CHAPTER 3

GAS TRANSPORT THROUGH LAYERED POLYMER NANOCOMPOSITE MEMBRANE

Chapter 3

Gas Transport through Layered Polymer Nanocomposite Membrane

3.1. Introduction

Gas transport phenomenon can be modified somehow by changing the barrier properties which can make alteration in the diffusion rate as the exposed feed first interact the membrane surface. Gas diffusion application by thin film coating depends on the requirement such as barrier diffusion and selective transport of gas molecules. The deposition of thin film layer to the polymer membrane is generally applied for food and medical packaging applications in the case of barrier diffusion whereas selective transport is applied in the separation of different gas species from the gas mixture. The metalized coating on the polymer substrate was reviewed by Chatham to investigate oxygen diffusion barrier properties. Comparison of oxygen permeability by coating deposition methods such as evaporation, sputtering and plasma deposition was performed using oxides and organic coating compositions. Initially the permeability was reduced with increasing the coating thickness depending on the layer deposition method. The oxygen permeation is dominated through high barrier coating as the gas molecules are diffused through the coating layer [1]. Palladium coating was used to combine with ceramic support by sputter deposition for separation of hydrogen gas from nitrogen. The presence of grain boundaries due to small crystallite size within the Pd lattice facilitates hydrogen transport through the dense metal coating. Thus the dislocations in the palladium lattice easily permeate hydrogen gas molecules [2]. Palladium/silver alloy coated on the polymer membrane are effective in the separation of hydrogen from the other gasses. It also includes CO_2 and He separation which are difficult to achieve by polymer membranes. Due to very thin metallic layer, such membranes are inexpensive and can be operated at ambient temperature and pressure. The metallic coating drastically improves the selectivity and shows stability even after continuous operation up to 6 weeks. Therefore, not only resultant point of view but also stability point of view such modification represents an intermediate stage between present state of the art of polymer membranes and high temperature metallic membranes [3]. The coating film of silicone oxide acts differently compared to the glass coating on the polymer substrate. Diffusion of inert gas molecules occurs in the silicone oxide coating on the polymer substrate due to presence of nano and micro defects within the lattice. Nanodefects in the oxide layer are more similar to nanoporous solid than the coating of silica glass with respect to the permeation properties. The permeability of oxide coated polymer membrane is increases and the activation energy reduces compared to the glass coating on the polymer substrate. Thus the modification in the coating composition also improves the barrier properties [4]. The MMM developed by coating of imidazolate framework ZIF-8 nanoparticles incorporated into a poly(vinylamine) (PVAm) coating solution on to PSF support membrane were fabricated to obtain CO_2 permeance and CO_2/N_2 selectivity. By increasing the feed pressure, MMM shows rapid decrease in the CO_2 permeance and results in the high degree of plasticization because the polymer chain segments becomes more flexible at higher pressure. The separation performance also improves due to deposition of selective layer. Thus the coating layer on to polymer membrane effectively changes CO_2 plasticization [5].

The transport mechanism by metal coated polycarbonate membrane has been discussed in the present chapter. The gases used for the test are He, H_2, CO_2, O_2, N_2 and CH_4. Pt-Pd alloy coated polycarbonate membranes are analysed for gas permeation testing using constant volume/variable pressure system described by **Figure 2.3** given in **Chapter 2**. The study describes the effect of kinetic diameter (KD) of gasses on their permeability by polycarbonate membrane and also the effect of leak rate of the system on gas permeability. The influence of gas flux through metal coating has been compared by its permeability with the neat polycarbonate membrane given in section **3.2**. The SEM analysis of PC/Pt-Pd composite membrane was performed to determine the surface morphology of membrane in the same section. As He and H_2 are having smallest kinetic diameter compared to other gasses, they diffused faster within the membrane matrix. Therefore, they do not show time lag whereas the other gasses takes time to diffuse called time lag given by the equation **1.4** in **Chapter 1**. The solubility coefficient of such gasses can be calculated by the relation of diffusion coefficient and permeability coefficient using equation **1.2** as described in the **Chapter 1**. Permeability coefficients were calculated by extrapolation of downstream pressure-time graph using origin 8 software using equation **2.1** given in **Chapter 2**. The selectivity of the gasses was also calculated for the selective gas pairs. Moreover, the plasticization effect of CO_2 at different operating pressure has been obtained and the effect of feed pressure on the selectivity is also discussed in section **3.3**. The whole analysed work is summarized in section **3.4**. The test was performed at 30 psi constant upstream pressure and at 35 ºC temperature. As the system was exposed to vacuum prior, the unit conversion of pressure must require. The gauge pressure was kept at 30 psi which is termed as psig. But for general notation the pressure displayed in the pressure gauge is denoted by psi. Therefore, 14.7 psi atmospheric pressure must be added to the gauge pressure which is termed as psia. Thus the absolute upstream pressure will be 44.7 psia.

3.2. PC and PC/Pt-Pd membranes

3.2.1. Gas permeation

The rate of change in gas flux and permeability are calculated using the expression of constant volume/variable pressure system given in **Chapter 2**. The permeability of penetrant with their kinetic diameter is shown in **Table 3.1**. As the system leakage is also included in the calculation, permeability with leak test and without leak test is listed for the gasses used. The leak rate of the system is 4.46E-07 cmHg/s when pure PC is used. The rate of gas flux i.e. $(dP/dt)_{ss}$ and $(dP/dt)_{leak}$ are also listed in **Table 3.1**. The transport of gas molecules through membrane depend on their shapes and size. The size dependent sequence has been followed by the gas molecules through the pure PC as well metal coated membranes. The smaller kinetic diameter gasses show faster permeation rate. Therefore, as shown in the **Table 3.1**, the rate of gas flux reduces with increase in KD of gasses. Permeability deceases with increasing the kinetic dimeter of penetrant. The permeability behavior follows the sequence: He > H_2 > CO_2 > O_2 > N_2 > CH_4. Due to excessively fast transport rate of He and H_2 even at low feed pressure, it is difficult to find their steady state. Due to smallest KD, He permeates faster as compared to rest of the gasses and for N_2 and CH_4 permeability coefficient fell down to relatively lower value.

