Int.J.Nano Dim. 2(4): 217-221, Spring 2012
ISSN: 2008-8868

Contents list available at **IJND**

International Journal of Nano Dimension

Journal homepage: *www.IJND.ir*

Comparative investigation on the correction factors of hydrogen permeability on CNTs-Mixed matrix membrane

A. Solaymani[1]
M. M. Doroodmand[2]
S. Sabbaghi[1,*]

[1]*Department of Nano Chemical Engineering, Shiraz University, Shiraz, Iran.*
[2]*Department of Chemistry, College of Sciences, Shiraz University, Shiraz 71454, Iran.*

Received: 27 July 2011
Accepted: 10 October 2011

ABSTRACT

This paper discusses different important gas permeation models such as "Maxwell", "Bruggeman", "Lewis-Neilson", and "Pal" models to predict "Mixed Matrix Membranes" (MMMs) performance. The main parameter considered and discussed is the permeability of Hydrogen on Carbon Nanotubes (CNTs)-MMM. For evaluation of the theoretical models, experimental data of permeability for H_2 were compared to the theoretical models. The results revealed that, the existing models are not appropriate for evaluation of the permeability of the carbon nanostructure-based MMMs. Therefore, correction factors are needed to fit the selective permeability of carbon nanostructure-based MMMs for selective separation of various gaseous such as H_2 or CO_2. This correction factor robustly depends on the morphology of carbon nanostructures, the defect, kind and amount of metal/metal oxide nanoparticles, doped on carbon substrate and functional groups in the carbon matrix. Hence, to be in a good agreement with experimental data for separation of H_2 from CO_2, the correction value was estimated to -0.0022 for single-walled carbon nanotubes (SWCNTs), -0.0032 for pure multi-walled carbon nanotubes (MWCNTs), -0.0044 for carbon nanofibers (CNFs).

Keywords: *Mixed Matrix Membrane; Permeation model; Gas separation; Permeability.*

INTRODUCTION

Function of membranes in gas separation process is playing an important role in lessening the operating energy requirements and environmental impact [1, 2]. Polymeric membranes have the advantages of attractive mechanical properties and economical costs. On the other hand, existing polymeric membrane materials misplace their selectivity in the presence of heavy hydrocarbons [3]. Inorganic materials can be used as membranes as a purpose of gas separation equipments [1, 4].

* Corresponding author:
Samad Sabbaghi
Department of Nano Chemical Engineering, Shiraz University, Shiraz, Iran.
Tel +98 7116133709
Fax +98 7116286421
Email sabbaghi@shirazu.ac.ir

Inorganic membranes like zeolite have significant advantages such as high thermal, chemical stability and good resistance at high pressures [4]. Nevertheless, the use of these materials as membranes has some limitations such as high cost production and brittleness. Thus, new types of composite membranes can be considered as permeable membrane.

(MMMs) stand for Mixed Matrix Membranes that are hybrid membranes of contain organic fillers, embedded in polymer matrix [5, 6]. MMMs have huge potentials such as good lifetime; high selectivity and permeability, superior mechanical and thermal stability that make them as a good candidate for gas separation. In recent times, "Carbon Nanotubes" (CNTs) are used as fillers in MMMs due to their important properties [6]. CNTs are known for their high surface area, active site and superior gas flux. CNTs are tubes composed of rolled-up graphite sheets with diameters in nanometer scale [7]. There are two types of CNTs [8–10]: single-walled CNTs (SWCNTs) and multi-walled CNTs (MWCNTs). SWCNTs are composed of a single graphene plane, while MWCNTs consist of two or more concentric tubes shells of graphene sheets. Using CNTs as dispersed fillers in MMMs offer a very attractive option approach. In order to make professional use of the MMMs, the permeability of membranes should be modeled. The existing models have been reported to predict the performance of MMMs. These models are also capable to estimate the permeability of membranes. Suitable models include "Agari", "Higuchi", "Bottcher", "Maxwell", "Bruggeman", "Pal", "Lewis-Nielsen" and "Felsk" models [11–20]. The aim of this study is to briefly discuss the existing models and also compare and evaluate the well-known theoretical gas permeation models for permeability of H_2 in mixed matrix membranes. This study is focused on the examination of more popular models such as the "Maxwell", "Bruggeman", "Pal", "Lewis-Nielsen" models.

COMPUTATIONAL METHODS

Some theoretical permeation models have been used to forecast the permeation properties of MMMs as functions of the permeabilities of the continuous and dispersed phases.

The "Maxwell" model was extended for electrical conductivity of composites and can be modified by permeability as [18]:

$$P_r = \frac{P}{P_m} = \left[\frac{2(1-\phi) + (1+2\phi)\lambda_{dm}}{(2+\phi) + (1-\phi)\lambda_{dm}} \right] \qquad (1)$$

Where P_r is the permeability relation of P/P_m, P is defined as the permeability of MMM. P_m and λ_{dm} are considered as the permeability of the continuous phase, and the permeability relation of P_d/P_m, respectively. Also, P_d and ϕ are defined as the permeability of the dispersed phase and ϕ the volume fraction of the dispersed phase, respectively. This model is appropriate to evaluate the amount of the permeability of MMM, when ϕ is less than 0.2.

