

Review

# A review on the latest development of carbon membranes for gas separation

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## Abstract

Inorganic membranes have been developed before 1945. The earlier application of inorganic membranes was primarily concentrate on military purpose. Carbon membrane is one type of porous inorganic membrane. Although the concept of carbon membrane for gas separation has been found in the early 1970, the interest to develop carbon membrane only increased, since Koresh and Soffer successfully prepared apparently crack-free molecular sieving hollow fiber carbon membranes. Nowadays, plenty of researchers have used different polymeric materials; including polyimides, to prepare carbon membranes by using pyrolysis. In general, carbon membranes can be divided into four major configurations: flat sheet, membrane supported on tube, capillary, and hollow fiber. Permeation properties of carbon membranes have been improved greatly in these 20 years. Carbon membranes offer advantages over polymeric membranes especially in terms of selectivity as well as thermal and chemical stability. More attention will be paid to carbon membranes in this century. This paper will review the development of carbon membranes in the last 30 years and give a clear future direction in research for carbon membrane. © 2001 Elsevier Science B.V. All rights reserved.

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## 1. Introduction

The development of porous inorganic membranes dates from before 1945, long before the development of today's synthetic organic membranes. Not much publicity was given to the early development of inorganic membranes because the first porous inorganic membranes were developed for separation of uranium isotopes, therefore, they were mainly used for military purposes or nuclear applications [1].

Non-nuclear applications of inorganic membranes started at the beginning of the 1980s with Membralox produced by Ceraver (now SCT), Carbosep produced by SFEC (now TECHSEP) and Ceraflo produced by Norton (now by SCT) [2]. The potential of inorganic membranes was not widely recognized until high quality porous ceramic membranes were produced for industrial usage on a large scale [3]. Nowadays, inorganic membranes are used primarily for civilian energy-related applications. They have become important tools for beverage production, water purification and the separation of dairy products [1]. In addition, they play a significant role in the gas separation processes of industrial sector. Numerous

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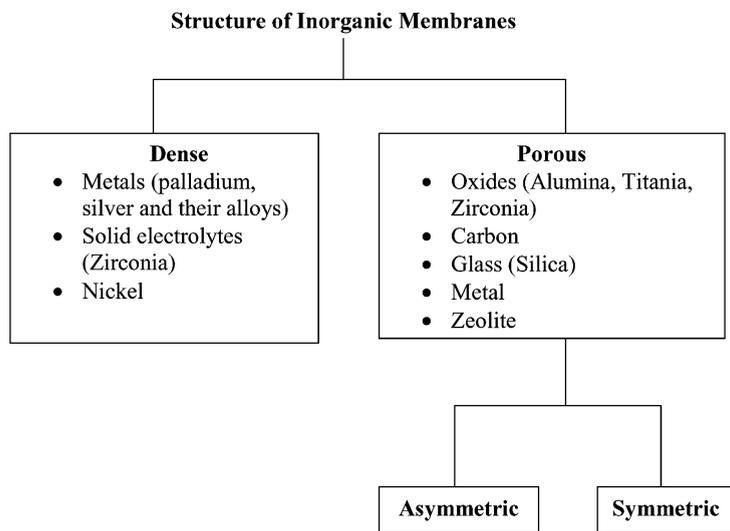


Fig. 1. Structures of inorganic membranes.

European, American and Japanese companies are now competing to produce inorganic membranes [2].

Hsieh has provided a technical overview of inorganic membranes in his paper [3]. He divided the inorganic membranes into two major categories based on its structure: porous inorganic membranes and dense (non-porous) inorganic membranes as shown in Fig. 1. Besides that, porous inorganic membranes have two different structures: asymmetric and symmetric. Porous inorganic membranes with pores more than 0.3 nm usually work as sieves for large molecules and particles. Glass, metal, alumina, zirconia, zeolite and carbon membranes are commercially used as porous inorganic membranes. Other inorganic materials, such as cordierite, silicon carbide, silicon nitride, titania, mullite, tin oxide and mica also have been used to produce porous inorganic membranes. These membranes vary greatly in pore size, support material and configuration. On the other hand, dense membranes made of palladium and its alloys, silver, nickel and stabilized zirconia have been used or evaluated mostly for separating gaseous components. Application of dense membranes is primarily for highly selective separation of hydrogen and oxygen; transport occurs via charged particles. However, the dense membranes have limited industrial application due to their low permeability compared to porous inorganic membranes. Therefore,

today's commercial inorganic membranes market is dominated by porous membrane [1–3].

Although inorganic membranes are more expensive than organic polymeric membranes, they possess advantages of: temperature and wear resistance, well-defined stable pore structure, and chemically inertness. These advantageous characteristics encouraged many researchers in the early 1980s to investigate the gas separation properties of these membranes, especially porous inorganic membranes. Furthermore, many studies regarding applications of inorganic membrane reactors have been carried out [1].

At present, interest in the development of porous inorganic membranes providing better selectivity, thermal stability and chemical stability than polymeric membranes has grown. The attention has focused on materials that exhibit molecular sieving properties, such as silica, zeolites and carbon [4], which appear to be promising in separation of gas as shown in Fig. 2. Silica-based inorganic membranes selectively separate hydrogen from other gases but permselectivity between similar-sized molecules, such as oxygen and nitrogen is not sufficient [5]. Zeolites can separate isomers, but it is difficult to obtain a large, crack-free zeolite membrane. Hence, it is more feasible to form carbon molecular sieve membranes [5,6]. Therefore, the purpose of this paper is to give an overview

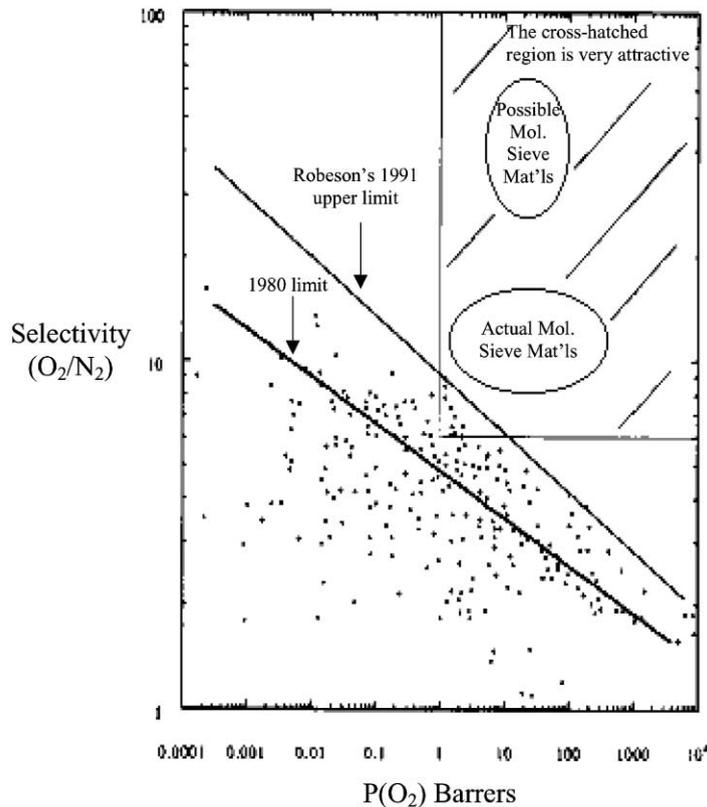


Fig. 2. Comparison between properties of polymeric membranes and molecular sieve membranes with the upper limit of performance [7].

regarding development of carbon molecular sieve membranes in the past 30 years. This paper also looks towards the future direction of carbon membranes development in the new millennium.

