10

Study of Gas Transport Phenomenon in Layered Polymer Nanocomposite Membranes

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Abstract

The transport of mass through a variety of polymer membranes has been reported over the last few years. Researchers have attempted a range of samples from pure polymer to modify its structure by blending, filling micro/nanoparticles in the polymer matrix, synthesizing mixed matrix membranes, etc. The change in free volume due to modification in polymer chains directly alters the transport mechanism. However, very little attention has been paid to layered polymer composites. In this work, the transport behavior of different gases across the metal coated membrane has been studied and compared with that of standard polycarbonate membrane. Deposition of nanolayer affects the transport properties due to the modification in sorption-diffusion process. Permeability coefficient is the product of diffusivity coefficient (D) and solubility coefficient (S). A platinum-palladium (Pt-Pd) alloy thin film of around 8 nm was coated on thick polycarbonate substrate using sputtering technique to make layered polymer nanocomposite membrane. The tests were carried out at upstream pressure of 30 psia. Gases used for the study herein were He, H_2, CO_2, O_2, N_2 and CH_4 and the selectivity was calculated for a particular gas pair. Pure

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gas permeability coefficients were calculated using constant volume/variable pressure method at 35 °C temperature.

***Keywords*:** Gas transport, thin film coating, selectivity, composite membrane

10.1 Introduction

Membrane science and technology has led to the development of industrial applications by technologies such as microfiltration, ultrafiltration, reverse osmosis, electrodialysis, gas transport and pervaporation. In addition to industry, membrane technology has also focused attention on applications in the medical field such as artificial lungs, artificial kidneys and controlled drug delivery systems [1, 2]. The separation process concerns material having some specific properties (chemical or physical) that can exist under the operating conditions [3]. Polymer membranes are widely used to perform mass transport process in the chemical industry due to a wide range of applications in fluid separation. Additionally, the polymer membrane can be produced cost-effectively and the separation process based on membrane is environmentally friendly [4]. The flow of gas molecules across the membrane is influenced by several factors: gas properties, material used to design the membrane, morphology of membrane structure and operating conditions [5]. The permeation as well as separation properties can be improved by chemically modifying the structure or by physical modifications. Different modifications are practiced to improve the performance of membranes like mixed matrix, cross-linking, grafting, polymer blending, making composite or hybrid membrane [6–9].

To fulfill the high gas barrier property, polymer surface can be modified by depositing thin film coating. Cellulose coating on silica-carbide improves gas flux permeation for H_2, CO_2, O_2 and N_2, and even gives better selectivity compared to virgin material [10]. A silica layer coated on polymer membrane reduces permeation flux, which improves the selectivity [11]. Metal coating can reduce permeability, which enhances the separation factor, or in some cases it may rise due to a defect in the coating layer [12]. Ti coating on polycarbonate membrane reduces the permeability of H_2 and CO_2 and simultaneously increases the selectivity of H_2 [13]. In the last decades, H_2 has become a major energy source, which needs to be extracted from water, hydrocarbons, coal or natural gases [14]. In addition, H_2 fuel is considered to be a clean energy source because the by-product of its combustion produces water. Its production from hydrocarbon forms CO_2, which is one of the gases responsible for the greenhouse effect. Pd is considered highly selective material to attract H_2 molecule. Even its composite form performs better for separation of H_2 from mixed state with other gases [15]. For this purpose Pd membrane have received growing consideration due to its separation ability with respect to all other gases [16]. Moreover, Pd membrane is unambiguously selective to H_2, which is a favorable response to separate it from other gases [17]. But several factors limit the gas permeation application for pure Pd membrane such as its high cost and irreversible damage by sulfide formation. Moreover, above 450 °C temperature it is subjected to deactivation by carbon compounds and below 300 °C temperature, when exposed to pure H_2, hydride formation takes place. To overcome this difficulty, Pd can be alloyed with other metals. For this purpose Pt gives better performance with Pd [18]. Herein, Pt-Pd alloy has been coated over polymeric support.

The supportive polymer has been chosen in such a way that it can provide good thermal resistance and mechanical strength. For this purpose polycarbonate (PC) is coated by Pt-Pd alloy and suspended for the gas permeation process, as explained in [19, 20]. Polycarbonate provides better backbone rigidity so that it permeates faster rate flow of gas flux, therefore it was chosen as polymer matrix [21]. H_2 and CO_2 permeability increase with an increase in temperature for polycarbonate as the diffusivity increases [22, 23]. Moreover, CO_2 treated polycarbonate enhances the solubility, which is credited to the plasticization effect [24]. In this study, gas permeability of pure PC as well as Pt-Pd coated PC has been compared with respect to their kinetic diameter for various gases. The key parameter for permeability measurements is the gas flux through the given membranes, which has been measured by a constant volume/variable pressure system [25]. Our goal was to develop a membrane which would have improved permeability along with selectivity. In this study, a new type of layered hybrid membrane was synthesized, consisting of thin inorganic bridged platinum-palladium layer deposited onto the surface of polycarbonate.

10.1.1 Transport Phenomenon

The permeability of gas through dense polymer membrane depends on the solubility and diffusivity of the reentrant. Figure 10.1 explains the steady-state permeation of gas molecules through polymer membrane. This process is classified into three steps:

- Absorption of gas molecules at upstream side;
- Diffusion through membrane with respect to pressure gradient;
- Desorption at downstream side.

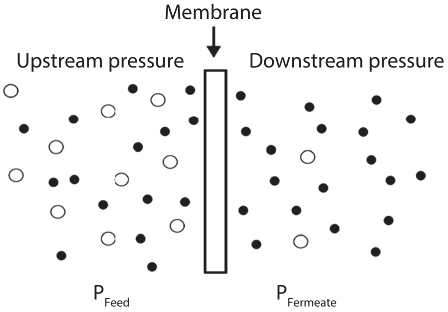

Figure 10.1 Transport of gas through membrane.

The upstream side at high pressure provides feed gas and the downstream side at low pressure, permeate gas. The gas molecules first dissolve into upstream side, diffuse across the membrane and desorb from downstream side.

Gas permeation is the flux of gas molecules through an object normalized by the pressure gradient. The driving force behind the transport of gas molecules which involves sorption, diffusion and permeation, is mainly due to the pressure difference between two phases. The principle of transport phenomenon is explained by Fick's first law of diffusion according to which the flux J in the direction of flow is directly proportional to the concentration gradient $\left(\frac{dC}{dX}\right)$ given by the equation:

$$J = -D\left(\frac{dC}{dX}\right) \tag{10.1}$$

where D is the diffusion coefficient. The equation is only applicable for steady-state diffusion process. Fick's law gives the linear relationship between the flux of substance diffusing through the membrane and the concentration gradient between two phases [4, 12].

Gas permeability coefficient P of a pure gas for polymeric membrane is given by the following formula:

$$P = \frac{\mathbf{JL}}{\mathbf{P}_2 - \mathbf{P}_1} \tag{10.2}$$

where J is the steady state flux across the membrane, L is the membrane thickness, P_2 is the upstream pressure and P_1 is the downstream pressure [4]. Permeability is expressed in barrers, where 1 barrer = 10^{-10} [cm^3(STP) cm/(cm^2 s cm-Hg)]. For dense polymeric membrane, the downstream pressure is much less than the upstream pressure. Gas permeation is explained by a simplest solution-diffusion model as follows:

$$P = D\,S \tag{11.3}$$

where D is the diffusion coefficient and S is the solubility coefficient. Diffusion coefficient can be estimated by the intercept of steady state line and the time axis of downstream pressure versus time curve:

$$D = L^2 / 6\theta \tag{11.4}$$

where θ is the time lag, L is the membrane thickness and D is diffusion coefficient. Solubility coefficient can be determined by the ratio of permeability over diffusion coefficient [29].

The selectivity of a polymer membrane for gas pair A and B is defined as the ratio of their permeability:

$$\alpha = P_{\mathrm{A}}/P_{\mathrm{B}} \tag{11.5}$$

Permeation across membrane takes place via solution diffusion process, i.e., feed gas absorbed at upstream pressure decided by chemical affinity of penetrated gas with polymer material of membrane. Further, the reentrant gas diffuses inside the polymer matrix within the available free volume and finally desorption occurs at downstream side. For dense membranes permeability is the product of diffusion coefficient and solubility coefficient; hence modification in either diffusion coefficient or in solubility coefficient alters directly to the overall gas permeability. Therefore, selectivity of gas A relative to gas B can be expressed in terms of ideal selectivity defined by the relation:

$$\alpha_{AB} = \frac{P_A}{P_B} = \frac{D_A}{D_B} \cdot \frac{S_A}{S_B} \tag{11.6}$$

where the ratio D_A/D_B is described as selectivity of diffusion and ratio S_A/S_B is viewed as solubility selectivity. Generally, glassy polymers are hard and brittle and have restricted chain mobility. The diffusion coefficient decreases with an increase in the size of molecule. This decrease of diffusivity depends on the flexibility of polymer backbone. For more rigid polymer structure, higher selectivity is achieved for a given gas pair. The diffusion selectivity is a controllable factor for most of the glassy polymers. Therefore, smaller molecular transport is favored. Whereas, the solubility of gases increases with molecular size due to increase in intermolecular force between gas and polymer [1].

10.1.2 Metal Coating

Metal coating over polymer membrane uplifts the permeation as well as performance of the membrane. This hybridization improves surface interaction of gas molecules, which leads to better thermal properties and mechanical strength [26]. The gas transport parameter is also influenced by polymer chain flexibility, segmental mobility and interaction with penetrant. These three factors can be controlled by surface coating as the feed gas does not interact directly with the host material. Before its transport through the polymer film, it diffuses through the metal coating which serves barrier properties. Coating can improve the selectivity of CO_2/CH_4 separation performance under different operating conditions when exposed to polysulfon mixed matrix membrane with silicate coating [30]. Palladium is extremely selective for H_2 gas but at low temperature, if Pd is exposed to H_2, it can become locked inside the Pd lattice, which causes stress inside the membrane and failure of membrane. The remedy to this problem is to dope Pd with other metals such as silver or platinum. The doping will improve the interaction with gases and protect the lattice structure. The transport of H_2 through Pd membrane occurs in six steps [31]:

- Dissociation of H_2 molecule at gas/metal interface;
- Sorption of atomic hydrogen on membrane surface;
- Dissolution into palladium matrix;
- Diffusion through membrane;
- Recombination of atomic hydrogen into molecule at gas/metal interface;
- Desorption of H_2.

Moreover, charge transfer occurs as the gases are interacted with metal surface, which may play a vital role in improving sorption of gas molecules [8, 27].

