Chapter 9

Advanced Functional Membrane for CO₂ Capture

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Abstract

The capture of carbon dioxide directly from the air has been shown a growing interest in the mitigation of greenhouse gases but remains controversial among the research community. Due to the high dilution factor of CO₂ in air, simultaneously increases the energy requirement as well as the charge of the respective technology. Membrane/Thin film technology has been conceded as the most investigated as well as most appealing technology to attenuate carbon dioxide from the atmosphere. The membrane and membrane process technique are found to be alluring and eco-friendly to mitigate the carbon due to its cost efficiency, low expenditure of energy as well as comprehensibility in operation. Traditionally, the materials are cast into dense membranes with a standard thickness and after the formation of the membranes, their applications such as carbon capture/separation are evaluated by commutation between permeability and selectivity. In present scenario, efficient separation of CO₂ from other gases has become a worldwide issue. Coal/Natural/Flue gases are evolving as the primary source of CO₂, so the capture of CO₂ from the mentioned sources are extensively contemplated as the next opportunity for the large-scale deployment of gas separation membranes. Although, current researches indicate the advances in material process designs that can crucially enhance the membrane capture systems as well as the separation systems, which make membrane process technique contentious with other technologies present till date for carbon capture. The aforementioned application requires novel polymeric materials which have the ability for efficient carbon capture and possesses high CO₂ separation properties from different mixed gases, along with high mechanical and thermal stability for a longer time. Herein, the present report precisely highlights the recent advancement on the membrane technology based on the functional materials and their applications in the field of CO₂ capture.

Keywords

Functional Materials, Composite, Membrane, Carbon-Dioxide Capture

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1. Introduction

Carbon dioxide (CO₂) is a prime chemical gas present in the atmosphere, which is censorious to continuance of life on earth. It is the main component of photosynthesis with the help of which plants fuel themselves, which assist as the prime origin of food for all living things. Moreover, it yields oxygen which is crucial for human beings for respiration. Researches have proved that a little assemblage of carbon dioxide in the earth's ambience

is needful, where glaciation is inhibited, thereby yielding a surrounding where plants and animals life can flourish. However, in this present world, mankind related to the creation of energy generates ampleness of carbon dioxide in the atmosphere which no longer can be stabilized by the earth's natural cycles, which can cause serious environmental problems that confront mankind in the future. Chemical industries are always the dominant sources for creating global warming by increasing the average global temperature by 5.8 °C. According to the International Energy Agency (IEA), CO₂ emission can be controlled by half by 2050 only when the reduction of industrial growth of CO₂ occurs by 21% in 2050 compared to today's CO₂ levels. Global carbon outpouring has been growing expeditiously anticipated by the growing demands of energy output and also by the use of fossil fuel dominantly for energy supply [1]. CO₂ is among the highest produced greenhouse gas, that has been directly implemented in global warming [2,3]. CO₂ is also an element of biogas, natural gas, as well as in landfill gas. It emitted to the atmosphere from flue gas is the main issue contributing to climate change together with global warming. The calorific value of biogas or natural gas is reduced by CO₂, making such gas streams corrosive and acidic, which leads to the removal of CO₂ from such gases. Also, the apprehend of CO₂ from such gases leads to CO₂ separation technologies [4]. There is a vital importance of removing CO₂ for the economic value and an issue of immediate investigation [5,6]. Some reports show natural gas formed 95% CH₄ and 5% of C₂H₆ while biogas contains 45%-65% CH₄ and 30%-40% CO₂. However, energy resources like natural gas, syngas, biogas, shale gas, and have impurity as CO₂ which reduces the heating qualities and values of the gases, demands high energy utilization for the altering as well as transport of corrodes pipelines and other equipment's [7-10]. It is foretelling that if the enormous CO₂ production persists in the future, it could have deleterious consequences which include rising sea levels, melting ice caps, weather changes, ozone layer depletion, poor air quality index, acidification of the ocean, and desertification, which can simultaneously harm the human lives, animals, plants, therefore, mitigation of CO₂ is of utmost importance [11,12]. Till now, there are many methods present for the separation of CO₂ [13-25].

But, due to the intricacy of the gas components and conditions, various technologies invented so far yet suffers from higher cost, high energy consumption, and severe secondary pollution [26-29]. Therefore, developing new technologies to separate such toxic gases and fabrication of new materials and novel processes are necessary. Several methods investigated and evolved in the past few decades to capture CO₂ from various gas mixtures, such as solid absorption, chemical and physical absorption, membrane, cryogenic, and gas hydrates chemical looping (Fig. 1). Among all the methods membrane separation holds many advantages like smaller unit size, lower capital and processing costs,

more elementary operation, better energy efficiency, more superficial up-down scaling, and much lower environmental impact [30].

Figure 1 Different modern and conventional techniques for CO₂ capture.

The CO₂ separation from a gas mixture is conducted by numerous techniques such as cryogenic distillation, membrane technology, absorption, and adsorption [31]. Among all the separation methods, adsorption is of strategic importance in the industry. Different materials like carbons, molecular sieves, zeolites, metal-organic framework, and clays gain more attention to separate mixtures of CO₂ and other gases [32-40]. Selectivity of the adsorption process over other separation methods is due to the unique and vital features of the adsorption process. Besides adsorption, membrane and membrane process is contemplated as one of the most appealing mechanization to mitigate CO₂ emission. The separation of CO₂ using membrane technique has accomplished as notably improved, with fast progress in the past decennium. The following figure (Fig. 2) shows several reported membrane/membrane processes placements into various classes.

Figure 2 Classification of membranes.

Han *et al.*, have showed the advances of using polymeric membranes and utilized the membranes for the capture of CO₂. They mainly focused on material design and formation for CO₂ capture. They grouped the materials on the basis of gas transport mechanism, i.e., facilitated transport and solution diffusion transport. Study of solution diffusion membrane encloses the current endeavors to shift the upper bound barrier and improved solubility of CO₂ in divergent polymers and introduces the new procedures to fabricate the shape persisting macromolecules with high sieving ability.