## 2. Transport mechanism of carbon membranes

Mass transfer of gas through a porous plug can involve several processes, depending on the nature of the pore structure and the solid [8]. There are four different mechanisms for separation of a gas mixture through a porous membrane: Knudsen diffusion, partial condensation/capillary condensation, surface diffusion/selective adsorption and molecular sieving [3,9]. The predominant transport mechanism of most carbon membranes is molecular sieving as shown in Fig. 3. The carbon membranes contain constrictions in the carbon matrix that approach the molecular

dimensions of the absorbing species [10]. In this manner, they are able to separate the gas molecules with similar size effectively. According to this mechanism, the separation is caused by passage of smaller

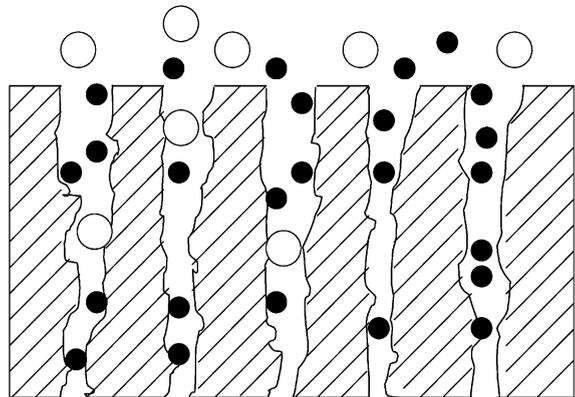


Fig. 3. Typical molecular sieving transport mechanism.

molecules of a gas mixture through the pores while the larger molecules are obstructed. It exhibits high selectivity and permeability for the smaller component of a gas mixture [9]. The carbon matrix is assumed to be impervious, and permeation through carbon membranes is attributed entirely to the pore system. The pore system consists of relatively wide openings with narrow constrictions. The openings contribute the major part of the pore volume and are thus responsible for the adsorption capacity, while the constrictions are responsible for the stereoselectivity of pore penetration by host molecules and for the kinetics of penetration [11]. Hence, the diffusivity of gases in carbon molecular sieve change abruptly depending on size and shape of molecules because the carbon molecular sieve has pores size close to dimension of gas molecules [12].

Carbon molecular sieve membranes have been identified as very promising candidates for gas separations, both in terms of separation properties and stability. Carbon molecular sieves are porous solids that contain constricted apertures that approach the molecular dimensions of diffusing gas molecules. At these constrictions the interaction energy between the molecule and the carbon is comprised of both dispersive and repulsive interactions. When the opening becomes sufficiently small relative to the size of the diffusing molecule, the repulsive forces dominate and the molecule requires activation energy to pass through the constrictions. In this region of activated diffusion, molecules with only slight differences in size can be effectively separated through molecular sieving [13]. The mechanism of gas permeation and

uptake through porous solids is thus closely related to the internal surface area and dimensions of the pores and to the surface properties of the solid, rather than to the bulk properties of the solid as in the case with polymers [11].

Molecular sieve carbon membranes suitable for gas separations have been prepared by pyrolyzing thermosetting polymers. Carbon molecular sieve membranes with pore diameters 3–5 Å have ideal separation factor for various combinations of gases ranges from 4 to more than 170. The ideal separation factor for N<sub>2</sub>/SF<sub>6</sub> and He/CO<sub>2</sub> are 4. The values are in the range of 20–40 for He/O<sub>2</sub>, He/N<sub>2</sub> and He/SF<sub>6</sub> separation. Meanwhile, ideal separation factor for O<sub>2</sub>/N<sub>2</sub>, H<sub>2</sub>/N<sub>2</sub> and O<sub>2</sub>/SF<sub>6</sub> are 8, 10–20 and more than 170, respectively [3]. The permeation characteristics of the molecular sieve carbon membrane can be varied by changing the high temperature treatment parameters [14].

Another transport mechanism of carbon membranes is selective adsorption/ surface diffusion mechanism. Adsorption-selective carbon membranes separate non-adsorbable or weakly adsorbable gases (O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub>) from adsorbable gases, such as NH<sub>3</sub>, SO<sub>2</sub>, H<sub>2</sub>S and CFCs. The difference between structure of adsorption-selective carbon membranes (ASCM) and carbon molecular sieve membranes (CMSM) concerns the micropores. Adsorption-selective carbon membranes (ASCM) have a carbon film with micropores slightly wider than carbon molecular sieve membranes (CMSM), probably in the range of 5–7 Å [15].

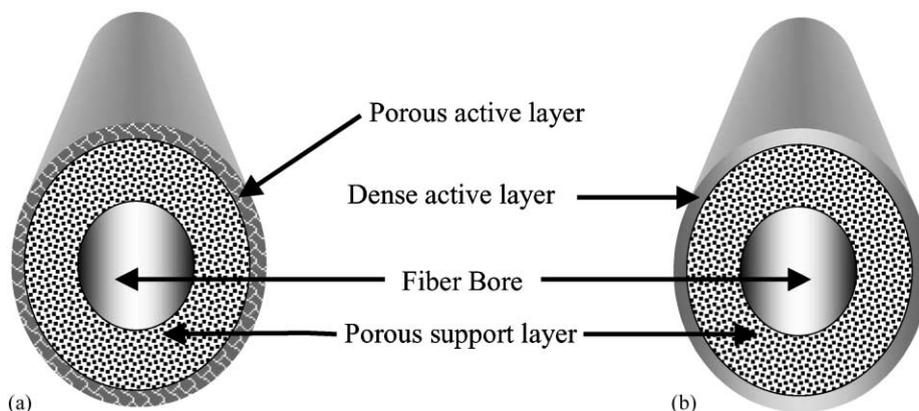


Fig. 4. Comparison of (a) carbon hollow fiber membrane with the (b) polymeric hollow fiber membrane.

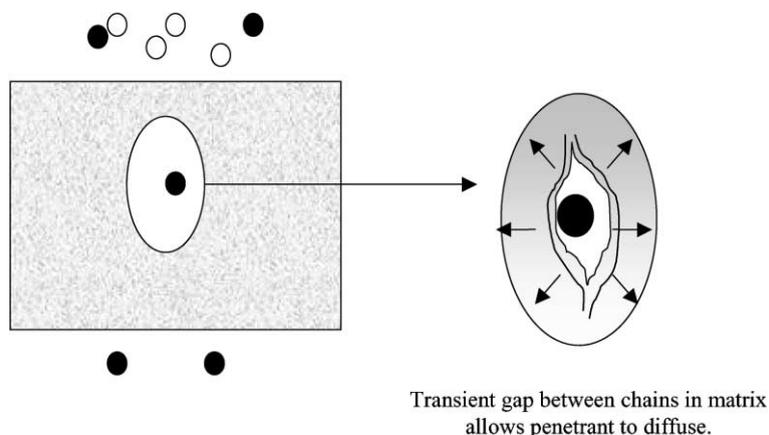


Fig. 5. Solution–diffusion transport mechanism [17].

