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Molecular Sieve Carbon Permselective Membrane. Part I. Presentation of a New Device for Gas Mixture Separation

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Abstract

A molecular sieve carbon membrane (MSCM) that contains no pores greater than those of molecular dimensions was produced by pyrolysis of organic compounds. The MSCM, an outcome of recent studies on molecular sieve carbon adsorbents, shows gas permeabilities and selectivities that are considerably greater than any of the presently known polymer membranes. The permeates examined were He, CO_2, O_2, N_2, and SF_6. The pore dimensions of the same starting carbon membrane may be adjusted by simple thermochemical treatments to achieve optimal separation power for any gas mixture composition.

INTRODUCTION

Carbons are produced by pyrolysis of a great variety of organic residues, synthetic polymers, and natural coals in an inert atmosphere. The products obtained are highly porous. They may contain, depending on the morphology of the organic precursor and on the chemistry of pyrolysis, pores of very diversified dimensions. In order to prepare a molecular sieve permselective membrane, the precursor must be of a type that, upon pyrolysis, yields no pores larger than those of molecular dimensions.

Of special interest are certain thermosetting polymers, typically cellulosic and phenolic resins and oxidized polyacrylonitrile and pitch mesophase, which do not liquify or soften during any stage of the pyrolysis process. In such materials the porosity which is due to morphology and that which is due to the chemistry of pyrolysis are completely distinct. The porosity which is

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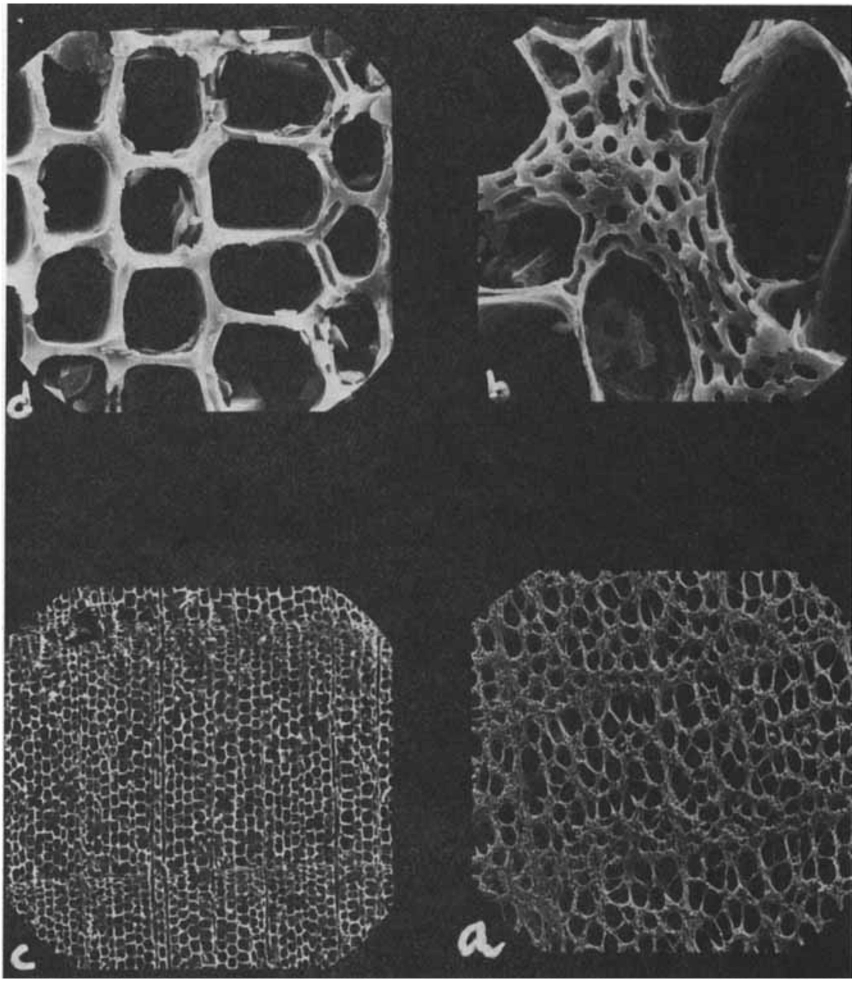

