

## Short Communication

# Membranes and membrane processes for CO<sub>2</sub> separation: MEMFO's long-term effort in reducing carbon emissions

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## ABSTRACT

Urgent actions are needed to reduce CO<sub>2</sub> emissions and mitigate the increasingly severe impacts of climate change. Since the 1990s, the membrane research group (MEMFO) at the Norwegian University of Science and Technology has been committed to developing effective membranes and membrane processes for CO<sub>2</sub> separation. MEMFO's research can be categorized into five main themes: facilitated transport membranes, hybrid membranes, carbon membranes, membrane contactors, and related modeling and process simulation. These themes are tied to industrial applications in CO<sub>2</sub> capture from flue gas, biogas upgrading, natural gas sweetening, and hydrogen purification. Promising membranes, identified based on their laboratory-scale performances, have been selected for onsite testing in industrial processes to validate their performances as well as stability and durability. Verified membranes are upscaled for pilot tests. This account paper summarizes MEMFO's research and development outcomes over the past decade and discusses our research strategies and perspectives for future work.

## 1. Introduction

The escalating level of greenhouse (GHG) emissions, particularly CO<sub>2</sub> emissions from fossil fuel-based energy generation, is widely recognized as the primary driver of global climate change. There is an urgent need to reduce carbon emissions and effectively mitigate the accelerating impact of climate change. CO<sub>2</sub> capture, utilization, and storage (CCUS) is commonly accepted as the most immediate and effective solution (Pedersen et al., 2022; IPCC 2022). Among the various carbon capture technologies (i.e., absorption, adsorption, membrane separation, and cryogenic separation), amine-based absorption dominates the market today due to its high efficiency and process maturity (Cachola et al., 2023). However, with the increasing urgency to reduce CO<sub>2</sub> emission, more CO<sub>2</sub>-containing streams with diverse gas compositions and process conditions must be processed, which provides enormous opportunities for alternative carbon capture technologies, especially membrane technologies.

Membrane separation is increasingly considered a greener and more efficient alternative to amine absorption, garnering significant attention from industries seeking solutions for CO<sub>2</sub> separation. Its unique features, such as small footprint, ease of operation, and linear up-scaling, make it particularly advantageous for small- to medium-sized processes (He et al., 2022). However, the market share of membrane technology

for industrial CO<sub>2</sub> separation remains small compared to absorption due to the following common challenges, i.e., membranes' moderate selectivity and the consequent difficulty in obtaining high-purity products, the need for complex pre-treatment in some processes, and the fact that, overall, CO<sub>2</sub> separation membrane technology is still at a relatively low Technology Readiness Level (TRL) compared to absorption (Dai et al., 2016; Hong, 2022).

"MEMbranFORskningsgruppen" (MEMFO), the membrane research group at the Norwegian University of Science and Technology (NTNU), was founded by Prof. May-Britt Hägg in the 1990s. Since then, MEMFO has embarked on a long journey to develop gas separation membranes, primarily focusing on CO<sub>2</sub> separation applications (Hägg and Lindbråthen, 2005; Kim et al., 2004; Lie et al., 2007; Hägg et al., 2003; Deng et al., 2006; Hägg, 2000; Deng et al., 2009). After Prof. Hägg's retirement about ten years ago, Prof. Liyuan Deng took over the reins. Over the past 10 years, MEMFO has not only continued to advance membrane research for CO<sub>2</sub> separation but also expanded our research into emerging fields to apply membranes in batteries and hydrometallurgical processes, and direct air capture (DAC) of CO<sub>2</sub> through implementing various research projects in collaboration with international and national partners and the Norwegian industry (Razaq et al., 2023; Tekinalp et al., 2023; Tekinalp et al., 2023; Tekinalp et al., 2024; Wang et al., 2023). Nevertheless, the core research task in MEMFO has

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constantly been developing techno-economically feasible CO<sub>2</sub> separation membrane processes. In MEMFO, industrial perspectives in membrane design, material selection, and choice of fabrication techniques are always considered before initiating a project in order to maximize the potential for industrial applications. It is worth noting that part of the MEMFO's facilities was funded by the European Carbon Dioxide Capture and Storage Laboratory Infrastructure (ECCSEL) project (Quale and Rohling, 2016)(<https://www.eccsel.org/>), which provides free lab access for users from all over the world.

This account summarizes MEMFO's research on CO<sub>2</sub> separation membranes over the past decade, roughly divided into six subsections: facilitated transport membranes, CO<sub>2</sub>-philic polymeric membranes, hybrid membranes, carbon membranes, membrane contactors, and modeling and process simulation. The applications studied include CO<sub>2</sub> separation from the four most common CO<sub>2</sub>-containing sources, namely flue gas, natural gas, biogas, and syngas, each with specific separation requirements and process conditions.

## 2. Solution

As CO<sub>2</sub> is an acidic, highly condensable polar gas with a molecular size between H<sub>2</sub>, N<sub>2</sub>, and CH<sub>4</sub>, the property differences of CO<sub>2</sub> from other components are the key to designing high-performance membranes. The mechanisms to separate CO<sub>2</sub> can be based on one or several of the properties, such as the reactivity of CO<sub>2</sub> as the basis of the facilitated transport mechanism, CO<sub>2</sub> affinity/solubility and gas diffusivity differences in membrane materials for the solution-diffusion mechanism, and size differences of gases for the molecular sieving mechanism. Different CO<sub>2</sub>-containing streams have varying components and process conditions. To achieve the desired separation efficiency, membrane material, morphology, and process design for CO<sub>2</sub> separation must be optimized on a case-by-case basis according to the feed gas compositions (especially the concentration of CO<sub>2</sub> and the 2nd key component. i.e., N<sub>2</sub>, H<sub>2</sub>, or CH<sub>4</sub>), types of impurities (NO<sub>x</sub>, SO<sub>x</sub>, water vapors, H<sub>2</sub>S and CO, etc.) and their respective properties, the process conditions (e.g., temperature, pressures, and flowrate of the gas streams), and the required product specifications.