Table 3.1 Permeability of pure PC within and without leak

Gases	**Kinetic Diameter (Å)**	**Rate of gas flux × 10^{-5} (cmHg/s)**		**Permeability of PC (barrer)**			**% change**
		$(dP/dt)_{leak}$	**$(dP/dt)_{ss}$**	**With Leak Test**	**Without Leak Test**	**Reference**	
He	2.60	7.44	7.49	13.56	13.64	17.6 [6]	0.6 %
H_2	2.89	7.26	7.31	13.23	13.31	11.5 [6]	0.6 %
CO_2	3.30	4.74	4.79	8.64	8.72	8.4 [7]	0.9 %
O_2	3.46	1.83	1.79	3.26	3.35	3.8 [8]	2.6 %
N_2	3.64	0.24	0.19	0.36	0.44	0.44 [8]	18 %

The leak rate of the system was determined by keeping the system under vacuum and permeability of pure PC was calculated with leak test and without leak test. As shown in the **Table 3.2** system leakage affects minor change in the gas permeability which is within error. The effect of gas leakage on permeability by the system depends on the KD of the gasses. Hydrogen and helium have smaller kinetic diameters. Therefore, the effect of leakage was found to be less. The system leakage changes with KD of the penetrant changes. It was observed that for CO_2, the leak rate percentage increases compared to H_2 and He. Without leakage 0.9% permeation raises for carbon dioxide whereas for oxygen it is 2.6% which proves that the KD affects the leak rate. The highest leak rate effect was noted for nitrogen which proves the larger KD of the gas molecule affects the leakage. In case of larger molecules, the $(dP/dt)_{ss}$ and $(dP/dt)_{leak}$ are compatible, while smaller molecules $(dP/dt)_{ss} >> (dP/dt)_{leak}$. Hence the overall contribution of leakage is less effective. The permeability coefficients of various gasses for PC membrane are compared with the literature values. Permeability of the gases determined by the system was also compared with the reported data given in the **Table 3.2**.

Table 3.2 Permeability of pure and Pt-Pd coated PC membranes

Gases	**Kinetic Diameter (Å)**	**Permeability (barrer)**		**% change**
		PC	**PC/Pt-Pd**	
He	2.60	13.64	117.37	227.38
H_2	2.89	13.31	16.91	27.06
CO_2	3.30	8.72	12.95	48.46
O_2	3.46	3.35	10.66	218.64
N_2	3.64	0.44	2.30	427
CH_4	3.80	*0.4	1.59	297

*Data used from reference [7]

Table 3.2 provides gas permeability of metal coated polycarbonate membrane for the gasses used for the present study. Under the same operating conditions, gas permeability of PC/Pt-Pd increases compared to pure PC. This may be due to gain in the solubility parameter as the exposed gasses first interact with the coating layer as shown in the schematic of sample in **Figure 3.1**. The transport of gasses through metal composite differs relative to that of polymer material. The interaction of gas and the metal is physiochemical process, which is thermodynamic phenomenon. Permeability is influenced mainly by two factors: (i) diffusivity and (ii) solubility. Diffusion coefficient is the kinetic parameter and the solubility coefficient is the thermodynamic parameter. Therefore, permeability of the gasses is enhanced due to sorption of gas molecules in presence of metal coating. Moreover, the metal alloy used for the test is catalytic in nature which may produce catalytic effect on the gas transport. For larger kinetic diameter gasses, permeability is influenced in vast amount of percentage relative to that of pure PC. It is observed that for H_2 and He, coating has affected in smaller percentage while the rest of the gases are more influenced by the modification. It was also observed that there is increase in gas permeability for all gases due to coating effect while for N_2 permeation it reflects highest percentage change relative to pure PC membrane. As reported by Lee et al., some defect sites, such as vacancies, grain boundaries and dislocations exist in metal structures promote to diffuse even for larger gas molecules. N_2 being larger atomic size, lattice expansion often occurs compared to the size of interstitial sites. Introduction of N_2 in to metal, forms “nitriding” and in the initial step it occurs as N_2 permeation [9]. Therefore, nitrogen permeation is more influenced by metal coating.