FIG. 1. SEM micrographs of wood charcoals viewed perpendicular to the fiber. a, b: Hardwood. c, d: Pinewood. Magnifications: a and c, 100×; b and d: 1000×.

due to morphology is coarse macroporosity. It is an exact, although a shrunken mimic of the structure and porosity of the solid precursor. An example is wood charcoal, the pores of which exhibit the cellular structure of the wood as shown in Fig. 1. It is therefore implied that in order to obtain a membrane free from pores larger than those of molecular dimension, one should start from an even, flawless, thermosetting polymer membrane as a precursor for pyrolysis. (The fact that many thermosetting polymers preserve their morphology upon pyrolysis is the basis of the art of producing high strength and high modulus graphite fibers utilized in composite material production.)

The second type of porosity which depends on the chemistry of pyrolysis is of molecular dimensions, and it is responsible for the molecular sieve property of carbons. It is termed ultramicroporosity (*1*) and is probably initiated by the small gaseous molecules channeling their way out of the solid matrix during pyrolysis. Ultramicroporosity is inherent to almost all carbons obtained by pyrolysis. It composes 30–70% of the apparent volume of the solid as observed from the low apparent density of carbons (1.3–1.8 g/cm^3 as compared to 2.2 for graphite). Clear evidence of the molecular sieving property of carbons was first observed by Franklin (*2*) who found that fluids were excluded from heat-treated coals in the order of their molecular size. Dacey and Thomas (*3*) published later a thorough study of the molecular sieve properties of polyvinylidene chloride charcoal. Since then the subject has constantly been investigated and reviewed (*4, 5*). The ultramicropore structure can be opened (widened) by activation (oxidative burnoff) (*4, 6*), or closed by high temperature sintering (*7*).

It has been shown previously that by careful and gradual air activation steps (*8, 9*) and recently by gradual nitric acid activation steps (*10*), it is possible to obtain from a single starting material, a series of adsorbents of extremely high adsorption stereoselectivity. According to the extent of air activation, pore dimensions can be fitted to separate any two adsorbate molecules having a critical (smallest) dimension in the range 3 to 5.2 Å with stereoselectivity greater than 100:1 if the two molecules differ by merely 0.2 Å in their critical dimension (*8, 9*). These adsorbents have been utilized to assess the dimensions of small molecules (*11*). The adsorption kinetics and molecular sieving mechanism (*12*) were also investigated in an attempt to find out how an amorphous carbon with nonhomogeneous ultramicropore dimensions can exhibit high adsorption stereoselectivity.

Knowledge of molecular sieve carbon adsorbents, together with the technique of obtaining homogeneous flawless and well-defined shapes of carbon from thermosetting precursors, stimulated us to proceed to carbon molecular sieve membranes which, as the heart of continuous gas separator processes, may lead to an advantage over the cyclic process of adsorption and desorption. Carbon membranes are supposed to withstand much higher working temperatures than polymeric membranes. They may serve, therefore, for the separation of hot gas mixtures.

EXPERIMENTAL

Permeability System

The metallic system is depicted in Fig. 2. It is suited for working with pure gases at stationary conditions. The pressures ranged from moderate vacuum (10^{-2} torr), necessary for pore development at high temperature, up to 10 atm. Gas pressures were generated by means of the pressure regulators of the gas cylinders. They could be increased further by introducing the gas into the pressurizing vessel PV while cooled to 77 K, closing valve 5, and heating the vessel PV back to room temperature.