2. Porous polymeric membrane

The separation of CO₂ through membrane exhibits superiority over the other investigated traditional techniques. Although using membranes with high permeability and selectivity is still a significant challenge [41]. Selective utilization of porous membrane is an unconventional concept applied to flue/fuel streams for separating CO₂. There are five mechanisms for separating CO₂ through the permeable membrane: ionic transport, molecular sieve, adsorption/surface diffusion, Knudsen diffusion solution/diffusion separation, and capillary condensation. The membrane performances are still a challenge and are based on two primary characteristics; selectivity and permeability. The former one in this context allows gas particles to pass over the other, and the latter is the flux. Flux can be defined as the transfer of a definite volume of gas per unit time across the membrane. Gas streams can significantly affect the selectivity and permeability of a particular membrane due to their properties (e.g., the molecular weight of the gas component, the kinetic diameter of the gas molecules, velocity), synthetic material, particular method used

for the synthesis of the membrane. Stating pressure, temperature, and polymer concentration during synthesis and membrane fabrication can control the permeability and selectivity. The use of membranes can be an advantage for the separation process. The complex material based on polymer exhibits a particular attachment of a thin layer to a non-selective, cost-effective, thicker coating that demonstrates high mechanical strength [42].

There is tremendous progress of membranes for the separation of CO₂ results in a considerable number of reports in the past ten years. There are reports on polymeric membranes, micro-porous membranes, carbon membranes, polymer blend membranes, ZIF membranes, MOF membranes, facilitated membranes, PEG-containing membranes, mixed matrix membranes, and polyimide membranes ionic membranes liquid-based membranes [43]. These methods for the separation of CO₂ are based on biogas upgrading, petrochemical industry application, olefin/paraffin separation, and natural gas sweetening [44-62]. In most of them, the thickness of the self-standing membrane was around 50-150 μm , and the separation performance was compared with 'Robeson upper bound' [63]. However, there are mainly two reasons for the disparity of such values in contrast to industrial values. Firstly, the prediction of pure gas measurements on an industrial scale is inferior, especially for CO₂. Secondly, the permeation properties of composite membranes depend on the thickness of polymeric films, which results in different separation and transport performances [43,64]. There are numerous reports regarding thin-film composite, primary cornerstones on inorganic materials with a selective layer for gas separation. Therefore, it is necessary to furnish a recent advance for the separation of CO₂ using multilayer composite membranes [43]. Polymeric separation demonstrates a very high permeability of CO₂ with lower selectivity values comparing with other separation methods. However, for the CO₂ separation, membranes only allow CO₂ to pass through the membrane, excluding the other components present in flue/fuel gas streams. Fabrication of ultra-thin, defect-free composite achieves a high gas flux. It ensures an economically viable membrane for the separation of gas. The main advantage of using composite membranes over other asymmetric membranes is the material because of its mechanical processability and properties. A minimal amount of the material is needed for deposition in the composite membrane (0.1-2 g/m²).

Figure 3 Structure of multilayer composite.

Composite layers contribute different functions to the membranes, and thus requirements of each layer are also other, as shown in Fig. 3. High mechanical strength resulting in low mass transfer resistance and high porosity obtained by porous support of the composite membrane. Additionally, such materials should be cheap as well as quickly processed into a permeable membrane. The selective and absorbent layers contain a gutter layer, which reduces the possible penetration into the membrane's pores of the coating solution and the surface roughness. The main separation properties of the membrane offer by the core part of the membrane is the selective layer.

Along with lifetime, aging, cost, and stability, the first two main criteria for the selectivity of membrane material are high selectivity and gas permeance. If needed, a protective layer can also be employed to protect the membrane during handling and fabrication. The selection of layers such as protective layers, selective layers, gutter layers, and porous support is of significant importance.

2.1 Porous support

The support comprises the phase inversion method immersed in a non-solvent bath involving precipitation of a casting solution. However, gas separation membranes can be primarily prepared by using this method commercially, such as poly-sulfone (PSF) and polyimide (PI). With the control of the synthetic condition of membranes, the supporting material should possess finger-like structures or sponge-type [65]. In the phase inversion method, the polymer consumption is about 50 gm/m² for asymmetric porous support where both the support and dense top layer are of the same material. The commercialization of membranes with expensive polymers is challenging if the phase inversion methods work

for them. Another technique is used to synthesize the not soluble polymers in commonly used solvents, including heating, annealing, extruding, and stretching. As a non-porous polymer film, heating is the melting stage followed by extruding the polymer. For the improvement of the crystalline structure of the polymer film (e.g., membranes like porous polytetrafluoroethylene (PTFE) and polypropylene (PP)), annealing is used. This stretching step leads to easy pore formation, and the annealed film was extended to form micropores [66]. As porous support, only a handful of commercial polymeric membranes are available. The most common porous supports are PSF, PAN, CA, PEI, PVDF, PPO, PP, PTFE, Teflon, etc. The coated porous support should have at least ten times much higher gas flux than the coated one, which corroborates the resistance of the selective layer. The main criterion of porous support is a smooth and clean surface for uniform and defect-free coating. Based on the intrinsic properties, supporting medium have also contribution to the selectivity of the process. Simultaneously, porous support present on the material surface can diminish the resistance of the mass transfer.

2.2 Gutter layer

The porous and selective layers contain a gutter layer between them and contributes different characteristics for different cases. The primary purpose is to avert the diluted polymer solution from blocking pores and penetrating the porous structure. However, this layer should be smooth to coat and make it defect-free easily. The most routinely used polymer for the fabrication of such layer is the poly(1-(trimethylsilyl)-1-propyne) (PTMSP) and polydimethylsiloxane (PDMS) due to their high porosity. Nevertheless, PTMSP loses its performance, although highly porous, within a concise period [67,68]. During an operation of 14 days, 80 % reduction was observed in the PTMSP composite membrane casted on polyacrylonitrile (PAN) support. A drop of about 5 % was observed using PDMS. The most commonly used polymer for a gutter layer is the PDMS, as it is rubbery and is reasonably stable. To increase the long-term stability cross-linking PDMS polymer is most frequently used. The physical aging issue of PTMSP can also be solved by cross-linking.

2.3 Selective layer

In the separation of gases, many contrasting polymers have been studied in the last decades in the form of dense, thick membranes (thickness~50-150 μm) like polyamides, polyimides, hydrophilic polymers, and block copolymers with copious amino groups. There are many advantages of using a thin-film composite membrane and having commercial applications [69]. A thin film's superior gas transport properties can be lost by physical aging in a short period [70]. Poor contact in a thick membrane at the interface of inorganic filler/polymer causes the interfacial defects to bring enormous challenges in

maintaining gas selectivity. This layer offers the function of separation and is the most crucial part of the composite membrane. A well-known route is the mixed matrix membrane to enhance the properties of the polymeric membrane. Mixed Matrix Membranes are fabricated by inorganic filler which will be incorporated into a polymeric matrix. The material used should be easily constructed in to different membrane modules, which founds to be more competitive with the methods that were already reported for separation and efficiency in cost. The main criteria for the preference of such layer of a composite membrane are: (i) high gas permeability, (ii) high selectivity of CO₂, (iii) resistance to aging, (iv) resistance to CO₂ plasticization, (v) good thermal and chemical stability.