It is known that the performance of an asymmetric membrane is dependent on the thin active layer [16]. Meanwhile, the great difference between carbon asymmetric membranes and polymeric asymmetric membranes is in the skin layer as shown in Fig. 4. Comparing with polymer membranes, carbon membranes may be considered as a refractory porous solid where, the permeates are non-soluble and merely penetrate through the pore system [14]. It is greatly different with the transport mechanism of polymer membranes — solution–diffusion mechanism. Fig. 5 shows the solution–diffusion mechanism in the dense layer of a polymeric membrane. Size (diffusivity) and condensability (solubility) selectivity factors determine which component passes through the membrane faster [17].

However, carbon membranes require very fine control of the pore sizes and require operation at an elevated temperature in order to provide practically acceptable flux for the smaller molecules due to membrane thicknesses several microns [9]. The influence of adsorption of permeates on the pore walls of carbon have to be taken into consideration, especially in the case of penetrants with relatively high boiling points [14].

### 3. Carbon membranes

The concept of carbon membrane or film for gas separation can be found in the early 1970. Ash et al.

compressed non-porous graphited carbon into a plug, called as carbon membrane [18]. Bird and Trimm used polyfurfuryl alcohol (PFA) to prepare unsupported and supported carbon molecular sieve membranes. During carbonization, they met shrinkage problem, which lead to cracking and deformation of the membrane. Hence, they failed to obtain continuous membranes [8].

Carbon molecular sieves produced from the pyrolysis of polymeric materials have proved to be very effective for gas separation in adsorption applications by Koresh and Soffer [19–22]. Molecular sieve carbon can be obtained by pyrolysis of many thermosetting polymers such as poly(vinylidene chloride) (PVDC), poly(furfuryl alcohol) (PFA), cellulose, cellulose triacetate, saran copolymer, polyacrylonitrile (PAN), phenol formaldehyde and various coals such as coconut shell [19]. They described that the pore dimensions of carbon depend on morphology of the organic precursor and the chemistry of pyrolysis [23]. During the research on molecular sieve carbon adsorbents, they have shown that the molecular sieving effect of non-graphitizing carbons was extremely specific and adjustable by mild activation and sintering steps to the discrimination range 2.8–5.2 Å [14].

Pyrolysis of thermosetting polymers typically cellulosic, phenolic resin, oxidized polyacrylonitrile as well as pitch mesophase has been recognized to yield an exact mimic of the morphology of the parent material. They do not proceed through a melt or soften during any stage of the pyrolysis process. Hence, pyrolysis processes can produce carbon molecular sieve

membranes from thermosetting polymer membranes [23]. The interest in developing carbon membranes only grew after Koresh and Soffer [11,14,23] had successfully prepared apparently crack-free molecular sieving hollow fiber membranes by carbonizing cellulose hollow fibers. They have shown the dependence of permeabilities and selectivities on temperature, pressure and extent of pore for both adsorbing and non-adsorbing permeates [14,23]. However, those membranes would be lack of mechanical strength for practical application.

#### 4. Configurations of carbon membranes

Carbon membranes can be divided into two categories: unsupported and supported carbon membranes [4]. Unsupported membranes have three different configurations: flat (film), hollow fiber, and capillary while supported membranes consisted of two configurations: flat and tube. Fig. 6 shows the configurations of carbon membranes.

##### 4.1. Flat (supported and unsupported) carbon membranes

A group of Japanese researchers, Hatori and coworkers have prepared porous carbon films from Kapton-type polyimide, including supported and unsupported carbon membranes [24–26]. Hatori et al. reported that the carbon molecular sieve film used for gas separation is required to be as thin as possible in order to enhance the separation efficiency. However, the thin film should be supported with a porous plate

for handling convenience. The flat homogeneous carbon films prepared by pyrolysis at 800°C had O<sub>2</sub>/N<sub>2</sub> selectivities of 4.2 [26].

Rao and Sircar [9,27,28] have introduced nanoporous supported carbon membranes, which were prepared by pyrolysis of polyvinylidene chloride layer coated on a macroporous graphite disk support. The diameter of the macropores of the dried polymer film was reduced to the order of nanometer as a result of a heat treatment at 1000°C for 3 h. These membranes with mesopores can be used to separate hydrogen-hydrocarbon mixtures by the surface diffusion mechanism, which selectively adsorbs gas molecules on pore wall. This transport mechanism differs from the molecular sieving mechanism, therefore, these membranes were named as selective surface flow (SSF<sup>TM</sup>) membranes. They possess a thin (2–5 μm) layer of nanoporous carbon (effective pore diameter in the range of 5–6 Å) supported on a mesoporous inert support such as graphite or alumina (effective pore diameter in the range of 0.3–1.0 μm). The procedures for making the selective surface flow membranes were described in those two authors' papers [9,28]. The requirement to produce a surface diffusion membrane has been described clearly in the author's paper [28].

A solution to overcome reproducibility problems of nanoporous carbon (NPC) membranes has been introduced by Acharya and Foley [29]. They have used spray coating system for the production of thin layers of nanoporous carbon on the surface of a porous stainless steel support. A solution of poly(furfuryl)alcohol (PFA) in acetone was sprayed onto the support in the form of a fine mist using an external mix

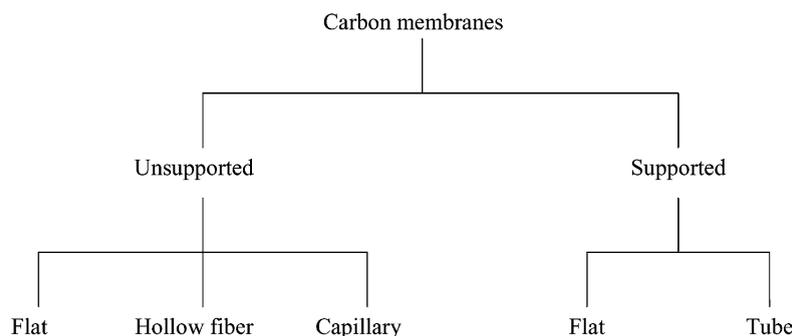


Fig. 6. Configurations of carbon membranes.

airbrush with nitrogen gas. This was the first reported technique for supported carbon membrane synthesis. The advantages of this preparation method are reproducibility, simplicity and good performance for oxygen–nitrogen separation. The resulting membranes were found to have oxygen over nitrogen selectivities up to 4 and oxygen fluxes on the order of  $10^{-9}$  mol  $m^{-2}$   $Pa^{-1}$   $s^{-1}$ .

Chen and Yang [6] have prepared large, crack-free carbon molecular sieve membrane supported on a macroporous substrate by coating a layer of polyfurfuryl alcohol followed by controlled pyrolysis. Diffusion of binary mixtures was measured and the results were compared with the kinetic theory for predicting binary diffusivities from pure-component diffusivities. Good agreement was obtained between theoretical predictions and experimental data for binary diffusion.