10.2 Experimental

10.2.1 Fabrication of Nanocomposite Membrane

Solution cast method, which is easy and reliable, was used to develop polycarbonate membrane [28]. Initially, the desired quantity of bispheneol A (polycarbonate), which is commercially available, was dissolved in dichloromethane and stirred overnight at room temperature using a magnetic stirrer. The mixture was poured onto a flat-bottomed glass surface covered with glass ring. The system was allowed to evaporate the solvent overnight for complete removal of the solvent. The next day, the membrane was taken for the measurements and commercially available film was also used for study. Uniformity in membrane thickness was confirmed by several thickness measurements using a digital thickness meter. Average thickness 180 (±2) μm was purchased for permeability calculation. Standard vapor deposition sputtering technique has been used to make layered composite membrane at ICMB facility of University of Texas at Austin, TX, USA. In this technique the target and substrate material were placed in a vacuum chamber. Pt-Pd thin film of about 8 nm thicknesses was deposited over PC thin film. In this technique, the polycarbonate substrate and target material were placed in high vacuum of 10^{-6} torr [32].

10.2.2 Gas Permeability Test

Figure 10.2 shows a schematic diagram of cell permeation in which membrane is placed normal to the upstream pressure. The membrane is placed under metal support inside the permeation cell and its diameter is the same size as the inner diameter of the cell. As the flat membrane is placed inside the cell, the system is divided into upstream and downstream compartments. The upstream side is at higher pressure from which feed gas enters into the cell and the downstream side is at lower pressure from which gas is permeated. O-rings are placed inside the cell at the upstream

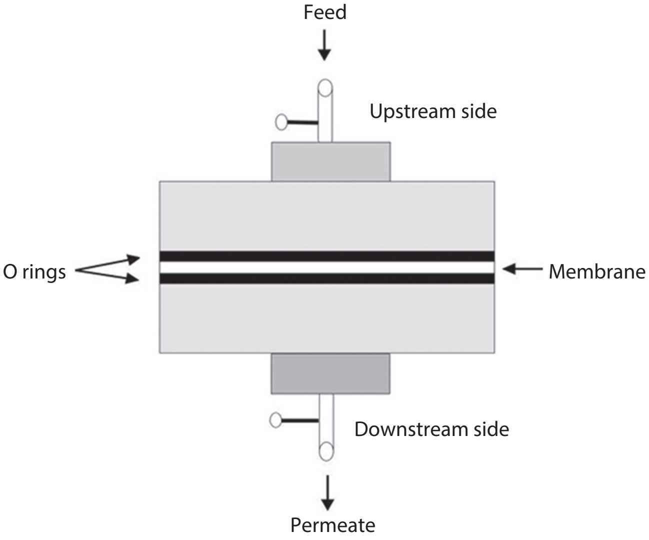

Figure 10.2 Schematic diagram of gas permeation cell.

and downstream sides of the membrane to prevent gas leakage as well as exchange of air particles from outer atmosphere. Thus, only feed gas from the higher pressure side can permeate within the membrane which is collected towards the downstream side.

The key parameter for permeability measurements is the gas flux through the given membranes. As illustrated in Figure 10.3, a constant-volume variable pressure system measures permeate flux by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer.

First of all, the whole system is exposed to vacuum prior to perform the experiment. This action can remove any volatile impurities inside the system. To degas the film, the upstream as well as the downstream volume are evacuated. Then the valves connecting the permeation cell to the vacuum pump are closed. Now a slow pressure rising towards the downstream volume is observed, which is called the leak rate of the system. The leak rate should be around 10 times less than the steadily permeating gas flow. Then the feed gas is introduced within the cell towards the upstream side of the membrane and at the downstream side the pressure rise is recorded as function of time [25]. The permeability of He, H_2, CO_2, O_2, N_2 and CH_4 was measured using a constant volume/variable pressure method. The tests were carried out at constant 30 psia upstream pressure and constant temperature of 35 °C. For pure polycarbonate, the surface area and thickness of membrane were 1.97 cm^2 and 180 μm respectively. For Pt-Pd coated PC, the surface area was 0.6529 cm^2. A constant-volume/variable pressure system measures permeate flux by monitoring the pressure increase of collected permeate gas in a closed

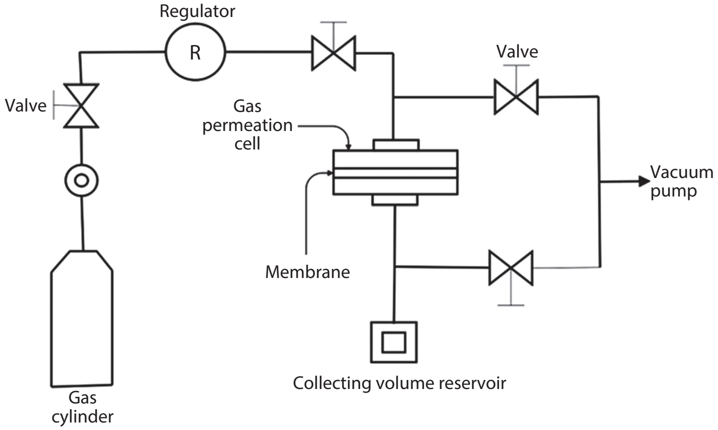

Figure 10.3 Constant volume/variable pressure system setup.

volume using a pressure transducer. Membrane was placed in such a way that the coated side was at the upstream, which was purged with penetrate gas, and the downstream side of the permeation cell was evacuated with the help of a rotary pump before taking the individual measurements. The following formula was used to calculate the permeability:

$$P = \frac{Vd}{pART}(m1) - (m2) \tag{10.7}$$

where *P* is the pure gas permeability, *V* the total volume of the downstream side, i.e., 39.43 cm^3, d the thickness of the membrane, *p* the upstream absolute pressure in psig, m1 the steady state slope of the downstream pressure versus time calculated in cm-Hg/s, and m^2 the leak rate calculated in cm-Hg/s which was maintained at 10^{-7} cm-Hg/s during the experiment [25]. Permeability was measured in barrers, where 1 barrer = 10^{-10} {cm^3 (STP) cm/(cm^2 s cm-Hg)} [25].

10.3 Results and Discussion

In Table 10.1, the comparison of permeability of all experimental gases within their kinetic diameters is shown. It is obvious that the decrease of gas permeability is proportional to the degree of kinetic parameter of gas molecule. The gases with larger kinetic diameter experience lower permeability. Permeation behavior was found in the following order: He > H_2 > CO_2 > O_2 > N_2 > CH_4, for both the pure and Pt-Pd layered PC membrane. All the data were statistically analyzed after steady state towards the downstream side. Hydrogen and helium have excessively fast permeation even at low upstream pressure, hence it is difficult to find the steady state for such gases. Compared with reference data for pure polycarbonate, the permeability of He has decreased in this experiment, which can promote its selectivity. It can be seen that He gives the highest permeability with respect to other gases that have a lot smaller kinetic diameter, while for N_2 and CH_4 it reduces permeability. Hence, according to the literature survey and the performance of this experiment, the transport of molecules from matter totally depends on their size. Compared with H_2 reference data, its permeability increases, which enhances its application as an energy tool. Additionally, as shown in Table 10.1, the percentage increase of kinetic diameter and the permeability also increase in the same manner. There is no further change in the permeability for CO_2, O_2, and N_2 gases with respect to the references given in Table 10.1. Moreover, for H_2 and He the percentage due to leakage

Table 10.1 Permeability of pure PC compared with leak test.

Gases	Kinetic diameter (Å)	Permeability of PC (barrer)			% change due to leakage
		With leak test	Without leak test	Reference data	
He	2.6	13.56	13.64	17.6 [21]	0.6%
H_2	2.89	13.23	13.31	11.5 [21]	0.6%
CO_2	3.3	8.64	8.72	8.4 [19]	0.9%
O_2	3.46	3.26	3.35	3.8 [20]	2.6%
N_2	3.64	0.36	0.44	0.44 [20]	18%
CH_4	3.8	–	–	0.4 [19]	–

is the same, as they are smaller in magnitude. But again, a rise in molecular size affects the leakage. For CO_2, 0.9% permeability arises without leakage and for O_2, its 2.6%, which provides evidence for the effect of molecular size. Finally, N_2 gives the highest percent change in permeability due to leakage, which proves that larger molecular size restricts its leakage. The permeability coefficient decreases as the kinetic diameter increases.

The same trade-off is followed by Pt-Pd coated PC membrane. There is marginal change which can be acceptable due to leakage in the permeability of pure PC. Moreover, under the same operating conditions Pt-Pd coated PC shows enhanced permeability for all gases with regards to their kinetic dimension given in Table 10.2. For all gases, Pt-Pd coating tends to increase the permeability compared to pure PC. This is due to an increase in solubility by surface coating and it is assumed that a rise in solubility may be due to the catalytic effect of Pt-Pd coating. For H_2 and He, permeability rises with nearly the same percentage. As previously stated, for H_2 interaction with Pt-Pd surface, Pd is considered an attractive tool for H_2 molecule.

The polycarbonate used as host material in this study was glassy polymer. In glassy state, the molecular motion is due to chain segments and substitute group. As the segmental motions are more confined, the selectivity is performed by enhanced mobility selectivity. It is shown in Table 10.3 that the permeability decreases and in Table 10.4, the diffusion selectivity rises due to coating. The selectivity for almost all gases decreases due to the coating effect, which follows the trade-off relationship for glassy polymers. Selectivity of different gas pairs is shown in Figure 10.3, which shows a decrease for layered composite membrane as compared to pure

Table 10.2 Permeability of pure and Pt-Pd coated polymers.

Gases	Kinetic diameter (Å)	Permeability (barrer)		% change by coating
		PC	PC/Pt-Pd	
He	2.6	13.64	17.37	27.38%
H_2	2.89	13.31	16.91	27.06%
CO_2	3.3	8.72	12.95	48.46%
O_2	3.46	3.35	10.66	218.64%
N_2	3.64	0.44	2.3	427%
CH_4	3.8	0.4	1.59	297%

polycarbonate; however, permeability of all the measured gases increases for nanocomposite membrane, which follows the trade-off relation of glassy polymer. For gas pairs H_2/N_2, CO_2/N_2 and O_2/N_2 the selectivity is reduced by 76%, 72% and 39% respectively.