Mechanism of gas transport can be divided into two types: one is facilitated transport of gases and the other one is solution-diffusion mechanism. There are no chemical reactions involved in the gas transport mechanism. Both solubility and diffusion of the gas contribute to the permeability of the gas in the solution diffusion method. Such a membrane type is usually engaged in the trade-off between selectivity and gas permeability. [71]. The transport mechanism is another mechanism involved, where a reversible reaction between functional groups in the membrane and CO₂ occurs.

Comparing these two membranes with relatively low driving force indicates that facilitated membranes have higher selectivity and permeability. Observed pressure-dependent CO₂ permeability is another characteristic. At elevated partial pressure of CO₂, there is a chance that the mobile carriers will be saturated and because of this, mobile carriers have the probability to lose their transport properties, including selectivity and permeability of CO₂ over other gases. The most commonly used facilitated transport carriers are the amino groups which includes primary amine, secondary amine, or any sterically hindered amine). Polyvinyl Amine (PVAm) is the most widely and intensively explored polymeric material. Such polymeric material is reactive reversibly and facilitates CO₂ transport where amino moieties are explained as 'fixed site carriers' [72,73]. Such transport includes the reaction of CO₂ with water, promoted by the functional group present, and then convey rapidly in HCO₃⁻ ions.

In contrast, gases like CH₄, H₂, and N₂, i.e., the non-reactive gases, will exclusively transferred via the membranes through the solution diffusion mechanism. Thus, transport and high selectivity of CO₂ are more significant as compared to the other gases. There are also reports where this transport affects the transport of ions such as potassium (K⁺), calcium (Ca²⁺), carboxylate group (COO⁻), and carbonate group (CO₃²⁻) [74-76]. CO₂ transport in membranes has also been reported to facilitate by mimic enzymes with a metal activation center [77,78].

2.4 Protective layer

In a multilayer composite selective layer can be coated with a protective layer if needed. The primary function of such a layer is to improve the selectivity by plug the minor defects in the membranes and protecting a distinct soft layer (e.g., Pebax, polyactive). Such modification can protect the membrane from being defaced in the fabrication process as well as handling, mainly in the module membrane construction with high membrane packing density [79,80].

3. Ionic liquid based membrane

In the past few years, these liquids are considered to be one of the most developing candidates for separation and capture of CO₂ owing to their structural features as they consist of anions and cations, and unique functional groups and have some exciting properties such as non-volatility, design ability, selectivity, and higher CO₂ solubility [81]. Exploration of ionic liquids (ILs) in CO₂ separation is based on their inherent structural tunability, good affinity with CO₂, and novelty, which led to unprecedented interest from both industries and academics. ILs can capture the CO₂ efficiently released from saturated solvents due to the absence of volatility lead to a decrease in energy consumption and environmental concerns than the traditional one [82]. The IL-based CO₂ capture, in single/multi stage, have the ability to reduce the total energy contrast to the well-known methyl diethanolamine (MDEA) process, including thermal energy and electricity, by 42.8 % and 66.04 %, respectively [83]. ILs can be tuned based on their structure, creating a degree of freedom for designing solvents with distinct properties. Thus, designable ILs are considered to be efficient for cost-effective and energy-efficient capture of CO₂. It can replace the nonvolatile solvent and circumventing solvents to go in the ejected gas in order to intercept the environmental pollution originated from the organic materials [84-86]. However, in comparison to the other organic solvents, tuned ILs are unique in nature [87]. The physicochemical properties of ILs can be tailored by many possible functional groups, anions, and cations, their CO₂ separation performances [88-90]. The structural framework for the capture of CO₂ by ILs is depicted in Fig. 4.

3.1 CO₂ selectivity in ionic liquids

Various impurities are found to be present in natural gas, biogas, and flue gas such as CO, H₂S, SO₂, O₂, CH₄, N₂, CO₂ and H₂. Therefore, the separation and purification of such gases are also crucial. It is of up most importance to explore the selectivity in comparison to other gases because the CO₂ solubility data is inadequate to examine the adsorbents separation performance [91].

Anderson *et al.*, in their report, used 1-hexyl-3-methyl pyridinium bis(trifluoromethylsulfonyl)imide [Hmpy][Tf₂N], which indicate the different solubilities of gases. They have shown that the selectivity of SO₂, CO₂ is high compared to N₂, O₂, etc. [92]. The ideal gases selectivity in ILs can be determined using Henry's law under the same temperature for different gases [93]. Thus, selectivity for [Hmpy][Tf₂N] of CO₂/O₂ and CO₂/N₂ is higher than the CO₂/hydrocarbon selectivity because of the lower O₂ and N₂.

Figure 4 Schematic representation for the mechanism of CO₂ absorption in ILs.

3.1.1 CO₂/hydrocarbon selectivity

Zheng *et al.*, and Noble *et al.*, have delineated the CH₄ and CO₂ solubility in imidazolium-based traditional ILs i.e., [Bmim][Tf₂N], [Bmim][dca], [Bmim][NO₃], and [Bmim][BF₄] [94-98]. This shows the higher solubility of CO₂ as compared to the CH₄ in some of the ILs. Though the selectivity value is lower than 12 in case of CO₂/CH₄, still inadequate to take part with the traditional physical absorbents sulfonate and rectisol.

Ramdin *et al.*, studied the solubility as well as selectivity of CO₂/CH₄ in different ILs based on ammonium, pyrrolidinium, piperidinium, and phosphonium. Among all these ILs, selectivity showed for CO₂/CH₄ are 1-butyl-1-methylpyrrolidinium dicyanamide [Bmpyrr][dca] and 1-allyl-3-methylimidazolium dicyanamide [Amim][dca] as the CH₄ solubility is low. Compared with the imidazole-based ILs, selectivity in different ILs is not significantly improved due to the simultaneous increase of CO₂ and CH₄ solubility [99]. However, with an increase in the molecular weight and free volume of ILs, the selectivity of CO₂ is also increases. At the same time, the solubility of CH₄ is not dependent on the molecular weight of ILs and is mainly determined by the interaction between the two [100]. Thus, there is a quid-pro-quo between the CO₂ and CO₂/CH₄ for their solubility and selectivity.

3.1.2 Selectivity of CO₂/Diatomic gas mixture

The solubilities of different gases, viz. H₂, CO, N₂, O₂ in ILs were found to be lowest for H₂ and highest for CO₂, which indicates the selectivity towards CO₂.

