CO_2 Permeation Behavior through Carbon Membranes: A Short Review of the Progress during the Last Decade

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Abstract: Although carbon dioxide is not classified as a toxic or harmful gas the necessity for its capture is enforced not only by scientists but also by governments worldwide. In this attempt the technologies which are proposed to attend this role are various. Contrary to the traditional thermal methods (distillation, adsorption, cryogenic), which require high energy sources, the membrane technology seems to be the prevalent solution mainly thanks to its low operation cost. To this aim, both polymeric and inorganic membranes are reported as good candidates for CO_2 separation–capture. The main advantages of the inorganic membranes, in terms of the polymeric, are their higher selectivity factors and the better stability at both high temperatures and chemical environments. The preparation of the carbon membranes takes place mainly by the controlled pyrolysis of different thermosetting polymeric materials and the final configuration can be divided into the following configurations: i) flat sheet membranes, ii) supported on tube membranes, iii) capillary membranes and iv) hollow fiber membranes. During the last fifty years, more attention has been devoted, not only for the simultaneous increase of both permeability and selectivity factors but also for the large–scale production of crack free carbon membranes. The reproductivity is also one critical point which has to be achieved if we really aim for the industrial application of the carbon gas selective membranes. Therefore, carbon membranes have the potential to be the materials of the future for many gas separation processes including the one of carbon dioxide separation–capture. This paper is reviewing the development and the achievements of the carbon membranes in the direction of the CO_2 separation giving emphasis on the last 10 years.

Keywords: CO_2 permeation, CO_2 selectivity, inorganic membranes, carbon membranes, gas separation.

1. INTRODUCTION

The first studies on separation membranes start in the 18th century (1748) when the Abbé Jean–Antoine Nollet, a French experimental physicist, proved that the bubbling phenomenon in decompressed liquids might be caused by the dissolved air. In 1824, René–Joachim–Henri Dutrochet, a French physiologist, discovers the phenomenon of osmosis in natural membranes [1]. In 1855, Adolf Eugen Fick, a German physiologist, introduces the Fick's law of diffusion, which describes the diffusion of a gas through a fluid membrane [2]. In 1861, Thomas Graham, a Scottish chemist, studied the diffusion of gases and laid the foundation of gas and vapour separation through polymeric membranes [3]. He could be probably called the father of modern dialysis that occupies the biggest share of membrane market. In 1887, Jacobus Henricus van’t Hoff, a Dutch physical and organic chemist, proposes the famous van’t Hoff equation for the osmotic pressure (π). This work was awarded the first Nobel Prize in Chemistry in 1901 [4]. After the above fundamental works much more pioneer papers were published due to the first half of 20th century, but the golden age of membrane technology (1960–1980) began in 1960 with the invention by Loeb and Souriraja [5] of the first asymmetric integrally skinned cellulose acetate reverse osmosis (RO) membrane.

Carbon dioxide (CO_2) is a naturally occurring gas that existed in the atmosphere long before human. Carbon dioxide is the fourth earth gas in concentration after the nitrogen (N_2), oxygen (O_2) and argon (Ar). In Earth's atmosphere it is considered as a trace gas which presents an average concentration between 0.036% (360 ppm) and 0.041% (410 ppm), depending on the location [6]. Although carbon dioxide is not classified as a toxic or harmful gas, the rising of CO_2 levels causes an enhanced greenhouse effect. Over the past ten thousand years, the level of atmospheric CO_2 in the atmosphere has remained at relatively stable levels. However, human CO_2 emissions over the past few centuries have upset this balance [7,8]. The increase of CO_2 concentration has some direct effects on the environment. For example, as the oceans absorb CO_2 from the atmosphere, it leads to acidification that affects many marine ecosystems [9]. However, the rise of CO_2 has a main impact on the environment provoking warmer temperatures.

To this end, the development of new technologies for the reduction of CO_2 emissions as well as the

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E-ISSN: 1929-6037/16

improvement of new technologies for CO_2 separation and capture [10] have been established as main priorities for scientists and governments worldwide. On the other hand, the ability to use the CO_2 by its transformation as a resource for the production of chemicals [11], materials (polymers) and fuels increase the necessity to dispose technologies for CO_2 separation. The current existing gas separation processes are mainly based on pressure swing adsorption (PSA), temperature swing adsorption (TSA), vacuum swing adsorption (VSA) and cryogenic separation (mainly for air separation) [12]. All these traditional techniques are characterized as highly energetic processes. The natural gas processing, the air separation, the helium and hydrogen recovery, the landfill gas recovery, the olefin/paraffin separation, the CO_2/N_2 separation are some of the many processes where membranes are candidates for use [13].

To this purpose, membranes can play an important role thanks to their ability to separate gases with different physical and chemical properties. One of the main targets for the membrane technology is the development of robust membranes with acceptable gas selectivity values and high permeabilities at the same time [14]. The advantage of the membrane technology to separate gas mixtures without high energy requirement makes this field more and more attractive. The materials that are mainly referred in the membrane technology are: polymeric membranes [15,16], carbon membranes [17], metal membranes [18], ceramic and zeolite membranes [19,20] and also mixed–matrix membranes [21–23].