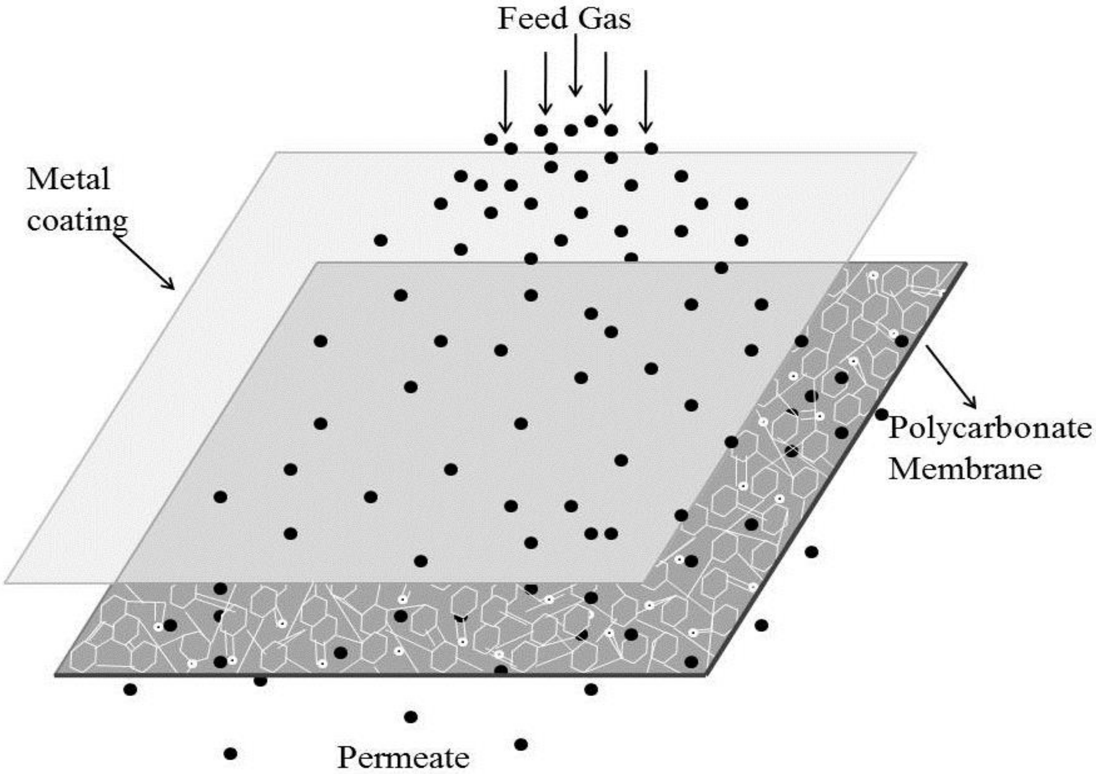

Figure 3.1 Gas transport through Pt-Pd coated PC membrane

3.2.2. Effect of metal coating on selectivity

The selectivity of various gas pairs for pure and modified membrane is given in the **Figure 3.2**. Usually, permeability and selectivity follows trade-off relationship as explained in **Chapter 1**. The metallic layer influences permeability coefficient for all the gasses which will certainly inhibit the selectivity. Selectivity of He is not given in **Figure 3.2** as H_2 and He permeation changes in similar way due to modification. Permeability for H_2 and CO_2 increases, whereas the selectivity was not much affected due to the coating. Only 14 % reduction in selectivity is obtained for hydrogen over carbon dioxide. Hydrogen separation from the rest of the gasses is inhibited by the fabrication compared to that of metallic layer. Selectivity of hydrogen over oxygen was reduced up to 60% whereas over nitrogen and methane, it gives 76% and 68% respectively. For CO_2/O_2, CO_2/N_2 and CO_2/CH_4 the values of selectivity reduce and vast domination have been observed with nitrogen and methane gas.

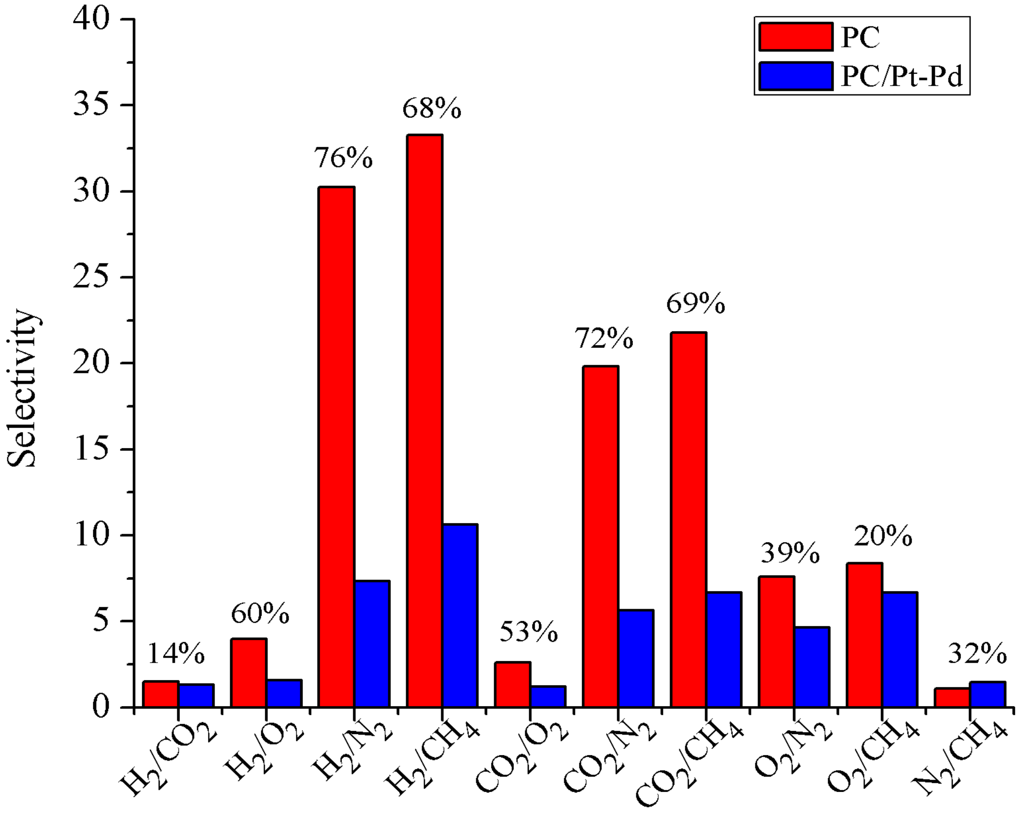

Figure 3.2 Selectivity comparison of pure PC and Pt-Pd coated PC

The selectivity by diffusion and by solubility for pure and metal coated membrane is given in the **Table 3.3**. Diffusivity selectivity is promoted by metal coating and solubility selectivity is inhibited in large amount. The separation factor for CO_2/O_2, CO_2/N_2 and O_2/N_2 gas pairs changes mainly by the solubility selectivity. For CO_2/N_2 gas pair solubility parameter is more influenced by the coating layer. CO_2 is condensable gas and N_2 forms nitride formation as discussed earlier which promotes the sorption of gas molecules by the metallic coating and tends to increase solubility of both the gasses. Therefore, the reduction in the solubility selectivity is larger for this gas pair. Oxygen separation from nitrogen and methane are not more affected compared to the previous gasses.