Jacquemin *et al.*, under different conditions, determined the solubilities of various gases in [Hmim][PF₆] and found some dissimilarity in their solubility with other reported works [101]. Despite such discrepancies, these gases with low solubilities in ILs also have followed the similar trend as cited above. Due to the presence of free volume, which is shown by [PF₆] anion, these above cited gases are better soluble in [Bmim][PF₆] than those in [Bmim][BF₄], directing to higher selectivity of CO₂/CO, CO₂/N₂, and CO₂/O₂ in [Bmim][PF₆] [102].

Finotello and his team mainly focused on the solubility of gases like CO₂, CH₄, H₂, and N₂ as well as the selectivity of CO₂ in ILs such as [Emim][BF₄], 1-hexyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide ([Hmim]-[Tf₂N]), 1,3-dimethyl imidazolium methyl sulfate ([mmim][MeSO₄]) and, [Emim][Tf₂N] at divergent temperatures. According to their studies, the selectivity of gas pairs is directly related to the smaller molar volumes of ILs [96].

Shi *et al.*, in their report, confirmed that the molar volumes of the ILs plays a major role in the solubility of H₂, established with the help of experimental as well as theoretical studies. According to their report, the use of ILs with small molar volumes such as 1-ethyl-3-methylimidazolium acetate ([Emim][Ac]) and intense interaction with CO₂ to attain high CO₂ selectivity and solubility. The result of H₂ solubility in [Emim][Ac] is six times smaller as compared to [Hmim][Tf₂N] which was confirmed by theoretical studies. The main reason behind the low solubility of H₂ in [Emim][Ac] is the smaller volume of IL and the weak interaction between IL and H₂ [103].

4. Metal-organic framework (MOF)

MOFs, due to their versatility, are the potential candidates to be implemented in real-time applications for carbon capture. Omar Yaghi was the first who introduced MOF to the scientific community in the 1990s, after that MOF becomes the most important material that has gained momentum being cited in renowned journals and gains countless patents with applications in variable fields [104-107]. Metal-Organic Frameworks are framed by linking of metal ions through some organic linkers forming 1d-, 2d-, 3d-frameworks with appealing features. The basic MOF framework along with its synthetic procedure is displayed in Fig. 5. The most advantageous feature about the MOFs is that they can be engineered to have a desirable shape with ultra-high porosity, different pore sizes, surface area, and they can be tuned at ease for any application [108]. Due to the above-mentioned

advantages, MOFs becomes the potential candidate for variable applications viz. gas storage [109,110], separation of gases [111,112], catalysis [113], sensing [114], drug delivery [115], semiconductor [116], photovoltaic device fabrication [117], etc.

Figure 5 General Synthesis Scheme for Metal-Organic Framework.

Concentrating on process, Carbon Capture and Sequestration (CCS), due to the highly tunable nature of Metal organic frameworks, they become the most appealing candidate, because MOFs can be specifically fabricated to capture CO₂ at variable conditions with high selectivity. MOFs, in comparison to other porous materials, are superior as MOFs structure can be tuned easily to fulfill the desired application, whereas other traditional porous materials such as zeolites have limited structure motifs. Therefore, logical design [118], theoretical model development [119-122], and synthesis schemes with high throughput instrumentation [123-126] are the prime focus of several evaluations to predict systematic properties and characteristics for CCS and other applications as well.

4.1 MOF membranes

Membranes are the potential candidate that can be utilized in real-time applications because of their most advantageous features. The most appealing feature is that the membranes does not have any moving parts and the membranes can be utilized for continuous separation process. Membranes can be employed for solubility, diffusion, and adsorption of analytes for separation. There are several materials used for membrane fabrication which are explored for carbon capture application that includes both porous as well as non-porous structure [127]. The porous/non-porous membranes incorporated with polymeric matrices either discrete or on a support comprising of a combination of dissimilar matter, which are often denoted as hybrid membranes. These hybrid membranes can be synthesized with a couple of polymers mixed or phase-separated, can also include the filler particles.

The shift of powder MOFs to membranes [128] or thin films [129] has magnetized the attention of scientific community for variable utilization which includes Carbon Capture and Sequestration (CCS) [127,130-132], liquid separations [133-136], gas separations [137-140], and sensor related devices [141-143]. The emphasis of the aforementioned applications entails harvesting the characteristics of a metal organic framework to fabricate the membrane/device and examined their execution for real time applications. The tailored MOF membranes for carbon capture are envisaged to have a higher rate of selectivity for CO₂ over N₂ in high flux. Such characteristics are found to be difficult to achieved in capturing in the post-combustion conditions; the MOF membranes should be highly selective to take out at lower concentration of CO₂ in the flue gas. Moreover, when flux flow rate is large, a large surface area is required to perform the separation application. Moreover, specific designs of module and packing of membranes occurred as challenge to scientific community for carbon capture specifics [144].

4.2 Performance of MOF membranes

The implementation of gas separation membranes is governed by three factors: penetrability, permeation, and selectivity [127,145-148]. Penetration or permeability can be defined as the ability of fluids to pass through a porous material and is the change in concentration value of different gases that can be separated in between both the sides of membranes, and it is always reported by Barrer units (10⁻⁶ cm³ (STP)/cm² s cm Hg). With utilization of chemical modification technique in membrane moieties, the permeability can be changed. Moreover, the porous/non-porous membranes can be compared with the help of permeability values. Concerning the solution-diffusion model, solubility (S) and diffusivity (D) factors are employed to calculate the permeability (P) by the equation,

$$P = S \times D$$

Solubility can be defined as the value which indicates the extent of a gas that solubilizes in the matrix of membrane, whereas the diffusivity of gas is directly associated to the volume that are free for polymer and gas particles of a gas stream. Permeation or permeance can be related to the coatings of membrane on flat surface or on the hollow fiber sheets where the important aspect is the width of the respective sheet. Permeance is also considered to compare membrane performance and is always denoted in gas permeation units (GPU). Other units are also present which are widely used. The conversion relationship between different units are shown in Table 1. The gas permeation unit is related to Barrer units as Barrer/Thickness. The separation factor/selectivity is defined as the correlation between more and the less permeable gas, that can be evaluated by using ideal gas permeabilities of two-variable gases (say A and B),

$$\alpha_{A/B} = P_A/P_B$$

Moreover, for a mixture of gas, the selectivity can be evaluated by calculating the modified equation-

$$\alpha_{A/B} = (X_i/X_j)_{\text{permeate}} / (X_i/X_j)_{\text{feed}}$$

MTR (Membrane Technology and Research) Center's Polaris™ is the most widely utilized membrane for post-combustion carbon capture [144,149]. Polaris's membrane is a thin polymeric membrane with high porosity designed to support high carbon capture. In their reports, MTR mentioned that their membrane captures 10 times higher than other membranes that are available commercially, the membranes show permeance of CO₂ of 1000-2000 GPU at 23 °C and a CO₂/N₂ selectivity of 50-60 [144]. In addition to this, MTR has increased their membrane surface area (up to 1 meter) and achieved a steady carbon capture, conducted at a pilot plant that emits huge amount of CO₂ (~1 ton per day) [149]. Merkel *et al.*, have demonstrated that when selectivity of CO₂/N₂ is more than 30, membrane permeance is the most prominent factor for reduction of capture cost, more membrane permeance, less will be the area of membrane required which simultaneously leads to reduce the capture cost [144].

