

THE PORE STRUCTURE CHARACTERISTICS OF A TUBULAR COAL-BASED SUPPORT CARBON MEMBRANE

T. H. Wang, Y. H. Liu, Y. Q. Pan, J. Liu, X. S. Wang and T. X. Cai
Laboratory of Comprehensive Utilization of Carbonaceous Resources,
Dalian University of Technology, Dalian 116012, PRC

Introduction

Carbon membrane as a new kind of inorganic membrane has gained a great interest in the recent years due to its high thermal and chemical stability and unique characteristics in pore structure. Support carbon membranes are typically prepared by the pyrolysis of the carbonaceous materials such as graphite, coal, coal char or coke and the polymeric materials[1,2,3,4,5]. The understanding of the pore structure characteristics of carbon membrane is very important for the study on the mechanism of membrane formation, liquid and gas separation, especially for preparation of a carbon-carbon composite membrane. Unfortunately, the study on the pore structure of a support carbon membrane and the effects of pyrolysis condition on the pore structure of a support carbon membrane were seldom reported. In this paper, the pore structure characteristics of a tubular coal-based support carbon membrane (CSCM) were studied by the measurement of their gas permeation flux, porosity and pore distribution as well as their SEM photograph. The effects of pyrolysis condition such as temperature, heating rate, inert purge gas flow rate and atmosphere on pore structure characteristics of a support carbon membrane were also investigated.

Experimental

1. Preparation of the coal-based support carbon membrane

The support carbon membrane was prepared by mixing coal powder less than 74 μm with the binder to form into a dough which was extruded into a tube with 10mm outer diameter by a hydraulic extruder. The tube, then, was air-dried at room temperature. The dried tubes were pyrolyzed in a stainless-steel horizontal reactor which was placed in a tubular furnace at the temperature of 500-900 and heating rate of 0.5-7 /min in a inert purge gas or vacuum. After pyrolysis, the resulting support carbon membrane was cooled to room temperature naturally.

2. Determination of pore structure characteristics of the coal-based support carbon membrane

The pore structure characteristic of support carbon membrane was determined by gas-liquid displacement

porometry method with isopropanol as wetting liquid and nitrogen as porometry gas [6]. The mean pore diameter (MPD) and pore size distribution can be calculated using the method recommended by Venkataraman[7]. The SEM photograph and microstructure of support carbon membrane were measured by JEM-1200EX electron microscopy and AS-1-MP physisorption, respectively.

Results and Discussion

1. The effects of pyrolysis condition on pore structure of the coal-based support carbon membrane

The effects of pyrolysis condition such as temperature, heating rate and purge gas flow rate on pore structure, weight loss and contracted ratio of sample size of a CSCM were shown in table 1.

It could be seen that the pyrolysis conditions have a great influence on weight loss, contracted ratio of sample size and pore structure of the CSCM. The weight loss of CSCM at 450 had been reached to 31.83%, about 76% of total weight loss, and the contracted ratio on tube size was only about 4%, the 37% of total contracted ratio. At 600, the weight loss of CSCM was reached to above 95% of the total, and the contracted ratio on tube size was only 48% of the total. With the pyrolysis temperature increasing from 600 to 900, weight loss was only about 5% of the total, and the contracted ratio on tube size was up to 52% of the total. The degree of change in weight loss and contracted ratio was decreased as temperature increased. On the pore structure, with the increase of pyrolysis temperature from 450 to 900, the mean pore diameter(MPD) of the CSCM was up to the largest at 500, and the porosity and N₂ flux was at 600. That suggested that emission of volatile in the CSCM was almost finished below 600 and the contraction of the CSCM mainly occurred above 600. The pore structure of the CSCM was formed around 450 and finished at 600. The pore structure of the CSCM was further improved with the increase of pyrolysis temperature. At the high temperature, the pore size became smaller and some closed or semi-closed pores were opened and became throughout pores. The increase of

Table 1. The effects of pyrolysis condition on pore structure of a support carbon membrane

pyrolysis condition			weight loss (%)	contracted ratio of sample size(%)			pore structure characteristic		
flow rate (cm ³ /min)	T (°C)	heating rate (/min)		Length diameter	inner diameter	outer diameter	mean pore diameter (μm)	porosity (%)	N ₂ flux (GPU)
20	450	3	31.83	4.32	4.07	4.48	0.500	36.04	4.48
20	500	3	33.29	5.13	4.68	5.52	0.628	39.12	6.72
20	600	3	39.78	5.64	5.70	5.86	0.560	42.97	7.56
20	750	3	41.03	9.87	9.98	10.67	0.550	42.77	7.54
20	900	3	41.66	11.83	11.81	12.07	0.538	40.20	7.45
20	900	0.5	41.20	11.30	11.41	12.07	0.472	40.02	7.73
20	900	7	43.32	11.87	12.02	12.41	0.542	40.21	7.20
100	900	3	43.22	12.05	11.41	12.07	0.540	41.47	8.06
200	900	3	43.35	12.21	11.81	12.24	0.560	41.95	8.48

$$\text{GPU}=\text{m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\times 10^{-7}$$

heating rate and purge gas flow rate further more increased the weight loss and contracted ratio of CSCM and enlarged the MPD, porosity and N₂ flux of CSCM. The small pore size at low purge gas flow rate was probably due to the deposits of pyrolysis byproducts on the surface of the CSCM [8].

