

Capillary carbon molecular sieve membranes derived from Kapton for high temperature gas separation

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Abstract

The degradation of Kapton polyimide leads to a carbon membrane with a dense surface layer suitable for gas permeations. An integral asymmetric capillary carbon membrane was prepared by coagulation of a polyamic acid solution which was imidized to a Kapton capillary and finally pyrolyzed to a capillary carbon membrane. Various preparation conditions have been studied. Single and mixed gas permeation experiments had been performed. The carbon membrane showed high permselectivities of 2000 for He/N₂ and about 1000 for H₂/N₂ at 0°C, respectively. Even for a high temperature of about 250°C the He/N₂ selectivity reached 170.

Keywords: Carbon; Kapton; Molecular sieve; Gas separations

1. Introduction

The intensive exploitation of natural energy resources needs a separation of energy rich compounds at a gaseous stage. Power plants combined with coal gasification processes need a hydrogen separation step at about 300–500°C [1]. In those hot environments, only a membrane driven separation process could isolate the H₂ from other carbon compounds. However, organic polymer membranes cannot resist very high temperatures and begin to decompose or react with certain components. Inorganic carbon membranes are chemically inert and thermally stable up to more than 500°C [2], except for oxygen attack over 200°C.

Because of a graphite like structure with micropores, carbon membranes show a molecular sieving effect for the mixtures of small and large gas molecules [3,4]. Selectivities for H₂/CH₄ of about 550 were reported [5] for carbon membranes pyrolyzed from polyimide at the temperature of 550°C. At higher pyrolyzation temperatures the H₂ selectivity to other gases increases with increasing density of the carbon material and the formation of a turbostratic structure [6], which means the occurrence of graphite domains in amorphous carbon. The high selectivity of more than 1000 for H₂/N₂ observed in Kapton derived carbon membranes confirms a molecular sieving effect [7].

For commercial applications of membranes it is preferable to be fabricated in an asymmetric structure and capillary or hollow fiber configurations in order to increase permeation products. Several investigations

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have been carried out to prepare asymmetric flat sheet [8] and hollow fiber [5] carbon membranes. We have also reported a simple and novel fabrication method of capillary carbon membranes derived from Kapton [7]. The objectives of this work are to improve the fabrication method of capillary carbon membranes and to make their possibility clear for a use of high-temperature gas separations.

2. Experimental

2.1. Permeation measurements for single gases and gas mixtures

For a feed pressure up to 6 bar the gas permeation rate was detected by a pressure increase in a closed permeate-side volume. The permeation apparatus shown in Fig. 1 allowed the detection of permeation through a membrane as well as compositions of the feed and the permeate by a gas chromatography in a single run. The pressure detection was done with a thermostated Baratron sensor. The performance of any membrane is described by the permeance P_v defined

by a standard volume V_s of a gaseous permeant which passed through a membrane area A at a partial pressure difference of Δp during a time t : $P_v = V_s / (A \cdot t \cdot \Delta p)$. The permeance was expressed here in an unit of $[\text{cm}^3 (\text{STP}) / (\text{cm}^2 \text{ s cmHg})]$. The membrane test cell was equipped with a heat exchanger and was placed in a ventilated oven with a temperature range from 0 to 250°C.

Components of mixed gases were analyzed by a gas chromatography GL-Science GC 380 equipped with a System Instruments Chromatocorder 21. A portion of the collected permeate with a pressure between 3 and 7 Torr in the permeate-side volume was transferred into a sample loop and withdrawn by a carrier gas to the gas chromatography. Pressure ratios of the feed-permeate were kept around 200. Flow rates of the feed gas were maintained more than 500 times larger than those of the permeate.