As Hsieh and Ismail have classified the inorganic membranes [17,24], carbon membranes belong to the category of porous membranes (see Figure **1**). At the same category they also have been mentioned the metal, zeolites, oxide, alumina, zirconia and glass membranes. Additionally, silicon carbite, silicon nitride, titania, mica as well as cordierite are reported as promising materials for porous membranes production. Furthermore, the porous membranes are classified as asymmetric and symmetric depending on the anisotropic grade of the membrane structure. On the contrary, dense membranes made of palladium and its alloys, nickel, silver and stabilized zirconia, have been used mostly for gas separations. The main application of dense membranes is for highly selective separations, such as the hydrogen purification [25]. However, the dense membranes do not remarkably apply yet in the industry due to their low permeability compared to porous inorganic membranes and due to their high production cost. Therefore, the most known commercial inorganic membranes market is dominated by porous membranes [17, 26,27].

Among other fields of the membrane research, the gas separation processes and particularly the carbon dioxide separation is classified as one of the first priorities of the scientific community. Note that both polymeric and inorganic materials are good candidates

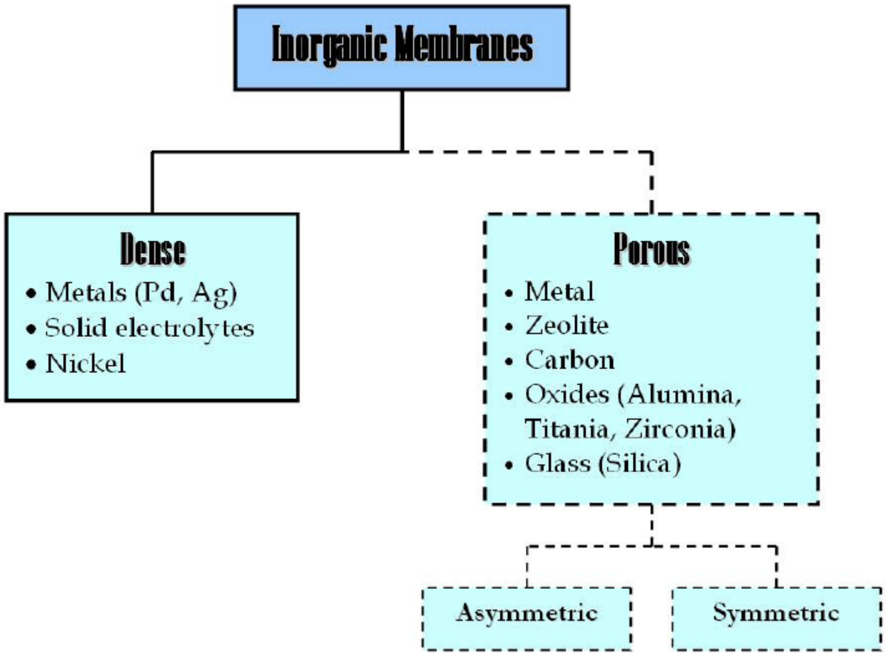


Figure 1: Inorganic membrane structures.

for CO_2 separation thanks to the remarkable separation mechanism of carbon dioxide [28]. In the present article special focus has been given to the recent remarkable results of the last decade regarding the CO_2 separation achievements in the case of carbon membranes.

2. CO_2 SEPARATION MEMBRANES

Carbon dioxide separation membranes are these membranes which are characterized by high fluxes of CO_2 compared to other feed gases. However, membrane gas separation (GS) technology is most of the time mentioned as potentially promising candidate for the CO_2 post–combustion capture and not as an already used technology. The main problem due to which membrane GS technology has not yet been established in industrial units is the low CO_2 concentration and pressure of the flue gas [29]. This fact became more difficult by taking into account the requested specifications by the International Energy Agency (IEA) in order to be a CO_2 capture technology acceptable for use. According to the IEA guidelines a CO_2 recovery ratio above 80% or 90% is required [30] and values below this do not offer a sufficient decrease in CO_2 released to the atmosphere. The permeate CO_2 mole fraction must also be in the range of 0.8–0.95, both to minimize the compression and transportation costs [31] and to prevent problems related to deep ocean or geological disposal [32]. Keep in mind that amine absorption processes easily achieve 99% CO_2 after condensation in the stripping tower (!!) [29].

Regardless of all these difficulties the efforts continue for the development of new membranes and materials for membrane GS technology application. The membrane GS technology has to supplant many other existing technologies before it can be acceptable by the final users. Some of the commonly used technologies for CO_2 separation/capture are the following [33]:

A. CO_2 Capture Schemes for Fossil–Fueled Power Plants

- Pulverized coal combustion CO_2 separation and capture process
- Gasification CO_2 separation and capture process
- Oxy–combustion CO_2 separation and capture process
- Chemical–looping combustion process

B. Carbon Fixation

- Forestation
- Ocean fertilization
- Photosynthesis process
- Mineral carbonation, natural or biomimetic
- In–situ CO_2 capture
- Hydrate–based separations

C. Carbon Separation Technical Options

- Amine absorption process
- Ammonium absorption process
- Dual–alkali absorption approach
- Molecular sieve adsorbent
- “Molecular basket” adsorbent for CO_2 separation
- Adsorption by activated carbon
- CO_2 adsorbents based on lithium compounds
- CO_2 capture based on membrane separation

This article is focused on the study of CO_2 separation by using carbon membranes. In order to be acceptable for CO_2 capture the candidate membrane has to satisfy a minimum number of properties, such as [34]:

- High CO_2 permeability
- High CO_2/N_2 selectivity
- Thermal and chemical resistance
- Plasticization resistance
- Aging resistance
- Cost effective
- Ability to be cheaply manufactured into different membrane modules

The plurality of industrial membrane GS, and liquid separations, applications are currently dominated by polymeric membranes. In the case of CO_2 separation/capture the recent research is directed towards the development of inorganic membranes. The advantages of inorganic membranes regarding the high temperature resistance, the aging resistance and the absence of plasticization phenomena have established them as one of the first priorities of the membrane research. However, both inorganic and polymeric membranes are expected to be more effective than conventional carbon dioxide separations [33,35,36].