In all three of these gas pairs, N_2 is the common gas even though the reduction in selectivity for the first two gas pairs has a change of barely 4%, whereas compared to these two pairs the O_2/N_2 selectivity reduction is 39%. This is due to the solubility selectivity, which is reduced by 77% for CO_2/N_2 and 49% for O_2/N_2. Here the reduction in solubility selectivity plays a vital role in changing the overall selectivity compared to pure polycarbonate membrane. As in gas pairs H_2/O_2 and CO_2/O_2, O_2 is a mutual gas which shows reduction in selectivity by 60% and 53% respectively. This can reduce the selectivity of H_2 and CO_2 by nearly the same amount. Selectivity by solubility for CO_2/O_2 is reduced by 54%. In the gas pairs H_2/CH_4 and CO_2/CH_4 the reduction in selectivity is 68% and 69% respectively, whereas for O_2/CH_4 and N_2/CH_4 it is 20% and 32% respectively, although CH_4 is a mutual gas. This may be due to the small kinetic diameter of H_2 and CO_2 compared to O_2 and N_2.

The selectivity for H_2/CO_2 was not more affected due to metal coating, as shown in Table 10.3. Pt-Pd coating plays an important role in enhancing the permeability of hydrogen and carbon dioxide by maintaining their selectivity. This is especially true for Pd, which absorbs H_2 in large amounts, but there are no more specific changes in the H_2 permeation. It can be seen from Figure 10.4 that selectivity was highly affected by H_2/N_2 gas pairs, which shows that the selectivity for PC/Pt-Pd is reduced 76% compared to pure PC due to coating. Selectivity for H_2/O_2 gas pair does not decrease

Table 10.3 Selectivity due to permeation.

Gas pair	Selectivity		% Change*
	PC	PC/Pt-Pd	
H_2/CO_2	1.52	1.3	14%
H_2/O_2	3.97	1.58	60%
H_2/N_2	30.25	7.35	76%
H_2/CH_4	33.27	10.63	68%
CO_2/O_2	2.6	1.21	53%
CO_2/N_2	19.81	5.63	72%
CO_2/CH_4	21.8	6.7	69%
O_2/N_2	7.61	4.63	39%
O_2/CH_4	8.38	6.7	20%
N_2/CH_4	1.1	1.45	32%

*For all gas pairs the selectivity decreases and only for N_2/CH_4 does it increase by 32%.

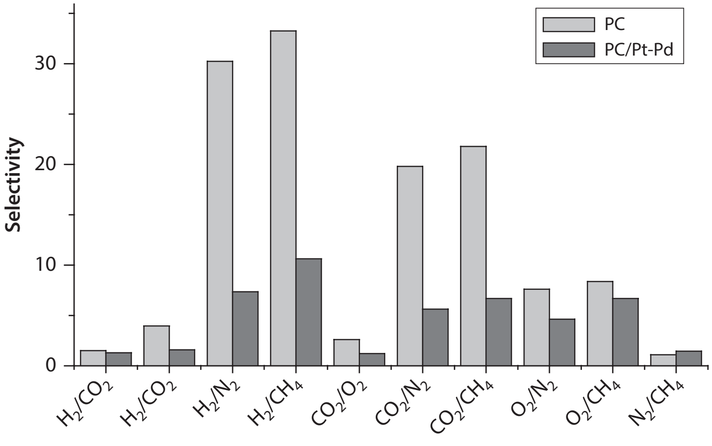

Figure 10.4 Selectivity comparison of pure PC and Pt-Pd coated PC.

in large amounts, i.e., 14%, which shows that it even is nearly stable due to surface modification. There is a prominent coating effect which promotes both permeability as well as selectivity for N_2 and N_2/CH_4 respectively. This results in the application of separation of CH_4 from natural gas.

Table 10.4 Selectivity due to diffusion and solubility.

	Selectivity by diffusion			Selectivity by solubility		
Gas pair	**PC**	**PC/Pt-Pd**	**% Change***	**PC**	**PC/Pt-Pd**	**% Change***
CO_2/O_2	0.88	0.9	2%	3.01	1.36	54%
CO_2/N_2	1.4	1.56	16%	17.33	3.98	77%
O_2/N_2	1.6	1.73	8%	5.76	2.93	49%

*Selectivity by diffusion increases whereas solubility selectivity is reduced.

10.4 Conclusion

The hybrid membrane fabricated by Pt-Pd metal coating permeates comparatively more gas flux than pure polycarbonate membrane. The constant volume/variable pressure system used for this study provides accurate data for calculation.

The conclusion is explained as follows:

- The above study shows that the permeability from hybrid membrane is directly proportional to the kinetic diameter of gas molecules.
- The leakage does not affect the gases having smaller kinetic diameter; as the kinetic diameter rises, the permeability difference due to leakage also increases.
- Permeability increases for all the gases but for N_2 there is a large difference in the permeability achieved by coating.
- The highest change of permeability due to coating has been recorded for N_2 gas compared to other gases and it is selective for N_2, as its selectivity increases for N_2/CH_4 gas pair as compared to other gases. This result is applicable for separation of N_2 with CH_4 from natural gas.

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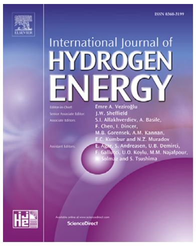

Metal coated and nanofiller doped polycarbonate membrane for hydrogen transport

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ABSTRACT

The modification in the polymeric membrane combined with metallic film as well as composites with inorganic nanofiller can be used for separation of various gases, with hydrogen gas as it is widely used as fuel material. The change in free volume due to modification in polymer chains alters the transport mechanism. In this work, the transport behaviour of H_2 across the different metal coated and nanocomposite membrane has been studied and compared with that of standard polycarbonate membrane. Transport properties changes due to the modification in the composition of nanofiller. A Pt–Pd alloy thin film and iridium thin film of around 8–10 nm was coated on polycarbonate substrate using sputtering technique to make layered polymer nanocomposite membrane. Moreover, SiO_2 nanocomposites with 10 wt% and 15 wt % were prepared by solution casting method and the uniform dispersion of silica nanoparticles was obtained by sonication before casting the membrane. Further, the tests were carried at constant upstream pressure 30 psi and at constant temperature 35 °C using constant volume/variable pressure method.

Introduction

Since last many decades hydrogen has become major energy source, it is necessary to extract it from water, hydrocarbons, coal or natural gases. In addition, hydrogen fuel is considered as clean energy source because its by-product by its combustion produces water. Its production from hydrocarbon forms CO_2 which is one of the responsible gases for greenhouse effect. Pd is considered highly selective material to attract H_2 molecule. Even its composite form serves better performance for separation of H_2 from mixed state with other gases [1,2]. The filtration of fair hydrogen gas requires semi permeable form of rigid material which can be applicable to separation of small species. Membranes science and technology leads to the industrial applications such as microfiltration, ultra-filtration, reverse osmosis, electrodialysis, gas transport, and pervaporation [3]. Polymer membranes are widely used to perform mass transport process in chemical industry due to wide range of applications in fluid separation. In addition to this, polymer membrane can be produced cost efficiently and the separation process based on membrane is environment friendly [4,5]. The polymer material used here is bisphenol-A polycarbonate which serves better physical as well chemical properties to its respected applications. It also provides better thermal stability, dimensional stability, mechanical strength, optical transparency, toughness and the most important it is cheaper in cost which makes its bulky applications in the industrial field [6,7]. Being glassy polymer, polycarbonate (PC) must face trade-off

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challenges for selectivity-permeability mechanism. As the permeability and selectivity both are the effective parameters for membrane performance, the modification in the structure property may defeat the trade-off challenges. Different modifications have been performed to improve the performance of membranes such as cross linking, grafting, irradiation, electron beam bombardment, etching [8–11] etc. Irradiation over the host polymer membrane can influence both permeability as well as the selectivity [12–14]. Polymer blending, mixed matrix, composite, layer deposition in polymer membrane can modify the polymer membrane to hybrid membrane material. This alteration can offer potential reward not only to the gas transport application but also in other industrial applications [9,15,16]. Hydrogen affinity to certain metallic membrane supports its flow but resist the penetration of other gases. Palladium (Pd) gives highest permeability as well better selectivity comparative to other membrane materials and at higher temperature exhibits good mechanical strength [17]. Pd is extremely selective for H_2 gas but at low temperature if H_2 is exposed to Pd, it can be locked inside the Pd lattice which cause stress inside the membrane and failure of membrane. The remedy of this problem is to dope Pd with other metals such as silver or Platinum. The doping will improve the interaction with gases and protect the lattice structure. Moreover, charge transfer occurs as the gases are interacted with metal surface which may play vital role to improve sorption of gas molecules [9,18]. Metal coating reduces permeability which enhances the separation factor or in some cases it may raise permeability due to defect in coating layer [19]. Nowadays it has been proved that Pd membranes have received growing consideration due to its separation ability. Also, Pd membrane is unambiguously selective to H_2 which is a favourable response to separate it from other gases [2,20]. But several factors limit the gas permeation application for pure Pd membrane such as its high cost and its irreversible damage by sulphide formation. Moreover, above 450 °C temperature they subject to deactivation by carbon compounds and below 300 °C temperature, when exposed to pure H_2, hydride formation takes place. To overcome this difficulty, Pd can be alloyed with other metals. For this purpose, Pt gives better performance with Pd [21]. Pd nanoparticles give better performance with CNTs in improvement of H_2 sensing. The sensor performance increases with increase in environmental temperature which improve hydrogen detection and mass production stability [22]. Pt alloyed with other metals modifies legend structure of Pt which results in weakening of CO adsorption on Pt. The poisoning effects of carbon monoxide can be filtered due to its inability to fully occupy the vacant sites on Pt nanoparticles. For fuel cell applications hydrogen oxidation become more effectively proceed on Pt and also the alloy structure can improve H_2 separation from CO. Pd provides vacant sites for H_2 molecules to dissociate results to improve desorption of H_2 gas from the downstream side [23]. Pt–Pd alloy results in FCC structure gives better performance as electrode materials and at 90 °C it enhances the ethanol fuel cell performance [24].