Suda and Haraya [30] have prepared flat, asymmetric carbon molecular sieve membranes, which exhibited the highest gas permselectivities among those in the past research by pyrolysis of a Kapton-type polyimide derived from pyromellitic dianhydride (PMDA) and ODA. They used the permeation measurements and X-ray powder diffraction to relate the relationship between the gas permselectivity and microstructure of the carbon molecular sieve membrane. They proposed that the decrease of the interplanar spacing, amorphous portion and pores upon heating might be the origin of the “molecular sieving effect”.

Suda and Haraya [31] also made a clarification of the factors that determine the microstructure and the permeation properties of carbon molecular sieve dense membranes derived from Kapton polyimide film. They have gained insight into the permeation mechanism through the study of permeability versus kinetic diameter in connection with diffusivity and sorptivity. They suggested that the factors determining the microstructure and gas permeation properties of carbon molecular sieve membranes are not completely open to controlled pyrolysis of a precursor, because these properties are significantly affected by several factors: the choice of polymer precursor, the membrane formation method and the pyrolysis conditions.

Shusen et al. [32] reported that the asymmetric carbon membranes produced by Le Carbon Lorraine using a two-step procedure (carbon support preparation in the first step and top layer deposition in the second step) seems to be complicated. By using this method,

the porous carbon support is made by pyrolysis of a tube with 1mm wall thickness. On top of the support, thin polymeric films are deposited; followed by controlled pyrolysis to the desired pore shape. Hence, Shusen et al. used simpler and more flexible one-step preparation method (one heat treatment step for support and functional top layer) to fabricate asymmetric supported carbon membranes, consisting formation of phenol formaldehyde film followed by pyrolysis and unequal oxidation.

In this process, micropores were achieved as a result of small gaseous molecules channeling their way out of the solid matrix of the polymer during pyrolysis. The micropore structure was further widened by oxidation, which removed carbon chains in the pores. The pore structure was made narrower by high temperature sintering which shrinks the pore size. All of the preparation conditions which shrink the pore size of the carbon membrane would be beneficial for improvement of selectivities while the conditions for widening pore size should be favorable for increasing permeabilities [33]. They have proposed that the key point to create a carbon membrane with asymmetric structure was to keep a different oxidation atmosphere on two sides of the membranes in the activation process, for example, a relatively strong activation condition on one side and a relatively weak activation conditions on the opposite side [32,33].

Kita et al. [34] synthesized an unsupported polypyrrolone film by means of a casting method. The authors found that the membranes, which have been carbonized at 700°C for 1 h gave the highest performance in their research. They observed that the membranes exhibited excellent stability up to 500°C under nitrogen atmosphere, without weight loss from the membrane.

Liang et al. [35] have produced carbon membranes for gas separation from coal tar pitch. The ‘separation power’, which is the production of permeability by selectivity of carbon membranes prepared from coal tar pitch was generally higher by at least three orders of magnitude compared with polymeric membranes for  $H_2/O_2$  and  $H_2/N_2$  separation.

Spain researchers, Fuertes and Centeno have investigated the preparation method of flat, supported carbon molecular sieve membranes by using different polymeric precursors. They used BPDA-PPDA [4,36], phenolic resin [12] as precursor to make flat carbon

molecular sieve membranes supported on a macroporous carbon substrate.

In another study, they chose polyetherimide as a precursor to prepare flat, supported carbon molecular sieve membranes [37]. Polyetherimide was chosen because it can be used economically. On the other hand, these polyetherimide carbon membranes showed similar performance with the carbon molecular sieve membranes prepared by Hayashi et al. [38], which were obtained from a laboratory-synthesized polyimide (BPDA-ODA).

Furthermore, they also used two other commercially available polyimide-type polymers, Matrimid and Kapton to prepare supported carbon composite membranes in a single casting step [39]. They reported that the different structures of carbon membranes could be obtained depending on the polymeric precursors, the casting solution and the preparation condition. However, preparation conditions have a great effect on the structure and separation properties of the Matrimid-based carbon membranes.

Recently, they have investigated the preparation of supported carbon molecular sieve membrane formed by a microporous carbon layer, obtained by carbonization of a poly(vinylidene chloride-co-vinyl chloride) (PVDC-PVC) film [40]. They discovered that the oxidation of PVDC-PVC samples did not significantly affect the micropore volume of the carbonized materials. However, the pretreatment in air at 200°C for 6 h led to a less permeable carbon membrane than the untreated membrane but much more selective. The selectivity of CO<sub>2</sub>/N<sub>2</sub> was increased from 7.7 to 13.8 after the pretreatment.

Some researchers have studied the entropic contributions to diffusivity selectivity as the polymer matrix evolved to a rigid carbon matrix [41]. Polymer precursor, membranes pyrolyzed at intermediate steps in the pyrolysis process and finally pyrolyzed membranes were tested for the purpose to study the development of gas separation properties as the material progresses from a polymer to a completely carbonized membrane.

#### 4.2. Carbon membranes supported on tube

Hayashi et al. [38] have produced carbon molecular sieve membranes by dip coating of BPDA-4,4'-oxydianiline (ODA) solution on an  $\alpha$ -Al<sub>2</sub>O<sub>3</sub> porous support

tube follow by pyrolysis at 500–900°C in an inert atmosphere. In their study, the sorptivity and diffusivity of penetrants in the carbonized membrane were greatly improved because of the increased micropore volume (free space) and segmental stiffness. The selectivity of CO<sub>2</sub>/CH<sub>4</sub> larger than 100 was achieved, although BPDA-ODA membrane usually can only reach 65 at 35°C. This indicated that the carbonization procedure was optimized and excellent selectivities of penetrants were obtained.

They modified the resulting carbon molecular sieve membranes by chemical vapor deposition (CVD) using propylene as carbon source at 650°C [5]. At pyrolysis temperature 700°C, the CVD modification was effective to increase the CO<sub>2</sub>/N<sub>2</sub> selectivity from 47 to 73 while O<sub>2</sub>/N<sub>2</sub> selectivity increased from 9.7 to 14 because the pore structure was further controlled and the micropores were narrowed.

Hayashi and coworkers [42,43] also found that a carbonized membrane prepared with a BPDA-pp'ODA polyimide gave higher C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> and C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> permselectivities than those of polymeric membranes. This was in accord with the fact that carbonized membrane possess a micropore structure, which was capable of recognizing size differences of alkane and alkene molecules. In addition, Hayashi et al. [43] evaluated the stability of a membrane based on BPDA-ODA polyimide and carbonized at 700°C by exposing it to air at 100°C for 1 month. It was suggested that the carbon molecular sieve membranes are usable for a prolonged period under an atmosphere that contains low levels of oxidants, which is refer to the level of oxidants in atmosphere air. Their study also showed that the permeation properties of carbon membrane could be improved by treating carbon membrane under an oxidizing atmosphere. Hayashi et al. [43] have oxidized BPDA-ODA carbon membrane with mixture of O<sub>2</sub>-N<sub>2</sub> at 300°C or with CO<sub>2</sub> at 800–900°C. Nevertheless, excessive oxidation fractured carbon membrane. They concluded that carbonization under optimum conditions shifted the trade-off relationship of the BPDA-pp'ODA polyimide membrane toward the direction of higher selectivity and permeability. The resulting membranes exhibited permeances approximately  $1 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  for C<sub>2</sub>H<sub>4</sub>,  $2 \times 10^{-9} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  for C<sub>2</sub>H<sub>6</sub>,  $4 \times 10^{-9} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  for C<sub>3</sub>H<sub>6</sub> and  $1 \times 10^{-10} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  for C<sub>3</sub>H<sub>8</sub>. The selectivities

were 4–5 for C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>6</sub> separation and 25–29 for C<sub>3</sub>H<sub>6</sub>/C<sub>3</sub>H<sub>8</sub> separation [42].