Table 3.3 Selectivity due to diffusion and solubility

Gas Pair	**Selectivity by Diffusion**		**Selectivity by Solubility**	
	PC	**PC/Pt-Pd**	**PC**	**PC/Pt-Pd**
CO_2/O_2	0.88	0.90	3.01	1.36
CO_2/N_2	1.40	1.56	17.33	3.98
O_2/N_2	1.60	1.73	5.76	2.93

Selectivity for N_2/CH_4 has increased for PC/Pt-Pd membrane. It enhances up to 32% for modified membrane compared to that of pure polymeric membrane. In Robeson 2008 upper bound plot, the selectivity of N_2/CH_4 with respect to the N_2 permeability tends towards the upper bound boundary line as shown in **Figure 3.3**. The graph is plotted on the same scales as given in the literature of Robeson upper bound for N_2/CH_4 versus nitrogen permeation given in 2008 [10]. The prominent effect of PC/Pt-Pd membrane improves both permeability and separation factor for N_2 and N_2/CH_4 respectively. The surface modification can be used for separation of CH_4 from natural gas.

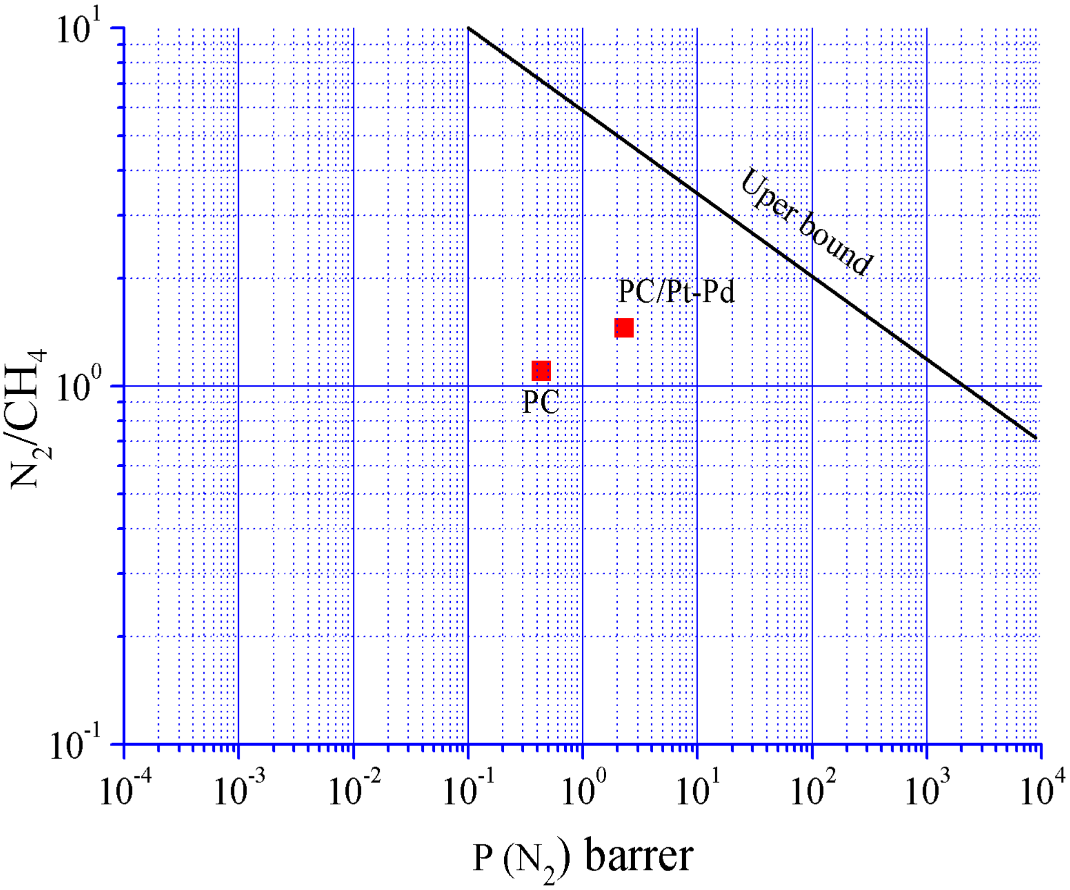

Figure 3.3 Robeson upper bound correlation for N_2/CH_4 separation [10]

3.2.3. Scanning Electron Microscopy (SEM)

The morphological structure of the PC/Pt-Pd membrane surface is shown in **Figure 3.4**. The surface of pure PC is dense in nature given by Alamin Idris et al. and the metallic coating produces surface roughness within the membrane surface [11]. Metal coating forms interfacial voids and rigidifies polymer chains at polymer/metal coating interface. Thus the metallic surface provides the interfacial gateway for transport of gas molecules [12]. The similar morphology was observed in this metal coated polycarbonate membrane. According to the solution-diffusion mechanism, the gas molecules are first absorbed at the membrane surface, the surface roughness of the membrane affects the gas transport parameters. Uniform coating is clearly seen in SEM image.