A typical pathway for membrane development from concept to industrial applications in MEMFO consists of five stages; each presents different challenges:

1. Screening and optimizing membrane materials by evaluating self-standing membranes using single gas permeation tests;
2. Fabricating flat sheet thin-film composite (TFC) membranes;
3. Developing TFC membranes in hollow fiber configurations; the TFC membranes are tested with simulated mixed gas streams.
4. Testing selected membranes in industrial processes to validate the performance and document the stability and durability of the membrane in real gas streams;
5. Upscaling the membrane module for pilot scale testing.

A modeling and process simulation approach has been taken when designing processes of our developed membranes and assessing their feasibilities in various applications. Membrane absorption (membrane contactor) has also been an important research topic in MEMFO to combine the advantages of membrane technology and chemical absorption, thereby dealing with a few special applications in CO<sub>2</sub> separation.

## 3. Outcomes & discussion

### 3.1. Facilitated transport membranes

Facilitated transport membranes for CO<sub>2</sub> separation have long been the highlight of MEMFO's research work. Given the reactivity of CO<sub>2</sub>, membranes based on the facilitated transport mechanism hold the greatest potential to achieve efficient CO<sub>2</sub> separation, as facilitated transport membranes can selectively permeate CO<sub>2</sub> through reversible reactions

of CO<sub>2</sub> with complexing agents (carriers) in the membranes, whereas unreactive gases such as N<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub> transport exclusively via the solution-diffusion mechanism, leading to both high CO<sub>2</sub> selectivity and CO<sub>2</sub> permeability (Rafiq et al., 2016). Hence, facilitated transport membranes are not subjected to the so-called "Robeson upper-bound" that limits the separation performances of most polymeric membranes relying solely on the solution-diffusion mechanism (Hägg and Deng, 2015). This unique feature makes facilitated transport membranes particularly promising in the field of CO<sub>2</sub> separation.

#### 3.1.1. Fixed site carrier membranes

CO<sub>2</sub>-reactive function groups in a facilitated transport membrane, such as amino groups, are called "CO<sub>2</sub> carriers", which can be directly attached or, more specifically, covalently bonded to the polymer backbones as fixed-site carriers (FSC) (Kim et al., 2004). MEMFO's research on FSC membranes began around 25 years ago with an extensive, ongoing study on polyvinylamine (PVAm) based membranes. Polyvinylamine has the highest content of primary amino groups in all polymers (Pelton, 2014), making it most likely to achieve the highest CO<sub>2</sub>-facilitated transport efficiency. Nevertheless, along the way in PVAm membrane development, we found that the performances of PVAm membranes varied significantly when the polymer status (molecular weight, protonation extent, cross-linking degree, etc.), preparation procedures (e.g., casting solution concentration, pH, temperature, blending polymers, casting methods, support substrate types, thickness of the selective layers), and separation conditions (relative humidity and flow rates in the feed and sweep sides) were different (Kim et al., 2013; Deng and Hägg, 2015; Sandru et al., 2022). Therefore, a series of approaches were taken to optimize the PVAm-based membranes with respect to their materials, fabrication conditions, and morphologies to improve their performances, including the mechanical properties and the processability of the membranes and modules. Later on, we explored other amine-containing polymers (e.g., polyallylamine (PAAm)) (Janakiram et al., 2020; Janakiram et al., 2020), of which the polymeric chains can be modified to optimize the chain space and make the carriers more accessible to enhance the CO<sub>2</sub> reaction. The accessibility of amino groups was found to be increased by introducing sterically hindered side groups, similar to what was reported by Han and Ho (2018) and Han and Ho (2021).

A strong correlation between CO<sub>2</sub> transport and the humidity levels of the feed gas streams was first identified by MEMFO researchers (Deng and Hägg, 2010; Deng et al., 2009). FSC membranes were found to swell significantly in the water-saturated feed gas, enhancing the facilitated transport effects. In water-swollen FSC membranes, CO<sub>2</sub> diffuses partially in the form of HCO<sub>3</sub><sup>-</sup> (Fig. 1a), resembling ion transport through a liquid, which can be two orders of magnitude greater than that of gas diffusing through solid polymers (Deng and Hägg, 2010; Deng et al., 2009). Hence, water saturated in the feed streams is not a troublesome impurity but a favorable CO<sub>2</sub> transport promoter in membranes based on the facilitated transport mechanism. According to the strong dependence of the CO<sub>2</sub> permeance on the relative humidity in the feed gas, CO<sub>2</sub> indeed transports differently from non-reactive gases, demonstrating that the facilitated transport effect is promoted by water vapor (Fig. 1b). The dependence of the membrane performance on CO<sub>2</sub> partial pressure and selective layer thickness also reflects the characteristics of facilitated transport mechanisms (Xu et al., 2023; Deng and Hägg, 2015).

FSC membranes, typically swollen by water during the separation process, are usually tested in the TFC form in the MEMFO studies, posing a challenge when determining the membrane thickness for the permeability data. In addition, as it is not possible to measure the actual driving force (partial pressures) along a hollow fiber membrane or inside the membrane module, we mainly reported the membrane performances using CO<sub>2</sub> permeance (not permeability) and separation factors (not ideal selectivity). The separation factor is defined as the ratio of gas compositions between the feed and permeate side of the membrane