3. POLYMERIC MEMBRANES

Generally polymeric membranes present higher permeability values than inorganic. This property can be attributed to the large free volume, the gaps between the polymer chains. Through them the molecules pass the membrane matrix from one side to the other. This free volume path depends on the material nature and the existence or not of cross linker ligands and/or any nano–filler material [22,23,37]. This is the main mechanism for gas separation in polymeric membranes and it is described as “solution–diffusion mechanism” [38] (see Figure **2**). Other mechanisms, including the molecular sieve effect and Knudsen diffusion, are also reported [39].

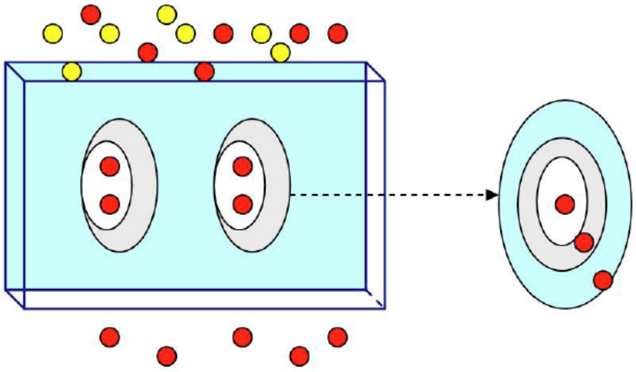


Figure 2: Solution–diffusion transport mechanism through polymeric matrices.

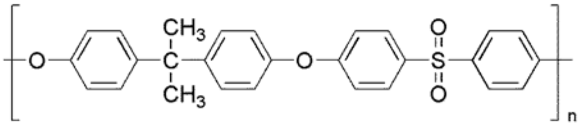
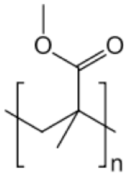
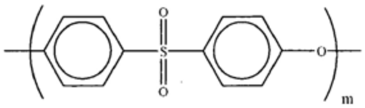
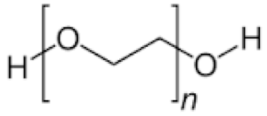
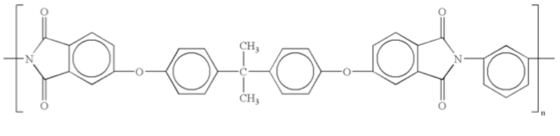
Regarding the CO_2 capture processes a crucial separation is this of CO_2/N_2. CO_2/N_2 separation factors of six “popular” polymeric membranes are summarized in Table **1** accompanied by their polymer chemical structure and their relative references. As it can be seen the achieved CO_2/N_2 selectivities are in the order of 10–30 and overall the permeation values are recorded also poor.

4. PREPARATION OF CARBON MEMBRANES

Carbon membranes are typically prepared by the controlled pyrolysis of thermosetting polymers. This way is allocated by four steps as described in Figure **3**. The pyrolysis conditions depend on the precursor material and of course on the suggested application at which the carbon membrane is aimed. An average ratio of the final carbonization (pyrolysis) temperature is between 500 and 1100 ^{o}C while the pyrolysis environment can be inert, for example helium or nitrogen, or oxidized, for example plasma. The above parameters combined with the heating rate and the isothermal zones conclude to the final structural characteristics of the prepared carbon membrane. According to this methodology many types of polymers are referred in the literature for carbon molecular sieve membranes preparation.

Afterwards, some important “stops” are mentioned in the carbon membrane preparation history in the period from 1994–2000, where many groups had been working in the field of carbon membranes from the pyrolysis of polymeric precursors. Chronologically, in 1994 Y. D. Chent and R. T. Yang [43] produced flat carbon molecular sieve membranes from pyrolysis of polyfurfuryl alcohol. The maximum pyrolysis temperature was 500 ^{o}C and the carbon molecular sieve membrane was formed by coating polyfurfuryl alcohol on the graphite support, followed by pyrolysis. This procedure was repeated until a film of the desired thickness was reached. The graphite disk was 1.75 in. (4.45 cm) in diameter and 3/16 in. (0.476 cm) thick and the reported diffusivity ratio for CH_4/C_2H_6 was approximately 10, which is typical of diffusion in molecular sieves. The diffusivity ratio for Knudsen or molecular diffusion (through cracks and crevices) would have been much lower, approximately 1.4. Two years later Wang Shusen *et al*. [44] produced an asymmetric carbon membrane in one–step. A thermosetting phenol formaldehyde resin film was chosen as a precursor. The film configuration was that of a fiat sheet which was formed by thermo–pressure molding process. The thickness of the precursor film was controlled in the range 0.05 to 0.10 ram. Pyrolysis of the polymeric film was conducted in an inert gas atmosphere. Then the activation gas, which contained 0.5–2.0% oxygen, was connected for the activation process. In order to create an asymmetric membrane structure, the key point was to keep a different oxidation atmosphere on the two sides of the membranes in the activation process. Single gas permeabilities for H_2, O_2 and N_2 were 5100, 2300 and 216 Barrer respectively, giving good permselectivity values, 23.61 for H_2/N_2 and 10.65 for O_2/N_2 attribute in molecular sieve separation mechanism. In 1997, Hidetoshi Kita *et al*. [45] published gas permeability and permselectivity data through poly(amidoamic acid)

