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이산화탄소 분리를 위한 이온성 액체 기반 복합 멤브레인: 총설

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Ionic Liquid Consisted of Composite Membrane for Carbon Dioxide Separation: A Review

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요 약: 가스 분리 방법 중에서도, 멤브레인을 이용한 CO_2 포집 및 분리는 지속적으로 개발되고 있는 꾸준히 성장하는 분야이다. 이온성 액체(IL) 기반 복합 막은 CO_2를 분리하는 데 있어 우수한 성능값을 보여준다. 유사하게, 다양한 공중합체/IL 복합막 또한 향상된 성능을 보여준다. 이러한 공중합체/IL 복합만에 산화그래핀과 같은 필러를 첨가하면 IL과 유기 필러 사이에서 발생하는 강한 상호작용으로 인해 필러의 효과가 더욱 향상되며, 이는 결과적으로 CO_2의 친화도, 선택도 및 흡착과 같은 요소를 향상시킨다. 금속-유기 구조체(MOF)를 사용하는 공중합체/IL 복합 막은 향상된 CO_2 투과도를 보여주었다. 이 총설에서는 이온성 액체와 공중합체복합막의 다양한 조합에 따른 이산화탄소분리성능에 대한 상관관계를 논의한다.

Abstract: Even among gas separation methods, CO_2 capture and separation via membranes is an ever-growing field, with many different membrane compositions continually being developed. Ionic liquid (IL) based composite membranes show excellent performance values in separating CO_2. Similarly, various copolymer/IL composite membranes also display improved performance. The addition of fillers such as graphene oxide to these copolymer/IL composite membranes shows a further enhanced version of these fillers, most likely due to the strong interactions that occur between ILs and organic fillers, which consequently improves factors such as the affinity, selectivity, and adsorption of CO_2. Copolymer/IL composite membranes utilizing a metal-organic framework (MOF) showed improved CO_2 permeability. This review discusses the study of various combinations of ionic liquid and copolymer composite membranes for carbon dioxide separation.

Keywords: *composite membrane, mixed matrix membrane, metal organic framework, ionic liquid, CO_2*

1. Introduction

The usage of membranes in the carbon dioxide separation process has been a constant source of interest[1-3]. This is mainly due to membranes requiring comparatively low energy consumption as opposed to the energy consumption levels in more common separation processes such as distillation, drying, extraction, adsorption, and so on. Using membranes requires low capital, and operating costs only increase the incentive for researchers to investigate the implementation and extension of membranes further to facilitate the separation process within industrial settings. As it relates to gas separation processes, permeability is defined as a measure of productivity, while selectivity can be defined as a measure of separation efficiency[4-7]. The separation of gases in a membrane separation process occurs due to differing levels of diffusivity and sol-

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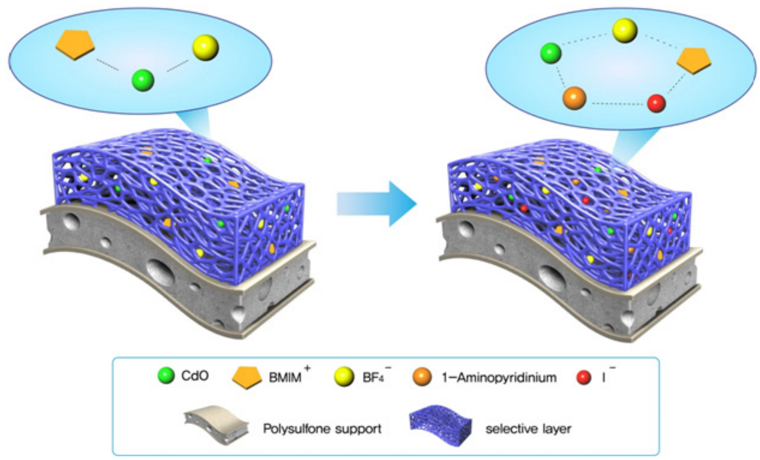

Fig. 1. Coordination behavior in 1-butyl-3-methylimidazolium tetrafluoroborate/CdO/1-aminopyridinium iodide composite (Reproduced with permission from Kim *et al.*[16], Copyright 2019, Springer Nature).

ubility between membrane and gas.