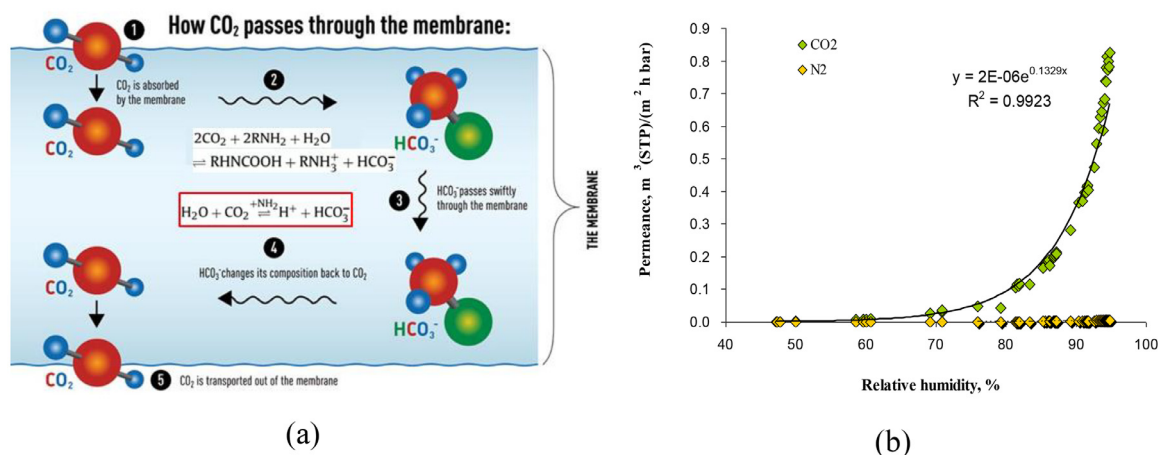


Fig. 1. (a) Illustration of the proposed facilitated transport mechanism in a fixed-site-carrier membrane, reprinted from (Oksholen, 2007). (b) Humidity dependence of the facilitated transport membrane on their performances (Deng and Hägg, 2010).

module. Our testing rig is equipped with humidifiers to regulate the humidity at both the feed and sweep gas sides to simulate the humid industrial gas streams.

### 3.1.2. Mobile carriers

Although the FSC membrane materials we selected usually have a high CO<sub>2</sub>-carrier density (e.g., sufficient amine groups), the “fixed” carrier may result in a less effective CO<sub>2</sub>-carrier interaction and a lack of CO<sub>2</sub>-complex mobility. Without enough active carriers, carrier saturation may occur when the feed gas has an elevated CO<sub>2</sub> partial pressure. To mitigate these challenges, we have introduced small CO<sub>2</sub>-philic molecules or reactive agents into FSC membrane matrices, which, as mobile carriers, enhance the facilitated transport effects. The selection criteria of mobile carriers typically include high CO<sub>2</sub>-philicity or the ability to form weak bonds with CO<sub>2</sub> inside the water-swollen membrane matrices, reactivity that enables reversible CO<sub>2</sub> association/dissociation in the presence of water, and low molecular weight for mobility. In MEMFO, we have investigated a variety of mobile carriers, including alkaline solutions and mimic enzymes (Zn-cyclen) (Saeed and Deng, 2015; Saeed and Deng, 2016), various amines, and amino acid salts (Janakiram et al., 2020; Dai et al., 2019; Saeed et al., 2017). The effects of these different mobile carriers have been reported to have significantly enhanced CO<sub>2</sub> permeance or selectivity of CO<sub>2</sub> over other gases. In many instances, improvements are documented in both CO<sub>2</sub> permeance and selectivity.

Indeed, the addition of CO<sub>2</sub>-philic mobile carriers not only enhances carrier mobility, making CO<sub>2</sub> transport more competitive, but also increases the carrier density (more CO<sub>2</sub>-reactive sites) in the membrane, alleviating carrier saturation phenomena. The introduction of liquid mobile carriers often also results in increased swelling in the membrane. In some instances, mobile carriers were not added to an FSC membrane as the supplement but rather to a hydrophilic polymer matrix without CO<sub>2</sub> reactive functional groups, such as polyvinyl alcohol (PVA) and polyvinyl pyrrolidone (PVP) (Saeed and Deng, 2016; Saeed et al., 2017; Torstensen et al., 2019; Lilleby Helberg et al., 2020). In these cases, mobile carriers are the primary contributors to the facilitated transport effect. These hydrophilic polymers serve as hosts for mobile carriers, maintaining membrane structure and optimizing swelling to provide balanced mechanical strength and carrier mobility.