Table 1 Relation between different Gas Permeation Units

	(GPU) 10 ⁻⁶ cm ³ (STP) cm ⁻² s ⁻¹ cmHg ⁻¹	10 ⁻⁷ cm ³ (STP) cm ⁻² s ⁻¹ kPa ⁻¹	10 ⁻¹⁰ mol m ⁻² s ⁻¹ Pa ⁻¹	10 ⁻³ m ³ (STP) m ⁻² h ⁻¹ bar ⁻¹
(GPU) 10 ⁻⁶ cm ³ (STP) cm ⁻² s ⁻¹ cmHg ⁻¹	1	7.50	3.35	2.70
10 ⁻⁷ cm ³ (STP) cm ⁻² s ⁻¹ kPa ⁻¹	0.133	1	0.447	0.360
10 ⁻¹⁰ mol m ⁻² s ⁻¹ Pa ⁻¹	0.299	2.24	1	0.806
10 ⁻³ m ³ (STP) m ⁻² h ⁻¹ bar ⁻¹	0.365	2.78	1.24	1

4.3 Design of MOF membranes

With the introduction of customized MOF for CCS into CO₂-permeable polymers, hybrid material can be created that will show high performance which reflects the properties of both. So, with the evolution of this, researchers are quite confident of mixing the organic polymer with inorganic MOF to fabricate a membrane which has the ability to cross the Roberson upper bound for CO₂/N₂ [150]. The diagram below (Fig. 6) will demonstrate the

CO₂ capture by MOF membranes. The blending of porous filler moiety and organic polymers to produce hybrid material is also called mixed matrix membrane (MMM). MMMs are fabricated by utilizing varying procedures such as direct mixing [134,151], and in-situ methods for growing [152,153]. But the blending of polymer with MOF are challenging as the two layers interface are often not compatible with each other. Koros *et al.*, [154] have demonstrated five non-ideal interfaces that are often observed during the fabrication of MMM: (1) stiffen of the organic polymer around the MOF; (2) large voids associated with MOFs within the MOF/polymer dispersion; (3) tiny gaps; (4) clogged MOF pore; (5) combination of all the above due to MOF particulate slows the gas permeability. For a membrane to overpass the limit of Robeson upper bound, the membrane should be fabricated with no or zero defects and should avoid the five interface cases. In this context, computational models are frequently employed to know the insight of the interface and compatibility of MOF and polymer [155,156]. Various instruments are also employed to show the interfacial defects such as Raman Spectroscopy, etc. [131].

Figure 6 Demonstration of CO₂ capture by MOF Membranes.

Universally there are few reports present till date to understand fully the interaction between the polymer and MOF composite. Moreover, all the MMM systems have different characteristics, due to which the idea to create membranes with no defects may not work universally for all the systems. Due to which a large number of fabrication techniques that involve chemical modification to both the MOF and the polymers are presented by different research groups to get a homogenous membrane where both the moieties mixed perfectly. However, post-synthetic adjustment of the MOFs is quite useful to enhance the interactions between both the moieties [151] which can lead to enhanced performance. There are other modification techniques present for the development of MOF, especially for CCS, which

includes MOF particle priming [157], polymer backbone modification [152], and reactive seeding of MOF precursors [139]. To get more detailed background of fabrication technologies of membranes, we hereby direct the reader to the references [145,158,159].

Asymmetric MOF membranes, in compared to the conventional MMMs, are also becoming potential separation membranes. Here, MOFs for thin film are deposited onto polymeric or ceramic supports. We hereby requested the readers to the references [135,137,140,160-165] to gain insight into different processes which are utilized to prepare asymmetric MOF membranes. There are some downfalls while fabricating asymmetric membranes on supports like ceramic (alumina), as this process can be discovered as more costly and mechanically weak. While the fabrication of asymmetric MOF membranes on polymer support is quite easy and is cost-efficient. However, controlling the MOF and polymer interface can be challenging. In this context, a continuous flow synthesis method has been developed which has the potential to reduce the steps of the MOF preparation, which simultaneously reduces the cost also. This method was first implemented on scale-up MOF synthesis materials [166-168], and then it is applied in membrane processing [169,170]. Marti *et al.*, [171] have illustrated the continuous flow process in the ZIF-8 MOF synthesis on the facade of Torlon Hollow fibers. Torlon is referred to as upper-level support, as it is mainly composed of polyimide which can resist the organic solvents and is stable at high pressures. ZIF-8 precursors are allowed to flow through the shell or the bore of the fiber with known concentration. The rate of flow generates fine membrane surface of MOF on the outer side of support. These membranes can show a high selectivity of CO₂/N₂ of 52, and 22 GPU high permeance. Comparing this work to others, it shows more efficient performance and strictly follows the green chemistry protocols. This is an example for many researchers to make such membranes that have application in various fields and can be utilized in CCS technology for higher performance values.

4.4 MOF membranes for CCS

Nowadays, the membrane separation technique emerges as a special separation method that can be used in CCS. It has many advantages as compared to other methods which include low cost, highly energy-efficient, recycling, and ease of operating. The insight mechanism of the separation method is based on molecular sieving towards the gas molecules. As the characteristics of the MOFs can be tuned easily to direct size-selective sieving effects, membranes of MOFs are evolved as the highly promising candidate for carbon capture, gas separation, and separation processes. The efficiency of the membranes of MOF towards carbon capture can be enhanced by inclusion of different functionalities to guide their variable interactions [172] and the post-synthetic functionalization can also be found as important to get improved carbon capture [172].

Lai *et al.*, have synthesized the first MOF membrane [174]. Zhu and Qui have synthesized the HKUST-1 MOF-membrane in a support of oxidized copper nets, which shows a good selectivity of H₂ gas over the other gases such as CH₄, CO₂, N₂, etc. as H₂ molecules due to their small size in nature, can easily permeate through the membrane. The same thing is also confirmed by one more group [175]. Ben and his team have synthesized a stainless-steel net/ PMMA-PMAA-supported HKUST-1 membrane. The same is also utilized in H₂/CO₂ separations from gases [176].