2.2. Membrane preparation

Since Kapton polyimide is nearly insoluble in any solvent, the membrane formation must start by its

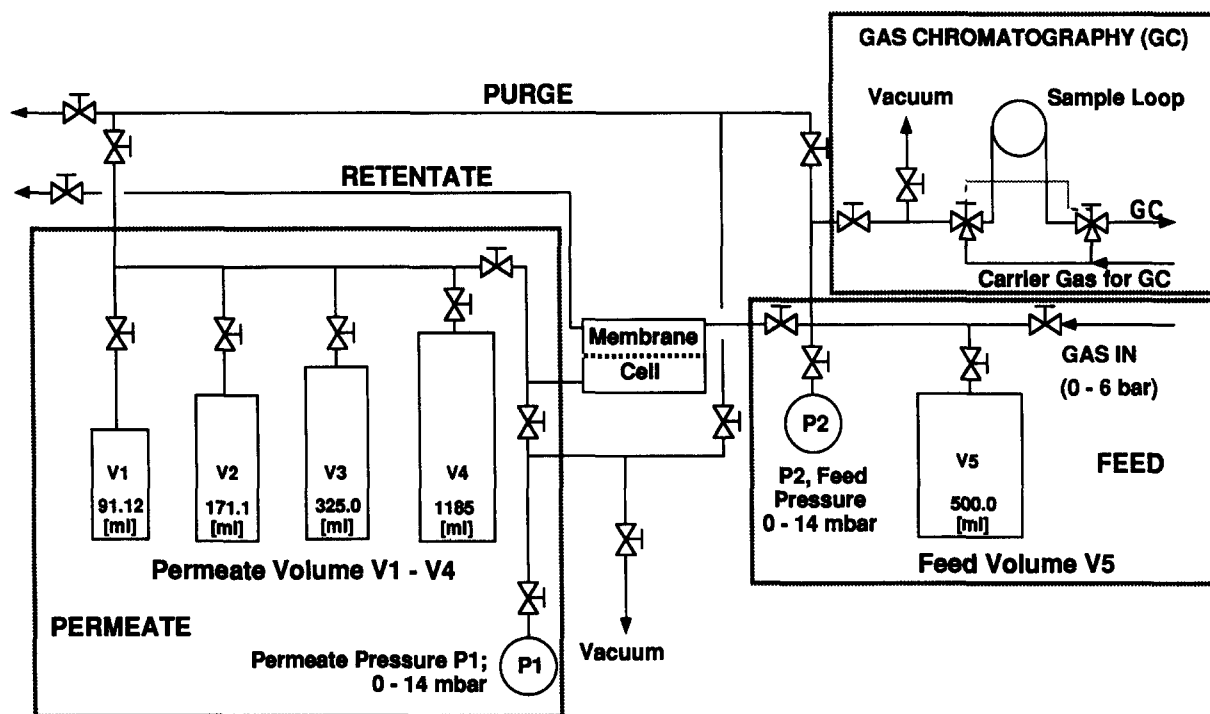


Fig. 1. Single gas and mixture gas permeability measurement device.

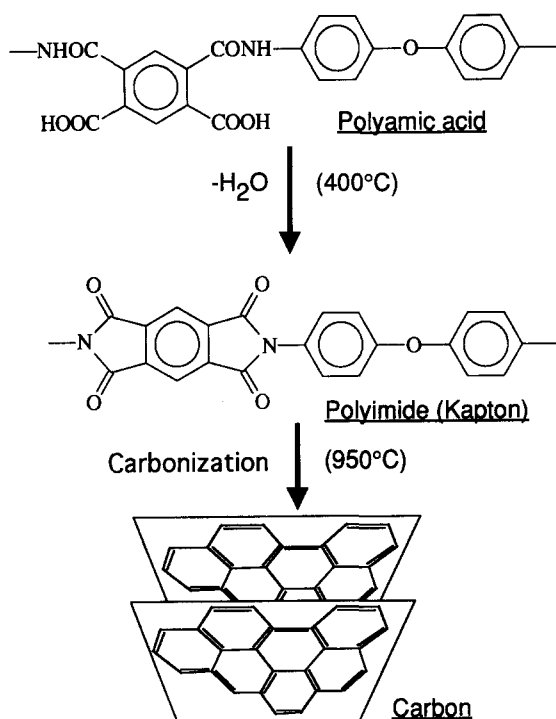


Fig. 2. Synthesis of a Kapton derived carbon membrane.