Table 1: Typical Polymeric Materials for CO_2 Permeable Membrane Preparation

Polymeric material	Chemical structure	CO_2 permeance / permeability	CO_2/N_2 selectivity	Ref.
Polyimide (BTDA–TDI/MDI)		9.8 (GPU)	10.43	[40]
Polysulfone (PSF)		450 ($m^3/m^2{\cdot}s{\cdot}Pa$)	31	[28]
Poly(methyl methacrylate) (PMMA)		6.6 (10^{-15} $mol{\cdot}m/m^2{\cdot}s{\cdot}Pa$)	23	[41]
Polyethersulfone		665 ($m^3/m^2{\cdot}s{\cdot}Pa$)	24.7	[28]
Polyethylene oxide (PEO)		0.64 (10^{-15} $mol{\cdot}m/m^2{\cdot}s{\cdot}Pa$)	42	[41]
Polyetherimide (PEI)		90 (GPU)	27	[42]

and polypyrrolone carbonized membranes. Polypyrrolone is a step–ladder polymer with high thermal and chemical stability and because of the rigidity of the main chain of polypyrrolone, intersegmental packing and segmental mobility should be inhibited, providing a precursor for a carbon membrane with high gas permeability and permselectivity similar than other polymers such as polyimides. Poly(amidoamic acid) was stabilized in 150 ^oC for 12 hours and gives permselectivity values 210 for H_2/CH_4, 49 for CO_2/CH_4, 20 for CO_2/N_2 and 6.1 for O_2/N_2. Additionally higher ideal selectivity values were evaluated by the pyrolysis of polypyrrolone membrane and specially in the case where the carbonization temperature was 700 ^oC, for 1 hour, giving selectivities of 1200, 180, 39 and 11 for H_2/CH_4, CO_2/CH_4, CO_2/N_2 and O_2/N_2 respectively. Yoshihiro Kusuki *et al*. [46] studied carbon hollow fiber membranes, from polyimide precursor (*prepared by 3,3',4,4'–biphenyl-tetracarboxylic dianhydride (BPDA) and aromatic diamine*), in H_2, CO_2, O_2, N_2, CH_4, C_2H_4 and C_2H_6 gas separation performance. These asymmetric carbon membranes, which were prepared at 700°C, displayed $P(H_2)=1.0\times10^{-3}$ cm^3 (STP)/(cm^2 s cmHg) and $P(H_2)/P(CH_4)=132$. The membranes prepared at 850°C displayed $P(H_2)=1.8\times10^{-4}$ cm^3 (STP)/(cm^2 s cmHg) and $P(H_2)/P(CH_4)=631$. Fuertes and Centeno [47] prepared carbon molecular sieve membrane by carbonization of a commercial polyimide (*polyetherimide*) with high gas permselectivity for permanent gas pairs (O_2/N_2 7.4, He/N_2 121, CO_2/CH_4 25 and CO_2/N_2 15 at 25 ^oC). The same group [48] reported another similar work where carbon molecular sieve membranes were prepared. In this work asymmetric disk–shape macroporous carbon substrates were used as the support and BPDA–pPDA polyimide deposited over this support. The formatted membranes were carbonized at 550 °C under vacuum and tested in gas separation performance. The separation factors of this membrane were 5.5, 26.5, 37.4 and 18.7 for O_2/N_2, He/N_2, CO_2/CH_4 and CO_2/N_2 respectively whereas gas transport through the carbon membranes occurs according to molecular sieving mechanism.

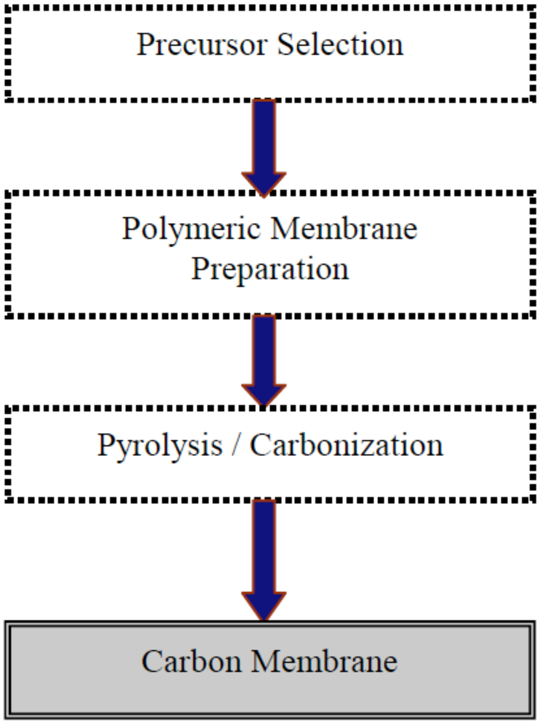


Figure 3: Diagram of the carbon membrane preparation route.

The same year, 1998, Katsuki Kusakabe *et al*. [49] developed BPDA–pp0ODA polyimide films on the porous alumina tube support, pyrolyzed at 700 °C and then oxidized under controlled conditions (*300 °C for 3 h ,O_2 fraction=0.05*). These membranes tested on CO_2/N_2 separation at 35, 65 and 100 °C and displayed separation factors from 15 to 51. Next year, Fuertes *et al*. [50] published their work, where both Matrimid and Kapton polyimides were selected as carbon molecular sieve precursors. In order to provide mechanical strength, macroporous carbon disks of 35 mm in diameter and 2.2–2.5 mm in thickness were used as support materials. From the millennium up today, many different polymers have been used as precursor materials in order to prepare high performance carbon gas separation membranes. For this purpose numerous pyrolysis environments, such as inert gases, oxidant curriers, vacuum etc, are reported, while the pyrolysis procedure fluctuates from low to high temperatures with a variety of heating rate protocols.