Katsaros et al. [44] have prepared microporous carbon membranes by carbonization and activation of an asymmetric phenolic resin structure comprising a dense resol layer, supported on a highly permeable macroporous novolak resin tube.

A BPDA-ODA/DAT copolyimide, which contains methyl groups; was used as a precursor for carbon molecular sieve membrane by Yamamoto et al. [45]. Methyl groups would be expected to be decomposed during the post-treatment under an oxidative atmosphere and result in expanded micropores. They reported that the permeation properties of the resulting membranes were dependent on the composition of the precursor films, carbonization temperature and oxidation conditions. In spite of the permeance increasing with increasing permeation temperature, the separation coefficients were not greatly influenced by the oxidation and carbonization treatments. They suggested that the oxidation in air by increasing temperature up to 400°C with a 1 h hold and carbonization up to 700°C was most suitable for increasing permeance with no damage in separation coefficient. The carbon membranes gave  $3 \times 10^{-8} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$  for CO<sub>2</sub> permeance and the separation coefficient of CO<sub>2</sub>/CH<sub>4</sub> reached 60 at permeation temperature of 35°C. In addition, the trade-off line for the BPDA-ODA carbon membrane for O<sub>2</sub>/N<sub>2</sub> system was three-fold higher in the direction of separation coefficient than that for polyimide membrane reported by Stern. They have concluded that optimization of the treatment procedure was more important than changes in diamine portion of the copolyimide.

Kusakabe et al. [46] made a further study regarding carbon molecular sieve membranes, which were formed by carbonizing BPDA-pp'ODA polyimide membranes at 700°C and then oxidized with either an O<sub>2</sub>-N<sub>2</sub> mixture or pure O<sub>2</sub> at 100–300°C under controlled conditions. The study showed that the oxidation increased permeance without greatly damaging the permselectivities. This was due to the oxidation at 300°C for 3 h significantly increased the micropore volume but the pore size distribution was not broadened. The result was similar with the author previous research [43] regarding the effect of oxidation on gas permeation of carbon molecular sieving membranes based on BPDA-pp'ODA polyimide.

They also formed the condensed polynuclear aromatic (COPNA) resin film on a porous  $\alpha$ -alumina support tube. Then, a pinhole-free carbon molecular sieve membrane was produced by carbonization at 400–1000°C [47]. The mesopores of the COPNA-based carbon membranes did not penetrate through the total thickness of each membrane and served as channels, which increased permeances by linking the micropores. Both COPNA carbon membranes having mesopores and micropores and BPDA-pp'ODA polyimides carbon membranes with only micropores showed similar permeation properties, although they had different pore structures. At permeation temperature 100°C, the selectivities of CO<sub>2</sub>/N<sub>2</sub> were 17 for pyrolysis temperature at 700°C and 19 for pyrolysis temperature at 800°C, respectively. This suggests that the micropores are responsible for the selectivities of the carbonized membrane.

Besides that, Fuertes [15] used phenolic resin to prepare adsorption-selective carbon membrane supported on ceramic tubular membranes. The dip coating technique was used in the research.

There are other different coating methods on porous stainless steel support media in the production of carbon membranes supported on tube: brush coating, spray coating and ultrasonic deposition of the polymer resin. Shiflett and Foley have reported various approaches to preparing carbon molecular sieve layers on the stainless steel support by ultrasonic deposition [48].

On the other hand, Wang et al. [49] used a gas phase coating technique, vapor deposition polymerization (VDP) to prepare supported carbon membranes from furfuryl alcohol. They reported that the membranes prepared by VDP have comparable CO<sub>2</sub>/CH<sub>4</sub> selectivities but lower CO<sub>2</sub> permeabilities than certain PFA-based membranes prepared by dip coating techniques. The selectivity for CO<sub>2</sub>/CH<sub>4</sub> separation was 80–90 with CO<sub>2</sub> permeances in the range of  $27 \times 10^{-10}$  to  $58 \times 10^{-10} \text{ mol m}^{-2} \text{ Pa}^{-1} \text{ s}^{-1}$ .

#### 4.3. Carbon capillary membranes

Haraya et al. [50] have reported a novel preparation of asymmetric capillary carbon molecular sieve membranes from Kapton polyimide membrane and their gas permeation properties. Capillary carbon molecular sieve membrane must have controlled asymmetric

structure, consisting of a dense surface layer with molecular sieving properties and a porous supporting layer in order to attain both high permselectivity and permeance. However, it is not easy to control the structure of the capillary carbon molecular sieve membrane. They described that the structure of membrane was formed in the gelation step of polyamic acid (PA) and was also maintained in the imidization and shrank about 30% at pyrolysis steps. They observed that the surface layer became thinner and the pore dimension became larger, with acceleration in the exchange rate of solvent with coagulant. Slow gelation process would result in a thicker dense surface layer.

Petersen et al. prepared carbon molecular sieve membrane (capillary tubes) by using precursor derived from Kapton [51]. They worked at improving the fabrication method of capillary carbon membrane for high-temperature gas separation applications.

#### 4.4. Carbon hollow fiber membranes

Linkov et al. [52] summarized a number of special techniques, which have been developed to obtain narrow pore-size distribution in carbon membranes. Those techniques consisted of introduction of monomers with low carbon content into polyacrylonitrile macromolecules, irradiation of polymer films with high-energy ions, in situ polymerization on the surface of dip-coated polymeric precursors, treatment with concentrated hydrazine solution and the dispersion of a finely divided inorganic material in the casting solution of polyacrylonitrile (PAN). They reported that the carbonization of highly asymmetrical PAN precursors, produced by the use of various combinations of solvent and non-solvents in precipitation media, resulted in the formation of a range of flexible hollow fiber carbon membranes with high porosity and good mechanical properties. Morphology of this type carbon membrane as well as the possibility of altering of the pore structure was studied. It was suggested that precursor preparation (solution formulation and fabrication procedure) and stabilization as well as carbonization conditions have possibility to alter the pore sizes of carbon membranes.

Linkov et al. [53] also used vapor-deposition polymerization method to coat hollow fiber carbon membranes. Then, the coated membranes were heated in a nitrogen atmosphere to produce composite

carbon-polyimide membranes. The composite membranes had low wall and active skin thickness with good mechanical properties. They have resistance against high pressures and high flexibility.

