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Ultra-permeable polymeric membranes containing ZIF-8 nanoparticles for CO_2 capture

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Abstract—Membrane technology is an attractive approach for CO_2 capture from flue gas derived from coal-power plants, due to its inherent advantages such as high energy-efficiency, small footprint and potentially low cost. The state-of-the-art membranes are based on polar poly(ethylene oxide) (PEO), which exhibit high CO_2 permeability and high CO_2/N_2 selectivity. In this work, these PEO containing materials were doped with zeolitic imidazolate framework (ZIF-8) nanoparticles to improve CO_2 permeability. Specifically, ZIF-8 was incorporated into polymers prepared from poly(ethylene glycol) diacrylate (PEGDA). These ZIF-8 nanoparticles had high porosities and average pore aperture of 0.34 nm that was between the molecule size of CO_2 (0.33 nm) and N_2 (0.364 nm), indicating their potential of achieving high CO_2 permeability and CO_2/N_2 selectivity. The in situ synthesis of ZIF-8 provided uniform nanoparticle size of about 100 nm, enabling a good dispersion in polymers at loadings as high as 50 wt%. Increasing the ZIF-8 loading dramatically increased CO_2 permeability. For example, adding 10 wt% ZIF-8 increased the CO_2 permeability from 130.8 Barrers in a polymer prepared from PEGDA to 318.3 Barrers without changing the CO_2/N_2 selectivity. At a loading of 50 wt%, the nanocomposite exhibited a CO_2 permeability of 1334.5 Barrers and CO_2/N_2 selectivity of 33.1 at 35 °C, which was one of the best separation properties reported in the literature.

Keywords—*CO_2 capture, membrane, ZIF-8, PEGDA*

I. INTRODUCTION

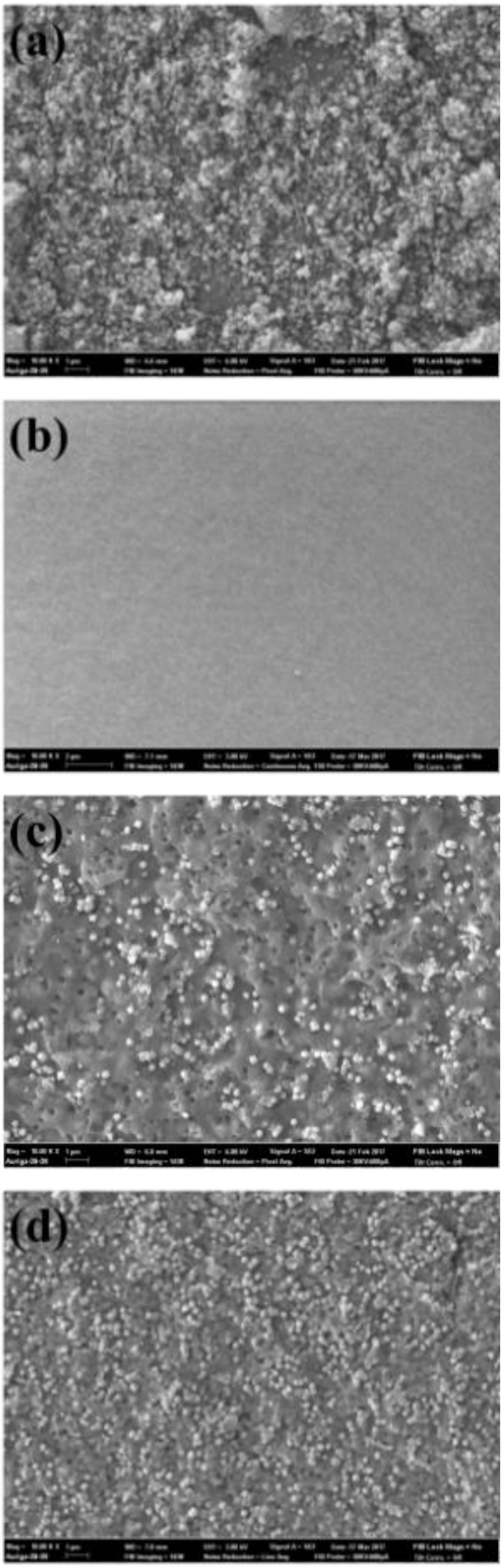
Nowadays, CO_2 separation is required in many fields like CO_2 capture from flue gas and syngas, purification of natural gas and biogas, etc [1]. Compared to conventional CO_2 separation technology (swing pressure adsorption and chemical absorption), membrane technology featured several advantages, such as small footprint, simplicity of operation and maintenance, high energy efficiency and potentially low cost [2]. As a branch of polymeric membranes, PEO-based membranes, including PEOs and copolymers like Pebax, showed high CO_2 permeability and high CO_2 selectivity against other gases such as H_2, CH_4 and N_2 [3,4]. However, for CO_2/N_2 separation, due to the trade-off between selectivity and gas permeability, PEO-based membranes are generally constrained by an upper bound performance limit [5]. Mixed matrix membranes comprising polymer bulk as the continuous phase and inorganic filler as the dispersed phase open new approaches to overcome the trade-off of polymeric membranes [1]. The majority of research concerns porous fillers, which include zeolites, carbon molecular sieves, metal organic frameworks (MOFs), zeolite imidazole frameworks (ZIFs) and porous organic cages (POCs), etc [6]. MOFs are porous crystalline coordination compounds, extending in one, two or three dimensions, composed of metal atoms or clusters linked by organic ligands [7]. ZIFs are a sub-family of MOFs that have tuneable pore sizes and chemical functionality, coupled with exceptional chemical stability, and exhibit versatile structures analogous to that of inorganic zeolites [5]. Herein, ZIF-8 nanoparticles had high porosities and theoretical pore aperture of 0.34 nm that was between the molecule size of CO_2 (0.33 nm) and N_2 (0.364 nm), indicating their potential of achieving high CO_2 permeability and CO_2/N_2 selectivity. Nafisi and Hägg [8] used ZIF-8 as inorganic filler in PEBAX®2533 polymer matrix, and obtained a high CO_2 permeability of 1287 Barrers with CO_2/CH_4 and CO_2/N_2 selectivity of 32.2 and 9 respectively when the concentration of ZIF-8 up to 35%. Multilayer composite membranes containing ZIFs were also researched. Sutrisna et al. [9] prepared ZIF-8/Pebax®1657 based dense flat sheet mixed matrix membranes and hollow fibre composite membranes, and found that the addition of ZIF-8 into the Pebax matrix improved the gas permeance with small loss of gas selectivity. Besides, a permeability of 758 Barrer with