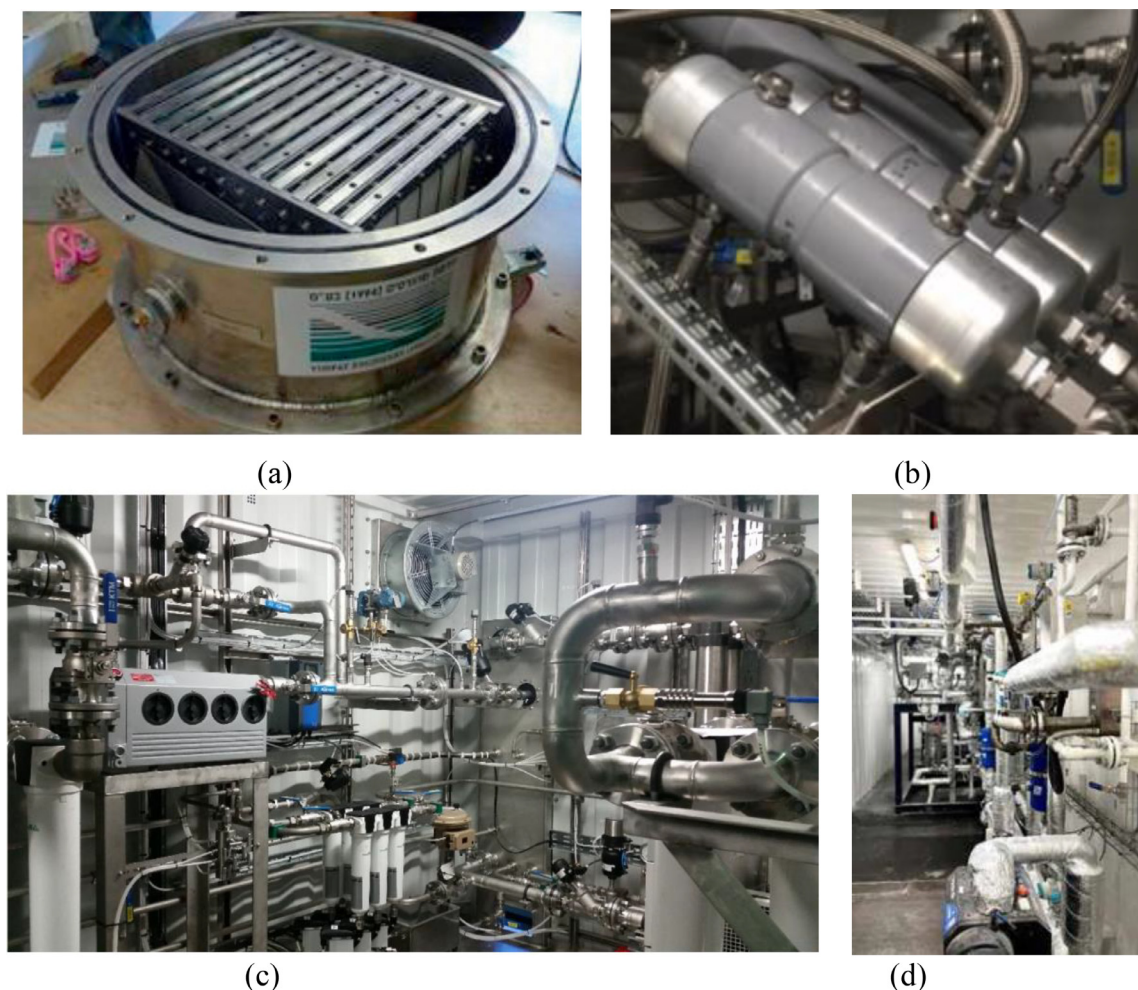
### 3.1.3. Ionic liquid-based membranes

In MEMFO, ionic liquids (ILs) have been extensively studied as mobile carriers in facilitated transport membranes or additives in other polymeric membranes. Ionic liquids are a class of low-temperature molten salts with organic cations and organic or inorganic anions and

are tuneable to obtain task-specific ILs with functional groups for CO<sub>2</sub> reactivity or high CO<sub>2</sub> affinity (Zhang et al., 2012). Since ILs are in the liquid phase, the long-term stability of most IL-based membranes is not sufficient, and many of them are challenging to fabricate into TFC membranes. Therefore, we polymerized task-specific ILs into poly(ionic liquids) (PILs) or interpenetrating frameworks (Deng et al., 2016). The polymerization eliminates the stability issues of free ILs in membranes (Dai et al., 2016).

### 3.1.4. Upscaling and pilot tests

In the early stage of facilitated transport membrane development in MEMFO, flat sheet configuration was our first choice. FSC membranes were developed up to approximately A4 sizes and tested in a plate-and-frame configuration at Sines, Portugal, for real flue gas over several months, showing promising results (Fig. 2(a)) (Sandru et al., 2013). Despite these encouraging results, there were two inherent challenges with the plate-and-frame approach: the relatively low packing density (membrane area/ membrane module volume) and the inefficient flow pattern, which, ideally, is the best as “cross-flow” (Han et al., 2019; Rivero et al., 2023; Sheng et al., 2021; Wu et al., 2021). As a result, we initiated a parallel development course in hollow fiber membranes. MEMFO recognized early on that it would be challenging (and likely time-consuming) to compete with large, mature commercial producers, so we initiated a partnership with a commercial company, Air-Products. FSC-membranes *in-situ* coated on hollow fiber-supported modules were produced (up to 4.2m<sup>2</sup> membrane area, Fig. 2b) (Hägg et al., 2017). In parallel, a pilot plant for onsite capture in the cement industry was designed and constructed by the commercial partner company (Fig. 2c). MEMFO has successfully run the pilot process for nine months, focusing more on understanding module efficiencies and exposing the FSC membrane to real-life contaminants with minimal pre-treatment. No evidence of significant drop in membrane performance was discovered. As part of the same development work, a pilot size flue gas exposure and concept try-out rig was constructed and put into service in close proximity to NTNU. This rig was used to test various mass transfer concepts in the up-scaled module, such as water permeation rate, extent of domination of the carrier effect relative to Fickian diffusion at (very) low CO<sub>2</sub> partial pressures, module back-mixing, and utilization of the available installed membrane area. In recent years, nanocomposite FSC membranes exhibiting improved performance were developed and tested in the Colacem cement plant in Gubbio (PG), Italy, for real stream tests (Janakiram et al., 2021; Dai et al., 2019). Surprisingly, the onsite testing results were better than those we obtained in the lab-scale. The higher temperature (90 °C) and good water distribution in the process are believed the causes of the nearly doubled CO<sub>2</sub> perme-



**Fig. 2.** (a) Pilot flat-sheet membrane tested at Sines Portugal (Sandru et al., 2013), (b-c) Pilot plant of hollow fiber membrane installed by Air-Product AS in the Norcem Cement factory (Hägg et al., 2017), and (d) Aqualung's hollow fiber membrane system installed at Nordkalk, Sweden (Aqualung, 2023).

ation rate. Studies of the impurity effect show that NO<sub>x</sub> and SO<sub>x</sub> have no evident impact on the membrane performance. The nanocomposite hollow fiber membranes have been commercialized by a company based in Norway, Aqualung Carbon Capture AS (Aqualung, 2023). Several processes have been installed/integrated into the industrial sites for CO<sub>2</sub> capture for further utilization, including a process at Nordkalk, Sweden (Aqualung, 2023) (Fig. 2, d).

Based on our experience, maintaining optimal flow conditions in an up-scaled membrane module is critical. Concentration polarization may not be a problem for most commercial gas separation membranes, but it becomes an issue when membranes are based on the facilitated transport mechanism. The concentration profile of CO<sub>2</sub> and water and the pressure drop along the membrane must be well understood in order to keep the membrane operating under optimal conditions. Special attention must be paid to water distribution; the lack of water may reduce the facilitated transport effect, causing the module performance below the laboratory results.

