J. Applied Membrane Science & Technology, Vol. 26, No. 2, August 2022, 43–48

Grand Challenges in Membrane Process for Gas Separation

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Submitted: 26/1/2022. Revised edition: 27/6/2022. Accepted: 27/6/2022. Available online: 25/7/2022

ABSTRACT

Membrane technology is the most promising technology in the post-combustion capture technology compared to absorption, adsorption and cryogenic distillation methods. It is an advanced new technology for recovery of carbon dioxide. It has several advantages when compared to other methods due to its' simple process, low cost, lower footprint, sustainable environment and energy saving method. The challenge is the fabrication method of the polymeric membrane, and it depends on the particular utilisation of the membrane. Different morphologies of the membrane structure can be produced using different methods.

Keywords: Membrane separation, fabrication method, modification techniques

1.0 MEMBRANE BASED GAS SEPARATION

Membrane technology is a highly promising technology for separation of carbon dioxide (CO_2) from flue gas [1]. It has advantages when compared to other types of separation technologies. Typically, there are two types of membranes, namely inorganic membrane and polymeric membrane. The classification of the membrane is based on the pore diameter, morphology, and porosity. The membranes can be further divided into porous and non-porous membranes [2].

Inorganic membranes can be fabricated from inorganic materials such as pyrolysed carbons, metals and ceramics [3]. These membranes can be divided into dense and porous membranes. By using porous inorganic membranes, porous metals or ceramic supports are used to provide the mechanical support during the process. The performance of the membrane can be improved by the interaction of the membrane surface with the inorganic material components; thus, resulting in higher efficiency of permeation. In view of thermal and chemical stability, porous membrane possesses good characteristic. However, the permeability and the selectivity are low in compared to other types of membranes. The dense (non-porous) membrane contains a thin layer of metal [4]. Examples are palladium or other types of alloy. The inorganic materials that are commonly used for membranes are zeolite, metals and ceramics. They perform well due to stable temperature and chemical. However, the production to fabricate this type of membrane is extremely high causing it hard to scale up in industrial scale. The brittle and fragile properties of the membrane also one of the main disadvantages compared to polymeric membrane [5].

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DOI: https://doi.org/10.11113/amst.v26n2.240

Polymeric membranes can be categorised as either glassy or rubbery based on the materials used to synthesise the membranes. They have porous and non-porous film. The selectivity and the permeability of the polymeric membranes are higher as compared to inorganic membranes [5]. When the permeability of the gas decreases, the selectivity of the membrane increases. Among glassy and rubbery membranes, the glassy polymeric membrane provides better performance compared to the rubbery polymeric membrane for separation of CO_2. This is because the glassy polymeric membrane has better selectivity and excellent properties in terms of mechanics [1]. Additionally, the rubbery polymeric membrane with its rubber properties that makes it flexible and soft, it has low selectivity and high permeability. Meanwhile, glassy polymeric membrane has higher selectivity with low permeability compared to the rubbery polymeric membrane [3].

There are several advantages of the polymeric membrane such as low production cost, excellent CO_2 separation, easy fabrication of membrane is easy, and high mechanical stability [6]. Unfortunately, the thermal stability is relatively low resulting in plasticisation of membrane when in contact with CO_2. Therefore, the flue gas is subjected to cooling down before the CO_2 separation. However, polymeric membranes are still the best option for CO_2 separation compared to inorganic membranes [4]. The polymeric membrane has several advantages over the inorganic membrane. This is mainly on the performance of the polymeric membrane such as the separation efficiency affected by the permeability and selectivity of the membrane. Permeability is the ability for the gas to permeate through the membrane affected by the solubility and diffusivity of the membrane [7]. Meanwhile, the selectivity of the membrane is measured by the ratio of permeability of particular gases. The relationship is always inversely proportional relationship between the permeability and selectivity. This indicates that when the selectivity of the membrane increases, the permeability of the gas passing through the membrane coherently decreases [1].

The solution-diffusion (SD) method is always adopted and is applicable to the membrane gas technology because it is a pressure driven process. The diffusivity selectivity is dependent on the free volume and rigidity of the membrane as well as the size of the molecules of the permeating gas [6]. The solubility selectivity is dependent on the interaction of the polymer chains with gas molecules.

The main challenge in membrane technology for gas separation process is producing a membrane with high permeability with high selectivity. A trade-off relationship between permeability and selectivity was carried out by the Robeson in 2008 [8]. Based on Robenson's upper bound correlation for CO_2/ CH_4 separation, the increment of selectivity through chain stiffness and the inter-chain spacing should be imposed to surpass the upper bound [8].

2.0 MEMBRANE FABRICATION METHOD

The fabrication methods for membrane gas separation are stretching, track-etching and the phase inversion.