Gas separation via membranes has been increasingly considered in gas separation applications as they are more attractive and practical than other methods. Three distinct types of membranes are currently being investigated for practical use: composite membranes, graphene oxide filler membranes, and metal-organic framework membranes. Composite membranes are combinations of ionic liquids (IL) and polymers[8-11]. Graphene oxide filler membranes utilize graphene oxide's gas barrier properties alongside IL/polymer composite membranes. Metal-Organic Framework Membranes are those which use MOFs partially organic nature in hopes of higher compatibility of a polymer chain within IL/polymer composite membranes[12-14]. This work will compare the performances of various types of membranes with a specific focus on CO_2 selectivity and permeability.

2. Ionic Liquid and Polymer Composite Membrane

Hayashi *et al*. prepared a composite membrane consisting of sulfonated polyimide (SPI) and cheap protic ionic liquid[15]. Composite membrane was prepared by solution casting method.

The properties of the composite membrane prepared by mixing of PIL is compared with another composite membrane when the same polymer was composited with aprotic ionic liquid (AIL) named as [N1123] [NTf_2]. Although the PIL composite membrane possess lower permeability but the selectivity of the membrane is higher than AIL composite membrane. Kim *et al.* reported prepares a composite membrane of 1-Aminopyridinium iodide and cadmium oxide for carbon dioxide separation[16]. The fabrication schematic of the membrane is presented in Fig. 2.

Composite membranes incorporate various combinations of polymers and ILs which results in unique performance values.

Hayashi *et al.* prepared composite membrane of SPI and ionic liquid to find out the role of cation in the sepation of CO_2 and their structure is represented in Fig. 3[17]. Phase separation in the composite membrane play an important role in the gas separation process. Gas separation behavior of PIL and AIL is presented in Fig. 3.

Cheng *et al.* examines the use of cellulose (CA) in synthesizing cellulose/IL composite membranes[18]. First, two completely new kinds of cellulose esters utilizing imadzaolium cations were synthesized, namely CA 1-butyl-3-methylimidazolium chloride (CA-BmimCl) and CA 1-butyl-3-methylimidazolium bis(trifluoromethane sulfonyl)imide (CA-BmimTf_2N). The resulting

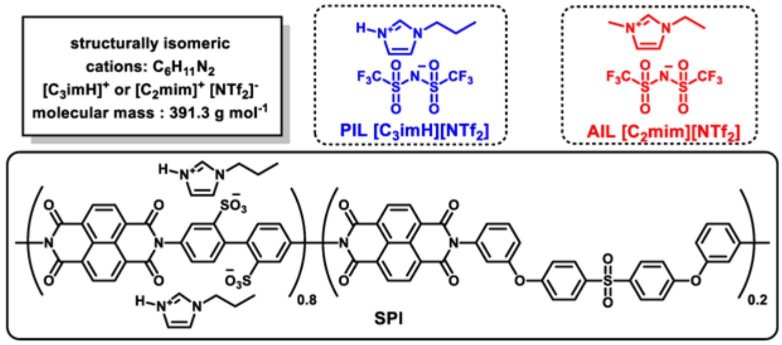

Fig. 2. Chemical structures of protic ionic liquid (PIL), aprotic ionic liquid (AIL), and sulfonated polyimide (SPI) used in this study (Reproduced with permission from Hayashi *et al.*[17], Copyright 2019, MDPI).

cationized cellulose esters were shown to effectively lock in various ILs such as $C_{10}mimTf_2N$ due to electrostatic interactions. As a result of strong attraction interactions, the resultant cellulose ester/ILs composite membranes were found to be uniform, smooth, and highly transparent. Of the two cellulose ester/IL composite membrane combinations, the CA-$BmimTf_2N$/$C10mimTf_2N$ membrane combination exhibited the highest CO_2 permeability, 38 times higher than CA membrane and 17 times higher than CA-$BmimTf_2N$ membrane with 91.1 Barrer, as well as showing a tensile strength of 10~55 MPa and an elongation break at 10~30% as well as-permselectivity of CO_2/N_2 levels at 24.3.