5. CARBON MEMBRANES FOR CO_2 SEPARATIONS

The usual pore sizes which are reported for carbon membranes are below molecular dimensions, <10 Å, and because of this characteristic carbon membranes are candidates for the separation of gases with very similar molecular sizes. In this case the main separation mechanism is molecular sieving while when the pore network is classified in the range of mesoporous then capillary condensation, surface diffusion and Knudsen diffusion may contribute to the gas flow through the membrane matrix. The four main transport mechanisms [51] for porous inorganic membranes are presented in Figure **4**.

In the case of a microporous carbon membrane the separation mechanism is the molecular sieving. This is the reason for the very high selectivity factors especially for gases with large difference in their molecular size. The existence of constrictions in the carbon matrix is responsible for the molecular size “windows” through which the gas molecular has to pass the membrane [52]. In this attitude, microporous carbon membranes are able to separate the gas molecules with similar effective size (kinetic diameter). According to this mechanism, the separation occurs by permeation of the smaller gas molecules through the pore network while the larger molecules are blocked. In the case of mixtures with large differences in their gas molecular size components both permeability and selectivity coefficients can be very high [53]. When the pore size and the constriction's size are enough larger than the molecule size then the narrow pore volume which is formed is the responsible for the adsorption capacity and the surface diffusion or/and the capillary condensation mechanisms contribute to the final separation factor [54].

The model of sorption–diffusion has been successfully used for the explanation of the gas permeation mechanism of molecular sieving media such as carbon molecular sieve and zeolite membranes [55]. Mainly by this model the mechanism of the CO_2 separation through carbon membranes has been explained [56]. Independently of the membrane type, the target of achieving high CO_2 separations remains the same for both scientists and industry. Regarding this purpose the works reported during the last decade are numerous. As it can be seen afterwards, the reported porous carbon membranes are configurated both as flat sheet and hollow fiber even if are characterized as symmetric or asymmetric. In general and in relevance with hydrogen selective

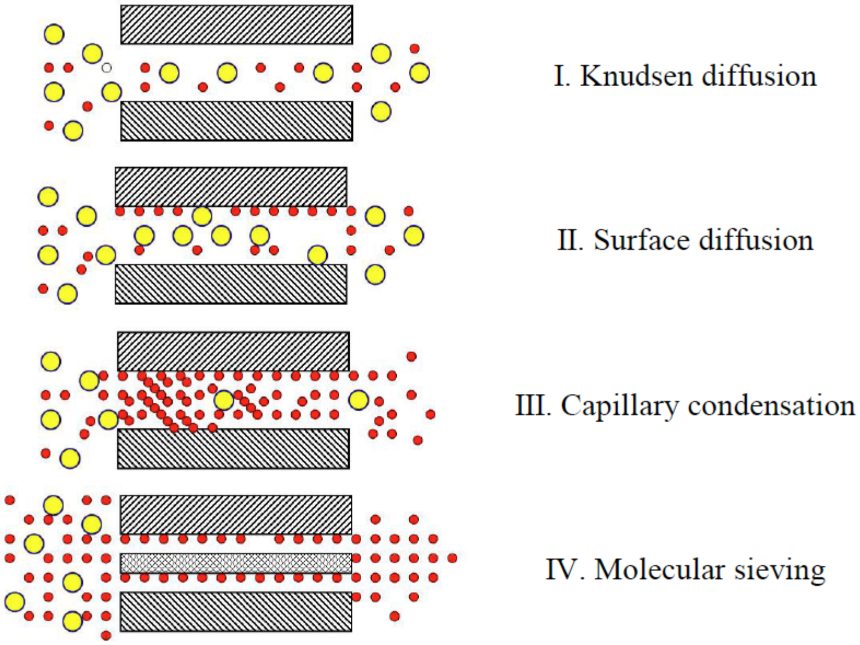


Figure 4: Gas transport mechanism through microporous membranes.

membranes [57], the carbon dioxide selective membranes must have at the same time the following characteristics: 1) high flux, 2) low cost and 3) high mechanical and chemical stability.

In 2005 Chung *et al*. [58] described a new concept of a dense, dual–phase membrane for selective permeation of CO_2 and O_2 at high temperatures. The reported membranes were synthesized by a direct infiltration method. Membrane preparation conditions were optimized to obtain stable, gas–tight dual–phase membranes at high temperatures (>450 °C). These dual–phase membranes exhibit low single–gas permeance for pure CO_2 and N_2 ($<5 \times 10^{-9}$ mol/s·m^2·Pa) in 450–650 °C but substantially higher CO_2 permeance for CO_2 mixed with O_2 at high temperatures. CO_2, after interacting with O_2, transports through the molten carbonate phase in a form of CO_3^{2-}, with electrons transporting through the porous metal support. With further improvement, the dual–phase membranes may be applied in producing O_2–enriched CO_2 streams for the oxyfuel combustion process. The concept can be also extended to prepare CO_2 perm–selective dense membranes for high–temperature CO_2 separation. Gas permeation properties through the studied membrane were measured at high temperatures (450–750 °C). CO_2 permeation flux was enhanced extensively by introducing O_2. The permeance of CO_2 in the presence of O_2 increases by increasing temperature (450–650 °C) and reaches a maximum value at 650 °C. The permeance of CO_2 with O_2 was 2.5×10^{-8} mol/s m^2 Pa, and the ideal separation factor of CO_2 over N_2 was about 16 at 650 °C. Under a CO_2/O_2 atmosphere, at high temperatures (>650 °C), the metal support can be oxidized to form $LiFeO_2$, causing a reduction in electronic conductivity of the metal phase and CO_2 permeance. The present metal–carbonate dual–phase membranes, if further improved, for example, using an electronically conducting oxidation–resistant porous inorganic support, can be used to produce an O_2–enriched CO_2 stream as the oxidant for the oxyfuel combustion process. The dual–phase membrane concept can be extended to prepare other dual–phase membranes, consisting, for example, of an oxygen ionic conducting phase and a carbonate phase, for permeation separation of CO_2 only at high temperatures.