precursor, the polyamic acid. The synthesis is described in Fig. 2. A solution of 16% polyamic acid in dimethylacetamide (DMAc) from TORAY Inc. was used without further purification. For changing the precipitation properties non-solvents were added to the DMAc/polymer solution pre-concentrated. A removal of solvent (DMAc) had to be done quickly by evaporation under high vacuum at a maximum temperature of 60°C to avoid imidization. A solution of the polyamic acid was cast on a PTFE Tube (Fig. 3 [7]) with a diameter of 1.8 mm which passed through a hole of the casting gate with a speed of 3 cm/s. The hole diameter was 2.8 mm so that a circled casting gap around the PTFE tube was 0.5 mm large. After precipitation in thermostated water at 3°C the cast membrane was washed with water over night. In case of a dual bath method the membrane was firstly coagulated in alcohol for a certain time and then treated with water. After removing the capillary polyamic acid membrane from the PTFE tube it was dried over night and later imidized to Kapton at 400°C. After imidization the capillary Kapton membrane was carbonized at

950°C. The chart in Fig. 4 shows temperature profiles for the imidization and pyrolysis.

The carbonized membrane was further treated by coating of a thin layer of polydimethylsiloxane (PDMS) to prevent gas flow through defect structures [9]. The membrane was immersed in a 2% solution of PDMS (WACKER E41) in heptane, and then withdrawn to harden coated layer. A two component epoxy glue was used for adhesion of the membrane and a metal tube sealed with the membrane test cell by Viton O-rings. This construction limited the maximum temperature to 250°C.

3. Results and discussion

3.1. Weight loss during pyrolysis

A preliminary pyrolysis experiment was done by using a thermogravimetric analysis apparatus MAC TG-DTA 2000S. The pyrolysis started at 550°C where a degradation of Kapton to carbon began to occur (Fig. 5). The decompose sharply improved up to 600°C, over which the rate of weight loss became slow. The main portion of the total weight loss of 42% already accomplished up to 600°C. The curve of weight loss observed was quite similar to that of Kapton film [10]. It was already found [6] that the pyrolysis at high temperatures causes a higher crystallinity, density and a smaller interplanar spacing of graphite layers of the carbon which lead to high gas permselectivities of a flat sheet carbon membrane. Therefore, best preparation conditions were expected to exist in high temperatures and long duration for the pyrolysis, in which high permselective membranes were actually obtained. Low heating rates also should assist the increase of crystallinity of carbon. The heating rate was finally set to 5°C/min and the heating duration was set to 120 min at 950°C.

3.2. Membrane structure

The macroscopic structure of the membranes was observed using scanning electron microscopy (SEM). The SEM pictures were taken by a Hitachi S-2400. The pictures in Fig. 6 shows cross sections of membranes obtained under different preparation conditions. The growth of macro-voids depends on an