3.The effects of pyrolysis atmosphere on pore structure of the coal-based support carbon membrane

The table 2 presented the effects of pyrolysis atmosphere and purge gas on pore structure, weight loss and contracted ratio of sample size of the CSCM.

The pyrolysis of carbon membrane in different atmosphere showed a different effect on pore structure, weight loss and contracted ratio of sample size of the CSCM. The weight loss and contracted ratio of sample size pyrolyzed in He was smaller than those in N₂ or Ar

while the porosity and N₂ flux pyrolyzed in He was larger than those in N₂ or Ar. The pyrolysis in N₂ showed a smaller MPD and in CO₂ got a CSCM with the largest MPD, porosity and gas flux, and the weight loss and contracted ratio of sample size pyrolyzed in CO₂ was also the largest among them due to its oxidization. Compared to the pyrolysis in a inert gas, a CSCM with a smaller MPD, gas flux and larger weight loss was obtained in vacuum although their porosity were no difference. That could be explained by their different mechanism of the carbonization reaction. When pyrolyzed in vacuum, carbonization reaction was via a unimolecular degradation mechanism. And in an inert gas, the degradation process was enhanced, presumably due to increased gas phase heat and mass transfer. By accelerating the carbonization reaction, the inert gas molecules appeared to produce a more “open” pore in carbon membrane[8].

Table 2. The effects of pyrolysis atmosphere on pore structure of support carbon membrane

pyrolysis purge gas	weight loss (%)	contract ratio of sample size(%)			pore structure characteristic		
		Length diameter	inner diameter	outer diameter	MPD (μm)	porosity (%)	N ₂ flux (GPU)
He	40.93	11.11	11.20	11.38	0.520	40.87	7.75
N ₂	41.86	11.54	11.41	12.16	0.500	40.13	7.55
Ar	41.66	11.83	11.81	12.07	0.538	40.20	7.45
CO ₂	44.94	12.21	12.02	12.07	0.550	41.31	7.76
Vacuum	42.30	12.57	11.41	11.21	0.448	40.42	5.32

$$\text{GPU}=\text{m}^3/\text{m}^2\cdot\text{s}\cdot\text{Pa}\times 10^{-7}$$

3. The pore structure characteristics of the coal-based support carbon membrane

As mentioned above, the pore structure of the CSCM was greatly affected by the pyrolysis condition and atmosphere. The pore structure of the CSCM was formed around 450 and finished at 600 and improved further with the increase of pyrolysis temperature. The increase of heating rate and purge gas flow rate enlarged the MPD, porosity and N₂ flux of the CSCM. The different pyrolysis atmosphere also affected the pore structure of the CSCM. The pore distributions of the CSCM measured by gas-liquid displacement porometry method were shown in Fig.2 and the cross-sectional microstructure of the CSCM under an SEM was shown in Fig.3. It can be observed that the pore distribution of the CSCM was obviously improved when pyrolyzed at the high temperature, low heating rate and low purge gas flow rate. At the high temperature, the pore structure of the CSCM became dense and uniform and possess a tortuous-pore structure, in which the pores were inter-connected with tortuous paths. The pore distribution of the CSCM pyrolyzed in vacuum was more narrow than that in inert gas. The micropore distribution of the CSCM measured by gas sorption method (shown in Fig. 1) suggested that the coal-based support carbon membrane also possessed some more micropores with the pore size between 0.3-2nm besides lots of throughout pores.

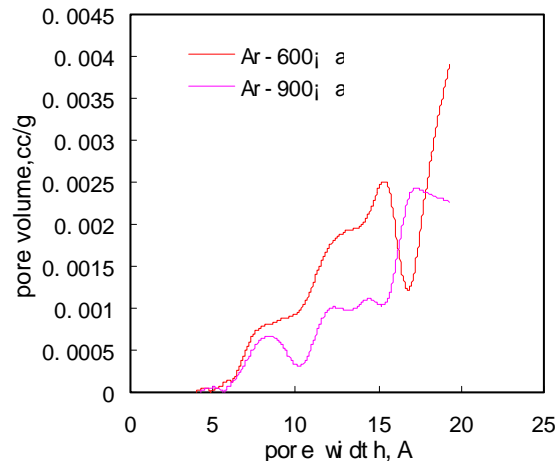
Conclusions

The coal-based support carbon membrane possessed a dense and uniform tortuous-pore structure. It not only had an abundant throughout pores, but also had some more micropores with the pore size between 0.3-2nm. It was formed around 450 and finished at 600 . Increasing the pyrolysis temperature further improved the pore structure of the CSCM. Besides, the pore structure of the CSCM was also greatly affected by the pyrolysis condition and atmosphere.