The permeability measurement was carried out by creating a pressure difference across the membrane and monitoring its decay with time. The gas volumes V_1 and V_2 on both sides of the membrane were calibrated utilizing the pressure transducers and the calibrated volume A. Assuming that the ideal gas law is valid, the rate of transport dc/dt (in cm^3 NTP) is given by

$$\frac{dv}{dt} = \frac{V_1 V_2}{RT(V_1 + V_2)} \frac{d(\Delta p)}{dt} \tag{1}$$

where $d(\Delta p)/dt$ is the rate of decrease of the pressure difference $p_1 - p_2$ across the membrane, and V_1 and V_2 are gas volumes on both sides of the membrane. Utilizing the permeability equation,

$$P = \frac{dv}{dt} \frac{l}{A \Delta p} \tag{2}$$

where A is the surface area and l is the thickness of the membrane, one obtains:

$$P = \frac{V_1 V_2}{RT(V_1 + V_2)} \frac{l}{A \Delta p} \frac{d(\Delta p)}{dt} \tag{3}$$

from which the permeability may be determined experimentally. The procedure of a permeability experiment was as follows: A certain gas pressure p was introduced through Valve 4 to both sides of the membrane.

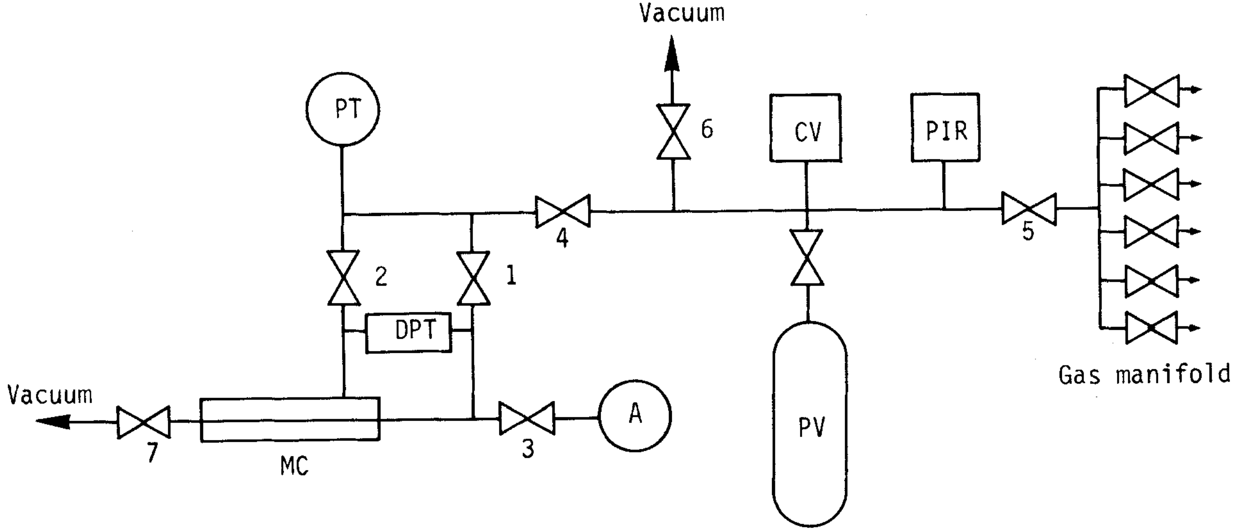

FIG. 2. The permeability measurement system: PIR, Piranni gauge; CV, check valve; PV, pressurizing vessel; PT, absolute pressure transducer; DPT. differential pressure transducer; A, calibrated volume; MC, membrane cell.