During the same year, 2005, one more interesting work was published from Kim and his coworkers [59]. In this work carbon molecular sieve (CMS) membranes were prepared using aromatic polyimide (PI) and polyvinylpyrrolidone (PVP) polymer blends as precursor materials. As the researchers reported, the O_2/N_2 selectivity of CMS membranes pyrolyzed at 550 ◦C was in the range of 7–10, while the H_2/N_2, He/N_2, and CO_2/N_2 selectivities of the CMS membranes pyrolyzed at 550 ◦C were 52–64, 26–35, and 20–31 respectively. The CMS membranes pyrolyzed at 700 ◦C showed an O_2/N_2 selectivity of 10–12, an H_2/N_2 selectivity of 214–250, an He/N_2 selectivity of 89–112, and a CO_2/N_2 selectivity of 30–38. As a general result of their work the selectivity of the CMS membranes decreased by increasing the molecular weight of PVP in the blended polymer precursors, and the selectivity of the CMS membranes increased with pyrolysis temperature.

It was in 2007 when Skoulidas and his colleagues [60] used the tool of atomistic simulation in order to examine the adsorption and transport diffusion of CO_2 and N_2 in single–walled carbon nanotubes at room temperature as a function of nanotube diameter. They found that the adsorption isotherms are qualitatively very similar to the spherical and linear CO_2 models, especially at lower pressures. Also, they concluded that at zero pressure the spherical CO_2 model has a diffusivity that is about a factor of 2 larger than the linear model. The transport diffusivities for CO_2 in nanotubes with diameters ranging from about 1 to about 50 Å were found that are roughly independent of pressure while the observed diffusion mechanism does not look alike the Knudsen one. In the case of nitrogen they predicted a permeance that is a factor of 30 larger than the one observed in the experiment. Rui *et al*. [61] worked with other theoretical models for carbon dioxide separations and especially for CO_2/O_2 permeation through a dual–phase membrane consisting of mixed–conducting oxide ceramic (MCOC) and molten carbonate (MC) phases. Overall, this kind of theoretical works can be proved as a useful tool for the design and development of new well defined inorganic and composite GS membranes.

Another membrane type is the composite carbon/polymer membranes. Carbon structures, carbon nanotubes, graphenes, etc are used as filler materials into a polymer matrix. Here we haven't a typical carbon membrane but a mixed matrix membrane (MMM) usually with improved properties. By this way not only the mechanical strength of the MMM but also their permeability/selectivity characteristics [22,23] can be simultaneously improved. Cong *et al*. [62] used brominated poly(2,6–diphenyl–1,4–phenylene oxide) (BPPOdp) and both pristine single–wall CNTs (SWNTs) and multi–wall CNTs (MWNTs) in order to form polymeric nanocomposite membranes with BPPOdp. The prepared composite membranes had an increased CO_2 permeability but a similar CO_2/N_2 selectivity compared to the corresponding pure–polymer membrane. The CO_2 permeability increased by increasing the CNT content and reached a maximum of 155 Barrer at 9 wt% of SWNTs, or 148 Barrer at 5 wt% of MWNTs. The CO_2/N_2 separation performance was insensitive to the MWNT diameter or length and recorder from 28 up to 34.

In 2009 Hosseini and Chung published a paper entitled "*Carbon membranes from blends of PBI and polyimides for N_2/CH_4 and CO_2/CH_4 separation and hydrogen purification*" [63]. In this work the researchers started by the preparation of poly(benzimidazole) (PBI) and various polyimides regarding their capabilities in formation of homogenous blends. The developed, homogeneous, membranes were used as precursor materials for fabrication of gas separating carbon molecular sieve membranes. They found that compared to Torlon and P84, Matrimid is a better choice for the preparation of blend precursors in combination with PBI. They also suggest that carbon membranes derived from PBI/Matrimid are congruous candidates for H_2/CO_2 separation. They also report that the modification of precursors by chemical cross–linking prior to carbonization provides membranes with enhanced selectivity suitable for separation of hydrogen from both nitrogen and carbon dioxide. These developed membranes surpass several separation performance trade–offs with great potentials for various industrial applications including CO_2/CH_4 (α=203.95), H_2/CO_2 (α=33.44) and particularly N_2/CH_4 separation with unprecedented high permeability (P_{N_2}=2.78 Barrer) and selectivity (α=7.99) for this gas pair.

A different membrane type, the one of carbonate–ceramic dual–phase membrane is reported by Anderson and Lin [64] in 2010. More specifically, the dual–phase membrane was synthesized from porous $La_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (LSCF) supports infiltrated with a eutectic molten carbonate ($Li_2CO_3/Na_2CO_3/K_2CO_3$) mixture. They performed high temperature CO_2 permeation experiments for several membranes of varying thickness under low oxygen partial pressure ($P_{O_2}=10^{-4}$ atm). Using the carbonate–ceramic membrane the researchers achieved a CO_2/Ar separation factor of at least 225 at 900 ^{o}C in the case of the 0.375 mm thick membrane. The calculated activation energy for CO_2 permeation was from 86.4 up to 89.9 kJ/mol depending on the membrane's thickness.