"Bruggeman" model was also developed to estimate the dielectric constant of composites. The equation given by:

$$(Pr)^{1/3}\left(\frac{\lambda_d - 1}{\lambda_d - Pr}\right) = (1 - \phi)^{-1} \qquad (2)$$

The "Bruggeman" model has significant limitations similar to those evaluated for "Maxwell" model [13]. "Lewis–Nielsen" model originally was recommended for the elastic modulus of particulate composites [16]. To estimate the permeability

$$Pr = \frac{1+2\phi(\lambda_d - 1)/(\lambda_d + 2)}{1-\psi\phi(\lambda_d + 2)} \qquad (3)$$

Where

$$\psi = 1 + \left(\frac{1-\phi_M}{\phi_M^2}\right)\phi \qquad (3a)$$

Where, ϕ_m is considered as maximum packing volume fraction of nanoparticles. This is usually equaled to 0.64. This model, as clearly revealed according to Eq. (3), is easily converted to the "Maxwell" model Eq. (1), when ϕ_m approaches to 1.

Also, models such as "Pal" model was originally developed for thermal conductivity. This equation is:

$$(Pr)^{1/3}\left(\frac{\lambda_d - 1}{\lambda_d - Pr}\right) = \left(1 - \frac{\phi}{\phi_M}\right)^{-\phi_M} \quad (4)$$

In this study, the permeability as well as volume fraction of chemical vapor deposition (CVD)-fabricated MMMs using different types of carbon nanostructures such as single-walled carbon nanotubes (SWCNTs), multi-walled (MWCNTs), carbon nanofibers (CNFs) and also the effects of functional groups such as hydroxyl (OH), or carboxylic group (COOH) and the influence of metal/metal oxide nanoparticles such Fe, Pd, Cu, Ag, TiO_2, doped on different forms of carbon nanostructures, were studied in detail. For this purpose, the adsorption percentages of H2 were then evaluated using a lab-made thermo gravimetric analysis (TGA) instrumentation system.

RESULTS AND DISCUSSION

The previously reported models have some limitations that cause to create some errors for special structure like CNTs. For example, some of these models are fitting when volume fraction is low. Also, various factors related to the morphology of nanoparticles such as shape, or size distribution is ignored. This study confirms the correctness and also the precision of previously reported models for evaluation of the calculated permeability of carbon nanomaterials to H2. As shown Figure 1, differences between the experimental and theoretical models are clear. Due to the decrease of the results of theoretical models and experimental data, some correction factors should be introduced. Figure 2 shows the amount of correction factors that should be applied to the existing models. These correction factors are evaluated to-0.0022 for SWCNTs, -0.0032 for MWCNTs, -0.0044 for CNFs respectively. Applying these correction factors to the permeability coefficients of the existing models, simply makes these models suitable for prediction of the intrinsic properties CNT-based MMMs.

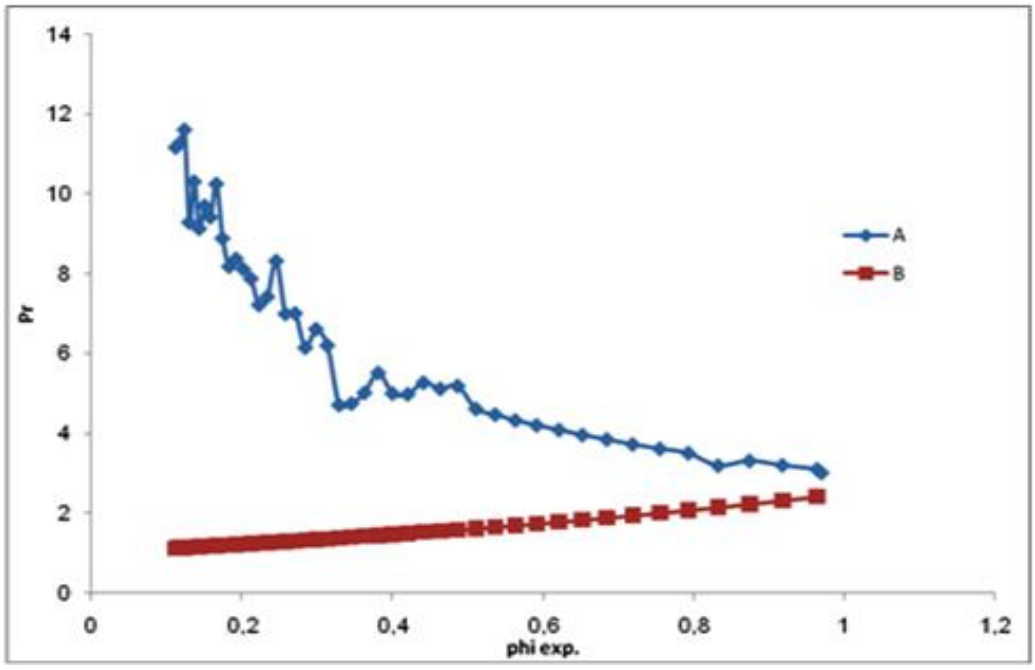

Fig. 1. Comparison between experimental and theoretical permeabilities for H2, A) Experimental B) Theoretical