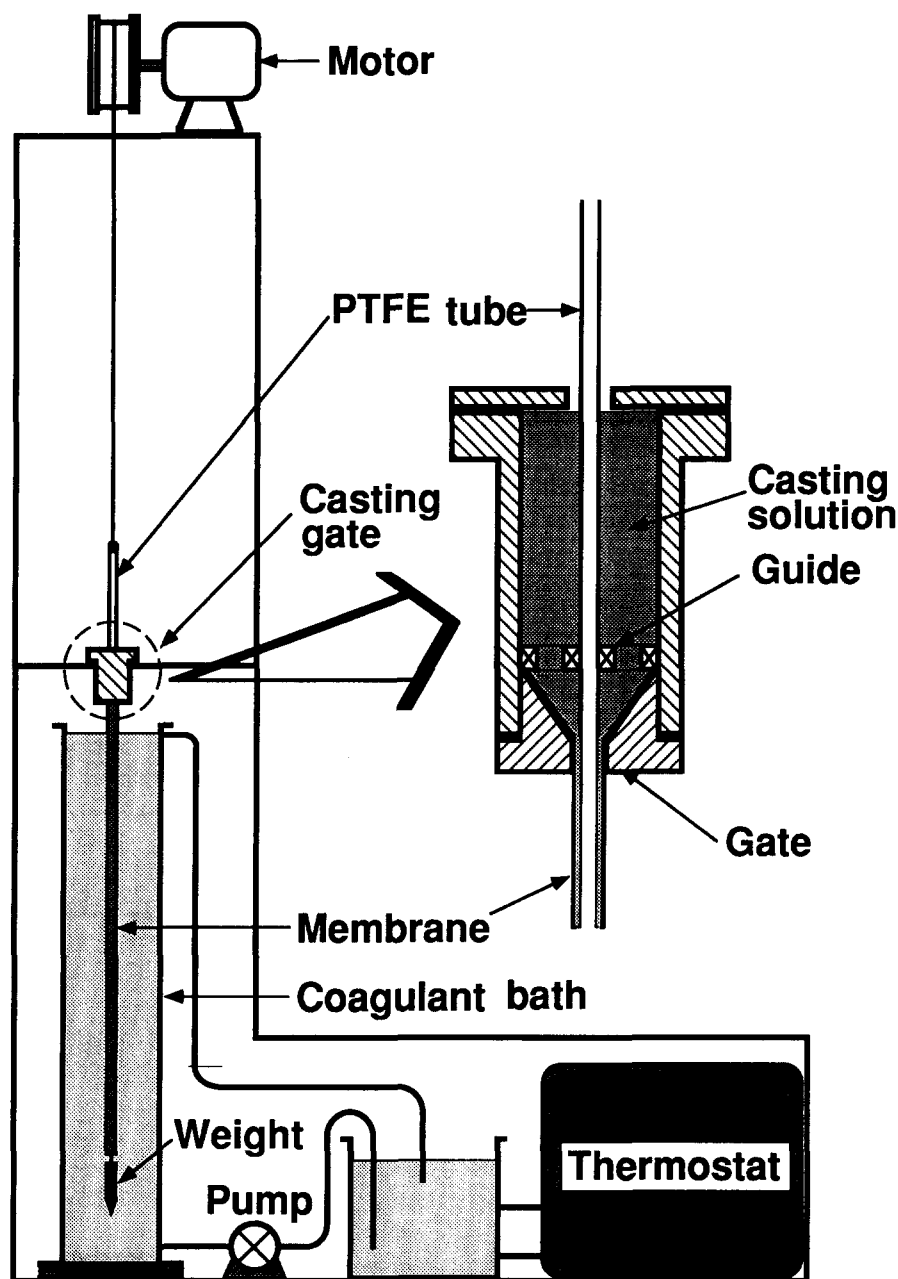


Fig. 3. Casting apparatus for membrane preparation.

exchange rate of a solvent with a coagulant. In the coagulation process two kinds of demixing, i.e., instantaneous and delayed demixing are reported [11]. The instantaneous demixing, which means immediate diffusion of the solvent into the coagulant and the coagulant into the polymer solution, leads to

forming macro-voids. The delayed demixing, in which the solvent slowly diffuses from the polymer solution into the coagulant bath while no coagulant diffuses into the polymer solution at first, causes a sponge like structure. This delay can be achieved not only in a case of highly concentrated polymer solutions, but also the

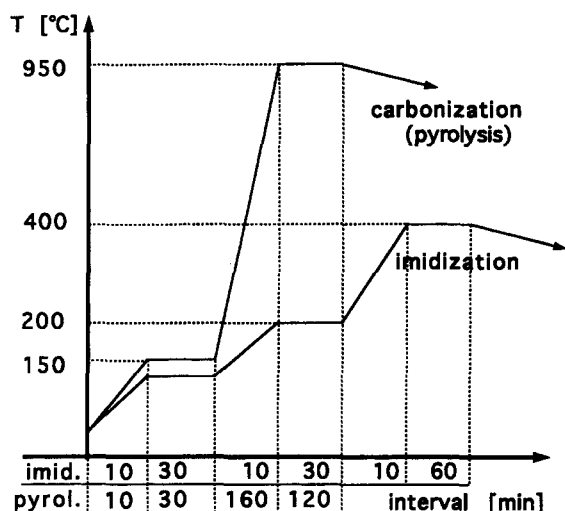


Fig. 4. Heating profile of imidization to Kapton and pyrolysis to carbon.