Dai *et al.* research investigates hybrid membranes of Nafion and the IL 1-butyl-3-methylimidazolium tetrafluoroborate ($[Bmim][BF_4]$) for applications in carbon [19]. CO_2 permeability was found to be greatly enhanced upon usage of the composite membranewhilst surrounded by water in the gas stream, most likely as a result of IL nanochannels forming within the Nafion matrix. $[Bmim][BF_4]$ in the Nafion/IL hybrid membranes functions as a "first promoter" to improve gas transport, whilst water vapor acts as a "second promoter". $[Bmim][BF_4]$/Nafion hybrid membrane exhibited CO_2/N_2 selectivity of about 30 at 100% RH, 3 times more than same membrane in dry state and 200 times more than dry nafion. $[Bmim][BF_4]$/Nafion hybrid membrane also exhibited mixed gas CO_2 permeability of 390 Barrer. These performance statistics strongly

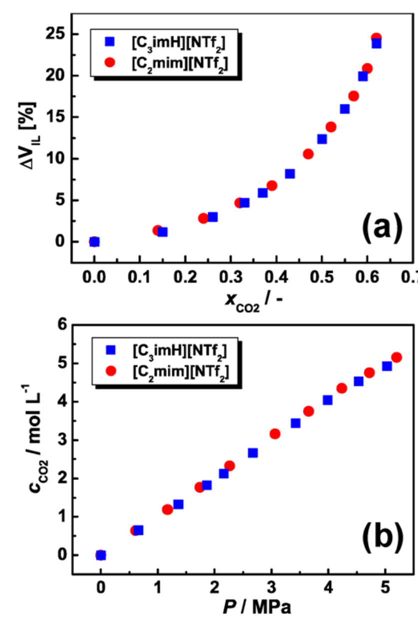

Fig. 3. (a) Volume expansion of IL as a function of mole fraction of dissolved CO_2 and (b) molarities of dissolved CO_2 as a function of the pressure of CO_2 for PIL $[C_3imH][NTf_2]$ and AIL $[C_2mim][NTf_2]$ at 30°C (Reproduced with permission from Hayashi *et al.*[17], Copyright 2019, MDPI).

suggest a synergetic relationship between IL and water vapor in regards to the gas transportation properties of Nafion.

Estahbanati *et al.* research investigates the incorporation of the superior characteristics of Pebax 1657 which includes strong mechanical resistance and outstanding gas permeability especially in regards to polar gases, with the IL 1-butyl-3-methylimidazolium

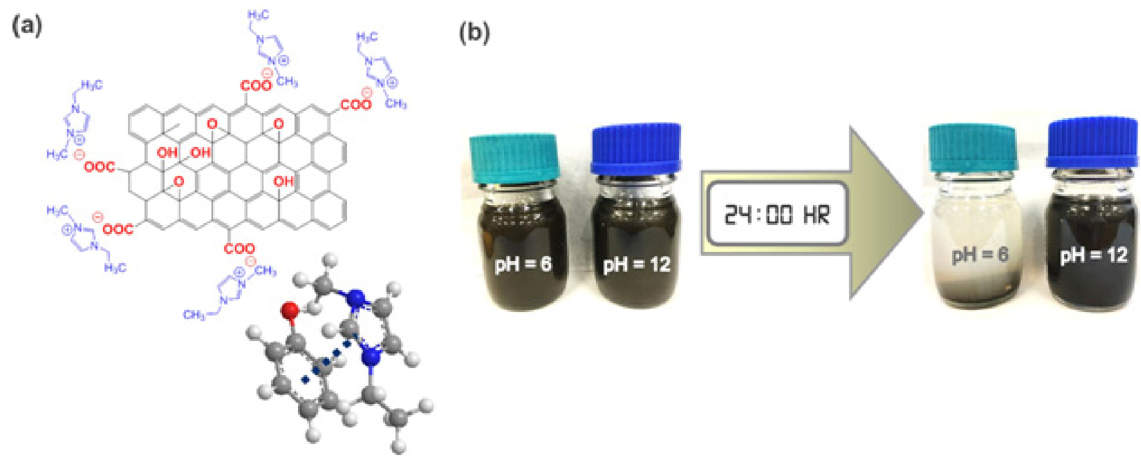

Fig. 4. (a) Interaction between GO sheets and IL in the form of ionic complexation (2-D model) at a high pH (21) and $\pi-\pi$ or cation$-\pi$ interaction between the GO basal plane and cation of IL (ball and stick model) and (b) stable dispersion of the Pebax/IL/GO-0.5 solution at pH = 12 (Reproduced with permission from Fam *et al.*[22], Copyright 2018, American Chemical Society).

tetrafluoroborate ([BMIM][BF_4])'s affinity to CO_2[20]. Synthesizing the polymer/IL composite membrane resulted in membranes that were more amorphous and less crystalline which was shown to be beneficial factors in increasing permeability. In addition, both CO_2 permeability and selectivity was shown to increase simultaneously as IL content was incrementally increased, most likely due to the high affinity of CO_2 of both components of the composite membrane synthesized in the research. In a 50% wt hybrid membrane, CO_2 permeability was found to be 190 Barrer while selectivity of CO_2/N_2 was found to be 105.6 as well as a tensile strength of 153.8 MPa. which results in increasing the permselectivity of the membranes for CO_2/light gases separation.