2.1 Stretching

The stretching method is adopted for the semi-crystalline polymer [9]. It is a technique that does not use solvent but melts the polymer to get to the desired morphology of the membrane. The synthesised membrane has to undergo two steps, which are cold and hot stretching. Cold stretching is used to nucleate the microspores of the membrane. Meanwhile, hot stretching is conducted to shape the morphology of the synthesised membrane [10].

2.2 Track-Etching

The track-etching method is a process that utilises the ion charges of the solvent to weaken the polymer via pre-irradiation of the polymer films [11]. The uniform diameter quasi-cylindrical microspores are formed by the following chemical etching. The size of the microspore is adjustable by manipulating the time of chemical etching. Besides that, the irradiation of the ion fluence controls the number of pores on the membrane [11].

2.3 Phase Inversion

Phase inversion is a commercial membrane fabrication method that has been used widely in the industries today. This process takes place during the shifting of the stability of the polymer solution when the temperature varies, solvent evaporates or mass exchange with non-solvent/coagulant bath [10]. The principle behind this method is to utilise the miscibility of the two solvents. At the miscibility gap in the phase diagram, the mixing of the polymer-solvent system is unstable resulting in formation of the polymer-rich and polymer-lean phases. Non-solvent induced phase separation (NIPS) is also known as the mass exchange between the non-solvent/coagulant bath [12]. These are wet and dry phase inversion processes resulting in asymmetric membrane with good porosity. The precipitation of polymer is carried out during the wet inversion phase Ideally, the asymmetric membrane is first fabricated and then immersed into a solution in a non-solvent/coagulant bath [11]. Meanwhile, the dry phase inversion method requires involvement of solvent, which has higher volatility compared to the non-solvent and additives used to enhance the viscosity [13].

3.0 MEMBRANE MODIFICATION TECHNIQUES

Four techniques are currently used to modify the membrane. They are discussed below:

3.1 Cross-Linking

Cross-linking is a process that creates a network structure between the polymer chains [1]. The advantages of the cross-linking are enhancing the thermal, chemical and mechanical stability of the synthesised membrane. In the cross-linking process, when the mobility of the polymer chain decreases, the permeability also reduce but the selectivity increases. Cross-linking can be achieved by chemical reaction, radiation, thermal treatment, and physical networking [13].

3.2 Ionic Liquids

Ionic liquids such as organic cations and inorganic anions are able to fabricate the membrane with high selectivity and permeability [1]. These ionic salt liquids are stored at temperature below 100 °C. Ionic liquids gained attention in the application of gas separation due to their unique physical and chemical properties. The common ionic liquids are used amino acids and amines ionic liquid [13].

3.3 Mixed Matrix Membranes

Mixed Matrix Membranes (MMMs) also known as nano-composite membranes are fabrication methods, which add the mineral fillers such as zeolites to the polymer matrix to increase the performance of the membrane [6]. By adding the mineral fillers, the membranes become denser and harder and form more rigid structures compared to the pure polymeric membranes. This combination also could enhance the membrane properties including the selectivity and permeability [6].

3.4 Polymer Blending

The polymer blending method is a commonly used method for fabrication of membrane. It has an attractive advantage in which it has inherited the characteristics of both different polymers resulting in new synthesised polymeric membranes [14]. The desired properties such as the distinctive physical, chemical and gas separation properties can be combined to synthesise an excellent performing polymeric membrane. For example when a glassy polymer blends with a rubbery polymer it results in a new polymer with higher strength and thermal stability when compared to a pure polymer [15]. This method has always been the preferred methods used for optimising the selectivity, permeability and the performance of the polymeric membranes. In addition, the cost of fabrication is also can be reduced. Wang *et al*. (2014) reported a new synthesised membrane with hollow fibre structure by blending two glassy polymers, which are poly(ethylene-glycol) and polydimethylsiloxane co-polymers were blended together and resulted in a high gas separation performance membrane [16]. Meanwhile, Quan *et al.* (2016) had blended a low molecular weight PEG into polyethylene oxide (PEO) membranes. The fabricated PEO membrane possessed high permeability, high selectivity and high fractional free volume. This research has proven that polymer blending is the most promising method for fabrication of polymeric membrane with good characteristics of gas separation [17].

FUTURE DIRECTION

The characteristics of synthesised polymeric membrane are usually has high permeability but low selectivity. Therefore, in order to enhance its performance various methods have been applied such as cross-linking, nanocomposite/mixed matrix membranes, ionic liquids and polymer blending.

REFERENCES

[1] Ali Kargari and Sheida Rezeinia. 2019. State of the Art Modification of Polymeric Membrane by PEO and PEG for Carbon Dioxide Separation: A Review of the Current Status and Future Perspectives. *J Ind Eng Chem.* 84(25): 1-22. https://doi.org/10.1016/j.jiec.2019.12.020.