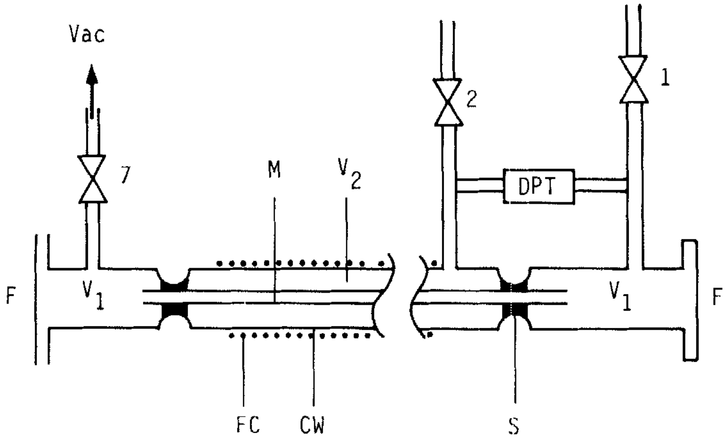

FIG. 3. The membrane cell: CW, cell walls; M, the tubular membrane; S, seal; FC, furnace coal; F, flange; V_1. V_2, gas volumes on both sides of the membrane (Eq. 1).

Valve 2 was then shut off and the pressure at V_1 was decreased back through Valves 4 and 6 to the desired value. Valve 1 was then shut off and the rate dp/dt was recorded by means of the differential pressure transducer (DPT). The rate of transport was obtained by means of Eq. (1).

The Membrane Cell

The membrane cell was of tubular construction. It was assembled into the cell as shown in Fig. 3. The heating element around the quarz tubing enabled heat treatment of the membrane in the presence of inert or oxidizing gas in order to modify its ultramicropore dimensions (*8*). The carbon membrane was of hollow fiber configuration, produced by pyrolysis of polymer hollow fibers. The dimension of the membrane was estimated with the aid of the SEM micrograph shown in Fig. 4. These were wall thickness $l = 6 \pm 1$ μm, inner diameter $d = 140$ μm, and the length $L = 5$ cm. Since $l \ll d$, the membrane may be considered planar so that Eq (3) becomes valid for $A = \pi dl$.

The gases studied so far are helium, oxygen, nitrogen, sulfur hexafluoride, and, to a lesser extent, carbon dioxide.

RESULTS AND DISCUSSION

According to the highest temperature of pyrolysis, two types of MSC membranes were prepared. The first type was pyrolyzed to 950°C and the

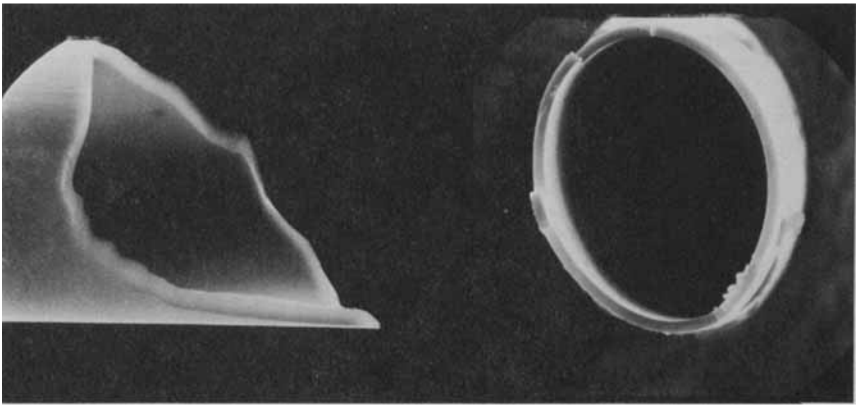

FIG. 4. SEM micrographs of the hollow fiber carbon studied. 1 cm = 36 μm.

second to 800°C. The highest temperature achieved determines the extent of sintering, i.e., of pore closure (*7, 8*). By means of this approach, membranes of various initial permeabilities and selectivities can be obtained. The pores of these membranes may be widened by gradual burn-off in oxidizing gas in order to achieve more varieties of permeabilities and selectivities. In the following, some of the varieties that were obtained from the same precursor are displayed.

The 950°C Membrane. This membrane was initially impervious at room temperature to all gases studied. We may therefore conclude that the carbon matrix is impervious and, at least in the case of the 950°C membrane, gas permeation proceeds only through the pore system which, if closed by constrictions (*8*), has to be opened by activation.

