the membrane correlated with kinetic diameter instead of molecular

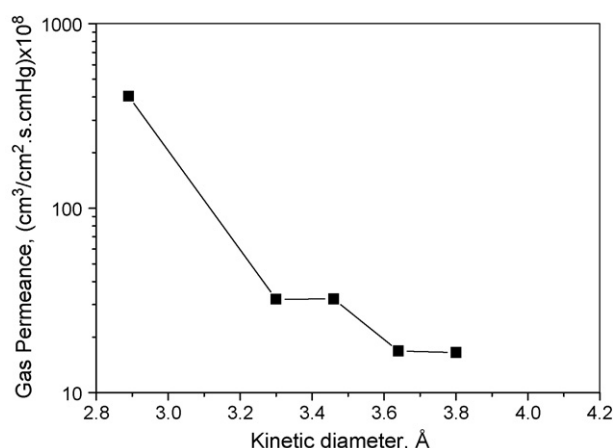


Fig. 6. Gas permeance with kinetic diameter of gas molecules.

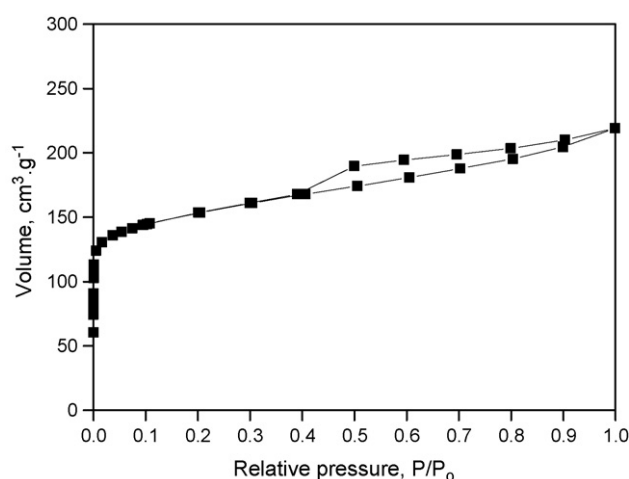


Fig. 7. Nitrogen adsorption isotherm of separation layer.

weight of gas molecules and decreased as the molecular size of gases increasing.

All these indicate that the pores of the separation layer are of molecular dimensions, which allows the separation of gases by molecular sieve mechanism.

We also used thermosetting phenol–formaldehyde resin as polymeric precursor. The preparation procedure is same as above. Experiment results demonstrated that the coating–pyrolysis cycle must repeat several times in order to get good selectivity. Table 3 showed the properties of carbon membrane coated by 60 wt.% thermosetting phenol–formaldehyde resin alcohol solution two times. The ideal selectivity was still low even two times coating.

The selectivity and permeance of carbon membranes from the literature are shown in Table 4 to compare with the present work. The virtue of this one-step method should not be obscured although the selectivity of present membranes is not impressive when compared with other membranes in the literature. It can effectively save energy, simplify the process and improve the reproducibility of defect free carbon membranes. Further study to improve the selectivity of carbon membranes is being conducted based on this method.

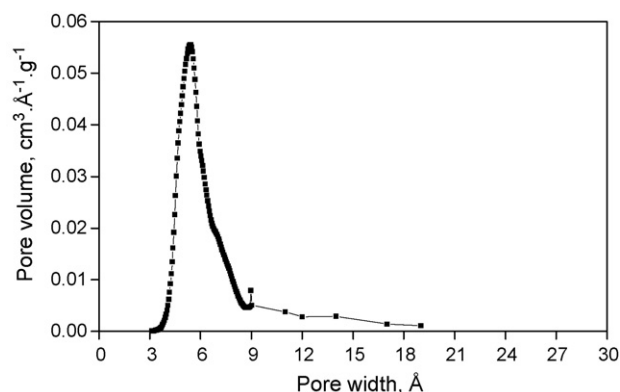


Fig. 8. Pore size distribution of separation layer.

Table 4

Selectivity comparison of carbon membranes prepared in this work with those in the literatures

Reference	Precursor	Membrane structure	Coat times	$\alpha_{(O_2/N_2)}$	$\alpha_{(H_2/N_2)}$
This work	Novolac PF resin	Resin tube supported	1	1.8–2.8	24.1–39.5
[18]	Polymide	Hollow fiber	–	7.4–9.0	64–110
[21]	Thermosetting PF resin	Alumina tube supported	5	5.7	28
[26]	Novolac PF resin	Resin tube supported	Spraying	12.8	471.3

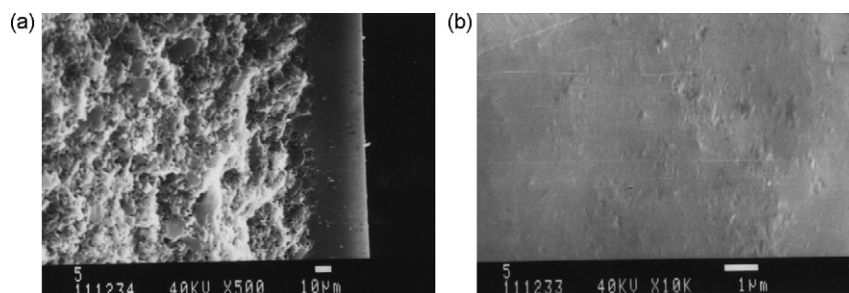


Fig. 9. SEM photographs of one-coated carbon membrane from novolac resin (a, cross-section; b, surface view).

3.3. Membrane structure

The replica of the separation layer was made through coating on a stainless steel tube the novolac resin solution and then heat-treatment as the preparation of carbon membranes. The replica was then removed from the tube in form of small chunks. The adsorption isotherm of nitrogen was measured volumetrically at 77 K. The sample was pre-outgassed at 10^{-7} mbar, and the isothermal profile was recorded following the adsorption–desorption path. Pore size distribution was calculated by HK method. The nitrogen adsorption isotherm (Fig. 7) implies that the membrane possessed micropores with a little mesopore volume. The pore size distribution was shown in Fig. 8. The mean pore size is about 0.5 nm. The mesopores have a negative effect on the selectivity of membranes for gas pairs although the mesopore volume is a small fraction of the total pore volume. The carbon membranes will be more selective if the mesopores are eliminated.

SEM photographs of one-coat carbon membrane from novolac resin are shown in Fig. 9. The structure of the asymmetric carbon membrane consists of a separation layer with a thickness around 35 μm and a macroporous matrix formed by uniform pores around 0.1 μm . The top layer is very smooth, defect-free. A good adherence between the separation layer and the macroporous carbon support is observed. The polymeric precursor substrate is porous matrix formed by finely ground particles and the polymeric precursor film is a dense film. On thermal treatment in inert gas atmosphere, the substrate was partially melted, rounded and the particles were connected, which formed macroporous carbon support. The dense films became a microporous structure because small volatile gaseous molecules channeled their ways out of the solid matrix during pyrolysis.

4. Conclusions

The carbon membranes were prepared by novolac phenol–formaldehyde resin in only one coating–pyrolysis cycle avoid-

ing complex and unpractical multicoating methods. The green support and separation layer were carbonized simultaneously which saves energy and avoids crack. The reproducibility of carbon membranes has been effectively improved. The carbon membrane had the asymmetric structure including microporous separation layer and macroporous support. The carbon membranes displayed high selectivity for the gas separation of H_2/N_2 and H_2/CH_4 .

Acknowledgments

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