The rising potential of new type of membrane material composed of organic frame and inorganic filler full fills the future applications in mixed matrix membrane. The comprised membrane of inorganic filler and polymer matrix provides the drastic change in the polymer chain packing and morphology of the matrix [25]. In the nanocomposite membrane, the particle loading not only promotes gas transport properties but also influence selectivity up to some extends [26]. The filler is preferred at nanoscale and it is chosen such a way that it would serve better contributively to respected field application. The incorporation of SiO_2 nanoparticles in to the host polymer matrix alter the intermolecular chain packaging of polycarbonate membrane which results in the change of morphology along with polymer structures reported by A. Idris et at [7]. Cong et al. studied the gas transport properties of nanosilica loading in brominated poly (2,6-diphynyl-1,4-phenylene oxide) nanocomposite membrane greatly enhanced CO_2 permeability maintaining CO_2/N_2 and CO_2/CH_4 selectivity compared to pure polymer. The selectivity was maintained by the concept of nanogap hypothesis mechanism of gas transport [27]. According to the free volume increase mechanism, nanofiller in the host polymer matrix disturb the polymer-chain packing which tends to enhance the fractional free volume. This turn arises specific voids in the polymer material to promote the diffusion pathway of transport gas molecule and results increase in the permeability [28]. Polycarbonate with 10 wt% SiO_2 nanoparticles gives raise in the permeability as the due to formation of excessive free volume in the polymer matrix. The voids created depend on the dispersion of nanofillers and the degree of de-agglomeration [29]. J.Ahn et al. have been reported that as amount of silica nanofiller has raised in the polysulfone matrix, the degree of agglomeration increase promoting void size which leads the permeability enhancement. There is more enhance in the permeability of large gas molecule by addition of silica which results from the increase in the free volume. The diffusion coefficient is also promoted by increasing the silica content [30]. Silica loading within polymer matrix results in improved thermal, mechanical and gas separation properties as reported by A. Idris et at [7].

In present work, it is proposed to prepare hybrid membranes by metal coating and nanocomposite using inorganic filler. A thin layer of metal was deposited on bisphenol-A polycarbonate using standard vapour deposition sputtering technique. The Pt–Pd alloy and iridium were used for deposition to make layered composite membranes. Silica nanoparticles were used as filler to synthesise polycarbonate nanocomposite membranes by solution casting method with various loading concentrations. These membranes were characterised by gas permeability measurements. The observations were carried out at constant temperature using constant volume/variable pressure method.

Experimental details

Material composition and FE-SEM

PC membrane of about 180 (±2) μm thickness was purchased from General Electrical Co, USA. Standard vapour deposition sputtering technique has been used to prepare layered composite membranes at ICMB facility of University of Texas at Austin, TX, USA. In this technique, the target and substrate materials are placed in ultra-high vacuum chamber. Pt–Pd

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thin film of about 8 nm thickness was deposited on polycarbonate substrate. In this technique, the polycarbonate and the target material are placed in ultra-high vacuum of 10^{-6} torr [31]. Iridium coated membrane was also fabricated the same way. The thickness of membranes was confirmed 180 (±2) μm by digital thickness metre before Pt–Pd coating. During the sputtering process, the surface atoms are physically ejected from the source material by momentum transfer from energetic bombarding particles and deposited on the host polymer film. The source to substrate distance is measured at different angles before and after sputter deposition process. Additionally, the amount of sputtered material is also measured. The average distance calculated and mass of deposited material gives the film thickness measurement [32]. In this way, the film thickness of Pt–Pd was calculated 8–10 nm. A thickness monitor was also attached with the system to observe deposited thickness. FE-SEM image of Pt–Pd coated PC membrane was taken using Carl Zeiss instrument at The University of Texas at Austin, USA. Silica nanoparticles (stock number 4860 MR), 20 nm in average diameter, were supplied by Nanostructure and Amorphous Materials, Inc,USA. The SiO_2 nanoparticles have density of 2.17–2.66 g/cm^3 at 20 °C and BET surface area of 160 m^2/g. The 10 wt% and 15 wt% nanocomposite membranes of around 40 μm were prepared by incorporation of silica nanoparticles in the polymer matrix using solution cast method. In this method, a desired quantity of PC was dissolved in the dichloromethane and stirred overnight at room temperature using magnetic stirrer. The next day, silica nanoparticles were placed in ultrasonic bath for a period of 5–6 h. They could disperse for additional sonication with polymer solvent for 30 min before casting the membrane. Then the mixed solvent was poured on a flat-bottomed glass surface. The system was kept overnight for complete evaporation of solvent. These membranes were pealed-off on next day and used for permeability measurements. The uniformity in thickness of membranes was confirmed by digital thickness metre [30].

Gas permeation measurements

Gas permeability measurements were carried out using gas permeability set up. A schematic diagram of permeation cell is shown in Fig. 1. Desired size of membrane was placed in permeability cell which creates pressure gradient across it. The membrane was supported by stainless steel grid inside the permeability cell. Upstream side was placed at higher pressure from which feed gas enters in the cell and the downstream side was at relatively lower pressure. O-rings were placed inside the cell at upstream and downstream side of the membrane to prevent leakage and exchange of air from outer environment. Thus, feed gas from higher pressure side can permeate through membrane which is collected towards downstream side.

Fig. 2 represents a constant/volume variable pressure system, measures permeate flux by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. Initially, the whole system was exposed to vacuum prior to perform the experiment. This action can remove any volatile impurity inside the system. To degas the film, upstream and downstream volume were evacuated with rotary pump. Then the valves connecting the permeation cell to vacuum pump were closed. Hence, pressure will rise towards downstream volume which was enables to measure leak rate of the system. The leak rate was maintained around 10 times less than the steadily permeating gas flow. Afterwards, the feed gas was introduced within the cell towards upstream side of membrane and at downstream side the pressure rise is recorded as function of time [33]. The permeability of H_2 was measured using a constant volume/variable pressure method. The measurements were carried out at constant 30 psi upstream pressure and constant temperature of 35 °C. A constant-volume/variable pressure system measures permeate flux by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. The metal coated membranes were placed in such a way that coated side was at upstream which was purged with penetrate gas and downstream side of permeation cell was evacuated with the help of rotary pump before talking the individual measurement. Following formula was used to calculate the permeability:

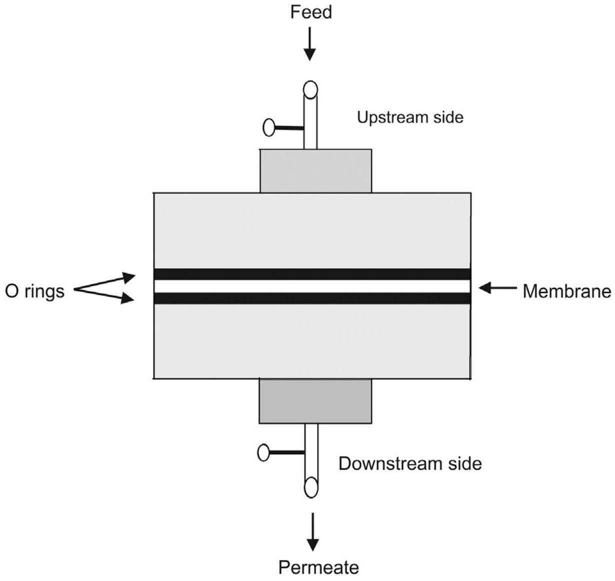

Fig. 1 – Schematic diagram of Gas Permeation Cell.

$$P = \frac{V\,d}{pART}(m1) - (m2)$$

P is the pure gas permeability, V total volume of downstream side i.e.39.43 cm^3, d thickness of the membrane, p upstream absolute pressure in psig, m1 is the steady state slope of downstream pressure versus time calculated in cm-Hg/s, m2 is the leak rate calculated in cm-Hg/s and it was maintained at 10^{-7} cm-Hg/s during the experiment [28]. Permeability was calculated in barrers, where 1 barrer = 10^{-10} [cm^3 (STP) cm/(cm^2 s cm-Hg)].

Result and discussion

The transport of H_2 gas across pure polycarbonate and their hybrid forms was observed at constant upstream pressure 30 psi. Polycarbonate being dense material follows solution

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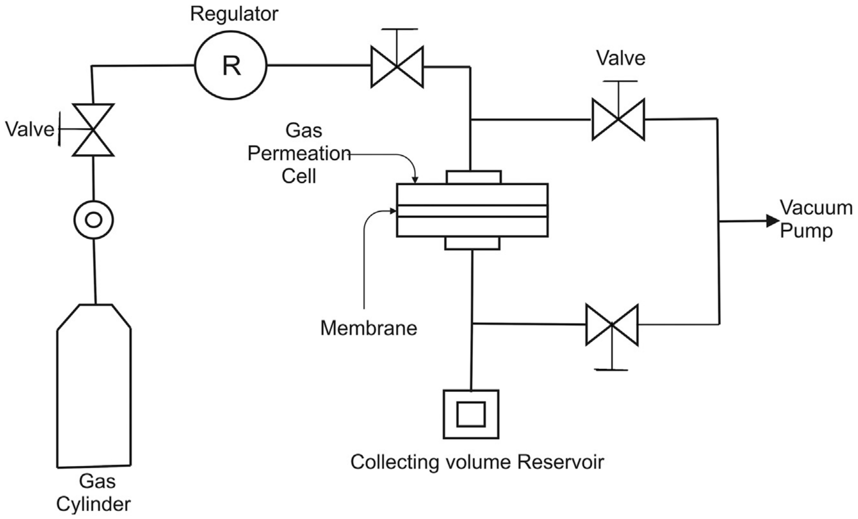

Fig. 2 – Constant volume/variable pressure system setup.

diffusion mechanism. The permeation tests were carried out at constant temperature 35 °C for pure polycarbonate, polycarbonate nanocomposite, Pt–Pd and Iridium coated polycarbonate membranes. Slopes of downstream pressure verses time were calculated by standard Origin8 software. Fig. 3 shows the comparison of H_2 flux over variety of membranes with respect to the pressure gradient. All the hybrid membranes give better transport rate as compared to the virgin polymer. Additionally, being smaller in molecular dimension H_2 gives quick response without achieving time lag.