Polyimide derived from a reaction of 2,4,6-trimethyl-1,3-phenylene diamine, 5,5-[2,2,2-trifluoro-1-(trifluoromethyl)ethylidene]-1,3-isobenzofurandione and 3,3',4,4'-biphenyl-tetra-carboxylic acid dianhydride was used by Jones and Koros to prepare carbon molecular sieve asymmetric hollow fiber membranes [13]. Those membranes were developed and optimized for air separation applications. However, they were also effective for the separation of other gas mixtures such as CO<sub>2</sub>/N<sub>2</sub>, CO<sub>2</sub>/CH<sub>4</sub> and H<sub>2</sub>/CH<sub>4</sub> with the selectivities 55–56, 140–190 and 400–520, respectively. On the other hand, the selectivities for conventional polymeric membranes only reached 15–25 for CO<sub>2</sub>/N<sub>2</sub> separation, 15–40 for CO<sub>2</sub>/CH<sub>4</sub> and less than 200 for H<sub>2</sub>/CH<sub>4</sub>. It is noteworthy that the selectivities obtained were much higher than those seen with conventional polymeric materials without sacrificing productivity.

Jones and Koros have found a few problems or weakness of carbon membranes in their studies [10,54]. Carbons generally have non-polar surfaces. As a result they are organophilic. Therefore, ultramicroporous carbon membranes would be very vulnerable to adverse effects from exposure to organic contaminants due to its adsorption characteristics of organics. Membrane performance will deteriorate severely if feed streams having as low as 0.1 ppm organics. As organic sorption proceeds, capacity for other compounds is diminished and membrane performance losses occur rapidly. Once a monolayer has been established, a prohibitive resistance to other permeating species exists. However, a unique regeneration technique developed by Jones and Koros [54] seem to be very promising for removing a number of organic contaminants. Pure propylene at unit or near-unit activity has found to be suitable for the regeneration process. The propylene most likely acted as a solvent, removing other sorbed compounds from the carbon surface. Propylene exposure resulted in a small "opening up" of the pore structure and membrane recovery was significantly boosted.

Jones and Koros [10] also found that the micropores of carbon membranes would gradually plugged with water at room temperature and resulting in the

decrease of the non-polar gases permeabilities and its selectivities. The reason is the surface of membrane carbonized at relatively low temperature is affected by oxygen remaining in the inert purge gas during pyrolysis [55]. The surface is partially covered with oxygen-containing functional groups, thus giving the membrane a hydrophilic character [46]. The resulting oxygen-containing surface complexes will act as primary sites for water sorption. Sorbed water molecules then attract additional water molecules through hydrogen bonding, leading to the formation of clusters. The cluster grows and coalesces, leading to bulk pore filling. As the amount of sorbed water in microporous carbon adsorbents increases, it will greatly diminish the diffusion rate of other permeating species [10].

The problem can be overcome by coating the membrane with a highly hydrophobic film, which does not prohibitively reduce the flux of other permeating species. Therefore, the resulting carbon composite membranes demonstrated a greater resistance to the adverse effects from water vapor while retaining very good separation properties [56]. Thus, Kusakabe et al. [46] reported that the modification of the surface properties of carbon molecular sieve membrane is a key technology for the selective gas separation.

Geiszler and Koros [55] have studied the effect of polyimide pyrolysis conditions on carbon molecular sieve membranes properties. They compared the carbon membrane performances prepared by vacuum pyrolysis and inert purge pyrolysis. In addition, they also studied other pyrolysis variables such as the processing temperature, purge gas flowrate and residual oxygen concentration in the purge gas. They observed that pyrolysis atmospheres and flow rates of purge gas strongly influenced  $H_2/N_2$  and  $O_2/N_2$  selectivities as well as permeability of carbon molecular sieve membranes. In argon purge pyrolysis, the  $O_2/N_2$  selectivity was 2.8–6.1 while the  $H_2/N_2$  selectivity was 6.8–31.2. The selectivities were increased to 7.4–9.0 for  $O_2/N_2$  and 64–110 for  $H_2/N_2$  when the membrane carbonized in vacuum condition. The purge gas flow rate changed from 20 to 200  $cm^3/min$  had resulted in the increasing of permeability of  $O_2$  from 0.05–0.54 to 71–284 GPU. It is noteworthy that pyrolysis condition has significant influence to the carbon membranes performance.

Kusuki et al. [57] have made the asymmetric carbon membranes by carbonization of asymmetric

polyimide hollow fiber membranes. The effects of different experimental conditions on the membrane performance have been investigated. They reported that those carbon membranes showed high permselectivities compared with polyimide hollow fiber membranes. They achieved the selectivity of  $H_2/CH_4$  ranging from 100–630 with permeation rate of  $H_2$  ranging from  $10^{-4}$  to  $10^{-3} cm^3(STP)/(cm^2 s cmHg)$ .

Tanihara et al. [58] have made the asymmetric carbon membranes by carbonization of asymmetric polyimide hollow fiber membranes. In their study, they found that the permeation properties of carbon membrane were hardly affected by feed pressure and exposure of toluene vapor. Furthermore, there was only little change in the permeation properties of the carbon membrane with the passage of time.

Ogawa and Nakano [59] have investigated the effect of gelation conditions on the properties of the carbonized membrane. The carbonized hollow fiber membrane was formed by gelation of polyamic acid solution in a coagulant by phase inversion method, imidization and carbonization. The microstructure of the carbonized membrane was evaluated by the micropore volumes, which depended on gelation temperature and pH of coagulant. Hence, the gelation process was important to control microstructure, permeance and permselectivity of the carbonized membrane. They observed that the gelation time was not a predominant factor to control the micropore volume, the permeances and  $CO_2/CH_4$  permselectivity. However, they found that the gelation temperature would influence the permeation properties of the carbon membranes.

They also reported that the permeance reduced with the increase of pH value of the coagulant. The micropore volume also decreased remarkably in the alkali region, resulting in reduction of micropore size. However, the permselectivity increased with the increase of pH. They proposed that the most important factor to achieve both high permeance and high permselectivity in the carbonized membrane was pH control of the coagulant (water). They realized that the high permeance of  $CO_2$  and the high  $CO_2/CH_4$  permselectivity were obtained under the specific conditions of gelation: time 6 h, temperature 275 K and pH 9.4. They concluded that the transport of  $CO_2$  was mainly governed by the adsorption effect and transport of  $CH_4$  was restricted by the molecular