Lu *et al.* research explored the design of a blending method of the various ILs including DEMSTFSI and polysulfone (PSf)[21]. The method devised by the researchers involves the ILs being immobilised, with-applications in high-pressure gas separation in mind. The method results inmembranes which are tunable and have a porous surface, The size and distribution of which were found to be dependent on both the type and the amount of IL blended with PSf. The best performance statstics in regards to gas separation was observed in a hybrid membrane using DEMSTFSI, with permeability of 580 Barrer and selectivity of 30. Based on these researches on IL/Polymer composite membranes it is clear that the polysulfone/IL composite membrane has the best performance values.

3. Ionic Liquid and Graphene Oxide Composite Membrane

IL/Polymer composite membranes that utilize graphene oxide as a filler are membranes that utilize GOs unique gas barrier properties to further increase membrane performance. Fam *et al.* first prepared blend of Pebax 1657 which is a block copolymer of polyamide and polyethylene glycol with ionic liquid[22]. By introduction of small amount of modified graphene oxide as shown in Fig. 6 into the blended system, tremendously increase the movement of ionic liquid to the membrane surface while reducing the interaction of BCP with IL in the bulk of the system.

Migration of IL to the membrane surface is observed by SEM which is presented in Fig. 5.

This membrane has excellent selectivity for CO_2/N_2 separation with CO_2 permeability of 1000 GPU.

Huang *et al.* looks into the synthesis of an alternate Pebax/IL composite membrane with GO fillers, this time using the IL 1-(3-aminopropyl)-3-methylimidazolium

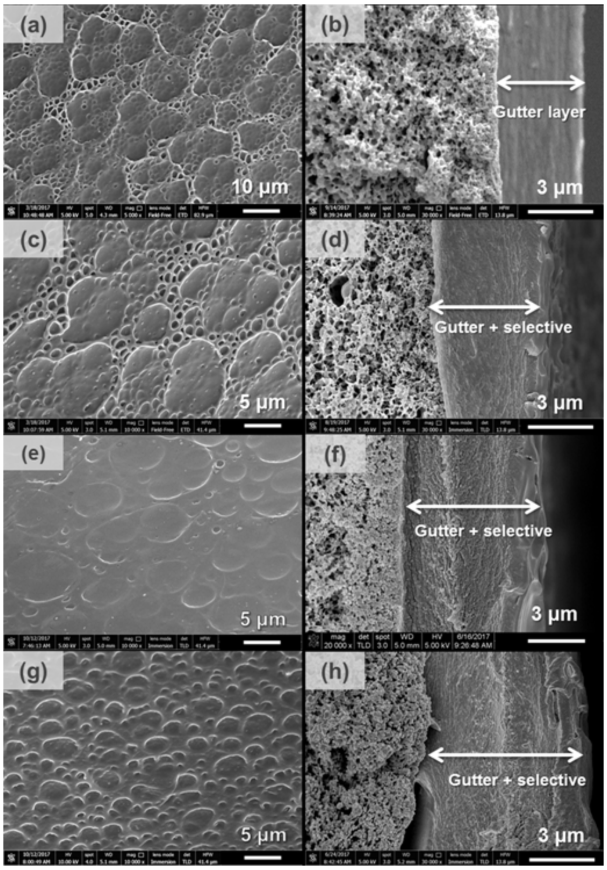

Fig. 5. SEM surface (left) and cross-sectional (right) images of the PVDF hollow fibers coated with (a, b) PTMSP and subsequent coating of (c, d) Pebax/IL/GO-0.5, (e, f) Pebax/IL/GO-2.0, or (g, h) Pebax/IL/GO-0.5 (pH = 12) (Reproduced with permission from Fam *et al.*[22], Copyright 2018, American Chemical Society).