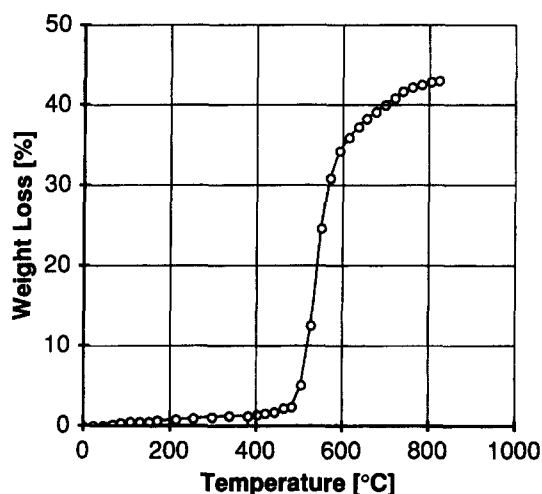


Fig. 5. Thermogravimetry of the carbonization from Kapton to carbon.

polymer solution contained weak or non-solvent like glycerol.

The usage of solutions up to 19% of the polyamic acid in simple DMAc produced open structures, with macro-voids very close to the surface layer and often membrane defect (Fig. 6(a)). High concentrated solutions up to 25% produced less macro-voids and a more sponge like structure (Fig. 6(b)), but a less permeable

top layer of about 2 μm thickness. Using a dual bath method, where membranes were firstly coagulated in ethanol and secondly coagulated in water, a very dense and thick top layer of about 2 μm was obtained (Fig. 6(c)) caused by the slow solvent exchange of DMAc with ethanol. The porous substructure was very open. Best results were obtained using the solution replaced 30% of DMAc solvent with glycerol and water as a coagulant. The membrane consisted of a thin top layer with a thickness of about 0.5 μm and a homogeneous substrate with a regular sponge like structure (Fig. 6(d)). An effective thickness of this membrane was estimated less than 0.3–0.5 μm by the calculation from permeability data measured on a carbonized membrane of commercially available Kapton film.

3.3. Single gas permeation

The temperature dependence of the gas permeance through an uncoated carbon membrane is shown in Fig. 7. The permeance of H_2 increased from $9.5 \text{ e-}7 \text{ cm}^3 \text{ (STP)/(cm}^2\text{s cmHg)}$ at 0°C to $5.3 \text{ e-}5$ at 250°C . The permeance of N_2 increased from $9.4 \text{ e-}10$ to $3.5 \text{ e-}7$. Unexpectedly, the selectivity for H_2/N_2 increased from 10 at 0°C to about 194 at 200°C in the same way as the He/N_2 selectivity increased from 12.7 to 270.6. At higher temperature of 250°C , the selectivities decreased to 151.4 for H_2/N_2 and to 174.3 for He/N_2 , respectively. The pure carbon membrane exhibited high permselectivities for small and large gas molecule pairs in the range of high temperature. The selectivity for He/H_2 was almost about 1.2.

Permeation measurements shown in Fig. 7 started from the temperature of 250°C and shifted to lower temperatures, and again shifted to higher temperature finally up to 200°C . Additional experiments were performed to ensure the stability of carbon membranes in the range of temperature around 250°C . The membrane was exposed in a hot gas mixture (except O_2) of 250°C under the pressure difference of 30 bar for one day. The followed permeation measurements confirmed the permeance data to be almost reproducible. The permeations of oxygen at higher than 200°C caused slight damage to the membrane with a small increase of the gas permeance.