### 3.2. CO<sub>2</sub>-philic polymeric membranes

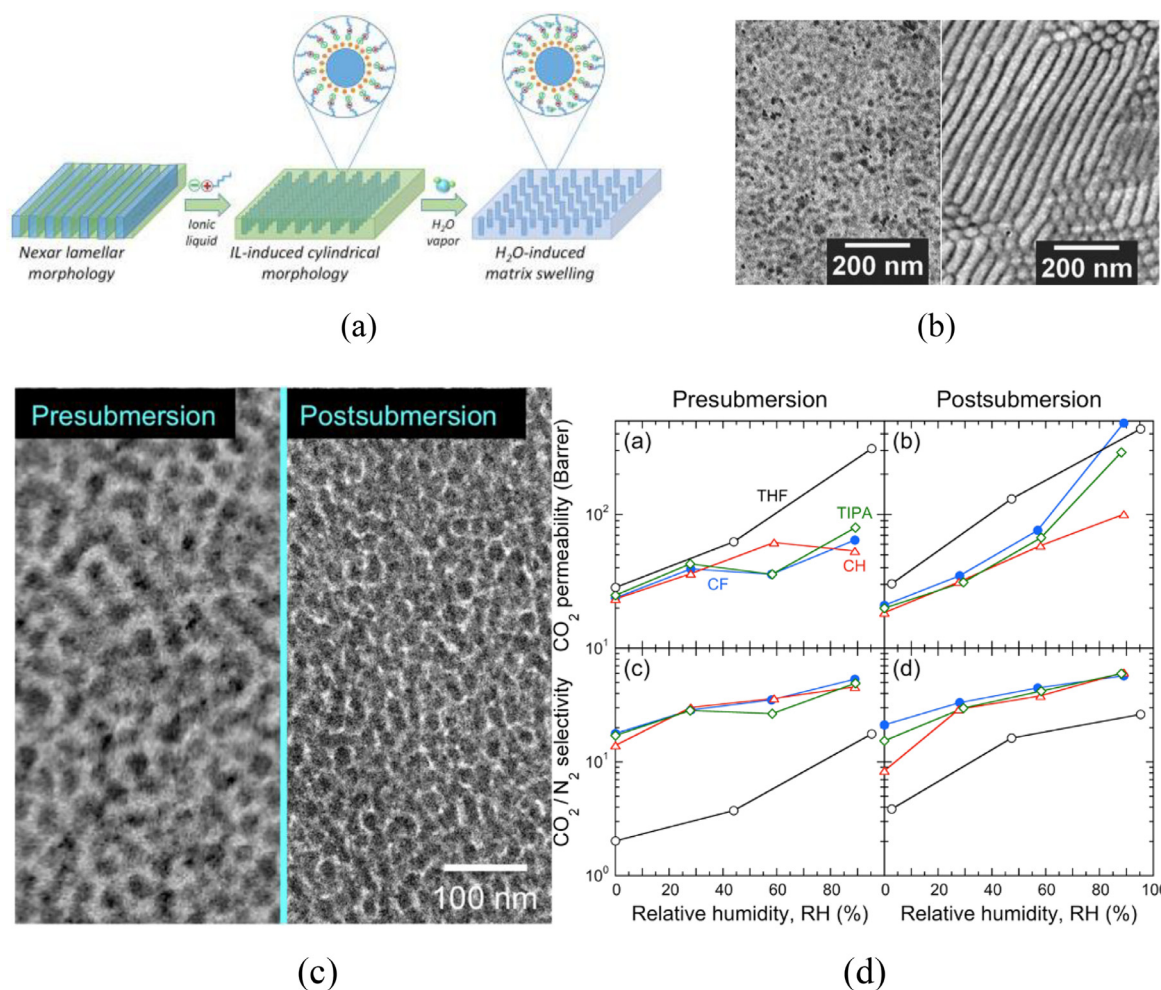
In addition to facilitated transport membranes, polymeric membranes based on the solution-diffusion mechanism have also been studied in MEMFO. Polymers containing various CO<sub>2</sub>-philic functional groups (but not reactive) have been synthesized and optimized to enhance CO<sub>2</sub> sorption in membranes, thereby improving the overall CO<sub>2</sub> separation performance.

#### 3.2.1. Polyether derivatives-based membranes

Polymers derived from polyether, such as poly(ethylene oxide) (PEO), are CO<sub>2</sub>-philic due to the strong dipole–quadrupole interactions with CO<sub>2</sub> molecules. PEO-based polymeric membranes favor CO<sub>2</sub> transport. However, high-molecular-weight PEO has an inherent tendency to crystallize, which reduces its CO<sub>2</sub> permeability. As a result, low-molecular-weight PEO, also known as poly(ethylene glycol) (PEG), has been used as a promising alternative. Several approaches have been investigated in MEMFO to introducing PEG-based CO<sub>2</sub>-philic segments to membranes, such as by creating cross-linked structures, grafting PEG groups to other polymers, retaining liquid PEG of various loadings in membrane matrix, and optimizing block-copolymers via PEG-induced nanostructure rearrangement. For instance, cross-linked PEG-based membranes with dual functional, interpenetrating polymer networks have been synthesized using amine-terminated Jeffamine through a solvent-free, two-stage reaction. Free PEG dimethyl ether (PEGDME) has been added into the optimized cross-linked matrix to enhance gas-transport properties further, resulting in a 48-fold increment in CO<sub>2</sub> permeability (Dai et al., 2017; Deng et al., 2020; Deng et al., 2019; Deng et al., 2019).

#### 3.2.2. Block co-polymer-based membranes

Polyether block amide (PEBA), under the tradename of Pebax®, is one of the most extensively studied polyether derivatives in membrane research. It is also a representative block copolymer, demonstrating enormous potential as a CO<sub>2</sub> separation membrane material. Pe-



**Fig. 3.** (a) Morphology optimization in block copolymers by adding ionic liquids and water (Dai et al., 2019), (b) TEM images of cylindrical and lamellar structure in Nexar illustrating two different solvent-templated morphologies wherein ion-rich microdomains are selectively stained (Ansaloni et al., 2017), (c) change in microchannels induced by water as a non-solvent (Dai et al., 2019), and (d) improved CO<sub>2</sub> separation performances after water submersion (Dai et al., 2019).

bax and other block copolymers have been widely studied in MEMFO. Block copolymers' unique molecular structures (consisting of soft (usually CO<sub>2</sub>-philic and hydrophilic) and hard (usually hydrophobic) segments) and the ability to spontaneously self-assemble to form nanoscale (ionic) channels greatly favor CO<sub>2</sub> transport, especially when the membranes are humidified. These features are taken into consideration when optimizing CO<sub>2</sub> separation membranes.