The last decade, our group has also published a series of papers regarding the preparation and gas performance of carbon hollow fiber membranes. At all these works we started from a polymeric hollow fiber membrane precursor and after controlled pyrolysis processes we produced the final carbon hollow fiber membrane. As polymeric precursor we studied two different polyimide structures, the Matrimid® 5218 and the BTDA–TDI/MDI (P84) co–polyimide. In 2007 we studied the permeation properties of a Matrimid® 5218 hollow fiber membrane as well as the pore structural characteristics and the gas permeance performance of three derivates carbon hollow fiber membranes [65]. The higher permselectivities for CO_2/N_2 and CO_2/CH_4 were 23.6 and 22.5 respectively and the CO_2 permeance in the range of 17 GPU. The membrane with these characteristics was the derivative of the Matrimid® 5218 polymeric hollow fiber precursor which was produced by the pyrolysis, with a heating rate of 5 ^oC/min, up to 900 ^oC, at water saturated N_2 environment.

In 2008 we prepared a carbon molecular sieve hollow fiber membrane (CMSHFM) by using BTDA–TDI/MDI (P84) polymeric co–polyimide hollow fiber membrane as precursor membrane [66]. The CMSHFM was prepared using a simple inert environment pyrolysis protocol, at a final temperature of 900 ^oC. Pure nitrogen was used as inert pyrolysis environment. During the carbonization process the temperature increased from 298 to 373 K with a ramp of 2 ^oC/min. The hollow fibers were left at 100 ^oC for 30 min in order to remove absorbed water molecules. Then, the following pyrolysis protocol was applied: heating rate of 5 ^oC/min up to 900 ^oC, stabilization at the maximum temperature for 5 min and then controlled quenching with a cooling rate of 10 ^oC/min down to ambient temperature. By this procedure we achieved, at 25 ^oC, the maximum permselectivities of 42.8 and 38.9 for CO_2/N_2 and CO_2/CH_4 respectively. The CO_2 permeance/permeability was measured 5.4 GPU or 2.7 barrer. Note that these values are in good classification regarding the reported ones in the literature for carbon hollow fiber membranes.

Similar carbon hollow fiber membranes were prepared again by carbonization of co–polyimide (P84) polymeric precursor hollow fiber membranes in 2011 [54] and 2014 [67]. In these works both inert and activation environment were used for the preparation of micro–meso porous carbon membranes. In specific, by this methodology both microporous and mesoporous carbon hollow fiber membranes were produced, while gas permeability experiments occurred from a wide range of feed pressures, from atmospheric pressure conditions up to 60 bars. A recent work, which is also focused on the application, was published in 2013 from He and Hagg [68] where they proposed a general technical route of Design–Preparation–Construction–Operation–Integration (DPCOI) platform for hollow fiber carbon membranes (HFCMs) in order to promote the development of carbon membrane material for commercial applications. By using HYSYS simulation and their experimental data, they concluded that this environmentally friendly process using carbon membranes could possibly become a promising technology for CO_2 capture in the future.

A very important graph in membrane technology is the Robeson plot. Robeson [69,70], first in 1991 and then in 2008, is the researcher who made the plots of a series of gas couples, where the behavior of the selectivity factor as a function of the permeability value

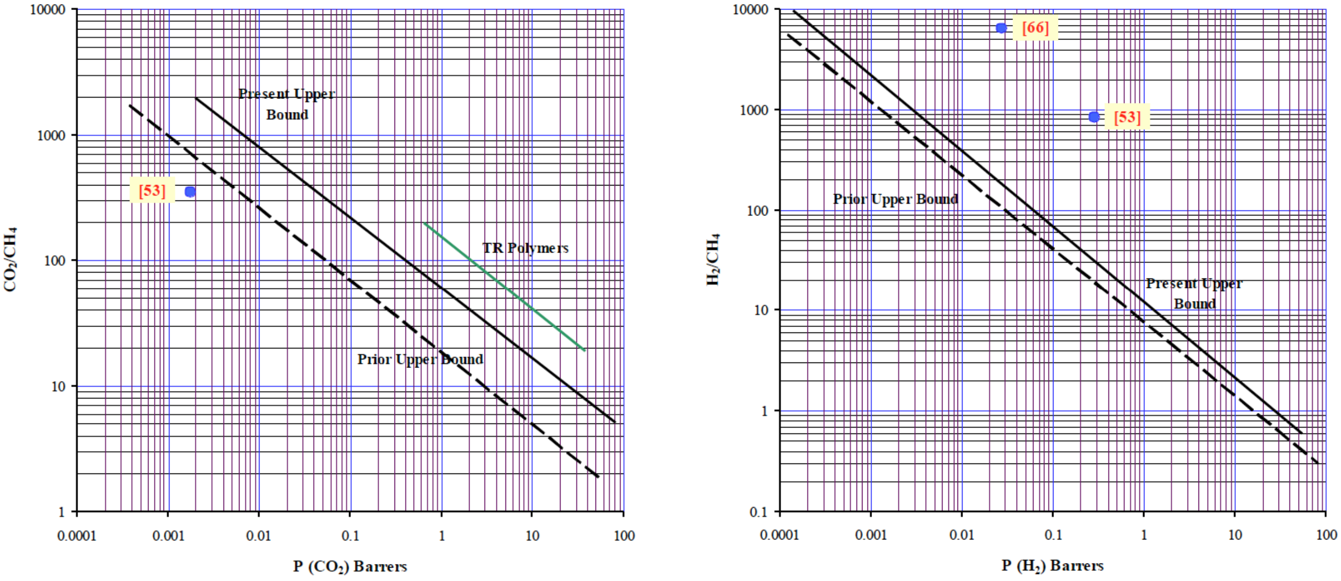


Figure 5: Present upper bound line (Robeson [70]) for CO_2/CH_4 and H_2/CH_4 separations.