The previous studies [6] showed, however, that the gas permeability of the carbon dense films derived



Fig. 6. Morphology of asymmetric Kapton membranes obtained under different kinds of preparation conditions: (a) 15–19% polymer in DMAc, coagulated in water, defect top layer, (b) 19–25% polymer in DMAc, coagulated in water, thick top layer: 2 mm, (c) 16% polymer in DMAc, 1. coagulation in ethanol, 2. coagulation in water, thick top layer: ~2 mm, (d) 15% polymer+30% glycerol in DMAc, coagulated in water, thin top layer: ~0.5 mm.

(c)



(d)

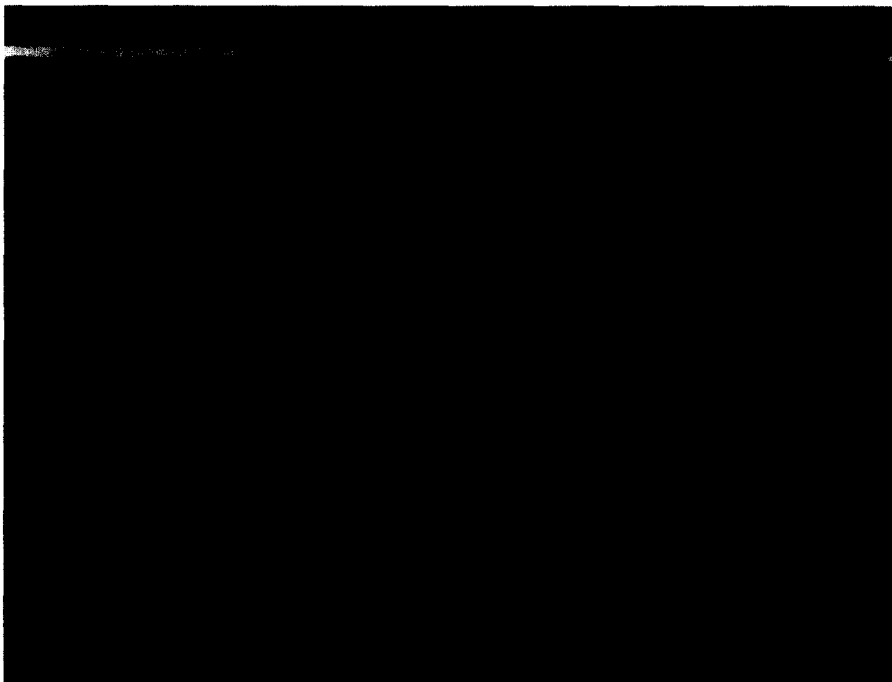


Fig. 6. (Continued)

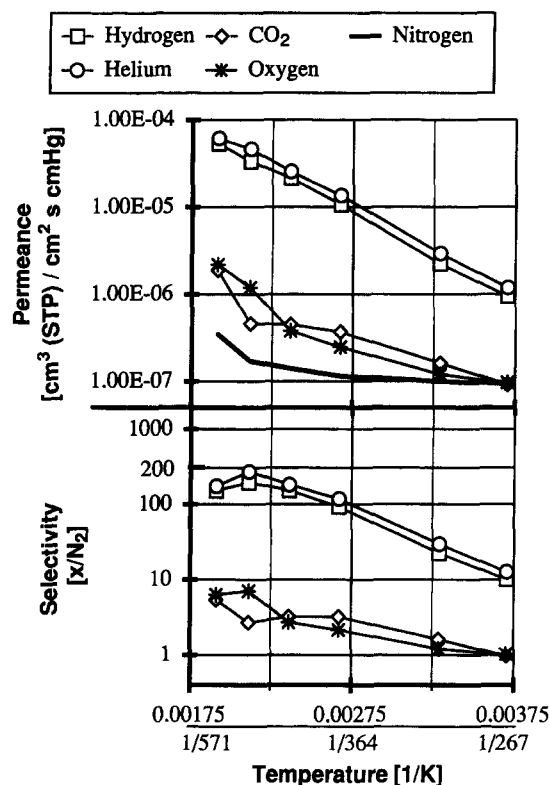


Fig. 7. Single gas selectivity and permeance versus temperature for a pure carbon membrane prepared from a polyamic acid/glycerol/DMAc mixture.