Zeolitic Imidazolate Frameworks (ZIF), which is nothing but a sub-branch of Metal Organic Framework, appeared as a potential moiety in the construction of membrane for the application in gas/hydrocarbon separation, which has a superior thermal as well as chemical stability and has a decent pore size of around 0.3-0.5 nm [177]. To date, different ZIF membranes are synthesized which have the potential for gas separation [178]. Caro and his team were the initial group to develop a ZIF-8 membrane and have showed Knudsen selectivity for H₂/CO₂ separation [179]. The same group has studied the membrane of ZIF-7 for selectivity and has concluded that they have prepared one novel rigid ZIF-7 membrane having nearby ~3 Å pore size [180]. A clear separation of both the gases is observed when H₂/CO₂ are in equal proportion, which are able to pass through the membrane of ZIF-7 [181]. The molecular sieving effect for the aforementioned system gives the separation factor (6.5) and gives a high value of H₂/CO₂ selectivity (6.7), higher than that of 4.7 (Knudsen separation factors). Moreover, they tried to upgrade the gas separation, H₂/CO₂ by a factor of 8.4 where the mixture contains equimolar amount of H₂/CO₂ at a temperature of 200 °C by changing the synthesis procedure. Additionally, they proved the separation of H₂/CO₂ gases through the ZIF-7 membrane can be varied with variable temperatures [182]. The results of the experiment were that the H₂ gas permeance quickly with an increase in temperature, but the permeance of CO₂ remains constant, which leads to the enhancement of separation factor from 5.4 (50 °C) to 13.6 (220 °C). Contrastingly, membrane of ZIF-22 which has the similar to ZIF-7 in case of pore size (~3.0 Å) exhibits more molecular sieving performance on separation of H₂/CO₂ and other gases as well [183]. ZIF-90 was often functionalized with different functionalities to attain selectivity. In comparison to the ZIF-90 membrane, post-synthetic functionalization of the same [86,184] by ethanolamine can significantly enhance separation factor of H₂/CO₂ and other gases as well to ~15.7. Later on, they synthesized APTES-functionalized ZIF-90 molecular sieving membranes that have improved separation of H₂/CO₂ (20) at 225 °C and 1 bar, which shows a high thermal and hydrothermal stability [185]. ZIF-90/Torlon membranes are obtained by Nair *et al.*, where membranes are formed with no defects and have a complete surface coverage, with a separation factor of 1.5 for CO₂/CH₄ and 3.5 for CO₂/N₂ [186].

MMMs, mixed matrix membranes, are nothing but the blending of MOF moieties with the polymer, has been explored and it emerges as an alternative strategy to obtain MOF membranes. Musselman *et al.*, have successfully synthesized MMM where ZIF-8 is the filler phase and polymer used is Matrimid®. When the ZIF-8 loading increased to 40% (w/w), the permeability also continuously increases for H₂, N₂, CO₂, O₂, C₃H₈, CH₄. Moreover, higher loading ratios up to 60% (w/w) of ZIF-8 into polymer Matrimid® enhances the selectivity for many gases. Matrimid® alone shows a 2.58 factor for selectivity in a 1:1 H₂/CO₂ mixture, that increases to a factor of 7.01 at 60 % loading of ZIF-8. Matrimid® alone shows selectivity of 42, which was further enhanced to 89 by a 50 % loading ratio of ZIF-8. Mixed matrix membranes framed with PVAc (Polyvinyl-Acetate) and Cu-TPA framework, show higher selectivity in case of CO₂/N₂ as well as CO₂/CH₄ separations [187]. Car *et al.*, have synthesized the HKUST-1/PDMS and HKUST-1/PSf membranes with 10% (w/w) loading of HKUST-1 enhances the selectivity for CO₂/N₂ and CO₂/CH₄.

5. Water facilitated mixed matrix membrane for CO₂ capture

The concept of mixed matrix membrane (MMM) emerges from the inclination of mixing of polymers and molecular sieves which are implemented for gas separation. The concept of MMM was enlarged in 2011 [188], and in the same time, organic/inorganic fillers are developed simultaneously. Mixed Matrix Membranes are elucidated as the inclusion of disseminate part onto a steady polymer part, to merge and produce new benefits. For Water Facilitated CO₂ capture (WFCC) MMMs, the polymer employed should be an ordinary polymer or high-performance hydrogel or the packing should be in such a way that it can furnish more transport highways for carbon dioxide or can enhance the further profits of the membrane. Here, the minimum criteria are that at least one part should show a good performance in the hydrated state.

Initial category of WFCC MMM was framed by using one inert inorganic filler and a hydrophilic polymer. Here “inert” refers to the filler that does not have any WFCC property. The thermal and mechanical stability of the filler is important so the filler is mainly composed of inorganic moieties [189-192]. The role that the polymer matrix does will be followed by the water (support) in this context. But the consequence of filler is complex. Xing *et al.*, [189] have submerged fumed silica into the carrier containing the PVA-POS network. While increasing the loading ratios of fumed silica from 4 wt.% to 17 wt.%, the permeability of CO₂ increases along with the enhancement of selectivity of CO₂/H₂ from 65 to 87. From the above results, they concluded that the fused silicas retarded the loading of the polymer chains, which is in accordance with reverse selectivity [193,194]. Deng *et al.*, have demonstrated the carbon nanotubes (CNTs) in PVAm-PVA

mixture showed two functions, viz., at lower pressure, CNTs slightly enhances the swelling of membrane due to the nano-spacer function and at higher pressure, it increases the swelling of membrane up to a higher strength due to the resistance against compaction effect. In general, CNTs improved the snit-compaction property, increases the mechanical strength, and enhances the separation performance of CO₂.