[2] Yutao Liu *et al.* 2020. Multifunctional Covalent Organic Gramework (COF)-Based Mixed Matrix Membranes for Enhanced CO_2 Separation. *J. Membr. Sci*. 618: 118693. https://doi.org/10.1016/j.memsci.2020.118693.

[3] Nidhika Bhoria *et al*. 2020. Composite Porous Nanostructures as Multi-action Adsorbents and Membrane

Fillers for Carbon Dioxide Separation: Comparative Performance of Metal Organic Framework – Grapheme Oxide Hybrids. *Mater. Today: Proc.* https://doi.org/10.1016/j.matpr.2020.07.466.

[4] Sogolzadeh Mohammad, Mansooreh Soleimani, Maryam Takht Ravnachi, and Reze Songolzaeh. 2014. Carbon Dioxide Separation Form Flue Gases: A Technological Review Emphasizing Reduction in Greenhouse Gas Emissions. *Sci. World J.* https://doi.org/10.1155/2014/828131.

[5] Wonji Jung *et al.* 2018. Water Membrane for Carbon Dioxide Separation. *Sep. Purif. Technol.* 203: 268-273. https://doi.org/10.1016/j.seppur.2018.04.054.

[6] Samaneh Bandehali *et al*. 2019. Advances in High Carbon Dioxide Separation Performance of Poly (ethylene oxide)-based Membranes. *J. Energy Chem.* 46: 30-52. https://doi.org/10.1016/j.jechem.2019.10.019.

[7] Xavier Duthie *et al.* 2007. Operating Temperature Effects on the Plasticisation of Polyimide Gas Separation Membranes. *J. Membr. Sci.* 294(1-2): 40-49. https://doi.org/10.1016/j.memsci.2007.02.004.

[8] L. M. Robeson. 2008. The Upper Bound Revisited. *J. Membr. Sci.* 320: 390-400. https://doi.org/10.1016/j.memsci.2008.04.030.

[9] Kar Kit Wong and Zeinab Abbsa Jawad. 2019. A Review and Future Prospect of Polymer Blend Mixed Matrix Membrane for CO_2 Separation. *J. Polym. Res.* https://doi.org/10.1007/s10965-019-1978-z.

[10] Wan Chin Cha and Zeinab. 2019. The Influence of Cellulose Acetate Butyrate Membrane Structure on CO_2/N_2 Separation: Effect of Casting Thickness and Solvent Exchange Time. *Chem Eng Commun.* https://doi.org/10.1080/00986445.2019.1605359.

[11] E. M. Awad *et al*. 2020. Strong Etching Investigation on PADC CR-39 as a Thick Track Membrane with Deep Depth Profile Study. *Radiat. Phys. Chem.* 177: 109104. https://doi.org/10.1016/j.radphyschem.2020.109104.

[12] Jingqian Zhou *et al.* 2008. Morphology Evolution Of Thickness-gradient Membranes Prepared by Wet-phase Inversion Process. *Sep. Purif. Technol*. 63(2): 484-486. https://doi.org/10.1016/j.seppur.2008.05.019.

[13] Wei Deng and Ying Li. 2020. Novel Super Hydrophilic Antifouling PVDF-BiOCl Nanocomposite Membranes Fabricated via A Modified Blending-phase Inversion Method. *Sep. Purif. Technol.* 254: 117656. https://doi.org/10.1016/j.seppur.2020.117656.

[14] Farzad Rayekan Iranagh *et al.* 2020. Dispersion Engineering of MWCNT to Control Structural and Gas Transport Properties of PU Mixed Matrix Membranes. J. *Environ. Chem. Eng.* 8(6): 104493. https://doi.org/10.1016/j.jece.2020.104493.

[15] Wai Fen Yong and Hao Zhang. 2020. Recent Advances in Polymer Blend Membranes for

Gas Separation and Evaporation. *Prog. Mater. Sci*. https://doi.org/10.1016/j.pmatsci.2020.100713.

[16] Yuanyuan Wang *et al*. 2014. Enhancing Membrane Permeability for CO_2 Capture through Blending Commodity Polymers with Selected PEO and PEO-PDMS Copolymers and Composite Hollow Fibres. *Energy Procedia*. 34: 202-209. https://doi.org/10.1016/j.egypro.2014.11.021.

[17] S. Quan *et al.* 2016. PEG-imbedded PEO Membrane Developed by a Novel Highly Efficient Strategy Toward Superior's Gas Transport Performance. *Macromol. Rapid Commun.* 36(5): 490-495. https://doi.org/10.1002/marc.201400633.