from commercial Kapton changed with an apparent activation energies of positive, with increase in selectivities of a smaller gas molecule over larger ones accompanied with decreasing temperatures. From these results we assumed that the unexpected dependency between permeances and temperatures in Fig. 7 was brought about by two competing transport mechanisms which was an activated diffusion with a negative slope (positive activation energies) through micropores and surface diffusion or Knudsen diffusion with a positive slope through defect macropores.

To ensure the assumption the pure carbon membrane described above was coated with a thin layer of PDMS for excluding gas permeation through possible porous defect structures [9]. The temperature dependency shows that after the coating of PDMS the H_2/N_2 selectivity increased dramatically in lower temperatures as can be seen in Fig. 8. The slight increase of He

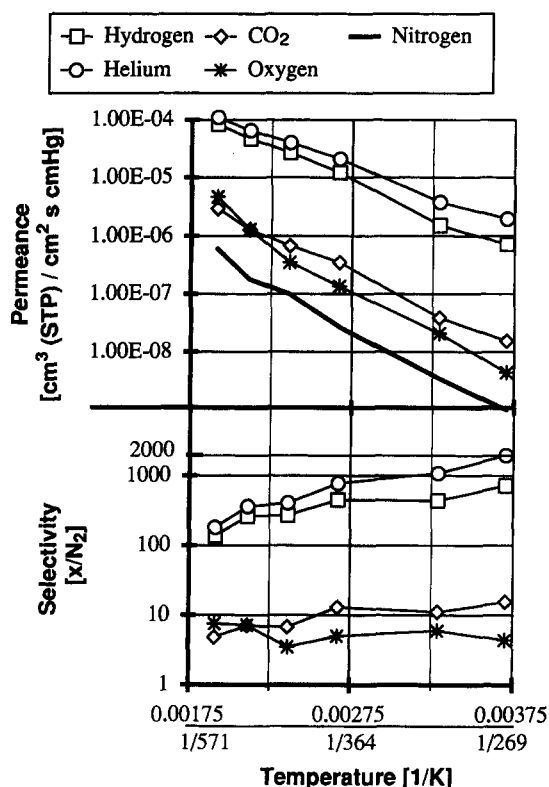


Fig. 8. Single gas selectivity and permeance versus temperature for a silicone rubber coated carbon membrane prepared from a polyamic acid/glycerol/DMAc mixture.

and H_2 permeances for this membrane may come from the previous permeations of O_2 at high temperatures above 200°C . Fig. 8 shows that permeances of H_2 increased from $7.2 \times 10^{-7} \text{ cm}^3 (\text{STP})/(\text{cm}^2 \text{ s cmHg})$ at 0°C to 8.3×10^{-5} at 250°C . The permeance of N_2 increased from 1×10^{-9} to 6×10^{-7} . The selectivity decreased from 720 to 136.4 for H_2/N_2 and from 1960 to 180.3 for He/N_2 .

3.4. Mixed gas permeation

For coal gasification gases separations of H_2/CO and H_2/CO_2 are important. Fig. 9 shows the results of separations for these mixtures with a PDMS coated capillary carbon membrane, which was different from the one used for permeations of single gases. In the measured temperature range of 0 to 150°C , with increasing temperature H_2 permeances increased while CO_2 and CO permeances firstly decreased