bromide[23]. A lower wt% of GO was used in this research, but displayed better performance values then the previous research. Best performance was observed in 0.05 %wt GO-IL Pebax membrane with permeability of 900 GPU and selectivity of 45 and a tensile strength of 17.3 MPa. Karunakran *et al.* investigated the design of a three component material consisting of the ionic liquids emimAc and emimBF_4, graphene oxide and a highly permeable low selective polymeric coating derived from polyacrylonitryle[24]. The resulting membrane displayed excellent performance statistics as well as stability spanning over 120 hours. As with all previous GO filler membranes, during membrane formation the GO films stacks create sieving nanochannels which result in improved performance levels. The unselective but highly permeable sealing layer and the GO incorporation are the key factors for the improved CO_2 selectivity. Best performance was observed in GO-IL hybrid membrane of 0.5 %wt GO and emimAc which showed a permeability flux of 37 GPU and selectivity of 130.

Wu *et al.* research investigated the synthesis of a GO supported ionic liquid membrane (GO-SILM) through the use of a strategy known as reduced pressure-assisted vapor penetration[25]. Researchers used the IL ([EMIM] [BF_4]) and GO, with Al_2O_3 for support. The vapors from the IL is shown to be capable of sealing any defects or pores in the GO membrane, as well as penetrate the 2D nanochannels. As seen across all GO/IL composite membranes, due to the interactions between GO and IL, the IL can be confined within the nanochannels, which results in fast and selective CO_2 transport. In addition, the transport distance is significantly shortened due to the ultrathin layers. All these factors help display high permeance of 56.6 GPU and selectivity of 63. Upon examining all the research, it can be concluded that the GO-filler membrane with the best performance is the one that was synthesized using Pebax1656 and 1-(3-aminopropyl)-3-methylimidazolium bromide.

4. Ionic Liquid and Metal Organic Framework Composite Membrane

Composite membranes which utilize MOFs refer to those that make use of the part-organic nature of MOFs that leads to increased compatibility with the organic chains of the polymers in the composite membranes. Casado-Coterilloet al research details the synthesis of mixed matrix membranes (MMMs) using the IL [emim][Ac] at 5 wt%, the biopolymer chitosan (CS), and nanometre-sized MOF ZIF-8 or HKUST-1 particles to improve the selectivity of the MMM[26]. The use of MOFs is shown to vastly improve the thermal stability of the resulting MMMs, which would al-low for applications in high temperature separation. The best CO_2 permeability and CO_2/N_2 selectivity performance is obtained for 10 wt% ZIF-8 and 5 wt% HKUST-1 at 5413 Barrer and 11.5 and 4754 Barrer and 19.3 respectively. The better performance of the ZIF-8 MOF MMM is attributed to a better adhesion and smaller particle size of ZIF-8 than HKUST-1 nanoparticles with respect to the IL-CS continuous matrix.

Hao *et al.* investigated into the effects of ZIF-8 MOF in applications in natural gas sweetening and capture of CO_2 post combustion when used with either polymerizable room temperature ionic liquids (poly(RTIL)) or free room temperature ionic liquids (RTIL)[27]. The research shows that ZIF-8 MOF in MMMs significantly improves permeability levels. The P[vbim][NTf_2]/[emim][$B(CN)_4$]/ZIF-8 system displayed an interesting phenomenon where the performance statistics improved as ZIF-8 wt% increased. Best performance was observed with P[vbim][NTf_2]/[emim][$B(CN)_4$]/ZIF-8 system with 25.8 %wt ZIF-8 with a permeability of 1062.4 Barrer and selectivity of 24.2.

Li *et al*. designed a toughened ZIF-8-pebaxMMMthrough the confinement ofthe IL [bmim][Tf_2N] at room temperature into ZIF-8 cages[28]. The diffusion of the IL out of the cages was restrained by water-washing. The resulting membrane's mechanical properties and gas separation performance were shown to have significantly improved. The molecular sieving properties were also shown to have improved in comparison to ZIF-8/Pebax membranes, as a result of the stiffer interphase between ZIF-9 and pebax as well as a reduction ofZIF-8's effective aperture size. The best performance of the resulting membranes showed permeability of 104.9 Barrer and selectivity of 83.9 as well as a tensile strength of 12.2 MPa. From exploring the various research into membranes that utilize MOF-fillers, it can be concluded that the membrane with the best performance is ZIF-8 filler membrane that was synthesized with the biopolymer chitosan and the IL emimAc.