One approach to optimizing the CO<sub>2</sub> separation performances of a block copolymer membrane is to introduce liquid additives to adjust the self-assembled nanochannels with respect to the channel size, interconnectivity, orientation, and affinity to CO<sub>2</sub>, thereby maximizing CO<sub>2</sub> transport. MEMFO researchers have introduced several types of ILs and PEG into selected block copolymers, including neutral (e.g., Pebax) (Dai et al., 2016; Dai et al., 2019) and charged sulfonated hydrocarbon pentablock terpolymers (Nexar) and sulfonated tetrafluoroethylene based fluoropolymer-copolymer (Nafion) (Ansaloni et al., 2017; Dai et al., 2018; Dai et al., 2019; Wei et al., 2023; Dai et al., 2019), resulting in more than two orders of magnitude improvement in CO<sub>2</sub> permeation rates. Fig. 3a illustrates the ILs-induced restructure of a midblock-sulfonated multiblock polymer (Nexar) in a CO<sub>2</sub>-selective membrane. Adding ILs to Nexar triggered a morphological change from a lamellar to a cylindrical nanostructure, significantly increasing CO<sub>2</sub> separation performance (Fig. 3b).

Nafion has never been considered a suitable membrane material for CO<sub>2</sub> separation due to its low CO<sub>2</sub> permeability of ~2 Barrer and

CO<sub>2</sub>/N<sub>2</sub> selectivity of around only 10. We introduced up to 40 wt% PEGDME as a liquid additive into Nafion-based membranes to form interconnected CO<sub>2</sub>-philic channels for enhanced CO<sub>2</sub> transport. The CO<sub>2</sub> permeability of 57.4 Barrer was obtained even at the dry state, 36 folds higher than the pristine Nafion (Dai et al., 2019). With the presence of water vapor, the CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity increase to 446 Barrer and 37, respectively, representing a more than 200 times increment in CO<sub>2</sub> permeability.

Efforts have also been made to tune the CO<sub>2</sub> separation performances of block copolymer-based membranes by controlling their nanostructures by manipulating the solvents or non-solvents (Fig. 3c) (Dai et al., 2019). It has been found that CO<sub>2</sub> separation performances of block copolymer-based membranes are strongly sensitive to both the casting solvents and the relative humidity in the feed gases (Ansaloni et al., 2017). Indeed, the CO<sub>2</sub> separation performances of selected block copolymer membranes can be dramatically enhanced by simply soaking these membranes in deionized (DI) water for some time due to the triggered micro-structure change by water. For instance, after DI water treatment with a Nexar membrane, a CO<sub>2</sub> permeability of up to 482 Barrer was documented, with a CO<sub>2</sub>/N<sub>2</sub> selectivity values of 57, surpassing the Robeson upper bound (Fig. 3 d). The excellent results indicate that nanostructure rearrangement of block copolymers in a membrane to a pattern favoring CO<sub>2</sub> transport constitutes a promising approach. More recently, it has been discovered that solvent also plays a critical role in CO<sub>2</sub> separation performances for Nafion membranes

(Wei et al., 2023). Due to the tight ionic nanostructure, pristine Nafion has never been exploited as a membrane material for CO<sub>2</sub> separation. By immersing Nafion membranes (prepared either from solution casting or melt extrusion) into liquid water, however, nanostructural rearrangement of this amphiphilic polyelectrolyte block copolymer was promoted by liquid water, and both CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity were significantly enhanced (472 Barrer and 61, respectively). Compared to the neat Nafion membrane, the chemical structure of the Nafion was not changing, and the original chemical/physical properties were nicely preserved. Similarly, favorable micro-structure rearrangement in Pebax has also been reported (Wei, 2023). More importantly, the DI-water-treated membrane demonstrated good long-term stability with no CO<sub>2</sub> permeability reduction after 300 days of storage.

### 3.3. Hybrid membranes

In MEMFO, nano-sized inorganic or organic fillers of various sizes and properties have been introduced into the above-discussed polymeric membranes, aiming to improve their CO<sub>2</sub> separation performance or other key properties, such as stability, mechanical strength, or fabrication possibilities, forming various types of hybrid membranes. Hybrid membranes are expected to combine advantageous features of their polymeric matrices (the continuous phase) with those of the fillers (as dispersed phases) (Ansaloni and Deng, 2017). The dispersed fillers may have ordered three-dimensional (3D) porous structures with desired properties, examples of which include metal-organic frameworks (MOFs), Zeolites, porous organic frameworks (POFs), or carbon molecular sieves (CMS) (Ahmadi et al., 2018), leveraging the fillers' inherent CO<sub>2</sub> transport/uptake capacities as the secondary transport mechanism in addition to the main mechanism in the polymer matrix. Hence, hybrid membranes containing 3D fillers are termed "mixed-matrix membranes" (MMM). Non-porous, nano-sized fillers of various properties and dimensions, from 0D nanoparticles to 1D nanofibers and 2D nanosheets, have also been incorporated into polymeric matrices, forming nanocomposite membranes. The transport properties of these membranes are altered according to the effects of these nanofillers' nature and morphology, thereby achieving different CO<sub>2</sub> permeation properties (Janakiram et al., 2018).

The most studied types of nanofillers for hybrid membranes in MEMFO include nanocellulose and carbon nanotubes (CNT) (nanofibers), graphene oxides (GO) (nanosheet), and various MOFs (3D nanoporous structures). The selection of nanofillers usually targets one or sometimes more specific property enhancements in a hybrid membrane. For example, in most cases, nanofillers with intrinsically high surface CO<sub>2</sub> affinity are preferred to increase CO<sub>2</sub> transport across the membrane. Besides, at least one dimension of the nanofiller should be in the range of a few nanometers to be able to coat a thin selective layer on porous supports in large areas. Dispersion of nanofillers is the most challenging part of developing hybrid membranes. Polymer-specific properties and attributes, such as molecular weight, hydrophilicity, and solvent requirements for dissolution, should be considered when searching for the most compatible nanofiller to result in a successful hybrid membrane. Nanofillers are often modified to enhance compatibility for better dispersion. It is also desirable that the selected nanofillers should influence the permeation properties at a small loading since low loading not only leads to a low cost in membrane production (as nanofillers are relatively expensive) but also reduces the risk of forming defects in membranes due to puncturing through by nanofillers (Hu et al., 2024).