Two modes of high temperature gas activation were applied to the 950°C membrane. One is stationary; the other dynamic. Equal gas pressures were maintained in the stationary mode, on both sides of the membrane, resulting in relatively slow and quite homogeneous pore openings throughout. An initial pressure difference of the activating gas was applied in the dynamic mode. This enabled monitoring the increase of the permeation rate of the gas during activation. It is faster than the first mode but may be catastrophic since, due to the pressure gradient, the oxidant is forced through the pore system. The dynamic mode is obviously unique to the membrane configuration and has not been tried by us to previous studies of MSC. All activation

TABLE 1
Permeabilities and Selectivities[a] of the 950°C Pyrolyzed Membrane

Experiment no.	Gas	Permeability ($cm^3 \cdot cm^{-2} \cdot cm \cdot S^{-1} cmHg^{-1}$) $\times 10^8$	Selectivity	Activation mode
1	He, O_2, N_2, SF_6	<0.3		No activation
2	He	6–12	>20	Stationary activation first step
3–5	O_2, N_2, SF_6	<0.3		
6	He	9.1	0.8	Dynamic activation first step
7	O_2	11.4	8.0	
8	N_2	1.4		
9	SF_6	<0.3		
10	SF_6	115	$0.19 \approx \sqrt{\frac{M_1}{M_2}}$	Dynamic activation second step
11	He	650	$2.8 \approx \sqrt{\frac{M_1}{M_2}}$	
12	O_2	228	$0.92 \approx \sqrt{\frac{M_1}{M_2}}$	
13	N_2	248		

[a] The selectivity is the permeability ratio of the gases shown above and below the given value.

modes may be applied to various extents by changing the temperature and duration of the treatment.

The permeability and selectivity results of the 950°C membrane are summarized in Table 1. After a single activation step by the stationary mode (Experiments 2–5), a significant increase in the He permeability was observed and the helium selectivity in comparison to the other gases studied became apparent. A subsequent activation step by the dynamic mode (Experiments 6–9) opened the pore structure toward oxygen and nitrogen, with a permselectivity of 8. This is a very significant value for this couple of gases as compared with the results achieved by others (*13–15*) with polymer membranes. It is worth mentioning that opening the pores in order to achieve an MS effect between N_2 and O_2 destroys this effect for the former (narrower pore) range. This behavior was met previously at the adsorption system (*8*, *9*). The fact that O_2 is only slightly more permeable than He is meaningful

TABLE 2
Permeability and Selectivity of the 800°C Pyrolyzed Membrane

Experiment no.	Gas	Permeability $(cm^3 \cdot cm^{-2} \cdot cm \cdot S^{-1} cmHg^{-1}) \times 10^8$	Selectivity	Activation mode
1	He	10.8	4.0	Non-activated
2	CO_2	2.7	>9	
3	O_2, N_2, SF_6	<0.3		
4	O_2	2.3	>8	Stationary first step
5	N_2	<0.3		
6	He	52	3.0	Stationary second step
7	O_2	17.1	7.1	
8	N_2	2.4	>24	
9	SF_6	<0.1		
10	He	44	1.1	Degassing at 600°C
11	N_2	39	2.3	
12	O_2	91		

and will be discussed later. A further activation step by the dynamic mode increased the permeabilities of He through SF_6 by a few orders of magnitudes and caused a breakdown of the molecular sieve permselectivity. This is evidenced by selectivity values which correspond to the square roots of the molecular weights (Experiments 10–13) according to the Knudsen diffusion or the viscous flow conditions. In both cases the pore dimension should be much greater than that of the diffusing molecule.

It seems, therefore, that by simple thermochemical modifications, different products, starting from low permeability and high selectivity toward any couple of gaseous molecules up to very high permeability and lower selectivity, approach the limiting $\sqrt{M_1/M_2}$ values.