CO_2/CH_4 selectivity of 16.1 was obtained in ZIF-8/Pebax®1657/PES flat membranes [10]. In summary, Pebax membranes containing ZIF-8 were well studied. However, other PEO-based polymers, such as PEGDA, PEGMEA, were rarely studied. Furthermore, for Pebax membranes, a relative long period was needed to evaporate solvents and form films or selective layers [11]. Therefore, the deposition and agglomeration of ZIF-8 would be happened in the solution.

In this study, pure PEGDA was adopted as PEO-based polymer materials. PEGDA showed good CO_2 permeability and CO_2/N_2 selectivity [12] . Meanwhile, relative to Pebax, PEGDA could be rapidly crosslinked and formed films under UV lights. Therefore, ZIF-8 nanoparticles could be rapidly fixed in polymer chains, enhancing the even distribution of ZIF-8 in the polymer and avoiding the deposition and agglomeration of ZIF-8. Besides, adopting ZIF-8/methanol suspension, rather than ZIF-8 powder, could avoid bulky ZIF-8 particles in the membrane and enhance selectivity. The synthesized ZIF-8 nanoparticles showed uniform size of about 100 nm. A good dispersion in polymers was obtained at loadings as high as 50 wt%.

II. Figures and Tables

The high-magnification SEM micrographs of pure ZIF-8 nanoparticles and the cross-section of representative composite membranes are shown in Fig. 1. Herein, for ZIF-8, the experiment was carried out using dried nanoparticles from the as-synthesized ZIF-8 solution. The cross-section of pure cross-linked PEGDA membrane was shown in Fig. 1 (b), which was normal. By using as-synthesized ZIF-8 suspensions, good dispersion and adhesion of ZIF-8 nanoparticles within the polymer matrix was obtained, even ZIF-8 loading up to 30 wt% (Fig. 1 (c) (d) and (e)). The cross-sections were homogeneous, and no aggregation of ZIF-8 particles was observed in SEM images. At higher loading of 50 wt%, continuous phase of ZIF-8 nanoparticles appeared in SEM, and the membrane became brittle and cracked easily. The method of direct mixing of as-synthesized nanoparticles in this study considerably improved the observed mixing and dispersion in polymer matrix, compared to previous work on other polymeric membranes blended with dry ZIF-8 particles [12].