(a) Hydrogen flux across metal coated polycarbonate

The H_2 transport rate through metal coated polycarbonate is shown in Fig. 3. It can be inferred that the flow of H_2 molecules varies for different coating materials. Polycarbonate gives better transport rate as compared to the PC/Ir and PC/Pt–Pd membranes. The flow rate also depends on the other parameters such as exposed area, working temperature, thickness of the membrane etc. Hence, these parameters affect the gas transport rate. The downstream flow rate of PC/Ir membrane was found to be lowest. Both the metal coated PC lowers the H_2 transport rate as compared to pure polycarbonate. Flow rate might be change due to change in sorption behaviour of different metallic coatings. For the metal coated hybrid membranes, the gas molecules first interact with thin metal layer which becomes physiochemical process. In this process, the H_2 adsorbed on the metal layer and dissociated in to atomic form and then diffused through the metal layer. This rate determining step for H_2 diffusion through metal layer promotes the sorption through the upstream side of membrane. Thus, the gateway of solution diffusion mechanism can be achieved easily by the metal coating. Moreover, Pd coating adds resistance which reduces with gain in temperature and the number of vacant sites also increases as the gas molecule penetrates the material which promotes the diffusion rate in effective membrane permeability [34,35]. Therefore Pt–Pd coated polycarbonate gives better flow rate as compared to Ir coated PC. Fig. 4 shows the diffusion rate of PC/Pt–Pd membranes at 35 °C and different

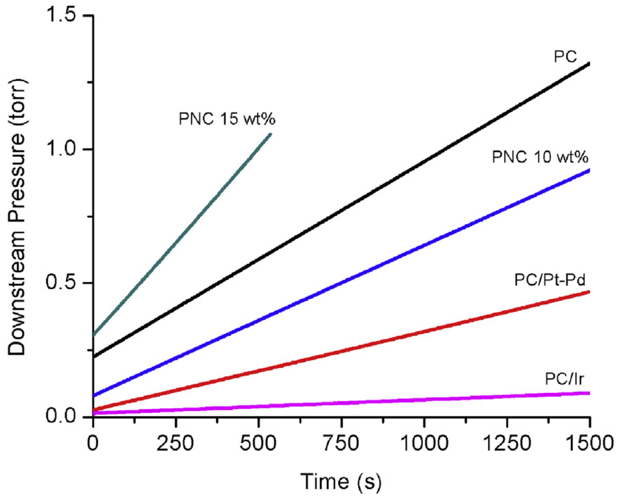

Fig. 3 – Downstream pressure verses time for pure as well hybrid PC at 30 psi upstream pressure.

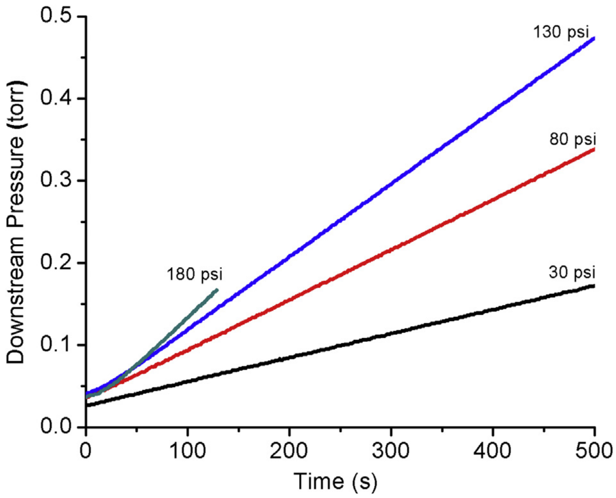

Fig. 4 – Downstream pressure verses time for PC/Pt–Pd at 35 °C and different upstream pressure.

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upstream pressure from 30 psi to 180 psi. As the upstream pressure increases the transport rate increases in negligible amount. This indicates that the increasing upstream pressure will not affect the transport rate of H_2 molecules. At 180 psi upstream pressure the slope gives small increment within 130 s of diffusion time.

(b) Hydrogen flux across Mixed Matrix Membranes

For pure polycarbonate the slope given in Fig. 3 is greater than that of nanocomposite and metal coated membranes. However, as the weight percentage of silica nanoparticles in the polymer matrix is raised the flow rate of hydrogen gas molecules increases which result gain in slope. Comparative study of H_2 permeation through various composite materials indicates that the gas flux rate depends on the composition of membrane material. The slope of downstream pressure versus time represents the flow rate of H_2 gas molecules within the membranes. The highest slope has been observed in 15 wt% silica nanocomposite polycarbonate membrane and the iridium metal coated polycarbonate gives lowest value of slope. Pure polycarbonate gives better flow rate comparative to that of metal coated and 10 wt% polycarbonate nanocomposite membranes (PNC) or mixed matrix membranes (MMMs). The permeability does not depend only on the slope value as the other parameters such as exposed area, thickness, temperature and pressure are also responsible for the transport mechanism. Mixed matrix membranes loaded with 15 wt% of silica, gives highest transport rate although having smaller area and lower in thickness comparative to other membranes. Due to this increased parameter of 15 wt% polycarbonate nanocomposite membrane, permeation of H_2 gas molecules increased relative to other presented membranes. During the synthesis of mixed matrix membrane, the particle agglomeration plays vital role to change the transport rate of gas molecules. Silica nanoparticles and polycarbonate having different physical and chemical properties, the composition may create inhomogeneous mixed matrix phase. There for silica can't compile properly with the polycarbonate and results in agglomeration. At the particle-polymer interphase, poor contact could be result in small voids and these voids provide extra path ways to the penetrant molecules [25]. Additionally, the silica nanofillers disturb the chain packing in the respected polymer and causes small pinholes. The gas molecules may refer these non-resistive modes to bypass and can easily transported through the material. As the silica content is increased, the rate of transport of gas molecules increases.

The permeability obtained for pure polycarbonate, metal coated polycarbonate and nanocomposite polycarbonate has been given in Fig. 5. The maximum permeability has been obtained for 15 wt% SiO_2 polycarbonate nanocomposite membranes and is lower for pure polycarbonate membrane.

(c) Hydrogen permeability for metal coated polycarbonate

Metal coated polycarbonate represents better transport efficiency compared to that of virgin polymer. It is observed that the permeability obtained in Ir coated is almost double then that of pure polycarbonate membrane as shown in Fig. 5.

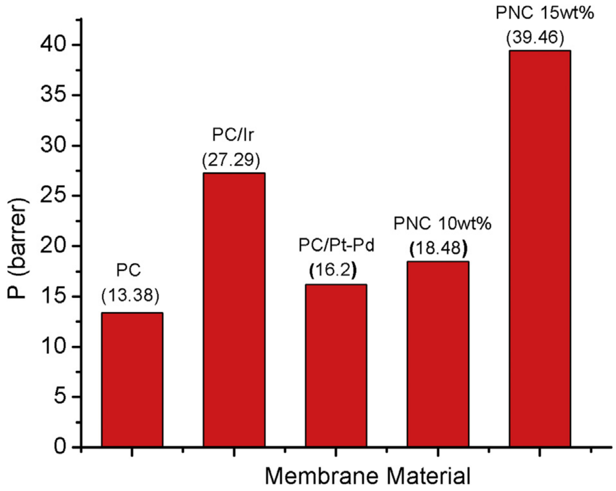

Fig. 5 – Permeability of pure and hybrid polycarbonate.

Moreover, Pt–Pd coating also effects the H_2 permeation as the permeability value gains by 17% as compared to the host material. Ir coating becomes better compatible for H_2 gas compared to Pt–Pd alloy material. It is expected that thermal property of exposed surface was changed due to metal coating and condensation occur which affect solubility factor. Condensation of gaseous penetrant and mixing of penetrant with polymer segments give rise to the solubility which promotes the permeability. Fig. 6 describes the nature of H_2 permeation with respect to upstream pressure for Pt–Pd coated polycarbonate. Permeability remains almost same as per gain in feed pressure in increased. The scattered values of permeability at 30 psi and 80 psi are almost same and there is small loss at 130 psi upstream pressure. As further the feed pressure is raised up to 180 psi small jump in H_2 permeation can be achieved. The marginal variation has been obtained within 130–180 psi range of feed pressure which is not remarkable.

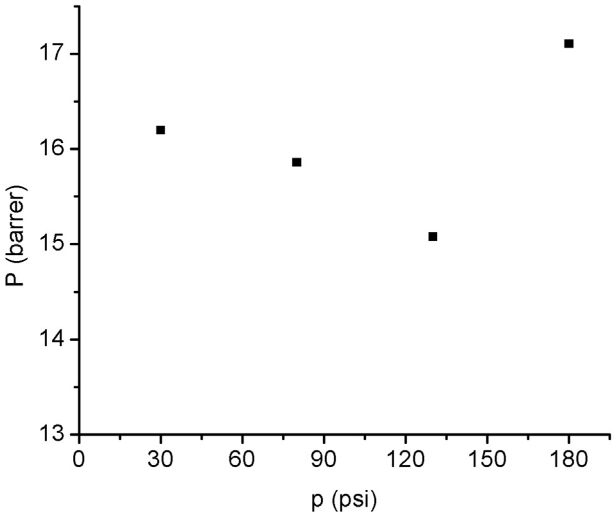

Fig. 6 – Permeability of PC/Pt–Pd at 35 °C and different upstream pressure.

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(d) Hydrogen permeability for Mixed Matrix Membranes (MMMs)

Permeability obtained in MMMs is shown in Fig. 5. It shows enhancement in permeability by incorporation of SiO_2 incorporation in polycarbonate matrix. MMMs with 10 wt% silica nanoparticles gains permeation of H_2 flux up to 27% than the polycarbonate. By increasing the amount of nanofiller up to 15 wt%, permeability enhances up to 66% with respect to pure polycarbonate membrane. Usually, the permeability depends on diffusivity and solubility of the penetrant through the membrane phase. Therefore, in MMM, the transport mechanism is based on free volume increase mechanism and solubility increase mechanism. Free volume increase phenomenon is based on the interaction between the polymer chain segment and the nanofiller. The incorporation of silica nanoparticles within polymer matrix modify the polymer segmental mobility which interrupt polymer chain-packing and increase the free volume between the polymer chains which in turns enhances penetrant permeability. As the amount of nanofiller in increased the fractional free volume increases which promotes the gas permeability. Solubility mechanism is based on the interaction between penetrant and filler material in which polar gas molecules interacts with the functional group on the filler surface [28]. In present case H_2 is not the polar gas which implies the gain in the overall permeability is caused by the free volume formed due to incorporation of nanofillers. It can be observed that the 10 wt% PC/SiO_2 nanocomposite gives better H_2 permeation than the pure polycarbonate membrane and as the amount of silica content increased up to 15 wt% the gas permeability was also increased.

Fig. 7 gives the comparison of selectivity of H_2/CO_2 gas pair by pure polycarbonate, Pt–Pd coated PC and 10 wt% SiO_2 PNC membranes. Usually, top surface of PNC membrane shows different roughness and the roughness parameter is associated to nanofiltration applications. As the increase in surface roughness increases effectual membrane surface area up to some extent which results to change in permeation rate of different gases [25]. Thus, the roughness parameter may affect the selectivity parameter. In present work the permeation of H_2 increases in 10 wt% PNC as compared to that of pure polycarbonate and the selectivity of H_2/CO_2 for both the membranes remain unchanged. The permeability and the selectivity parameters are in trade-off relationship with each other but the SiO_2 nano fillers plays vital role to maintain the selectivity. The maintenance of selectivity may be due to the nanogap hypothesis. According to the nanogap hypothesis an empty nanolayer is surrounded to the nanofiller due to poor interaction with the polymer chain. This cause to promote shorten mode for penetrant diffusion and results the gain in permeability. Once the nanofiller surface becomes somewhat compatible to the polymer chain the nanogap reduces and helps to uphold the selectivity [28]. Permeability obtained by PC/Pt–Pd is better as compared to that of pure polycarbonate but there is small loss in selectivity by PC/Pt–Pd for same gas pair.