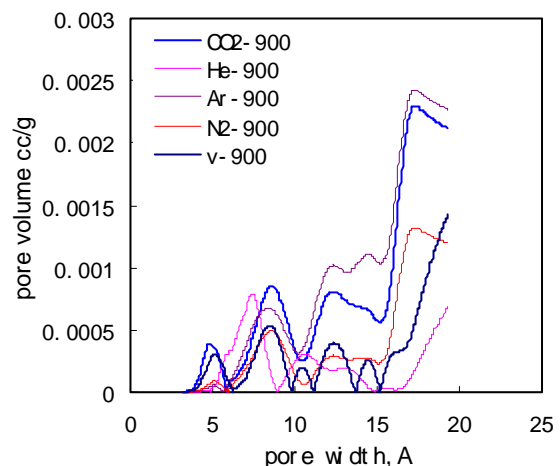
References

1. Schumacher H., Juntgen H.,US Patent: 4,261,832, 1981
2. Schindler E., Maier F., US Patent: 4,919,860, 1990
3. Bromhead J., Clint J.H., European Patent: 0 474 424 , 1991
4. Rao M.B., Sircar S., US Patent: 5,104,425, 1992
5. Wang T.H., Wei W., Cai T.X., New carbon materials, 2000, Vol.15,No1: 6-11
6. ASTM Procedure No. ASTM F316-80

7. Venkatarman K., Choate W.T. and Torre E.R., J Membr. Sci., 1988,39:259-271
8. Geiszler V.C., Koros W.J., Ind. Eng. Chem. Res., 1996, 35:2999-3003

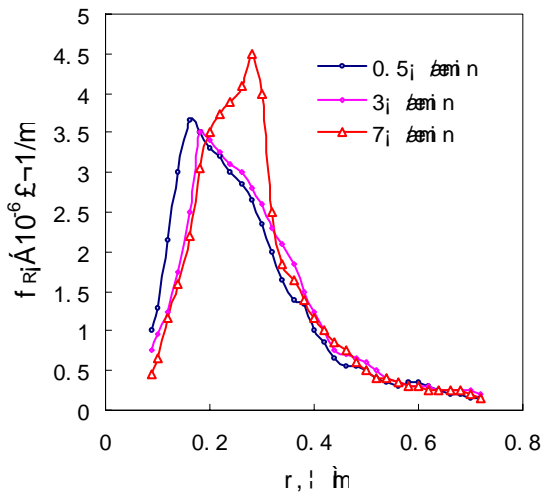


(a) an effect of temperature

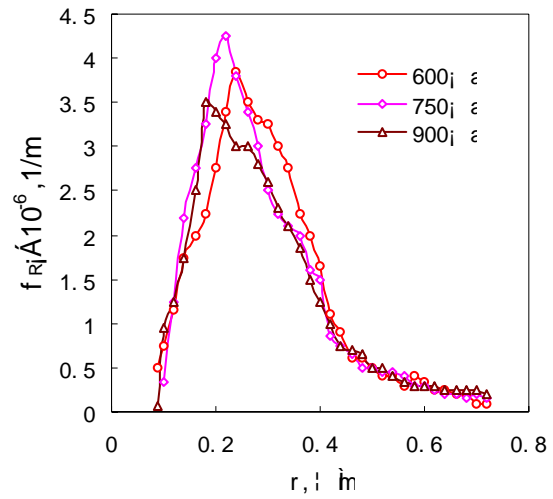


(b) an effect of pyrolysis atmosphere

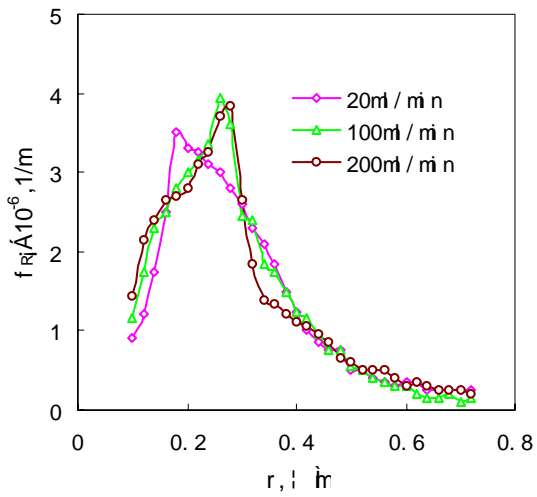
Fig.1. The pore distributions of the coal-based carbon membrane measured by gas sorption method