The 800°C Membrane. Unlike the 950°C membrane, the pore system of this membrane, which was sintered to a lower temperature, is a priori open to allow the passage of helium. Carbon dioxide has also passed through as shown in Table 2. The sequence $CO_2 > O_2 > N_2 > SF_6$ that can be obtained from the results presented so far corresponds with the adsorbability sequence that has been obtained previously (*8, 11*). Slight activation steps gradually open the pore system (Table 2, Experiments 4–9), as has been shown for the 950°C membrane. We tried a third mode of activation with this membrane which includes degassing of surface CO groups at high temperature. It is a mild mode which has been successfully applied in previous work (*8*). By degassing the 800°C membrane at 600°C after the two oxidative steps applied formerly (Table 2, Experiments 6–8), we achieved an intermediate pore opening which introduced the permeability values into the range(40–100) $\times 10^8$ $cm^3 \cdot cm^{-2} \cdot cm \cdot S^{-1} CmHg^{-1}$. The resulting decrease in selectivity has been reported above and is due to the breakdown of the MS effect. However, the inversion of He to O_2 selectivity is surprising. Recognizing that permeability depends on both the mobility and the concentration of the gaseous molecules within the membrane pores, we may speculate, at this stage of the study, that the O_2 concentration is greater than that of He due to some physisorption of the former at room temperature, but its mobility is very low as compared to that of He when the pore dimensions are very narrow. Upon activation (pore enlargement), the mobility of this adsorbed layer is increased and provides a greater contribution to O_2 permeation which supersedes that of He (Table 2, Experiments 6, 7, 10, 12). However, excessive activation (Table 1, Experiments 10–13) enabled massive gas phase transport by the Knudsen mechanism which obeys the mass root law.

Comparison with Polymer Membranes

Permeation through polymer membranes proceeds mainly by the dissolution-diffusion mechanism (*16*). Permeation through the carbon membrane proceeds exclusively through the pore system. This has been proven by the fact that the 950°C carbon membrane is impervious at room temperature to all gases studied unless its porosity is developed by activation. It should, therefore, be expected that carbon membranes would behave quite differently. In Table 3 we compare some permeabilities and selectivities of currently studied polymer membranes with our carbon membranes. Since these two magnitudes are inversely related, their product, namely the separation power, is a more adequate criterion for the quality of the permselective membrane and is also given in Table 3. The most remarkable feature that comes out is the much higher separation power exhibited by the variously activated carbon membranes studied in this work. Also, the high O_2–N_2 selectivity is noteworthy.

CONCLUSION

Combining the high separation power with higher working temperature that may be allowed by carbon membranes and with the ability to optimize

TABLE 3
Permeability, Selectivity, and Separation Power of Various Polymer Membranes and of the MSC Membrane

Membrane	Gas	Permeability ($cm^3 \cdot cm^{-2} \cdot cm \cdot S^{-1} cmHg^{-1}$) $\times 10^8$	Selectivity	Separation power	Ref.
Cellulose acetate	He	0.136	97	13.2	17
	N_2	0.0014			
Polysulfone	H_2	0.12	40	4.8	18
	CO	0.003			
Silicon rubber	H_2	5.2	2.08	10.8	18
	CO	2.5			
	He	2.3	1.5	3.5	19
	N_2	1.5			
	O_2	3.96	2.15	8.3	14
	N_2	1.84			
Du Pont, unspecified material	H_2	2.7–1.2	130–157	350–369	20
	N_2	0.02			
MSC membrane	O_2	17.1	7.1	124	
	N_2	2.4			
	He	52	22	1140	
	N_2	2.4			
	He	52	3.04	160	
	O_2	17.1			
	He	6	>20	>120	
	O_2	<0.3			
	N_2	2.4	>24	>58	
	SF_6	<0.1			

the permselectivity of the same precursor for the separation of any given mixture, one may conclude that a unique membrane material is at hand. The group of gases examined is far from being comprehensive. The separation power for several gas mixtures that are of practical interest is awaiting exploration. Deep mechanistic studies must be performed.

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