Table 1  
Configurations of carbon membranes produced by previous researchers

Researcher(s)	Configuration	Period (year)	Reference(s)
Ash et al.		1967–1968	[13]
Barrer et al.		1973	[18]
Bird and Trimm	Flat	1983	[8]
Koresh and Soffer	Hollow fiber	1980–1987	[11,14,19,23]
Kapoor and Yang		1989	[13]
Bauer et al.	Tube	1991	[61]
Hatori and coworkers	Flat	1991–1992	[24–26]
Rao and Sircar	Flat	1993	[9,27,28]
Chen and Yang	Flat	1994	[6]
Linkov et al.	Hollow fiber	1994	[52,53]
Jones and Koros	Hollow fiber	1994–1996	[10,13,54,56]
Hayashi and coworkers	Tube	1995–1997	[5,38,42,43]
Suda and Haraya	Flat, capillary	1995–1997	[30,31,50,62]
Shusen et al.	Flat	1996	[32,33]
Kita et al.	Flat	1997	[34]
Petersen et al.	Capillary	1997	[51]
Kusuki et al.	Hollow fiber	1997	[57]
Tennisson et al.	Tube	1997	[44]
Yamamoto et al.	Tube	1997	[45]
Kusakabe and coworkers	Tube	1998	[46,47]
Geiszler and Koros	Hollow fiber	1999	[55]
Tanihara et al.	Hollow fiber	1999	[58]
Okamoto et al.	Hollow fiber	1999	[63]
Liang et al.	Flat	1999	[35]
Acharya and Foley	Flat	1999	[29]
Fuertes and Centeno	Flat	1998–2000	[4,12,15,36–40]
Ogawa and Nakano	Hollow fiber	1999–2000	[59,60]
Ghosal and Koros	Flat	2000	[41]
Shiflett and Foley	Tube	2000	[48]
Wang et al.	Tube	2000	[49]

sieving effect, yielding high CO<sub>2</sub>/CH<sub>4</sub> permselectivity [59].

They also investigate the difference in permeation behaviors of CO<sub>2</sub> and CH<sub>4</sub> between single component and multicomponent of CO<sub>2</sub>/CH<sub>4</sub> system from the viewpoint of the microporous structure, which was created through the formation process of the carbonized membrane [60].

Table 1 has summarized the configurations of carbon membranes prepared or produced by the previous researchers. It is observed that most of the carbon membranes produced during 1980 until early 1990 were flat disk or flat sheet membranes. Only approaching the middle of 1990, carbon membranes supported on tube has been made followed with carbon capillary membranes as well as carbon hollow fiber membranes. Flat sheet carbon membranes are

more suitable for laboratory or research applications while carbon membranes supported on tube, carbon capillary membranes and carbon hollow fiber membranes are more practical and suitable to apply in industry.

## 5. Application of carbon membranes

The most important large application of carbon membrane is in the production of low cost and high purity nitrogen from air. Other separations are hydrogen from gasification gas and purification of methane [36]. In addition, carbon membranes are used to recover a valuable chemical (H<sub>2</sub>) from a waste gas without further compression of the feed gas while rejecting a substantial portion of the hydrocarbons [9].

Carbon membranes are promising candidates for the separation of light alkenes/alkanes especially propene/propane separation. It was reported that carbon membranes possess excellent propene/propane permselectivities. They are expected to be superior to other methods such as distillation, adsorption and absorption based on energy consumption. Separation of light alkenes/alkanes has been recognized to be a key technology in the petrochemical industry [62]. They have also shown good performance for the 1,3-butadiene/*n*-butane separation [63].

The combination of reaction and separation at high temperature in a membrane reactor offers interesting new possibilities. In a membrane reactor, the separate product and feed compartments allow more ways to optimize both selectivity and conversion [1].

## 6. Advantages of carbon membrane compare with polymeric membrane

1. Carbon membranes display superior permeabilities-selectivity combination than polymeric membranes [11,13,14,35,58].
2. Carbon membranes are mechanically much stronger and can withstand higher pressure differences for a given wall thickness [11]. Carbon membranes have higher elastic modulus and lower breaking elongation than the polyimide membranes [58].
3. The permeation properties of carbon membranes are hardly affected by the feed pressure [12,58] because carbon membranes do not possess compaction and swelling problems [3].
4. The permeation properties of carbon membranes will not be time dependent [58].
5. The activation energies required for the diffusion in the carbon membranes are smaller than those in the polyimide membranes. It means that the diffusing gas (especially with large molecule size) is much influenced by the activation energies when it diffuses in the polyimide membranes compared with carbon membranes. Therefore, the selectivity of polyimide membranes decreases remarkably if the measurement temperature increases [57]. This situation will not happen in the carbon membranes.
6. Carbon membranes offer the advantage of operation in environments prohibitive to polymeric

materials and have superior stability in the presence of organic vapor or solvent and non-oxidizing acids or bases environments [11,13,35,58]. They can perform very well with high purity and dry feeds [10]. They are ideal for corrosive applications [61].

7. Carbon membranes are far more stable thermally than polymeric membranes. They are suitable to be used in the separation processes with high temperature in the range of 500–900°C. On the other hand, organic polymer membranes cannot resist very high temperature and begin to decompose or react with certain components. [11,13,14,51,61].
8. The same starting material can be used to develop membranes of different permeation properties for different gas mixtures [11].
9. The pore dimension and distribution of the carbon membranes can be finely adjusted by simple thermochemical treatment to meet different separation needs and objectives [11,35].
10. Carbon membranes have a superior adsorptivity for some specific gases, which can enhance its gas separation capacity [35].
11. Carbon membranes have the ability to be back flushed, steam sterilized or autoclaved [3].

## 7. Disadvantages of carbon membranes

Carbon membrane is very brittle and fragile. Therefore, it requires more careful handling [11,35,65]. This may be avoided to a certain degree by optimizing precursors and preparation methods [35]. Therefore, it is difficult to process and expensive to fabricate carbon membranes [65].

Carbon membranes require a pre-purifier for removing traces of strongly adsorbing vapors, which can clog up the pores due to the transport is through a pore system rather than through the bulk system. This is typical of many industrial adsorption separators. This problem may be avoided by operating at sufficiently high temperatures [11].

Carbon membranes only demonstrated high selectivities for certain gas mixture, which limited to gases with molecular sizes smaller than 4.0–4.5 Å. Carbon membranes are not suitable to separate gas mixtures, such as *iso*-butane/*n*-butane and gas–vapour mixtures, for instance air/hydrocarbons, H<sub>2</sub>/hydrocarbon [15].

## 8. Current research and future direction

At this century, membrane systems process more than 4000 million m<sup>3</sup> of gas annually [64]. Increasing interest in gas separation by organic membranes had lead to exploitation of inorganic membranes for high temperature or corrosive gas separation applications [3]. Nowadays, inorganic membrane producers are generally in the start-up and technology push stage. Meanwhile, the end-user industry has exhibited a “wait-and-see” attitude when it comes to adopting advanced inorganic membrane applications. Industries currently have a major interest in basic quantitative knowledge of inorganic membranes particularly the performance of inorganic membranes in separation process and their stability in aggressive environment [1].

In general, gas separation inorganic membranes can be categorized into three types: microporous, amorphous membranes; microporous, crystalline membranes; and dense, high temperature membranes. Much attention will be focused on realizing complex, well-defined porous architectures and all three types of membranes will be combined to give separation properties with improved long-term stability in the next few years. In the near future, a gradual shift will take place from the exploration of new membrane concepts toward better control of membrane preparation and understanding of performance, long-term stability and process integration in the applications [1].

Today, 20 firms are manufacturing inorganic membranes; most of them were introduced to the market over the last 5–10 years. The inorganic membranes produced by these firms are presented in the Table 2. The oldest inorganic porous membranes manufacturers, SCT/US Filter and TECH-SEP now dominate the inorganic membranes market. Currently, porous ceramic membranes dominate commercialized inorganic membranes. The most prevalent membrane materials are metallic oxides and more precisely alumina and zirconia, but other materials, such as titania, carbon or glass are available [2].