#### 3.3.1. Nanocellulose-based membranes

Nanocellulose is the most extensively studied 1D nanofiller in MEMFO. It was selected as a natural replacement for CNTs, another 1D nanofiber we previously used as an effective nanofiller in FSC membranes for its nanopacer effect. However, unclear hazard effects of CNTs on the environment and health lead to unnecessary risks (Saeed and Deng, 2016; Dai et al., 2019; Deng and Hägg, 2014). Nanocellulose, due to its high specific surface area, mechanical strength, bio-based nature of origin, and chemically tailorable surface properties (Zhang et al., 2024; Dai et al., 2019), has huge potential to enhance CO<sub>2</sub> separation performance when added to membranes. Adding nanocellulose also reduces environmental impacts and carbon footprint in membrane production (Fig. 4a). The immense number of hydroxyl groups on the nanocellulose surface paves the way for functionalization, simultaneously contributing to hydrophilicity, favors nanofiber dispersion and water redistribution in the membranes, benefiting CO<sub>2</sub> transport.

Originally, the use of nanocellulose in gas separation applications was confined to barrier materials due to their inherent resistance

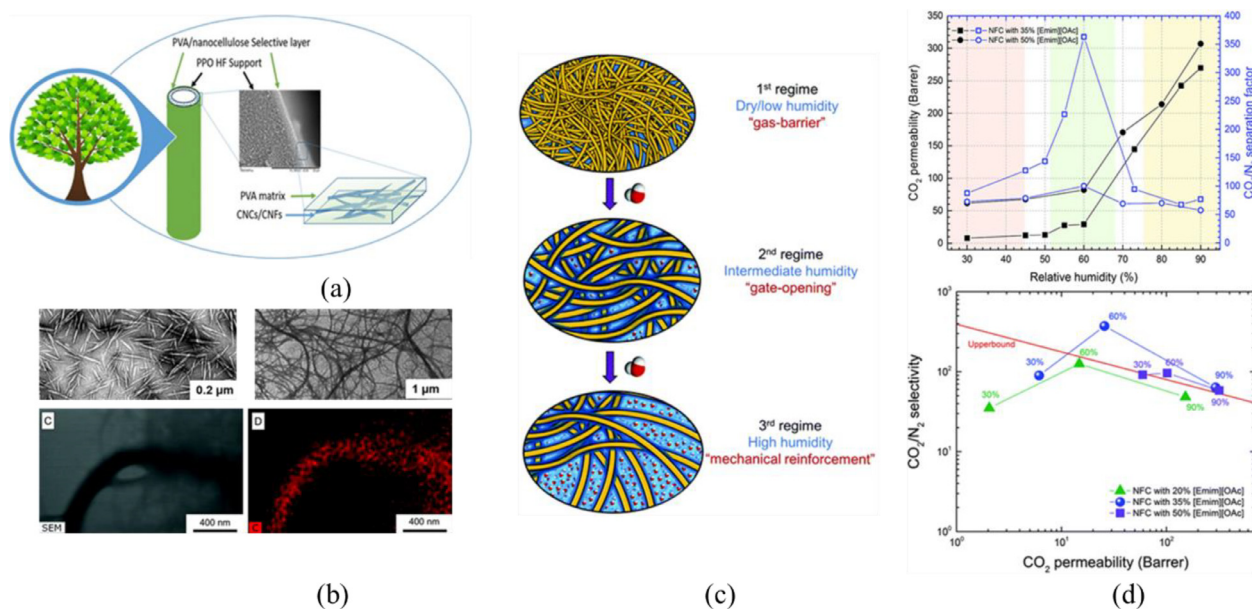


Fig. 4. Nanocellulose is a bio-nanofiller that is compatible with hydrophilic FSC membranes for TFC hollow fiber membrane fabrication (a) (Dai et al., 2019). Ionic liquids can soften the nanocellulose and improve the dispersion in membrane matrices (b), and regulating relative humidity in the feed can transform the membrane from a barrier to a CO<sub>2</sub>-selective membrane of different transport mechanism (c) with controllable separation performances (Janakiram et al., 2020).

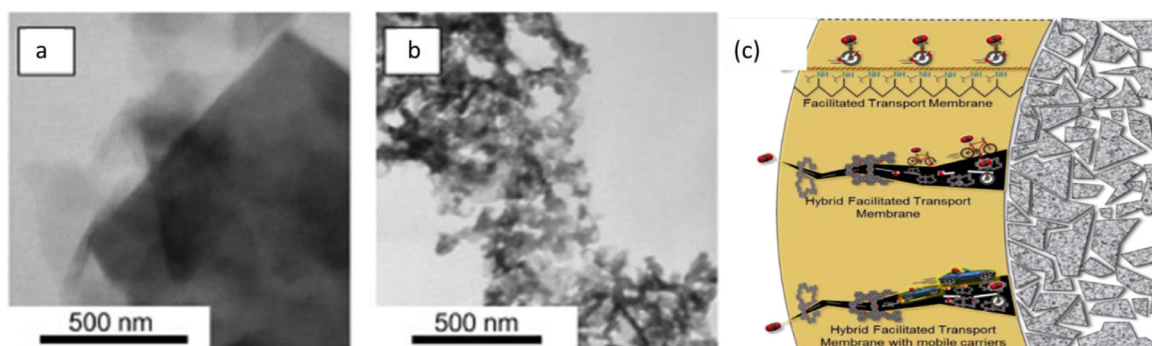


Fig. 5. (a) a GO nanosheet and (b) a physically processed porous GO. (c) Illustration of the three-phase membrane concept, including the FSC membrane matrix, porous GO as nanofiller, and mobile carriers.

to gas permeation. With increasing humidity, however, the synergistic use of nanocellulose in conjunction with compatible polymers was found able to enhance CO<sub>2</sub> transport and increase the performances of nanocellulose-based hybrid membranes for CO<sub>2</sub> separation (Dai et al., 2019). Depending on its gravimetric share in the selective layer relative to other components, nanocellulose can also be treated as a host polymer (e.g., >80 %). Ionic Liquids can then be used as softeners, enabling highly selective permeation of CO<sub>2</sub> under humid conditions (Fig. 4b). The inherent capacity and hydrogen bonding enables the film formation, but the resulting membranes exhibit barrier properties (Fig. 4c). As reported by Janakiram et al., humidity can be used as a key control parameter to tune separation performances primarily guided by different separation mechanisms simply by changing the water content in the membrane matrix (Janakiram et al., 2020) (Fig. 4d).