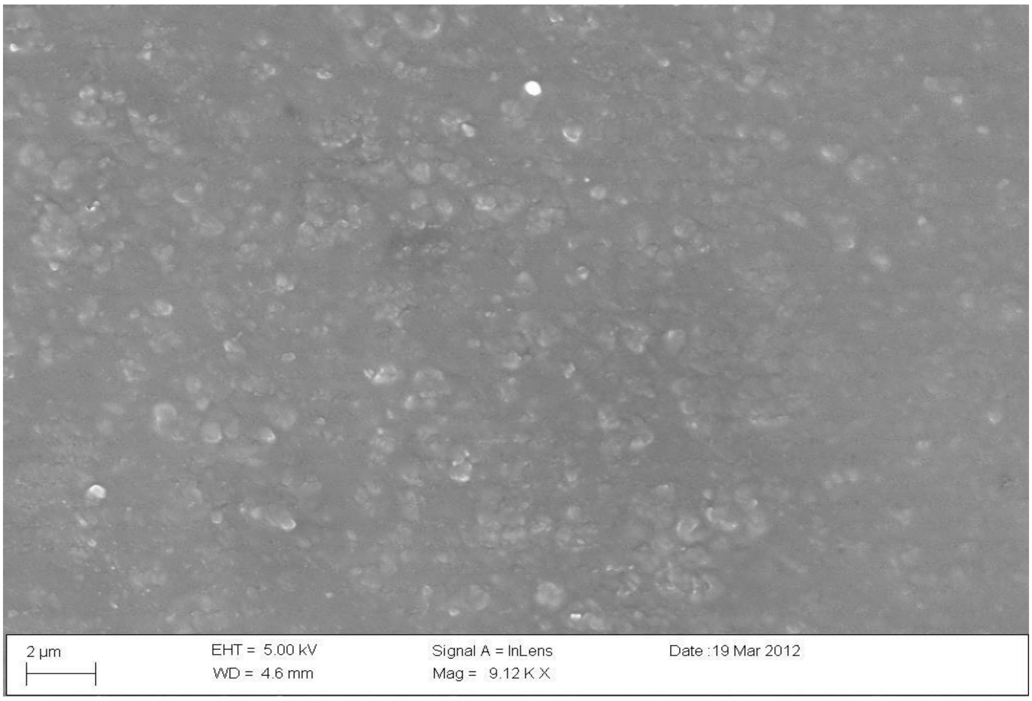

Figure 3.4 FE-SEM image of Pt-Pd coated PC membrane

3.3. CO_2 plasticization effect

3.3.1. CO_2 permeability

The CO_2 permeation tests were carried out at constant temperature 35°C for PC/Pt-Pd membrane and the operating upstream pressure ranges from 30 psi to 230 psi to investigate the effect of structural changes. The permeability obtained was compared with reported data. Gas permeability coefficient, diffusion coefficient and solubility coefficient are given in **Table 3.4**.

Table 3.4 Gas transport parameters at different feed pressure

Feed pressure (psi)	**Time lag (s)**	**D × 10^{-8} (cm^2/s)**	**S × 10^{-2} $cm^3(STP)/cm^3cmHg$)**	**P (barrer)**	**P (barrer)***
30	2295	2.35	5.27	12.40	7.71
80	1984	2.72	3.28	8.94	7.22
130	2121	2.55	3.49	8.90	6.71
180	1602	3.37	2.16	7.28	6.31
230	1669	3.24	2.28	7.41	5.98

*Reference data used from Jorden et al. [13]

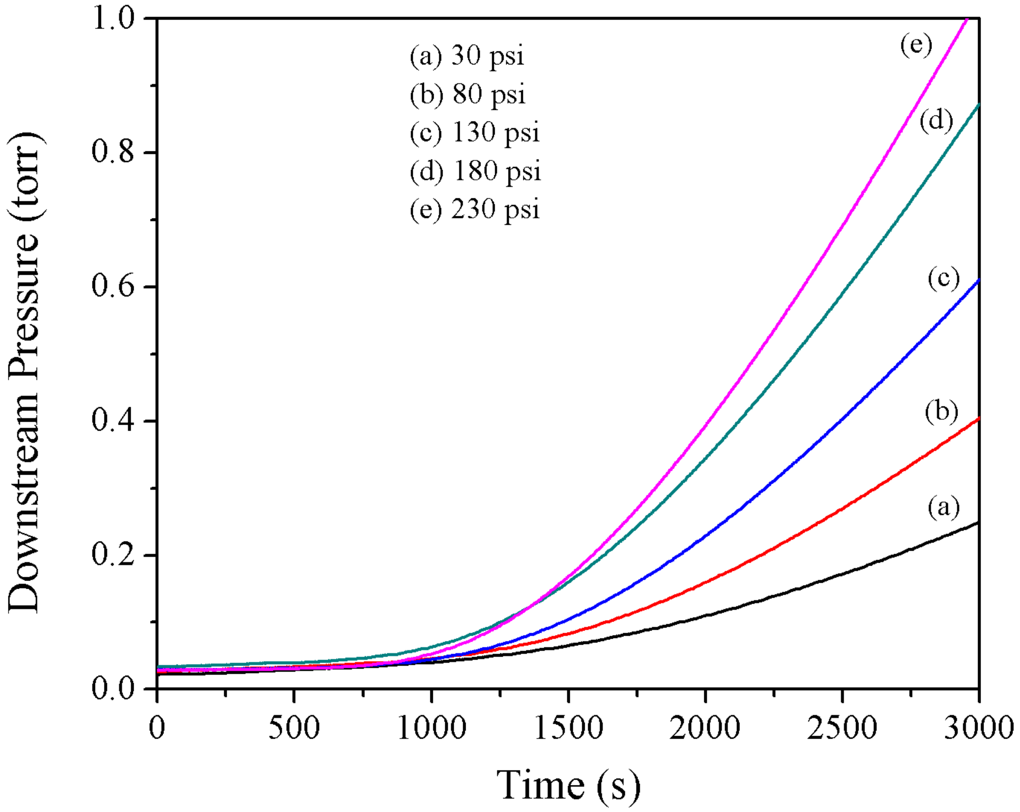

Figure 3.5 Downstream pressure versus diffusion time at different feed pressure for PC/Pt-Pd membrane

It can be inferred from **Figure 3.5** that time lag reduces as per increment in feed pressure. CO_2 gas molecule diffuses within 1000-2300 seconds from 30-230 psi operating range. Steady state time reduces with increase in upstream pressure, e.g. it falls down from 2295 seconds to 1984s second as pressure gains from 30 psi to 80 psi and the further increase in pressure up to 130 psi, the CO_2 diffusion becomes steady and shifts to 2121 seconds producing small fluctuation. Thus within 30-230 psi operating pressure time lag value reduces with small fluctuations. Diffusion coefficient and time lag are in inverse proportion to each other which have been discussed in **Chapter 1**. Therefore, diffusion coefficient increases by increasing upstream pressure. As explained in the **Chapter 1**, gas permeability is more affected by diffusion coefficient. Therefore, transport of carbon dioxide gas molecule becomes faster by increasing the feed pressure. The lowest flow rate is observed at 30 psi whereas at 230 psi it gives maximum transport rate. The **Figure 3.5** describes downstream pressure versus time range for CO_2 gas and denotes the dependence of transport rate for different upstream pressure. Being polar molecule, CO_2 forms dipolar interaction with the polar group of PC. The interaction of CO_2 with polar group is stronger than the interaction in-between the pendent segments. Therefore, the exposure of CO_2 at specific operating pressure to PC may break the weaker interaction providing additional diffusion routs [14]. But in case of metal coated PC, as CO_2 exposed to the membrane, initially it interacts with coating layer and it diffuses through the metallic region and then enters to polymer matrix causing very small mobility of polymer chain segments. Thus by increasing the feed pressure, diffusion also changes up to certain extent.