Table 2: Carbon or/and Carbon Based Membranes' Configuration and their CO_2 Permeation Characteristics as are Reported in the Literature During the Last Decade (Note that 1 Barrer = 1×10^{-10} cm^3(STP) cm/cm^2 s cmHg)

Researcher(s)	CO_2 permeability/ permeance	Configuration	Year	Ref.
Chung *et al*.	~5 X 10^{-9} mol/s·m^2·Pa	Disk	2005	[58]
Kim et al.	500 Barrer	Flat sheet	2005	[59]
Cong *et al*.	130 Barrer	Flat sheet	2007	[62]
Favvas *et al*.	0.08 – 17.30 GPU	Hollow Fiber	2007	[65]
Favvas *et al*.	0.30 – 1.00 GPU	Hollow Fiber	2008	[66]
Hosseini and Chung	7 Barrer	Flat films	2009	[63]
Anderson and Lin	4.77×10^{-8} mol/m^2 s Pa	Disk	2010	[64]
Favvas *et al*.	0.30 – 116.00 GPU	Hollow Fiber	2011	[54]
He and Hagg	1050 Barrer	Hollow Fiber	2013	[68]
Favvas	31.80 – 573.10 GPU	Hollow Fiber	2014	[67]

of the more permeable gas is presented. A devious line called as "upper bound" indicates if the candidate membrane will have the possibility to be commercialized or not. Membranes which simultaneously satisfy the requested values of selectivity and permeability are located above the "upper bound" line. The most interesting gas couples which are reported in Robeson's plot are: O_2/N_2, CO_2/CH_4, H_2/N_2, H_2/CH_4, He/N_2, He/H_2, CO_2/N_2, N_2/CH_4, H_2/CO_2 and He/CO_2. As shown in Figure **5**, the gas permeation data obtained were inserted into the trade–off plot devised by Robeson [70] to show the upper bound limits for CO_2/CH_4 and H_2/CH_4. Regarding our experimental data, the optimum attainment for the CO_2/CH_4 couple was achieved in the case of CMS–900/60 carbon hollow fiber molecular sieve membrane where the permeability of CO_2 is $7.5\cdot10^{-3}$ Barrer and the calculated CO_2/CH_4 selectivity about 260 [53]. The position of this cycle still remains down to the prior upper bound but close to this. On the other hand, in the case of H_2/CH_4 Robeson's plot the achieved properties of two of our carbon hollow fiber membranes place these two membranes well above the present upper bound. Specifically, these two membranes present H_2 permeability ~16 and 0.16 and H_2/CH_4 ideal selectivity 850 [66] and 5500 [53] respectively.

Following Table **2** shows information regarding the CO_2 permeance behavior, the membrane configuration type and the responsible researchers' team of ten recent papers in the field of carbon membranes.

In general, carbon membranes are preferable thanks to their high gas separation characteristics, low cost, high packing density, chemical and thermal stability. However, the main reasons that make carbon membranes difficult to use at real industrial processes are two: their brittleness and the existence of sensitivity to high temperature in the presence of oxygen [71–73]. Nonetheless, carbon membranes have been applied in a large scale such as in the production of low cost and high purity nitrogen from air. Other separations that can be achieved by using carbon membranes are: hydrogen separations, from both gasification gas and methane mixture purification, hydrogen from waste gases and without further compression of the feed gas [74], propene/propane separation [75], olefin/paraffin purifications [76], helium recovery [53] etc. Another very interesting topic is the one of membrane reactor technology, where the combination of reaction and separation, at the same time, at high temperature conditions seems to be already a very hot topic in the field with promising results to be in the near future extensively applicable in the real market [77].

CONCLUSIONS

The continuous interest in the development of new carbon materials has made carbon membrane technology a promising solution for industry separation process. These materials consist, as membranes, mainly of four major configurations: flat, supported on tube, capillary and finally, hollow fiber. Given the fact that carbon dioxide must be reduced at the earth atmosphere, one of the most developing technologies is the membrane technology. To this purpose, carbon membranes have great potential to be used widely in the gas separation processes, especially in CO_2 separations. Nowadays, hollow fiber membranes are the most used membrane geometry thanks to their high surface area per unit volume of membrane module and this is the reason that a high focus has been concentrated on the development of carbon hollow fiber membranes. It is no coincidence that carbon membranes, with optimum structural and permeation characteristics and advantages will compete with polymeric membranes and many other porous inorganic membranes. Conclusively, we must keep in mind that, much research and development effort is yet needed in order to commercialize carbon gas separation membranes in the international market.

ACKNOWLEDGEMENTS

The present work is a result in the framework of NSRF. The “NANOSKAI” Project (Archimedes Framework) of the Eastern Macedonia and Thrace Institute of Technology is co–financed by Greece and the European Union in the frame of the operational program “Education and lifelong learning investing in knowledge society”, of the Ministry of Education and Religious Affairs, Culture and Sports, NSRF 2007–2013.

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Received on 07-12-2015 Accepted on 15-01-2016 Published on 06-04-2016

DOI: http://dx.doi.org/10.6000/1929-6037.2016.05.01.1