The second category of WFCC MMM was framed by using one active filler and an ordinary polymer. Here, the active filler can absorb a high quantity of water and can permeate more CO₂ from it. Liu *et al.*, [195] have prepared for the first time the polyzwitterion@CNT (polyzwitterion coated CNTs), which was further coated in Matrimid® 5218. Here the filler shows to enhance the water uptake capacity of the membrane which was further attributed by strong hydrophilicity of polyzwitterion. Whereas Li *et al.*, [196] have incorporated poly(N-isopropyl acrylamide) nanohydrogels in the aforesaid matrix. The nanohydrogels inserted in the Matrimid® matrix act as pool for water which provides water for CO₂ dissolution and also gives pathways for CO₂ transport. The aforementioned Matrimid®/nanohydrogel mixed matrix membranes show an enhance in CO₂/N₂ and CO₂/CH₄ selectivity of 52 and 61, with CO₂ penetrability of 278 Barrer, which is much better than previous MMM that shows a selectivity factor of 36 for CO₂/CH₄ and 103 Barrer CO₂ penetrability. The reason behind the enhanced property is that the nanohydrogels are filled with water and are highly swollen, and main effective hydration layer was found at the CNT surface. The idea of blending nanohydrogels with a commercial polymer seems interesting because of the commercialization prospects as well as the mass transfer model.

The third category of WFCC MMM was framed by using an active filler and a hydrophilic polymer. Here the no mobile carriers are present on the polymer. The mobile carriers are provided by the active fillers to the inner channels. The active fillers also have roles in the structure modifier. Dry MMMs are prepared successfully and the hydrated MMMs should also include inner channels. Few researches have reported the microporous filler-based hydrated MMMs that show better separation of CO₂. Wu *et al.*, have disseminate the functionalized poly-ethylenimine with MCM-41 (PEI-MCM-41) into Pebax 1657. Poly-ethylenimine were present in the channels of pore as well as on the MCM-41 surface, which provides amine carriers for transport of CO₂. Comparing with the MCM-41, modified version of MCM-41, viz., PEI-MCM-41, results in more stiffness in the polymer chain at the polymer-packing interface. By referring mesoporous fillers-based morphological structure of MMMs [197], such interfacial structure enhances the selectivity and permeability. In the same context, Xin *et al.*, by using the facile vacuum-assisted method, have dispersed PEI into a mesoporous MIL-101(Cr), and then incorporate the obtained compound, i.e., PEI@MIL-101(Cr) into SPEEK. For the advantageous feature of SPEEK

like high mechanical strength, the loading ratio of 40 can be realized. PEI@MIL-101(Cr)-doped membranes show a 2490 Barrer for the CO₂ permeability, which is the highest as compared to the pristine SPEEK membrane by a 4.6-fold. In comparison to the pristine MIL-101(Cr), permeability, and selectivity of gases such as CO₂/CH₄ and CO₂/N₂ of PEI@MIL-101(Cr)-doped membranes show improvement by 62 %, 128 %, and 102 %. She *et al.*, [198] has also tried by adding sulfonated MIL-101(Cr) to SPEEK. They have found that separation data of CO₂ with comparison to that of the PEI@MIL-101(Cr) shows a little lower. The inclusion of sulfonated MIL-101(Cr) in membrane enhances the solubility of CO₂ which was further accounted for the sorption enhancement effect of adsorbed water. Moreover, new experiments were exploited by using TiO₂, a non-porous filler, and found that despite the surface have amines in it, still it shows the highest CO₂ permeability of 1629 Barrer only [199]. These results directly demonstrate the advantages provided by mesoporous fillers and incorporating such fillers in the hydrophilic matrix. So, by taking this into account, various researches have also been done with microcapsules as filler, due to their hollow structure, it can construct even more CO₂ transport pathways as compared to mesoporous fillers [200].

By considering the above context, PVAm based MMMs are also exploited. Zhao *et al.*, have demonstrated the disruption of the PVAm chain packing by polyaniline nanosheets and can furnish few weaker carriers, which simultaneously show a much higher CO₂/N₂ selectivity of 120 along with higher CO₂ permeance, 1200 GPU. The advantage of this is that, by decreasing the wet coating thickness of polyaniline nanorods, one can easily increase the CO₂/N₂ selectivity and permeance of CO₂ up to 240 and 3080 GPU [201]. Liao *et al.*, have successfully demonstrated an HT (hydrotalcite) channel in PVAm [202]. Here, the flexible carbonate acted as a semi-mobile carrier and shows a CO₂/N₂ selectivity and permeance of CO₂ by 296 and 3187 GPU respectively.

6. Hollow fiber membranes

Spinning is a process where polymer can be converted to fiber. In hollow fiber (HF) fabrication technique, there is the continuous production of single as well as multiple fiber by means of spinneret followed by returning to the solid state through solidification process [203]. The varying properties of fiber form during this fabrication process depends on several parameters. There are two common methods used in spinning process, solution spinning and melt spinning [204]. The common features used in both of these methods is the spinneret through where a polymer sample solution as well as solvent were extruded. After extruding, the polymer sample retain a hollow cylindrical shape through the solidification process generally called as the phase inversion. Melt spinning process is used for those polymer materials which can be melt easily. The process includes, in an extruder,

heating of the polymer flakes or pellets until it melts completely which later pumps the liquid polymer across a spinneret to form liquid spinning dope. The filament in the spinneret is cooled to undergo solidification and with the help of a godet roller, final fiber velocity can be fixed [203,205]. Finally, for the storage, the fiber is wound on a spool like a sewing thread [206].

On the other hand, solution spinning process [207] can be classified in two categories, wet and dry-wet spinning process. Wet spinning process consist of the methods where the dope solutions were ejected to an external bath that contains a non-solvent liquid which on later exchange themselves, referred to as phase inversion, that leads to the complete dismissal of solvent which is further followed by solidification/precipitation of the fiber. In solidification process, sometimes due to the improper mass transfer through the nonsolvent-dope interface, several voids as well as cross-sectional irregularities were observed which can be reduced by applying the air gap between the spinneret and end of the coagulation bath. This above discussed is called as dry-wet process [206]. Advantages of a Hollow fiber membrane over a flat membrane are that they have self-supporting properties which help them in reducing the complexity in fabrication of the component and the higher productivity, that can be related to its high area of surface with excessive packing density [208,209,210]. Different types of parameters that cause instability during the spinning of HF are draw resonance, cross-section, necking, and irregularity in fabrication of the fibers.

Membrane contactor, as the name suggests, is a mechanical device consisting of a membrane that employs separation or chemical changes between two phases using selective mass transfer. For example, membrane present in gas-liquid contactor is used to separate two phases of gas and liquid respectively, providing sufficient contact with two phases without mixing them directly. The solubility of the components in the liquid phase provides the selectivity of the membrane and for this reason, most gas-liquid contactors are employed with porous membranes with high mass transfer ability. In some cases, the composite or asymmetric membrane with thin non-porous polymer material is also used in the high-pressure separation process [211,212]. To minimize the resistance during mass transfer, a porous hydrophobic membrane is used which allowed the gas phase to enter the pore instead of penetration of liquid as shown in the Fig. 7. In the membrane separation technique, the contact area plays a vital role that can be illustrated as the area of the membrane pore mouths. The operating pressure in systems must be controlled to avoid the intermixing between gas and liquid phase. Especially when the operating pressure is not equal for both phases, gas bubbles dispersion may arise which affects the rate of mass transfer [213]. The mass transfer ability of a porous membrane is also affected when the liquid layer is immobilized in the pore. Wang *et al.*, [214] suggest that a 20 % decrease of

mass transfer coefficient is observed when membrane pore is 5 % wetting, while it increases up to 6 % when 2 % wetting of membrane pores.