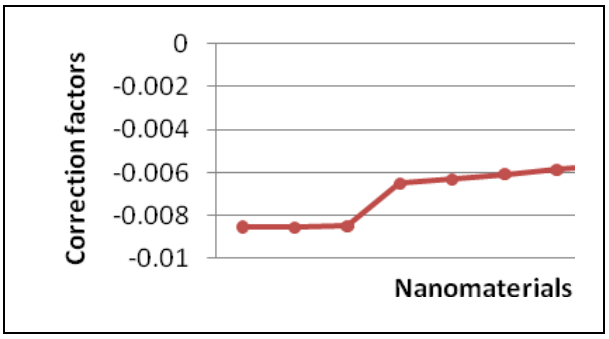

Fig. 2. Correction factors, evaluated for H_2 on different forms of carbon nanostructures

CONCLUSION

The theoretical models were developed to describe the permeability and selectivity of MMM systems. These models predicted MMM permeability but they have capability to particular fillers. The application of existing models for CNTs emerge some errors that presents the necessity to introduce the correction factors. By introducing the correction factors, the differences between experimental and theoretical models were disappeared.

REFERENCES

[1] Pandey Pratibha, Chauhan R.S, (2001), Membrane for gas separation, Prog. *Poly. Sci*. 26 853–893.

[2] Shimekit, Mukhtar B.H., Maitra S.,(2009) ,Ceramic membranes for the separation of carbon dioxide: A review, Trans. *Ind. Ceram. Soc*., 68 115–138.

[3] Shao Lu, Ting Low Bee,Chunga Tai-Shung, Greenberg Alan R.,(2009), Polymeric membranes for the hydrogen economy: Contemporary approaches and prospects for the future, *Journal of Membrane Science*, 327 18–31.

[4] Lu G.Q., Da Costa Diniz, Duke M.,Giessler S., Socolow R., Williams R.H.,Kreutz T., (2007), Inorganic membranes for hydrogen production and purification:A critical review and perspective, *Journal of Colloid and Interface Science*, 314 589–603.

[5] Zimmerman, C.M, Singh A., Koros W.J., (1997),Tailoring mixed matrix membranes for gas sparations, *J. Membr. Sci*., 137 145–154.

[6] Hashemifard S.A., Ismail A.F., Matsuura T., (2010), A new theoretical gas permeability model using resistance modeling for mixed matrix membrane systems, *Journal of Membrane Science* 350 259–268.

[7] Maa Peng-Cheng, Siddiqui Naveed A., Marom Gad, Kim Jang-Kyo, (2010), Dispersion and functionalization of carbon nanotubes for polymer-based nanocomposites: A review, Composites: Part A, 41 1345–1367.

[8] Dresselhaus MS, Dresselhaus G, Saito R., (1995), Physics of carbon Nanotubes, *Carbon* 33 883–91.

[9] Reich S, Thomsen C, Maultzsch J., 2004, Carbon nanotubes: basic concepts and physical properties, *New York, Wiley-VCH*, p. 31–40.

[10] Qian D, Wagner GJ, Liu WK, Yu MF, Ruoff RS.,(2002), Mechanics of carbon nanotubes. *Appl. Mech. Rev*., 55 495–533.

[11] Agari, Y., Uno T., (1986), Estimation on thermal conductivities of filled polymers, *J. Applied Polym. Sci.*, 32 5705–5712.

[12] Bottcher, C.J.F, (1945), The dielectric constant of crystalline powders, Recueil des Travaux Chimiques des Pays-Bas., 64 47–51.

[13] Bruggeman, D.A.G.,(1935), Berechnung verschiedener physikascher Konstanten von heterogen substanzen, *Annalen der Physics*, 24 636–679.

[14] Higuchi, W.I., Higuchi T., (1960),Theoretical analysis of diffusional movement through heterogeneous barriers. *J. Am. Pharm. Assoc. Sci*., 49 598–606.

[15] Felske, J.D., (2004), Effective thermal conductivity of composite spheres in a continuous medium with contact resistance. *Int. J. Heat Mass Transfer*, 47 3453–3461.

[16] Lewis, Nielsen T. and L., (1970), Dynamic mechanical properties of particulate-filled composites, *J. Applied Polym. Sci*., 14 1449–1471.

[17] Pal, R., (2008), Permeation models for mixed matrix membranes, *J. Colloid Int. Sci*., 317 191–198.

[18] Maxwell, J.C., 1954, A Treatise on Electricity and Magnetism, Dover Publications, Mineola, New York.

[19] Hashemifard, S.A., Ismail A.F., Matsuura T., (2010), Prediction of gas permeability in mixed matrix membranes using theoretical models. *J. Memb. Sci*., 347 53–61.

[20] Shimekit B., Mukhtar H., Maitra S., (2010), Comparison of predictive models for relative permeability of CO_2 in Matrimid-Carbon Molecular Sieve Mixed Matrix Membrane, *Journal of Applied Sciences* 10 1204–1211.