Permeability coefficient is also affected by thermodynamic parameter, solubility of gas molecules within the membrane. CO_2 solubility enhances within PC with constant diffusion parameter [15]. In case of PC/Pt-Pd composite membrane permeability reduces due to rejection in solubility at higher upstream pressure. Generally, solubility is governed by condensation of penetrants and its mixing with polymer segments. CO_2 interaction on metal surface becomes physiochemical process in which carbon dioxide forms stable structure with binding modes. According to Wang et al., highest binding energy is formed by carbon dioxide bond on platinum surface relative to other metals. The thermal properties of metal can be changed as metal composited with polymer material [16]. Therefore, thermodynamic coefficient has been affected by coating layer. Solubility reduces around 50 % with change in feed pressure from 30-230 psi and minor change in diffusion coefficient is recorded compared to solubility within the pressure range. Permeability verse upstream pressure plot is given in **Figure 3.6**. Carbon dioxide permeation steadily reduces in the operating pressure range with small deviation at 130 psi. There is gradual decrement in permeation with respect to feed pressure which follows the similar trend of CO_2 permeation for pure polycarbonate at operating pressure range. Permeability changes with CO_2 exposure at different feed pressure has been given by Jorden et al. in the graphical form compared with the values obtained for PC/Pt-Pd membrane. The permeability coefficient obtained from the graph using get data software was compared with values of the coated membrane. Jorden reported that the coefficient of permeability gradually decreases in the range of 1-20 atmospheric operating pressure [13]. The metal coating has improved the permeability compared to pure PC provided in literature. The comparison of permeability is provided in **Table 3.4** for pure and coated membrane. At 30 psi constant pressure, permeability of PC membrane is 7.71 barrer and for PC/Pt-Pd it is 12.40 barrer. As shown in **Figure 3.1** the feed pressure was applied on the metallic layered surface without direct interaction to host PC material. The occurrence of physiochemical process between the carbon dioxide gas and metal coating leads somewhat faster transport of the gas molecules relative to neat membrane materials. Plasticization of the membrane promotes penetrant permeability as the carbonyl group of polycarbonate significantly affects the polymer chain mobility. Due to condensable nature, CO_2 plasticize the polycarbonate composition and raise its chain motion at high pressure. As carbon dioxide is polar molecule, its interaction with carbonyl group of polycarbonate increase chain mobility at elevated pressure. The coating includes palladium composition and as reported by Valmikanathan et al., interaction of Pd nanocluster gains free volume between polymer chain segments. In addition, relative weak interaction of Pd and PC compositions results gain in free volume [17]. Therefore, at same elevated feed pressure, PC and PC/Pt-Pd membranes differ in permeation as the metal coating promotes carbon dioxide transport compared to that of PC membrane. Even the Pd adds resistance which reduces as gain in temperature. Therefore, number of vacant site increases as the gas molecules penetrates the material which enhances the effective gas permeability through the membrane. It was observed that the modified and virgin membrane differs by 5 barrer difference at 30 psi operating pressure. Permeability of PC/Pt-Pd and PC at 230 psi was 7.41 barrer and 5.98 barrer respectively. Thus plasticization of PC is affected by metal coating results the change in gas permeability.

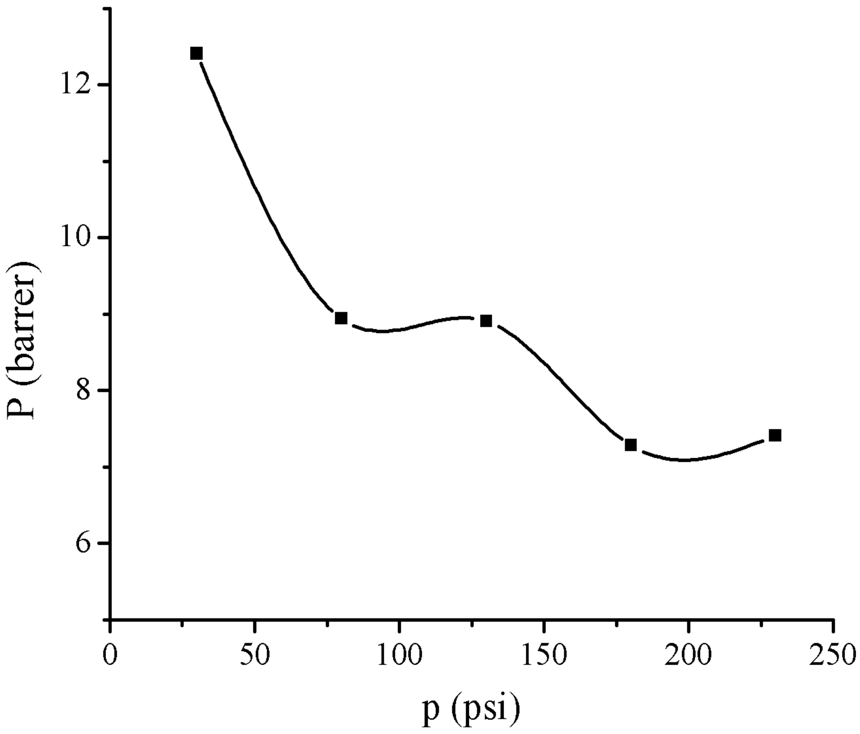

Figure 3.6 Permeability of CO_2 for PC/Pt-Pd at different feed pressure

3.3.2. Effect of feed pressure on selectivity

Selectivity of H_2/CO_2 gas pair for PC/Pt-Pd membrane at different feed pressures is given in **Figure 3.7**. H_2 separation factor enhances with increase in 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 extent which will be discussed in **Chapter 4** whereas CO_2 permeability inhibited for this pressure range. The selectivity is maintained with small loss at 30 psi [18]. The result indicates the better trade off relationship for H_2/CO_2 gas pair. Thus the selectivity of H_2 over CO_2 was improved within the pressure range for PC/Pt-Pd membrane.