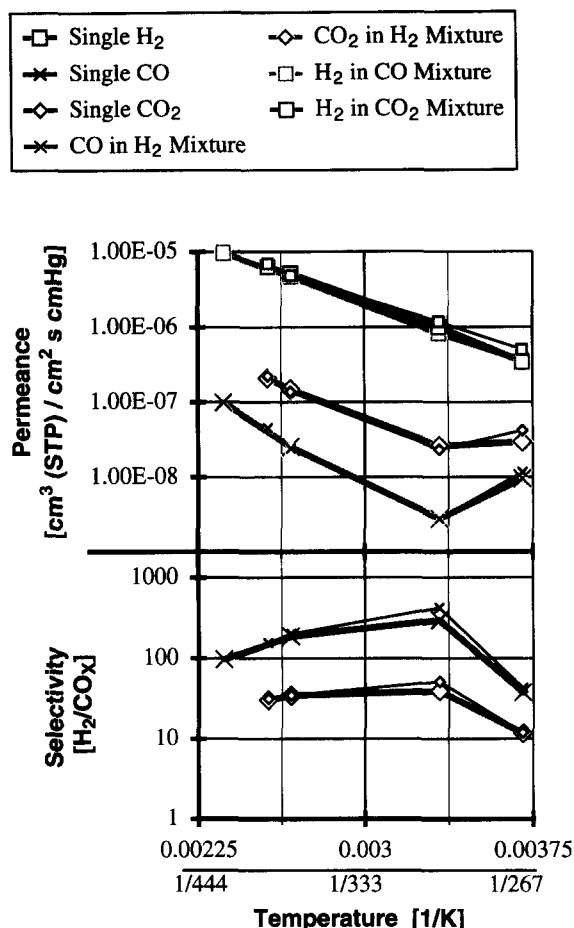


Fig. 9. Mixture gas and single gas selectivity and permeance of a CO/H₂ (20:1) and a CO₂/H₂ (10:1) system versus temperature for a silicone rubber coated carbon membrane prepared from a polyamic acid/glycerol/DMAc mixture.

and then increased. As a result selectivities for H₂/CO and H₂/CO₂ increased up to around room temperature and then decreased gradually. At low temperature surface diffusions became so apparent that the permeances of CO₂ and CO increased. Measured gas permeances were considerably smaller than those in Fig. 8. A reason may be brought about by imperfect reproducibility of membrane preparations. Membranes having low gas permeances at low temperatures may be more influenced by surface diffusion through macropores inside.

The selectivity of H₂/CO reached a maximum of 421.4 for single gas permeations and 327.3 for mixed

gas permeations at 30°C, respectively. At the same temperature the H₂/CO₂ system had its maximum selectivity of 51.1 for single gas and 39.1 for the mixed gas permeations. At higher temperature the permeances of all gases increased linearly with increasing temperature in the Arrhenius plot. For gas mixtures as well as single gases the gaseous compounds showed similar permeances, so that, the separation of mixed gases by the carbon membrane can roughly be estimated using data of single gas permeances.

However, compared to the single gas measurement, there is a small decline of permeance for H₂ and a small incline of permeance for CO and CO₂ in the mixed gas measurement. In the gas mixture the large excess (CO : H₂=20 : 1; CO₂ : H₂=10 : 1) of the bigger and stronger sorptive molecules with the lower permeability did not affect strongly the faster permeance of H₂ even at low temperature. In opposite to other molecular sieve membranes like zeolite membranes [12] the permselectivity of carbon membranes for a mixed gas consisting of light and heavy components did not show a large decrease caused by sorption effects of the heavy component [2]. One of the reasons considerably attributes to slit shape pores in carbons through which gas molecules can by-pass the sorbed molecules.

4. Conclusion

It was found that carbon capillary membranes derived from Kapton can be obtained with a desirable structure of a thin dense top layer and a fine sponge like substrate by adding the non-solvent glycerol to the casting solution. High gas permselectivities even at high temperatures were realized. Each component in gas mixtures showed nearly identical permeation behavior with that of the single gas. The permselectivity of the mixed gas consisting of light and heavy components did not show the decrease caused by sorption effects of the heavy components. Therefore, the permselectivity of those carbon membranes can roughly be estimated by data of single gas experiments. For future application of carbon membranes the existing problem of a gas tied sealing and fixing of the membranes in a high temperature applicable module (>500°C) must be solved.

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