5. Conclusions

Each composite membrane explored has shown potential to be used in various applications such as gas separation in water or gas separation in high heat environments. Ionic liquids are excellent materials used for adsorption of CO_2. Composite membrane prepared by compositing by various kind of polymer are applied as CO_2 separation membrane. Anion present in the ionic liquid be easily tuned to enhance the gas separation efficiency. MOF is another interesting type of material that can be incorporated into the polymer/IL binary system to make the ternary composite membrane more selective CO_2 separation membrane. Different type of functional group can be introduced into the inorganic-organic framework to enhance CO_2 dissolution ability along with enhancing the mechanical strength and thermal behavior like glass transition temperature. These are the issues discussed in this review.

Reference

1. H. Lin and B. D. Freeman, "Materials selection guidelines for membranes that remove CO_2 from gas mixtures", *J. Mol. Struct.*, **739**, 57 (2005).
2. M. Loloei, M. Omidkhah, A. Moghadassi, and A. E. Amooghin, "Preparation and characterization of Matrimid® 5218 based binary and ternary mixed matrix membranes for CO_2 separation", *Int. J. Greenh. Gas Control*, **39**, 225 (2015).
3. M. S. Park, J. H. Kim, and R. Patel, "PVA-based graft copolymer composite membrane synthesized by free-radical polymerization for CO_2 gas separation", *Membr. J.*, **31**, 268 (2021).
4. M. Rezakazemi, A. Ebadi Amooghin, M. M. Montazer-Rahmati, A. F. Ismail, and T. Matsuura, "State-of-the-art membrane based CO_2 separation using mixed matrix membranes (MMMs): An overview on current status and future directions", *Prog. Polym. Sci.*, **39**, 817 (2014).
5. H. Sanaeepur, A. Ebadi Amooghin, A. Moghadassi,