Commercialized inorganic membranes exist in three configurations: disks or sheets, tubes and multi-channels/honeycombs. Usually, flat disks or sheets are limited to small-scale industrial, medical and laboratory applications. They are used almost exclusively in flow-through filtration in contrast to cross-flow

filtration in tubes and multichannel monoliths. Meanwhile, tubes and monoliths are used for various industrial applications [2,3].

As we can see in Table 2, there are only a few manufacturers involved in the production of carbon membranes. It is because greater expenses in producing and packaging these carbon membranes in modules have prevented their use in large-scale membrane modules [17]. A lot of effort should be put in to study the optimum conditions to prepare carbon membranes with desired performance. However, the production of carbon membranes involves a very high cost. The cost of carbon membrane per unit of membrane area is reported to be between one and three orders of magnitude greater than for polymeric membrane [65].

Investigation on material selection of more suitable precursors is warranted. Finding a more economical material than polyimide is still a necessary trend in carbon membrane production. This indicates that discovering ways to provide excellent separation properties of carbon membrane without losing the economical processability of polymeric membrane materials would be a major breakthrough for this field [17].

Meanwhile, the challenges faced by the current membrane technology have been summarized by Koros and Mahajan [65]. The main challenges are: achieving higher permselectivity with acceptable productivity, maintaining these properties in the presence of complex and aggressive feeds and avoiding the need for recompression of the desired product.

In the future, the polymer carbon composites method will become important for producing membranes with mixed-matrix materials, which are able to overcome the challenges mentioned above. The concept of the polymer carbon composite is shown in Fig. 7. Mixed-matrix materials comprising molecular sieve entities embedded in a polymer matrix offer the potential to combine the processability of polymers with the superior gas separation properties of rigid molecular sieving materials [65]. The carbonization polymer blend will lead to the formation of porous structure due to the thermally unstable polymer (pyrolyzing polymer) decomposing to leave pores in the carbon matrix formed from the stable polymer (carbonizing polymer). Although polymer blends have been now widely used as important industrial raw materials as highly functional materials, this carbonization method is just at the starting stage [66].

Table 2  
Commercial porous inorganic membranes [2]

Manufacturer	Trade name	Material	Pore	Geometry
USF/SCT	MEMBRALOX <sup>®</sup>	ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	20–100 nm 5 nm–12 μm	Monolith
	CERAFLO <sup>®</sup>	Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.2–1.0 μm	Monolith
TECH-SEP	CARBOSEP <sup>®</sup>	ZrO <sub>2</sub> /C TiO <sub>2</sub> /C	10–300 kD 0.14 μm	Tube
	KERASEP <sup>®</sup>	TiO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub>	0.1–0.45 μm 15–300 kD	Monolith
Le Carbone Lorraine		C/C	0.1–1.4 μm	Tube
CERASIV		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.1–1.2 μm	Tube/monolith
		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> + TiO <sub>2</sub> /ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5–100 nm	
NGK		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub> +SiO <sub>2</sub>	0.2–5 μm	Tube/monolith
Whatman	ANOPORE <sup>®</sup>	Al <sub>2</sub> O <sub>3</sub>	20 nm–0.2 μm	Disk
Gaston Country	UCARSEP <sup>®</sup>	ZrO <sub>2</sub> /C	4 nm	Tube
Du Pont/Carre		Zr(OH) <sub>4</sub> /SS	0.2–0.5 μm	Tube
TDK	DYNACERAM <sup>®</sup>	ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	≈10 nm	Tube
		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	50 nm	
ATECH		SiC/SiC	0.05–1.0 μm	Tube/monolith
		Al <sub>2</sub> O <sub>3</sub>		
Asahi Glass		Glass	0.1–1.4 μm	Tube
Fuji Filters		Glass	4–90 nm	Tube
		Glass	0.25–1.2 μm	
Fairey	STRATA-PORE <sup>®</sup>	Ceramics/ceramics	1–10 μm	Tube/plate
	MICROFILTREX <sup>®</sup>	SS	0.2–1 μm	Tube/plate
Osmonics	HYTREX <sup>®</sup>	Ag/none	0.2–5 μm	Tube/plate
	CERATREX <sup>®</sup>	Ceramics/ceramics	0.1 μm	
Ceramem		Ceramics/cordierite	0.05–0.5 μm	Honeycomb
Trideltafiltration		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.1–7 μm	Tube/monolith
Hoogovens		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.1–1 μm	Tube
Steenecker		Al <sub>2</sub> O <sub>3</sub>	0.4 μm	Tube
NOK		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.2–6 μm	Tube
TOTO		Al <sub>2</sub> O <sub>3</sub> /Al <sub>2</sub> O <sub>3</sub>	0.1–0.2 μm	Tube
		ZrO <sub>2</sub> /Al <sub>2</sub> O <sub>3</sub>	5–30 nm	Monolith
Carre		ZrO <sub>2</sub> /SS		Tube

Much study is needed to identify the suitable pyrolyzing polymers and carbonizing polymers for blending.

It is clear from the above discussion, carbon membranes still require improvement before they

can become a dominant commercialized inorganic membrane. However, carbon membranes have great potential to replace other inorganic membranes in the market because they have many useful characteristics

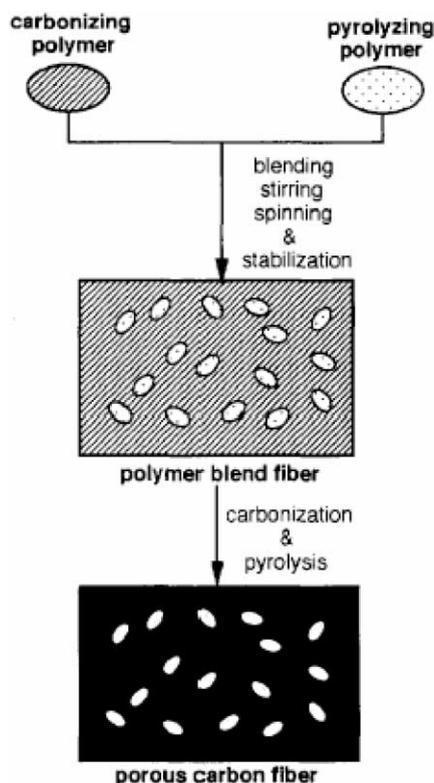


Fig. 7. Schematic diagram regarding the concept of the polymer blend carbonization [67].

and are able to separate gas mixtures, which have similar size of gas molecules efficiently.

## 9. Conclusions

Increasing research of carbon membrane technology indicates that carbon membranes definitely will become another alternative for industry separation process. They consist of four major configurations: flat, supported on tube, capillary and hollow fiber. Carbon membranes have great potential to be used widely in the gas separation processes, especially carbon hollow fiber membranes. Nowadays, hollow fibers are the most used membrane geometry due to their high surface area per unit volume of membrane module [64]. Carbon membranes with useful characteristics and advantages will compete with polymeric membranes and other porous inorganic

membranes. However, much research and development effort is needed in order to commercialize carbon membranes in the international market.

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