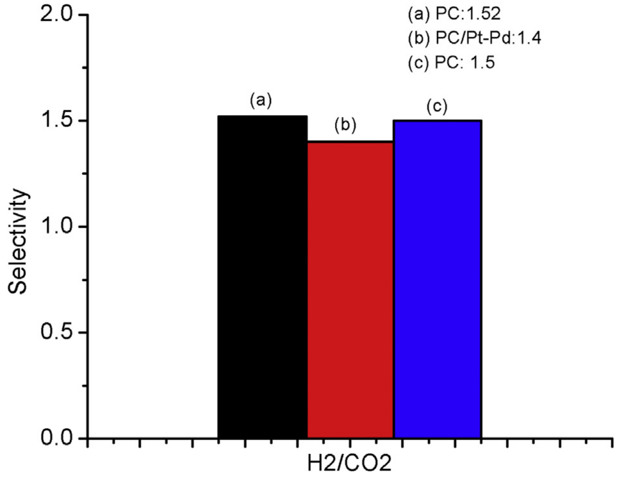

Fig. 7 – **Selectivity of H_2/CO_2 by pure PC, Pt–Pd coated PC and 10 wt% SiO_2 PNC membranes.**

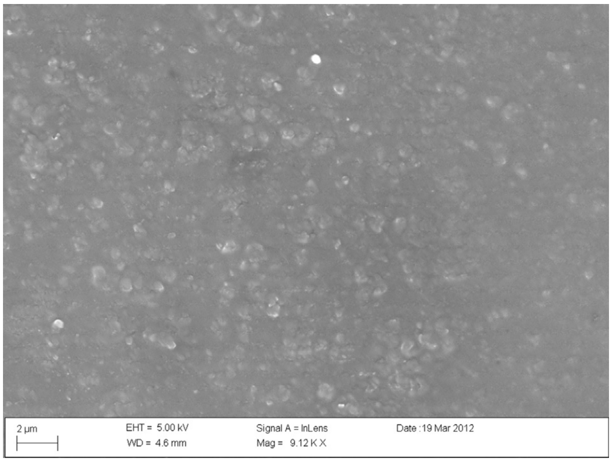

Fig. 8 – **FE-SEM image of Pt–Pd coated PC membrane.**

(e) FE-SEM of PC/Pt–Pd

Surface morphology of Pt–Pd coated polycarbonate membrane is given in Fig. 8. It revels the existence of metallic surface through the observation. As per the reference by Alamin Idris et al. SEM shows dense structure of pure PC [7]. The formation of coating layer provides interfacial voids and rigidifies polymer chains at polymer metal coating interface. There for the metallic surface layer becomes the interfacial gateway for transport of H_2 molecules.

Conclusion

The work was aimed to develop various hybridization of polycarbonate membrane to full fill better transport mechanism of hydrogen gas molecules. The alteration in the transport of hydrogen molecules reflects the performance of these modified membranes in terms of permeability along with selectivity. Nanocomposite form of polycarbonate, in which SiO_2 nanoparticles play vital role to improve transport modes of H_2 molecules. Moreover, as the silica amount is increased the excessive free space is increased and enhances the

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permeability. Metal coating provide better gateway to the penetrant to make them soluble in the membrane material which finally also reflect as an increment in permeability. The H_2/CO_2 selectivity factor is also maintained by the hybridization which is applicable to separate H_2 from gas mixture.

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ORIGINAL PAPER

CO_2 plasticization effect and selectivity for Pt-Pd alloy coated polycarbonate membrane

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Abstract

The transport of CO_2 through variety of polymer membrane has been reported since last few years. CO_2 shows plasticizing effect with glassy polymers facilitating molecular motion and increasing free volume which promotes the permeability. In this work, the transport behaviour of CO_2 across the metal coated membrane has been studied and compared with that of standard polycarbonate membrane as a function of pressure. Deposition of nanolayer affects the transport properties due to the modification in sorption-diffusion process. As CO_2 is a plasticizing agent and at definite pressure it gives plasticizing effect depending on the properties of material. A Platinum-Palladium (Pt-Pd) alloy thin film of around 8–10 nm was coated on thick polycarbonate (PC) substrate using sputtering technique to make layered polymer nanocomposite membrane. The permeability decreases with feed pressure for PC/Pt-Pd. As operating pressure is increased, the diffusion coefficient increases with small change and the solubility decreases. The tests were carried out at different upstream pressures i.e. in the range of 30 psi to 230 psi (2 atm to 16 atm) for PC/Pt-Pd at 35 °C temperature. Further, the selectivity of CO_2 over H_2, O_2 and N_2 at various upstream pressures has been reported.

Keywords Gas transport · Thin film coating · Selectivity · CO_2 plasticization · Polycarbonate

Introduction

Being the major factor of global warming as well climate change, CO_2 filtration from natural gas, bio gas and flue gas has become the need of hours. Polymeric CO_2/N_2 separation membranes have been developed for the capture of carbon dioxide. C.E.Powel has surveyed number of different classes of polymers with their utility as well provided the synthesis, fabrication and the role of novel polymeric materials for CO_2 separation [1]. Furthermore, the upstairs applied for better performance in the separation process give rise to the modification technologies in membrane material. A review given by Zhongde Dai et al. presents improvement in the separation performance of CO_2/CH_4, CO_2/N_2 and CO_2/H_2 by multilayer polymeric membranes. The selective coating layer applied to the membrane provides barrier properties that can improve two selective criteria such as high permeability as well high selectivity [2]. The separation process concerns for the material having some specific properties (chemical or physical) that can exist under the operating conditions. As per some specific transport routs of polymer membrane, one can select appropriate material that achieves purity as well as the recovery of specific species in the form of separation. Separation process performs the operations like detachment of a specific gas from the gas mixture such as hydrogen recovery from nitrogen, removal of carbon monoxide from air, separation of hydrogen from carbon dioxide, nitrogen enrichment, refinery gas purification, acid gas treatment etc. [3, 4]. The flow of gas molecules across the membrane is influenced by several factors: gas properties, material used to design the membrane, morphology of membrane structure and operating conditions [5]. Carbon dioxide being polar molecule, at higher pressure results in plasticization with some glassy polymers having polar pendent groups. Due to the plasticization of membrane material its permeability is changed which can modify separation ability of the membrane.

The plasticization is penetrant induced phenomenon which relay on the nature of penetrant, nature of material and the penetrant material interaction. Apart from various gases such as CO_2, SO_2, NO_2, CH_4 having plasticizing ability, the results

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from the literature supports CO_2 as better plasticizing agent compared to other mentioned gases. Plasticizing potential of CO_2 with glassy polymers having polar group promotes the permeability of gas molecules through the membrane material [6]. Instead of using pure polymer membranes, the hybrid materials can serve better to enhance gas permeability and selectivity. The mixed matrix membrane (MMM) dispersed with zeolitic imidazolate framework increases CO_2/N_2 selectivity at high pressure. This hybridization does not affect both the permeation performance of $CO_2$and its plasticization at increased feed pressure [7]. Moreover, the blending of carboxylated polymers of intrinsic microscopy (cPMI-1) and Torlon tends to imply significant increment in the gas permeability and its anti-plasticization property could gain in selectivity of O_2/N_2, CO_2/CH_4, CO_2/N_2 and H_2/N_2. This hybridization has driven the separation performance closer to the Robeson's upper bound for the gases [8]. As per explained by Salman Shid et al. mixed matrix membranes of metal organic framework (MOF) with matrimide-PI loading reduces plasticizing effect at high pressure which results gain in CO_2 permeability and CO_2/CH_4 selectivity due to increase in diffusion and sorption selectivity. The membranes sustain almost constant selectivity within whole pressure range as the MOF loading increases because the CO_2 plasticization is resisted in the presence of MOF particles [9]. CO_2 treated polycarbonate membrane shows enhancement in the O_2/N_2 selectivity which is attributed to gain in the solubility. Plasticized CO_2 absorbed by the polycarbonate and changed the morphology by redistribution of polymer chain [10]. The permeation as well as separation properties can be improved by chemically modifying the structure or by physical modification. Irradiation over the host polymer membrane can influence both the permeability as well as the selectivity [11, 12]. In addition, polymer blending, mixed matrix, making composite, layer deposition over polymer film can modify the polymer membrane to hybrid membrane material. This alteration can offer potential reward not only to the gas transport application but also in other industrial applications. To achieve the high gas barrier property, polymer surface can be modified by depositing thin film coating. Metal coating can reduce permeability which enhances the separation factor or in some cases it may raise due to defect in coating layer. Coating of inorganic layer over polymer membrane is also a better option for surface modification of the membrane. Titanium coating on polycarbonate membrane reduces the permeability of H_2 and CO_2 and simultaneously increases the selectivity of H_2 [13–15]. Bisphenol-A polycarbonate is found to have some unique physical and chemical properties as well as having good mechanical strength and toughness. Moreover, polycarbonate is transparent material and its heat distortion temperature is too high. It also supports molecular weight degradation and dispersion of colour formation. According to economical point of view polycarbonate is very cheap material and easily available so it is a good candidate for industrial applications. It supports the incorporation of nanofillers to modify its functional properties which can improve its applications for permeation as well as separation performance [16, 17].

The proposed work presents polycarbonate (PC) membrane coated with nanolayer of Pt-Pd alloy suspended for gas permeability test. The hybridised membrane was applied to study plasticization effect of CO_2 as per gain in operating pressure which can improve permeability and selectivity. In this study the metallic nanolayer was fabricated by vapour deposition sputtering technique. The transport of CO_2 gas molecules through the given membranes has been measured by a constant volume/variable pressure system.