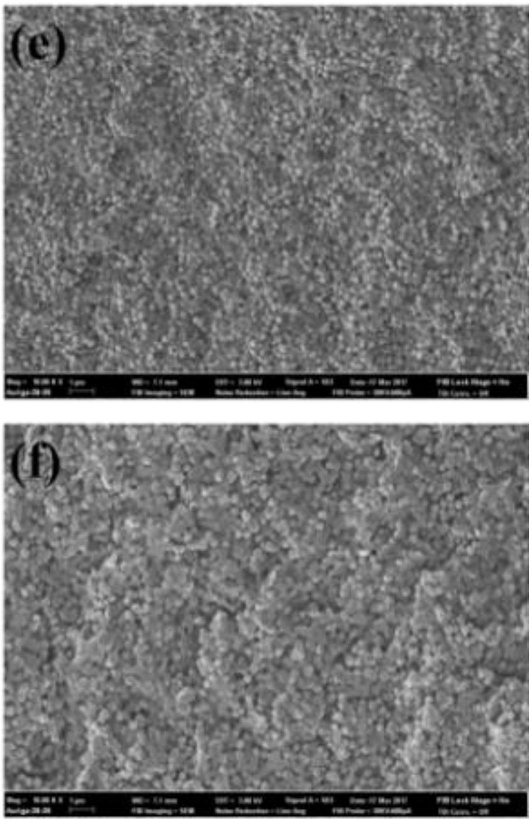


Figure 1: SEM images of pure ZIF-8 nanoparticles (a) and cross-section of membranes: XLPEGDA (b), 10 wt% ZIF-8/PEGDA (c), 20 wt% ZIF-8/PEGDA (d), 30 wt% ZIF-8/PEGDA (e), and 50 wt% ZIF-8/PEGDA (f).

Table 1 present the gas transport data of pure PEGDA membrane and nanocomposite membranes with various loadings. When the ZIF-8 loading is 10 wt%, CO_2 permeability increased to more than 2.5 times, from 130.8 Barrers to 318.3 Barrers. Meanwhile the high CO_2/N_2 selectivity was maintained. When the ZIF-8 loading increased further, CO_2 permeability increased while CO_2/N_2 selectivity decreased slightly. At the high loading as 50 wt%, CO_2 permeability increased to more than 10 times that of the pure polymer, however, the selectivity of typical gas pairs decreased obviously. This could be attribute that the high ZIF-8 loading in the membrane cause the continuous ZIF-8 phase, which provide the inner channel for gas transport, as shown in the SEM cross-section image (Fig. 1 (f)).

TABLE 1. PURE GAS PERMEABILITY OF THE PURE PEGDA MEMBRANE AND ZIF-8/PEGDA COMPOSITE MEMBRANES. THE DATA WAS OBTAINED UNDER 35 °C

Sample membrane	**Permeability (Barrer)**		**CO_2/N_2 selectivity**
	CO_2	**N_2**	
Pure PEGDA	130.8	2.4	54.5
10 wt% ZIF-8/PEGDA	318.3	5.6	56.3
20 wt% ZIF-8/PEGDA	500.4	11.4	44.0
30 wt% ZIF-8/PEGDA	723.4	18.2	39.7
50 wt% ZIF-8/PEGDA	1334.5	40.3	33.1

Gas solubility was measured by a dual volume and dual transducer system, and gas diffusivity was calculated through the equation 3. It can be found that both CO_2 solubility and diffusivity increased with the ZIF-8 loading. It was attributed to that ZIF-8 nanoparticles had good CO_2 adsorption ability and the pores of ZIF-8 could improve CO_2 transport through the membrane. If it is assumed that the gas adsorption ability of ZIF-8 nanoparticle and the gas solubility of the polymer PEGDA would be not affected after the ZIF-8 were loaded within PEGDA, an additive model for CO_2 sorption could be introduced. In Table 2, It can be found that the measured CO_2 solubilities of composite membranes were slightly higher than those estimated values. The increase of the gap between polymer chains could account for the phenomenon.

TABLE 2. CO_2 SOLUBILITY AND DIFFUSIVITY OF ZIF-8/PEGDA COMPOSITE MEMBRANES.

Sample membrane	**CO_2 solubility ^{a}**		**CO_2 diffusivity ^{b}**
	Measured	**Estimated**	
Pure PEGDA	130.8	2.4	54.5
10 wt% ZIF-8/PEGDA	318.3	5.6	56.3
20 wt% ZIF-8/PEGDA	500.4	11.4	44.0
Pure ZIF-8 ^{c}	1334.5	40.3	33.1

(Note: ^{a} ($10^{-3}cm^3(STP)/(cm^3cmHg)$); ^{b} the values of CO_2 diffusivity are calculated through the Equation 3 and the unit of CO_2 diffusivity is $10^{-7}cm^2/s$; ^{c} the data is obtained from the literature [13].)