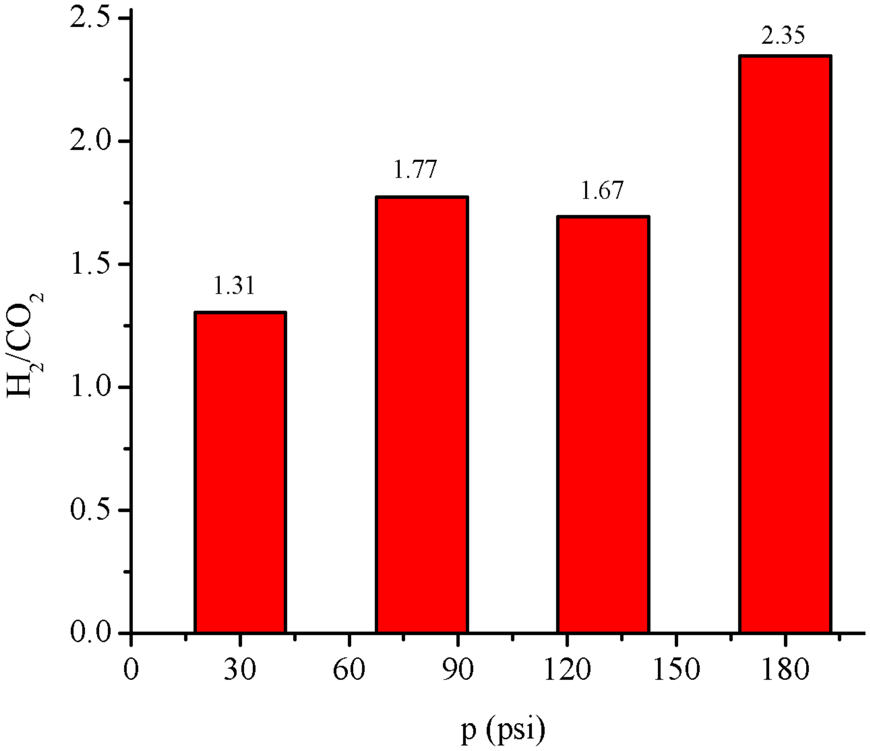

Figure 3.7 Selectivity of H_2/CO_2 at different upstream pressure from 30 psi to 180 psi

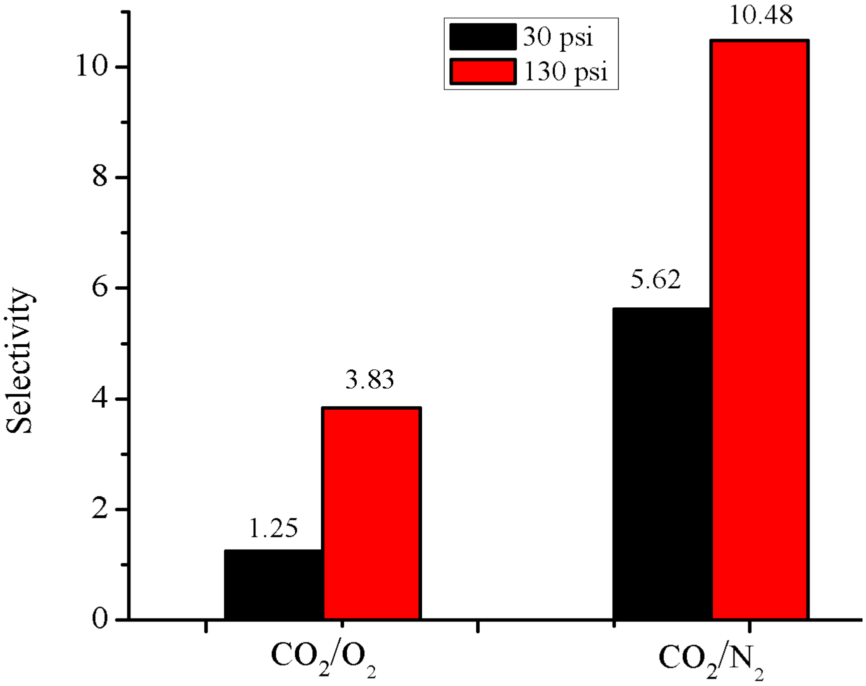

Figure 3.8 Selectivity of CO_2 with O_2 and N_2 at 30 psi and 130 psi upstream pressures

Figure 3.8 shows selectivity of CO_2/O_2 and CO_2/N_2 gas pairs at 30 psi and 130 psi operating pressures. In most of the membrane materials, gain in permeability causes reduction in selectivity. In case of metal composite, by increasing the feed pressure, the selectivity was also increased. The selectivity for CO_2/O_2 gas pair becomes double at 130 psi with respect to 30 psi feed pressure. The PC chain segments are rigid at higher pressure and they do not allow the N_2 permeation as in case of lower feed pressure. CO_2/N_2 gas pair also follows the similar trade as its selectivity becomes almost double.