Experimental

Material composition and FTIR

The host polycarbonate membrane was purchased from General Electrical Co, USA of thickness about 180 (±2) μm and was coated with thin nanolayer of Pt-Pd alloy by standard vapour deposition sputtering technique at ICMB facility of University of Texas at Austin, TX, USA. According to sputtering technique, the target and substrate materials are placed inside vacuum chamber and ultra-high vacuum up to about 10^{-6} Torr is obtained. The thickness of deposited film was about 8 nm and before coating the membrane thickness was confirmed 180 (±2) μm by digital thickness metre. From the source material, energetic bombarding particles by momentum transfer are physically ejected and deposited on the host polymer film during the sputtering process. Relative distance from source to substrate is measured at different angles before and after sputter deposition process. The film thickness measurement was obtained by calculating average distance and measuring mass of deposited material [2, 10]. The thickness of Pt-Pd coating layer was calculated around 8–10 nm. Additionally, to observe deposited thickness of coating material, thickness monitor was also attached with the system. The composite membrane was characterised for FTIR using Thermo-scientific instrument at university of Texas at Austin, Austin, USA.

Gas permeability measurement

Gas permeability measurement is determined as a function of gas flux through the given membranes as illustrated in Fig. 1, a constant-volume variable pressure system. Gas flux permeate through the membrane was measured by monitoring the pressure increase of collected permeate gas in a closed volume using a pressure transducer. To obtain accurate measurements, any volatile impurity inside the system was removed by exposing it to vacuum prior. Thus, the feed volume and permeate

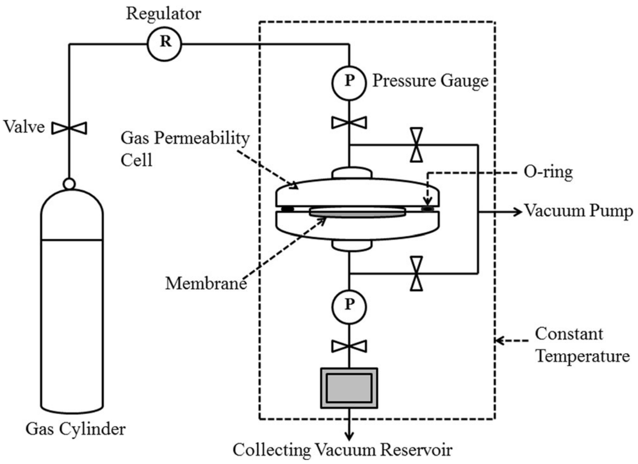

Fig. 1 Constant volume/ variable pressure system setup

volume were evacuated to degas the film. Then the valves connecting the permeation cell to vacuum pump are closed and slow pressure will rise towards downstream volume which is called the leak rate of the system. The system must be evacuated in such a way that the leak rate should be around 10 times less than the steady state permeation of gas flow. Then the feed gas is introduced within the cell towards upstream side of the membrane and at the downstream side the pressure rise is recorded as function of time. The experiment was performed at constant operating pressures from 30 psi to 230 psi and at constant temperature 35 °C. The exposed surface area of Pt-Pd coated PC was 0.6529 cm^2. Inside the gas permeation cell, the coated side of the membrane was faced towards upstream. Following formula was used to calculate the permeability:

$$P = \frac{V \quad d}{p \quad A \quad R \quad T}(m1) - (m2)$$

P is the gas permeability coefficient, V is total volume of downstream side which is 39.43 cm^3, d is thickness of the membrane, p is upstream absolute pressure in psig, m1 is the steady state slope of downstream pressure versus time calculated in cm-Hg/s, m2 is the leak rate calculated in cm-Hg/s. During the experiment, the leak rate was maintained up to 10^{-7} cm-Hg/s Permeability was calculated in barrers, where 1 barrer = 10^{-10} [cm^3 (STP) cm/ (cm^2 s cm-Hg)]. Polycarbonate being glassy polymer, gas permeation is explained by a simplest solution-diffusion model. As per the mechanism of this model, gas molecules are absorbed towards feed side surface of the membrane, diffused through the membrane with respect to the pressure gradient and then desorbs from downstream side surface. Gas permeability is also explained by following equation.

$$P = D\,S$$

D is the diffusion coefficient and S is the solubility coefficient. Diffusion coefficient can be determined by intercept of steady state line and the time axis of downstream pressure versus time curve and solubility coefficient can be determined by the ratio of permeability to diffusion coefficient.

$$D = \frac{L^2}{6\theta}$$

θ is the time lag, L is the membrane thickness and D is diffusion coefficient.

Result and discussion

Permeability is the rate of transportation of permeant through the membrane system. Generally, it depends on the operating conditions such as feed pressure, temperature, structure of polymeric material and size as well shape of penetrant. For glassy polymeric system, the transport of gases follows solution diffusion mechanism. The permeation tests were carried out at constant temperature 35 °C for Pt-Pd coated polycarbonate membrane. Slopes of downstream pressure verses time were calculated by standard Origin8 software and the resultant value of permeability is compared with reference data.

The effect of operating upstream pressure on CO_2 permeation was examined and the data is listed in the Table 1. For CO_2 gas molecule steady state time reduces with gain in upstream pressure. Even the steady state is achieved within 1000–2300 s for the range of 30 psi to 230 psi upstream pressure. It can be inferred that at 30 psi upstream pressure steady state is achieved within 2295 s, as the upstream pressure is raised to 80 psi the steady state decreases to 1984 s. Further the gain in pressure up to 130 psi, gas transportation become steady within 2121 s giving small fluctuation. It reduces up to 1602 s for 180 psi feed pressure and then gives small gain for 230 psi feed pressure. Thus, within the feed pressure range from 30 psi to 230 psi steady state value is decreased with small deviations. The change in steady state transport time tends to change diffusion coefficient as the diffusion is inversely proportional to steady state time. As given in the Table 1, the diffusion coefficient increases with feed pressure with small fluctuations within the pressure range. Figure 2 shows the steady state nature of all gases. As per the gain in upstream pressure, the rate of transport increases. Although there is small fluctuation in steady state time with respect to feed pressure, the slope of downstream pressure verses time continuously increases. For 30 psi feed pressure it shows lowest value of CO_2 flow rate whereas for 230 psi feed pressure it shows its highest value. It is clear from the graph that the rate of transport of gas molecules through the membrane is directly proportional to the upstream pressure. Since CO_2 is polar molecule, dipolar interaction will occur with polar group of polycarbonate (PC). The interaction between the pendent segments is weaker than interaction formed by CO_2 with polar group. As CO_2 is exposed up to specific

Table 1 Permeability, Diffusion coefficient and solubility coefficient at different feed pressure

Pressure (psi)	Steady state time (sec)	D (cm^2/s)	S (cc STP/cc cmHg)	P (barrer)	P (barrer)[a]
30	2295	2.35×10^{-8}	5.2×10^{-2}	12.40	7.71
80	1984	2.72×10^{-8}	3.2×10^{-2}	8.94	7.22
130	2121	2.55×10^{-8}	3.4×10^{-2}	8.90	6.71
180	1602	3.37×10^{-8}	2.1×10^{-2}	7.28	6.31
230	1669	3.24×10^{-8}	2.2×10^{-2}	7.41	5.98

[a] Reference data used from Jorden et al. [18]

feed pressure to the polycarbonate, it may break this weaker interaction by providing the additional rout of diffusion. Thus, permeability is promoted by gain in diffusivity [6]. The material presented is not pure polycarbonate, there for by exposing CO_2 to the membrane, firstly it interacts with the coating material. After interaction with metal layer the gas molecules start entering the polymer region which may cause very small chain mobility of polymer segments. The nature of transport of gas molecules through layered PC does not form the additional path ways by means of diffusion. Therefore, as the feed pressure is increased, the diffusion coefficient raises with small change. The penetrant interaction with the polymer matrix will aid to determine diffusion coefficient. This parameter is used to determine solubility coefficient.

Solubility and permeability data at corresponding operating pressure are also listed in the Table 1. As per the analysis given by S. H. Chen et al. CO_2 enhances solubility within polycarbonate whereas the diffusion remains almost constant [10]. In this case the decrement in permeation is responsible due to solubility factor. As the pressure is increased the solubility decreases which is governed by condensation of gaseous penetrant and mixing of penetrant with polymer segments. The feed gas firstly interacts with thin barrier i.e. Pt-Pd metal layer and the interaction of CO_2 on Pd surface becomes physio-chemical process in which CO_2 forms stable structures with binding modes. As per referenced by S. G. Wang et al., on the Pt surface CO_2 bond provides highest binding energy comparative to other metals [19]. According to previous studies thermal properties of membrane can be changed as Pd interacts with the PC material. Due to these reasons, the solubility has been affected by coating layer. Within the range of 30 psi–230 psi, the solubility becomes almost half. There is minor change in the diffusion coefficient comparative to solubility within this feed pressure range.

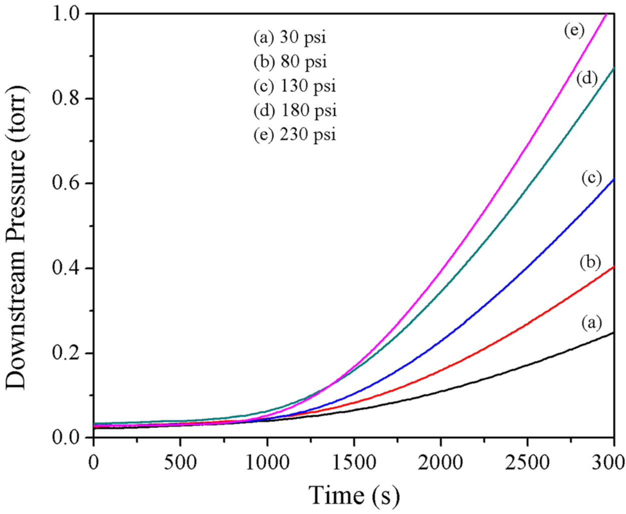

Fig. 2 Downstream pressure verses diffusion time at different feed pressure

Figure 3 represents permeability verses pressure in which permeability steadily decreases from 30 psi to 230 psi but takes a small uptake at 130 psi. However, there is gradual decrease in the permeability with respect to operating pressure which follows nature of pure polycarbonate membrane for CO_2 permeation for this pressure range. The data in the literature on CO_2 permeation through polycarbonate is available for comparison given by Jorden et al. Permeability values were calculated from the graphical figure given in this reference using get data software. Within the range of 1–20 atm pressure the permeability gradually decreases [18]. The metal coated PC with this feed pressure range changes around 13 to 7 barrers. At 30 psi upstream pressure, Pt-Pd coating plays vital role to permeate CO_2 gas molecules as compared to pure PC given in the reference data. From Table 1, the permeability at 30 psi for pure PC is around 7 barrer as per given reference