A. Kargari, S. Moradi, and D. Ghanbari, "A novel acrylonitrile–butadiene–styrene/poly(ethylene glycol) membrane: preparation, characterization, and gas permeation study", *Polym. Adv. Technol.*, **23**, 1207 (2012).
6. S. Park and R. Patel, "Recent progress in conductive polymer-based membranes", *Membr. J.*, **31**, 101 (2021).
7. M. Zamani Pedram, M. Omidkhah, and A. Ebadi Amooghin, "Synthesis and characterization of diethanolamine-impregnated cross-linked polyvinylalcohol/glutaraldehyde membranes for CO_2/CH_4 separation", *J. Ind. Eng. Chem.*, **20**, 74 (2014).
8. H. Rabiee, A. Ghadimi, and T. Mohammadi, "Gas transport properties of reverse-selective poly(ether-b-amide6)/[Emim][BF_4] gel membranes for CO_2/light gases separation", *J. Membr. Sci.*, **476**, 286 (2015).
9. S. Tachibana, K. Hashimoto, H. Mizuno, K. Ueno, and M. Watanabe, "Effects of polyimide sequence and monomer structures on CO_2 permeation and mechanical properties of sulfonated polyimide/ionic liquid composite membranes", *Polymer*, **241**, 124533 (2022).
10. M. Barooah and B. Mandal, "Synthesis, characterization and CO_2 separation performance of novel PVA/PG/ZIF-8 mixed matrix membrane", *J. Membr. Sci.*, **572**, 198 (2019).
11. Y. Y. Lee and B. Gurkan, "Graphene oxide reinforced facilitated transport membrane with poly (ionic liquid) and ionic liquid carriers for CO_2/N_2 separation", *J. Membr. Sci.*, **638**, 119652 (2021).
12. A. Ebadi Amooghin, M. Omidkhah, and A. Kargari, "The effects of aminosilane grafting on NaY zeolite–Matrimid®5218 mixed matrix membranes for CO_2/CH_4 separation", *J. Membr. Sci.*, **490**, 364 (2015).
13. A. Ebadi Amooghin, M. Omidkhah, and A. Kargari, "Enhanced CO_2 transport properties of membranes by embedding nano-porous zeolite particles into Matrimid®5218 matrix", *RSC Adv.*, **5**, 8552 (2015).
14. M.-T. Vu, R. Lin, H. Diao, Z. Zhu, S. K. Bhatia, S. Smart, "Effect of ionic liquids (ILs) on MOFs/polymer interfacial enhancement in mixed matrix membranes", *J. Membr. Sci.*, **587**, 117157 (2019).
15. E. Hayashi, M. L. Thomas, K. Hashimoto, S. Tsuzuki, A. Ito, and M. Watanabe, "Application of protic ionic liquids to CO_2 separation in a sulfonated polyimide-derived ion gel membrane", *ACS Appl. Polymer Mat.*, **1**, 1579 (2019).
16. H. Y. Kim and S. W. Kang, "CO_2 separation using composites consisting of 1-butyl-3-methylimidazolium tetrafluoroborate/CdO/1-aminopyridinium iodide", *Sci. Rep.*, **9**, 16563 (2019).
17. E. Hayashi, K. Hashimoto, M. L. Thomas, S. Tsuzuki, and M. Watanabe, "Role of cation structure in CO_2 separation by ionic liquid/sulfonated polyimide composite membrane", Membranes, **9**, 81 (2019).
18. Y. Cheng, X. Zhang, C. Yin, J. Zhang, J. Yu, and J. Zhang, "Immobilization of ionic liquids with a new cellulose ester containing imidazolium cation for high-performance CO_2 separation membranes", *Macromol. Rapid Commun.*, **42**, 2000494 (2021).
19. Z. Dai, L. Ansaloni, J. J. Ryan, R. J. Spontak, and L. Deng, "Nafion/IL hybrid membranes with tuned nanostructure for enhanced CO_2 separation: Effects of ionic liquid and water vapor", *Green Chem.*, **20**, 1391 (2018).
20. E. Ghasemi Estahbanati, M. Omidkhah, and A. Ebadi Amooghin, "Preparation and characterization of novel Ionic liquid/Pebax membranes for efficient CO_2/light gases separation", *J. Ind. Eng. Chem.*, **51**, 77 (2017).
21. S. C. Lu, A. L. Khan, and I. F. J. Vankelecom, "Polysulfone-ionic liquid based membranes for CO_2/N_2 separation with tunable porous surface features", *J. Membr. Sci.*, **518**, 10 (2016).
22. W. Fam, J. Mansouri, H. Li, J. Hou, and V. Chen, "Gelled graphene oxide-ionic liquid composite membranes with enriched ionic liquid surfaces for improved CO_2 separation", *ACS Appl. Mater. Interfaces*, **10**, 7389 (2018).
23. G. Huang, A.P. Isfahani, A. Muchtar, K. Sakurai, B. B. Shrestha, D. Qin, D. Yamaguchi, E.

Sivaniah, and B. Ghalei, "Pebax/ionic liquid modified graphene oxide mixed matrix membranes for enhanced CO_2 capture", *J. Membr. Sci.*, **565**, 370 (2018).

24. M. Karunakaran, L. F. Villalobos, M. Kumar, R. Shevate, F. H. Akhtar, and K. V. Peinemann, "Graphene oxide doped ionic liquid ultrathin composite membranes for efficient CO_2 capture", *J. Mater. Chem. A*, **5**, 649 (2017).
25. M. Wu, X. Song, X. Zhang, C. Jiao, and H. Jiang, "A reduced pressure-assisted vapor penetration of ionic liquid into the laminated graphene oxide membranes for efficient CO_2 separation", *Sep. Purif. Technol.*, **287**, 120514 (2022).
26. C. Casado-Coterillo, A. Fernández-Barquín, B. Zornoza, C. Téllez, J. Coronas, and Á. Irabien, "Synthesis and characterisation of MOF/ionic liquid/chitosan mixed matrix membranes for CO_2/N_2 separation", *RSC Adv.*, **5**, 102350 (2015).
27. L. Hao, P. Li, T. Yang, and T. S. Chung, "Room temperature ionic liquid/ZIF-8 mixed-matrix membranes for natural gas sweetening and post-combustion CO_2 capture", *J. Membr. Sci.*, **436**, 221 (2013).
28. H. Li, L. Tuo, K. Yang, H. K. Jeong, Y. Dai, G. He, W. Zhao, "Simultaneous enhancement of mechanical properties and CO_2 selectivity of ZIF-8 mixed matrix membranes: Interfacial toughening effect of ionic liquid", *J. Membr. Sci.*, **511**, 130 (2016).