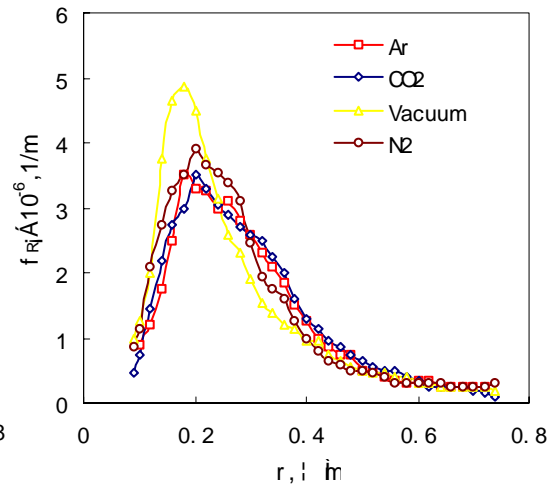
(a) an effect of heating rate



(b) an effect of temperature

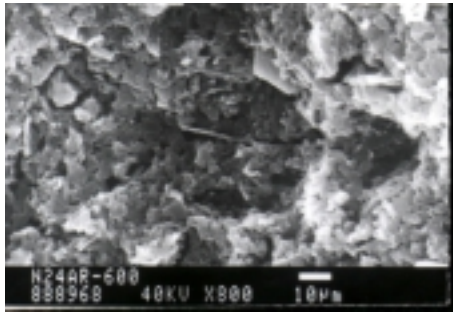


(c) an effect of purge gas flow rate

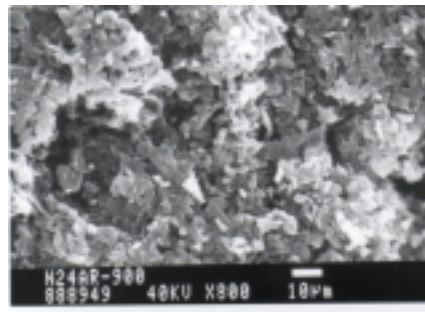


(d) an effect of pyrolysis atmosphere

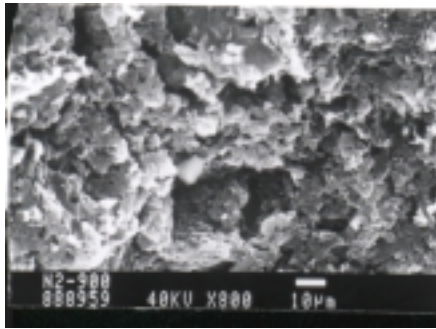
Fig.2. The pore distributions of the coal-based carbon membrane measured by gas-liquid displacement porometry method



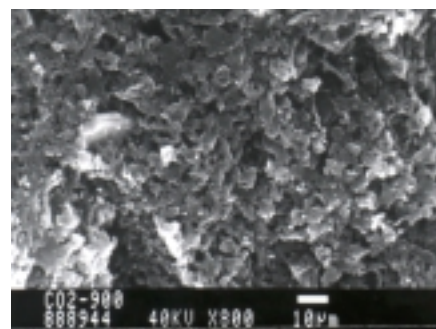
(a) pyrolysis at 600



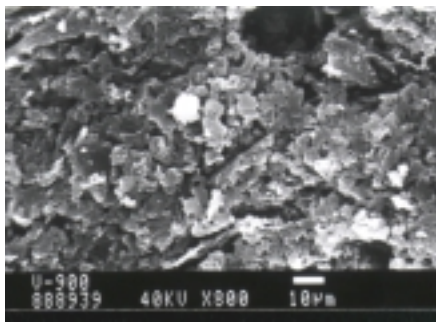
(b) pyrolysis at 900



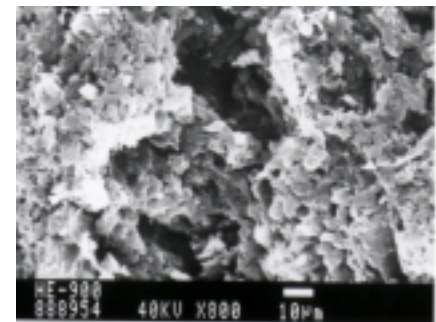
(c) pyrolysis in N₂



(d) pyrolysis inCO₂



(e) pyrolysis in vacuum



(f) pyrolysis in He

Fig.3. The SEM photograph of the coal-based support carbon membrane