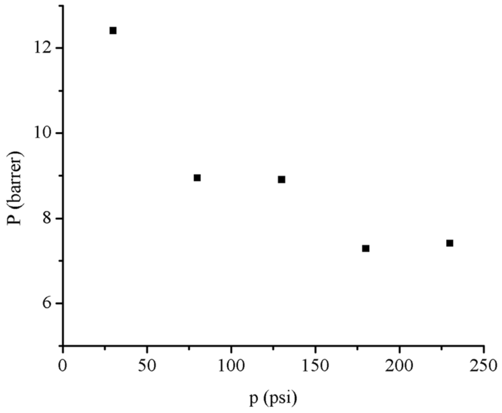

Fig. 3 Permeability of CO_2 at different feed pressure

whereas for metal coated PC it is 12.40 barrer. As per given in the Fig. 4, the feed gas is applied over the coating side surface of the membrane, it does not directly interact with the host PC material. There for the applied upstream pressure is first acquired by coating layer. CO_2 gas molecules first interact with thin metal layer and the interaction of gas molecule with metallic materials is physiochemical process. This may lead to the transportation of CO_2 molecules within the membrane. Usually, the raise in the permeability of PC can be due to plasticization effect of CO_2 gas because carbonyl group of PC has significant effect upon permeability of membrane. Being condensable gas, CO_2 plasticizes the membrane and increase polymer chain mobility at high pressure, subsequently rises in permeability. Additionally, CO_2 is polar molecule which interacts with carbonyl group of PC results increase in chain mobility at elevated pressure. It may possible that after the interaction with metallic film CO_2 molecules tries to penetrate PC membrane through the interaction with its chain segments and with the polar pendent groups. Valmikanathan et al. have reported that the interaction of Pd nanocluster can increase free volume between polymer chains. Moreover, relatively weak interaction exists in Pd/PC nanocomposite which results in raise in free volume. Thus, at same feed pressures for PC and PC/Pt-Pd membranes permeability values are different because coating layer promotes CO_2 permeation. Moreover, Pd coating adds resistance which reduces with gain in temperature and the number of vacant sites also increases as the gas molecule penetrates the material. This promotes in effective membrane permeability through the membrane [20]. Pure PC is going to be plasticized at particular pressure by the CO_2 but, as a barrier is introduced between PC and CO_2, it may alter the plasticization effect. The barrier, metal alloy plays vital role to change the plasticization pressure. At 30 psi upstream pressure the difference between modified and virgin membrane is 5 barrer. At 230 psi feed pressure composite PC membrane gives permeability of 7.41 barrer and PC membrane gives 5.98 barrer. Even at 230 psi operating pressure CO_2 permeability by PC becomes compatible to metal coated PC. Permeability of CO_2 acquires different value at same feed pressure for modified as well unmodified membranes. Thus, plasticization phenomenon can be altered by modification in the chemical structure of the membrane [21]. Thus, the plasticizing pressure can be raised for this modified membrane as compared to pure PC.

Figure 5 gives the comparison of selectivity of H_2/CO_2 gas pair by PC/Pt-Pd membrane at different upstream pressures. It is inferred from the graph that the H_2 selectivity gains as per raise in upstream pressure from 30 psi to 230 psi. The feed pressure for H_2 permeation does not affect for Pt-Pd metal coated PC membrane at large extend whereas CO_2 permeability decrease for this pressure range. It maintains the selectivity with very small loss at 30 psi [22]. Hence, the gain in pressure only affects CO_2 permeability. This result indicates the better trade off relationship for the given gas pair. Thus, the separation of H_2 from CO_2 can be obtained up to the plasticizing pressure of PC.

Figure 6 shows selectivity of CO_2/O_2 and CO_2/N_2 gas pairs at 30 psi and 130 psi upstream pressures. Usually, with the gain in permeability, selectivity drops down for most of the membrane materials. In this metal composite, by increasing the feed pressure, the selectivity is also increase. For CO_2/O_2 gas pair, the selectivity at 230 psi upstream pressure becomes more than doubles then the 30 psi. Same trade is followed for CO_2/N_2 gas pair in which the selectivity becomes almost double.

The FTIR spectra for pure and metal coated PC are presented in Fig. 7. It can be noticed that in both the materials the characteristic peak of carbonate stretching at wavelength

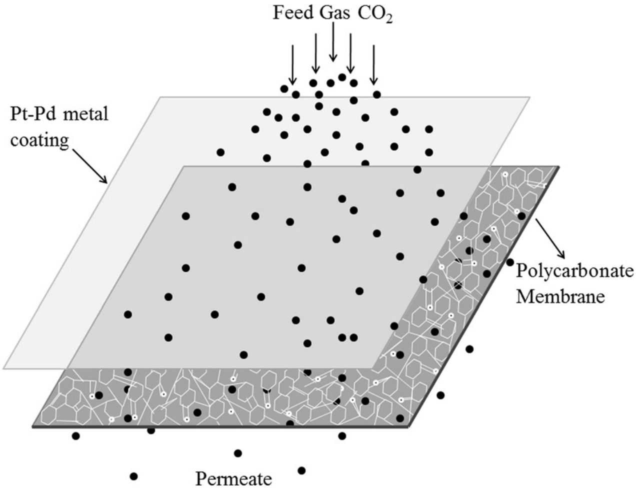

Fig. 4 CO_2 transport through metal coated PC

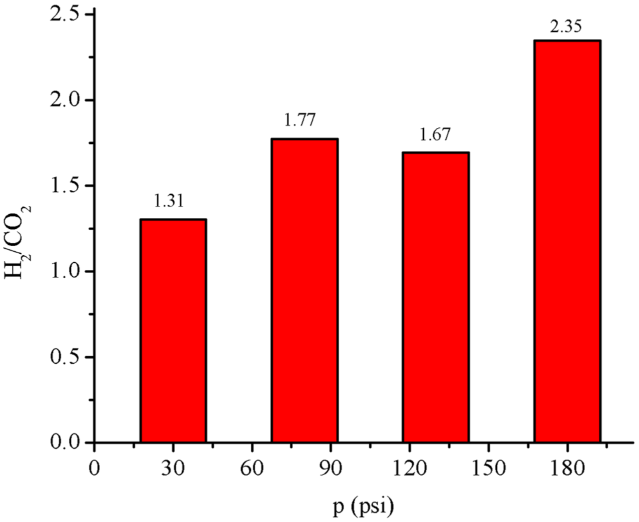

Fig. 5 Selectivity of H_2/ CO_2 at different upstream pressure from 30 psi to 180 psi

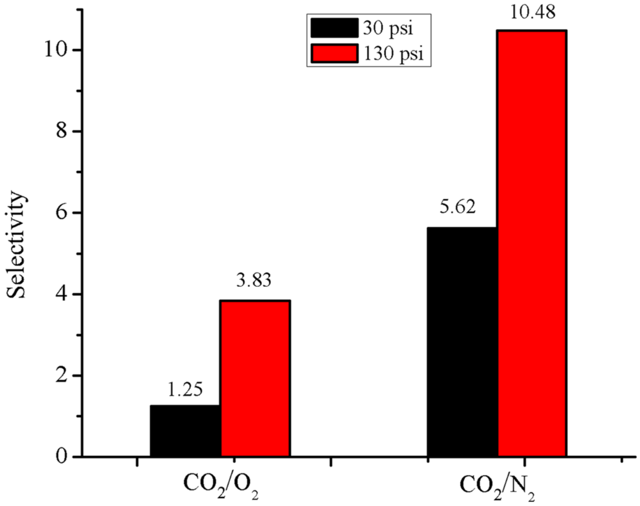

Fig. 6 Selectivity of CO_2 with O_2 and N_2 at 30 psi and 130 psi upstream pressures

around 1765.4 cm^{-1}. This specific peak is shifted due to metal coating of Pt-Pd alloy. The peak broadening for composite membrane conform the formation of nanolayer on PC. CH_3 symmetric deformation can be identified at 1378.7 cm^{-1}. C-O and C-H bonds stretch at 1765.4 cm^{-1} and 882.7 cm^{-1} respectively. The wavelength has shifted from 3170 cm^{-1} to 3188 cm^{-1} for PC and composite PC respectively. The peak broadening is more affected from 2000 cm^{-1} to 3200 cm^{-1}.

Surface morphology of Pt-Pd coated polycarbonate membrane has been described by Patel el al. [22] and it revels the existence of metallic surface. The formation of coating layer provides interfacial voids and rigidifies polymer chains at polymer metal coating interface. Therefore, the metallic surface layer becomes the interfacial gateway for transport of CO_2 molecules. Similar study has been reported by Alamin Idris et al. [16].

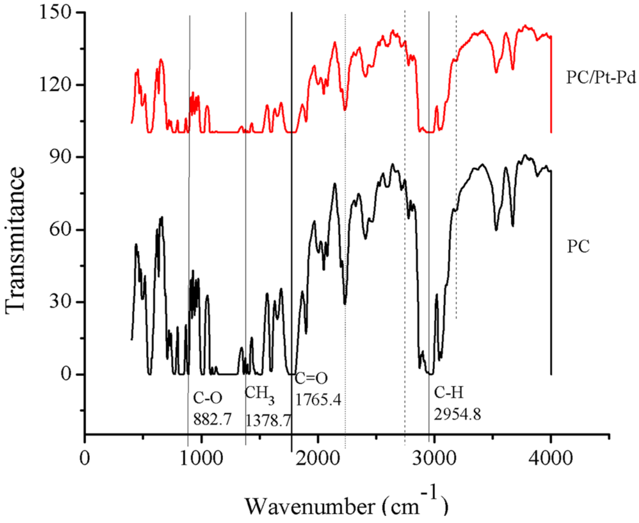

Fig. 7 FTIR of PC and PC/Pt-Pd membranes

Conclusion

Metal coated polymer composite membrane was prepared to analyse the effect of feed pressure on transport property of CO_2. As per the results obtained from this experiment, the metal coating plays a vital role for enhancement of diffusion coefficient which is responsible for gain in permeability. The hybridization of organic-inorganic material improves interaction of penetrant with the membrane as per increase in feed pressure. There is lose in solubility factor with respect to upstream pressure. Compared to diffusivity value, the solubility has changed and down up to half amount from 30 psi to 230 psi operating pressure. The metal layer has changed plasticization effect up to some extent. The effect can be observed in selectivity value which has gained as per raise in feed pressure for all three gas pairs. FTIR analysis confirms the metal coating and also the broadening of the peaks indicates the interaction of PC functional groups with Pt-Pd alloy. The surface roughness appears from FE-SEM analysis of the composite membrane. Due to the surface roughness, the interaction of gas molecules during sorption process changes which can be useful to enhance the separation factor. However, this modification appears as an effective approach for suppressing plasticization effect for polycarbonate membrane.

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