Figure 7 Mass transfer in a membrane contactor: symmetric hydrophobic porous support.

If the pressure of the liquid phase surpasses a critical level, the non-wetted mode can't be provided by the membrane's hydrophobicity [215,216,217]. Therefore, pressure plays a crucial role in the mass transfer process and is dependent on the surface tension and also on the contact angle at stated operating condition. Using Laplace's equation, pressure can be easily quantified-

$$\Delta P = \frac{2\sigma \cos\theta}{r_{p,max}}$$

where, ΔP is the critical transmembrane pressure, $r_{p,max}$ is maximum pore radius, σ is the surface tension of the liquid, and θ is the contact angle.

Figure 8 Mass transfer in a membrane contactor: a) Hydrophobic Porous Asymmetric Support.; b) Thin non-porous layer present in asymmetric composite support.

Asymmetrical membranes are those where pore size is different for opposite sides. In that case, without dispersion also it is possible to contact two phases from one phase to another even when operating pressure exceed from the larger side pore. As a result, partial wetting takes place from the side of large pore and gas-liquid interface appears inside the pore space. To increase the operating pressure of the contactor, composite membrane with polymer support is generally used which prevent the perforation of the liquid phase into membrane pore space. It can be seen that the operating pressure is further increase by using non-porous layer and laid the layer on the porous membrane surface (Fig. 8), however it must be highly permeable in order to avoid the membrane resistance to the mass transfer process [218-220]. Furthermore, gas-liquid membrane contactor can be utilized for absorption or desorption of the respective moiety in liquid absorbent (Fig. 9). For that hollow fiber membrane, be a promising candidate since it provides large surface area per apparatus volume, thus making the equipment compact.

Figure 9 Mass transfer in a membrane contactor: a) Component absorbed from gaseous phase.; b) Component desorbed from the liquid phase.

In addition to all the above literature, the main properties of pre- and post-combustion CO₂ capture by different membranes are summarizes in Table 2.

Table 2 Division and Properties of Membranes for Pre- and Post-combustion CO₂ Capture.

Type of Membrane		Membrane Material	Driving Force	Selectivity	Permeation
Polymer		Glassy & Rubbery	Solution Diffusion	Selectivity towards CO ₂ or H ₂	Low
		Mixed Matrix			Moderate
Inorganic Porous	Meso (2-50 nm)	Amine Grafted Silicas	Adsorption/Diffusion	Selectivity towards CO ₂	Low/Moderate
	Micro (<2 nm)	Amine functionalised Silicas	Adsorption/Diffusion	Selectivity towards CO ₂	High
		Stabilized Silicas	Molecular Sieving/Activated Diffusion	Selectivity towards H ₂	High
		Zeolites	Adsorption/Diffusion	Selectivity towards CO ₂ or H ₂	High
		MOFs/ZIFs	Adsorption/Diffusion	Selectivity towards CO ₂ or H ₂	Moderate/High
Hollow Fiber Membranes		Thin Polymeric Tubes	Phase Inversion	H ₂ /CO ₂	Moderate

Summary

In the past few years, there has been a steady work going on based on polymer and their composite membranes and different conventional ILs based on blending and functionalization. The most widely used polymeric membrane for the separation of CO₂ is the facilitated material-based membranes and glassy rubbery block polymers (e.g., Pebax, Polyactive). The primary mechanism of using such polymeric material is based on solution-diffusion. To make such polymeric membranes more efficient and improve their performances, additives like nanoparticles, PEG, and amines with low molecular weight can be used. Great efforts are needed to industrialize gas separation using polymeric membranes. Some prospective to make these membranes efficient are developing high-performance membrane material, eco-friendly membrane fabrication processes, testing under ambient conditions, long-term stability, and durability of such membranes.

Along with polymers, ILs also played an essential role in the absorption and separation of CO₂. Novelty and structural tunability make ILs a valuable media to utilized in separation/capture of CO₂. The absorption and separation of CO₂ especially depend on permeability and selectivity, and the mechanism can be understood with experimental methods and molecular simulation. However, the ILs based membranes are still new and are yet to be explored to persuade industrial needs. Therefore, more researches are required to explore the field thoroughly. The main criteria for efficient CO₂ capture are understanding the systematic and comprehensive relationship between ILs and CO₂ and their physicochemical and absorption/desorption properties. Instead of rapid progress in this field, there is still a significant research gap. To overcome such difficulties, the main possible thing is to design and prepare a composite membrane of ILs and porous material with high selectivity, permeability, and stability.

MOFs, due to their highly tunable nature, make them a potential candidate for CCS both as sorbents or membranes. MOFs due to their higher porosity and surface area, with tremendous choices of metals and ligands, show potential application in CO₂ capture and separation technology. Various researches reveal that the chemical nature of the MOFs can be changed on the surface, which makes them advantageous compared to other porous entities. Selectivity, Capacity, and regeneration are the most important factors that play role in the CCS process. However, investigations of these materials are ongoing, still many different processes and creative synthesis approaches are appearing to date. For this, the blending of both the chemical design and engineering strategies is still an appealing feature that can be implemented in real-time analysis. Within this chapter, we have discussed the importance of MOF membranes for CCS technology, different parameters, and how the appealing material can be fabricated/designed perfectly to use in the real world to mitigate the CO₂ from the environment. In addition, we have included one new process called continuous flow.

The capture of CO₂ efficiently in the presence of moisture by solid medium is relatively new content, yet it is of up most necessary for real time applications. Various impurities are present in adsorbents of CO₂ capture where water is quite known for the most unexpected impurity. In the same context, water also enables facilitated transport in some CO₂ capture membranes. So, the use of water in CO₂ capture material is worthy, moreover it gives the opportunity to many researchers to explore the WFCC materials. Various strategies are proposed to avoid the negative effects of water, but in the same time, WFCC membranes are widely explored. Among the various materials present till date, rigid framework materials are the most appealing candidate for excellent WFCC membranes/adsorbents. A well-established WFCC membranes have the ability to integrate hierarchical structures with different transport mechanism.

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