3.4. Summary

Platinum-palladium metal alloy was used as barrier material on polycarbonate substrate to alter the transport parameters of the resultant membrane composition. The study of gas permeability using constant volume/variable pressure system provides very reliable measurements with the introduction of system leakage even for very low pressure deviations. Gas permeability of the gasses follows the same sequence such of the kinetic diameters of the gasses. Metal coating influences the gas transportation in vast amount. Scanning electron microscopic image of the PC/Pt-Pd membrane conforms the morphological changes due to modification. The alteration of surface morphology promotes penetrant permeation as interfacial voids are generated by the coating layer. Moreover, at the metal-polymer interface, the polymer chain segments are rigidified due to the thin coating layer. Thus, the gas permeability increases by introduction of an additional nanolayer. The modified membrane structure forms large deviation in selectivity compared to pure polymer membrane. H_2/CO_2 selectivity was not much affected by layered PC membrane. For most of the gas pairs, the selectivity reduces with high percentage whereas for N_2/CH_4 gas pairs it gains. N_2/CH_4 selectivity within the Robeson upper bound plot shifts towards the upper bound limit due to the metal coating.

The effect of metal coating alters the plasticization pressure of carbon dioxide gas under operating pressure from 30 psi to 230 psi. The solubility of

CO_2 is enhanced by metal coated PC membrane which increases its permeability. The hybridization of organic-inorganic composition improves CO_2 interaction at penetrant/membrane interface under influence of pressure gradient. Diffusivity increases in small amount as the feed pressure is increased. Therefore, the improvement in the permeability is due to sorption of CO_2 by the membrane to be tested. The effect of plasticization has been compared with the reported data for the same pressure range. The plasticization effect can be restricted by metal layer deposition on the PC membrane. The coating plays vital role to enhance selectivity under the gain in feed pressure. It is concluded that the thin layer of metal alloy not only improves the gas transport through the membrane but also alters the plasticization phenomenon.

References

[1] T. Holo, Oxygen diffusion barrier properties of transparent oxide coatings on polymeric substrates, *Surf. Coatings Tech*. 78 (1996) 1–9.

[2] V. Jayaraman, Y.S. Lin, M. Pakala, R.Y. Lin, Fabrication of ultrathin metallic membranes on ceramic supports by sputter deposition, *J. Memb. Sci.* 99 (1995) 89–100.

[3] A.L. Athayde, R.W. Baker, P. Nguyen, Metal composite membranes, *J. Memb. Sci.* 94 (1994) 299–311.

[4] A.P. Roberts, B.M. Henry, A.P. Sutton, C.R.M. Grovenor, G.A.D. Briggs, T. Miyamoto, M. Kano, Y. Tsukahara, M. Yanaka, Gas permeation in silicon-oxide/polymer (SiOx/PET) barrier films : role of the oxide lattice, nano-defects and macro-defects, *J. Memb. Sci.* 208 (2002) 75–88.

[5] S. Zhao, X. Cao, Z. Ma, Z. Wang, Z. Qiao, J. Wang, S. Wang, Mixed-matrix membranes for CO_2/N_2 separation comprising a poly (vinylamine) matrix and metal−organic frameworks, *Ame. Chem. Soc.* 54 (2015) 5139–5148.

[6] D. Sen, H. Kalipclar, and L. Yilmaz, Gas separation performance of polycarbonate membranes modified with multifunctional low molecular

weight additives, *Sep. Sci. Tech.* 41 (2006) 37–41.

[7] S. Sridhar, T.M. Aminabhavi, M. Ramakrishna, Separation of Binary Mixtures of Carbon Dioxide and Methane through Sulfonated Polycarbonate Membranes, *J. App. Poly. Sci.* 105 (2007) 1749–1756.

[8] C. Hu, Y. Fu, K. Lee, R. Ruaan, J. Lai, Effect of sorption behavior on transport properties of gases in polymeric membranes, *Polymer.* 50 (2009) 5308–5313.

[9] K. Lee, S. Liguori, P. Psarras, J. Wilcox, Theoretical study of nitrogen absorption in metals, *Ame. Chem. Soc.* 121 (2017) 17016–17028.

[10] L.M. Robeson, The upper bound revisited, *J. Mem. Sci.* 320 (2008) 390–400.

[11] A. Idris, Z. Man, A.S. Maulud, Polycarbonate/silica nanocomposite membranes: Fabrication, characterization, and performance evaluation, J. *Appl. Polym. Sci.* 134 (2017) 1–17.

[12] B.A. Mccool, Y.S. Lin, Nanostructured thin palladium-silver membranes: Effects of grain size on gas permeation properties, *J. Mater. Sci.* 36 (2001) 3221–3227.

[13] S.M. Jordan, W.J. Koros, J.K. Beasley, Characterization of CO_2 induced conditioning polycarbonate films using penetrants with different solubilities, *J. Mem. Sci.* 43 (1989) 103–120.

[14] M. Wessling, H. Strathmann, A. Bos, I.G.M. Pu, CO_2 induced plasticization phenomena in glassy polymers, *J. Mem. Sci.* 155 (1999) 67–78.

[15] S. Chen, S. Huang, K. Yu, J. Lai, M. Liang, Effect of CO 2 treated polycarbonate membranes on gas transport and sorption properties, *J. Memb. Sci.* 172 (2000) 105–112.

[16] S. Wang, X. Liao, D. Cao, C. Huo, Y. Li, J. Wang, H. Jiao, Factors Controlling the Interaction of CO_2 with Transition Metal Surfaces, *J. Phys. Chem. C.* 111 (2007) 16934–16940.

[17] O.P. Valmikanathan, S.V. Atre, O. Ostroverkhova, V.K. Pillai, I.S. Mulla, The Effect of nanoparticle distribution on the structure and

properties of palladium/polycarbonate nanocomposites, *NSTI-Nanotech.* 1 (2007) 162–165.

[18] P.S. Tin, T.S. Chung, Y. Liu, R. Wang, S.L. Liu, K.P. Pramoda, Effects of cross-linking modification on gas separation performance of Matrimid membranes, *J. Memb. Sci.* 225 (2003) 77–90.