III Conclusions and recommendations

In summary, the ZIF-8 nanoparticles synthesized with an average size of 100 nm and were loaded into CO_2-selective polymer (PEGDA). SEM cross-sectional images showed the good dispersion and adhesion of ZIF-8 nanoparticles within the polymer. Increasing the ZIF-8 loading dramatically increased CO_2 permeability, from 110 Barrers in a polymer prepared from PEGDA to 318.3 Barrers with a loading of 10 wt%, and to 1334.5 Barrers at a loading of 50 wt%. Meanwhile, CO_2/N_2 selectivity dropped to 33.1.

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REFERENCES

[1]. Ban, Y., Li, Z., Li, Y., Peng, Y., Jin, H., Jiao, W., . . . Yang, W. (2015). Confinement of Ionic Liquids in Nanocages: Tailoring the Molecular Sieving Properties of ZIF-8 for Membrane-Based CO2 Capture. Angew Chem Int Ed Engl, 54(51), 15483-15487.

[2]. Barillas, M. K., Enick, R. M., O'Brien, M., Perry, R., Luebke, D. R., & Morreale, B. D. (2011). The CO2 permeability and mixed gas CO2/H2 selectivity of membranes composed of CO2-philic polymers. Journal Of Membrane Science, 372(1-2), 29-39.

[3]. k, H. B., Dal-Cin, M. M., & Guiver, M. D. (2012). Advances in high permeability polymeric membrane materials for CO2 separations. Energy & Environmental Science, 5(6), 7306-7322.

[4]. Jomekian, A., Behbahani, R. M., Mohammadi, T., & Kargari, A. (2016). CO2/CH4 separation by high performance co-casted ZIF-8/Pebax 1657/PES mixed matrix membrane. Journal Of Natural Gas Science And Engineering, 31, 562-574.

[5]. Lin, H., Van Wagner, E., Freeman, B. D., Toy, L. G., & Gupta, R. P. (2006). Plasticization-enhanced hydrogen purification using polymeric membranes. Science, 311(5761), 639-642.

[6]. Nafisi, V., & Hagg, M. B. (2014). Development of dual layer of ZIF-8/PEBAX-2533 mixed matrix membrane for CO2 capture. Journal Of Membrane Science, 459, 244-255.

[7]. Ordonez, M. J. C., Balkus, K. J., Ferraris, J. P., & Musselman, I. H. (2010). Molecular sieving realized with ZIF-8/Matrimid (R) mixed-matrix membranes. Journal Of Membrane Science, 361(1-2), 28-37.

[8]. Sabetghadam, A., Seoane, B., Keskin, D., Duim, N., Rodenas, T., Shahid, S., . . . Gascon, J. (2016). Metal Organic Framework Crystals in Mixed-Matrix Membranes: Impact of the Filler Morphology on the Gas Separation Performance. Advanced Functional Materials, 26(18), 3154-3163.

[9]. Song, Q. L., Nataraj, S. K., Roussenova, M. V., Tan, J. C., Hughes, D. J., Li, W., . . . Sivaniah, E. (2012). Zeolitic imidazolate framework (ZIF-8) based polymer nanocomposite membranes for gas separation. Energy & Environmental Science, 5(8), 8359-8369.

[10]. Sutrisna, P. D., Hou, J. W., Li, H. Y., Zhang, Y. T., & Chen, V. (2017). Improved operational stability of Pebax-based gas separation membranes with ZIF-8: A comparative study of flat sheet and composite hollow fibre membranes. Journal Of Membrane Science, 524, 266-279.

[11]. Wang, S. F., Li, X. Q., Wu, H., Tian, Z. Z., Xin, Q. P., He, G. W., . . . Guiver, M. D. (2016). Advances in high permeability polymer-based membrane materials for CO2 separations. Energy & Environmental Science, 9(6), 1863-1890.

[12]. Yave, W., Car, A., & Peinemann, K. V. (2010). Nanostructured membrane material designed for carbon dioxide separation. Journal Of Membrane Science, 350(1-2), 124-129.

[13]. Zhu, J. Q., Jiang, L., Dai, C. N., Yang, N., & Lei, Z. G. (2015). Gas adsorption in shaped zeolitic imidazolate framework-8. Chinese Journal of Chemical Engineering, 23(8), 1275-1282.