When used as nanofillers in polymer matrices, cellulose nanofibrils (CNF) or cellulose nanocrystals (CNC) require surface functionalization to form a compatible interface between the cellulosic surface and the main polymer matrix. A facile modification procedure was established for this purpose. Functionalization was found to play a crucial role in determining the transport properties of the nanocellulose-based hybrid membranes. Helberg et al. and Torstensen et al. systematically studied the effect of charges and sizes of nanocellulose (Torstensen et al., 2019; Helberg et al., 2021; Torstensen et al., 2018) and discovered that using CNF of high charge (5.4 mmol g<sup>-1</sup>) and reduced size (screening by centrifugation) results in the best membrane formation and CO<sub>2</sub> separation performance. Zhongde et al. and Janakiram et al. applied CNFs and CNCs in FSC membranes to improve the water distribution inside the membrane and reinforce the membrane stability, resulting in significantly increased CO<sub>2</sub> permeation (Dai et al., 2019; Dai et al., 2022; Janakiram et al., 2019; Dai et al., 2021).

### 3.3.2. Graphene oxide-embedded membranes

When nanosheets and 2D nanomaterials were considered as nanofillers to enhance the FSC membranes' stability and optimize the water distribution in the membranes, GO was our first choice. Graphene oxide has been identified as a unique 2D nanofiller in hybrid membranes due to its high aspect ratio, planar shape, and large surface area containing -OH groups as extra CO<sub>2</sub> sorption sites, contributing to reinforced polymer nanocomposites and significantly improved membrane stability and CO<sub>2</sub> affinity, beneficial to CO<sub>2</sub> separation in the industrial settings. Graphene oxide as nanofillers were either physically modified to make porous GO (pGO) for optimized sizes, chemically modified by wrapping GO with polymer chains (e.g., GO-PEG and GO-PVA) for increased CO<sub>2</sub> affinity and compatibility for better dispersion (Xu et al., 2023; Janakiram et al., 2020), or used without modification prior to fabricating TFC membranes (Fig. 5a and b); a selective layer as low as around 200 nm on flat sheet or hollow fibers was coated. The pGO nanoplatelets were found to positively disrupt polymer chain packing, increase CO<sub>2</sub> sorption, and reorient water distribution in favor of increased CO<sub>2</sub>-

facilitated transport at a very low loading of 0.2 wt% (Xu et al., 2023; Janakiram et al., 2020; Xu et al., 2023).

When added to ultrathin selective layers of facilitated transport polymers, hydrophilic GO nanosheets can induce the polymer chain disruption, leading to well-distributed water-rich channels and increased CO<sub>2</sub> solubility (with more CO<sub>2</sub> sorption sites at the GO surfaces). However, the dispersed GO is usually self-oriented during the dip-coating; the nanosheets are usually placed parallel to the surface of the support substrate, resulting in an enhanced barrier effect to gas diffusion. The decrease in gas diffusion due to the barrier effect is more profound for the smaller, more inert gases, such as H<sub>2</sub> and He.

Mobile carriers that reversibly react with CO<sub>2</sub> can also be added to the membrane matrix containing size-optimized GO nanosheets, resulting in a new class of three-phase hybrid facilitated transport membranes (Fig. 5c). The synergistic effects of GO and mobile carriers on the gas separation properties of such hybrid membranes highly rely on the size, distribution, and surface chemistry of the added nanosheets, their consequent lateral dimensions, and the properties of the added mobile carriers. The resulting membranes exhibited a CO<sub>2</sub> permeance of 825 GPU with a CO<sub>2</sub>/N<sub>2</sub> separation factor of 31 (Janakiram et al., 2020). This family of membranes developed at MEMFO was patented and is currently under commercialization by Aqualung Carbon Capture AS.

### 3.3.3. MOF-based membranes

MOF is one of the most intensively studied 3D fillers with structured and tunable pores in hybrid membranes (Chen et al., 2023). The properties and morphology of MOF play important roles in the performances of resulting membranes. MOFs with different morphology have been synthesized and used to study the morphologic effects into a Pebax matrix to form MMMs (Deng et al., 2020; Dai et al., 2018; Deng et al., 2020). It is found that nanofiller morphology significantly leads to different optimized loadings. Zeolitic imidazolate framework-8 (ZIF-8) was used to investigate the effects of shape and size on CO<sub>2</sub> separation performances of MMMs. For ZIF particles and microneedles, MMMs with 10 wt% loading display the highest CO<sub>2</sub> permeability and CO<sub>2</sub>/N<sub>2</sub> selectivity, while for ZIF leaves, the optimized value is around 5 wt%. Moreover, the increment in CO<sub>2</sub> permeability is related to the ZIFs' morphology, where the 2D ZIF shows the highest increment (Fig. 6d).

In addition, the effect of the thickness of plate-shaped MOF nanofiller was also investigated (Deng et al., 2020). Three different ZIF cuboid (ZIF-C) nanosheets with tunable thicknesses from 70 to 170 nm have been successfully synthesized and applied as nanofillers in the Pebax matrix. Gas permeation results demonstrated that the ZIFs with thinner thickness present better performance.

### 3.4. Carbon membranes

Carbon molecular sieve membranes (CMSMs) have great advantages in having high mechanical and chemical stabilities, where the mass

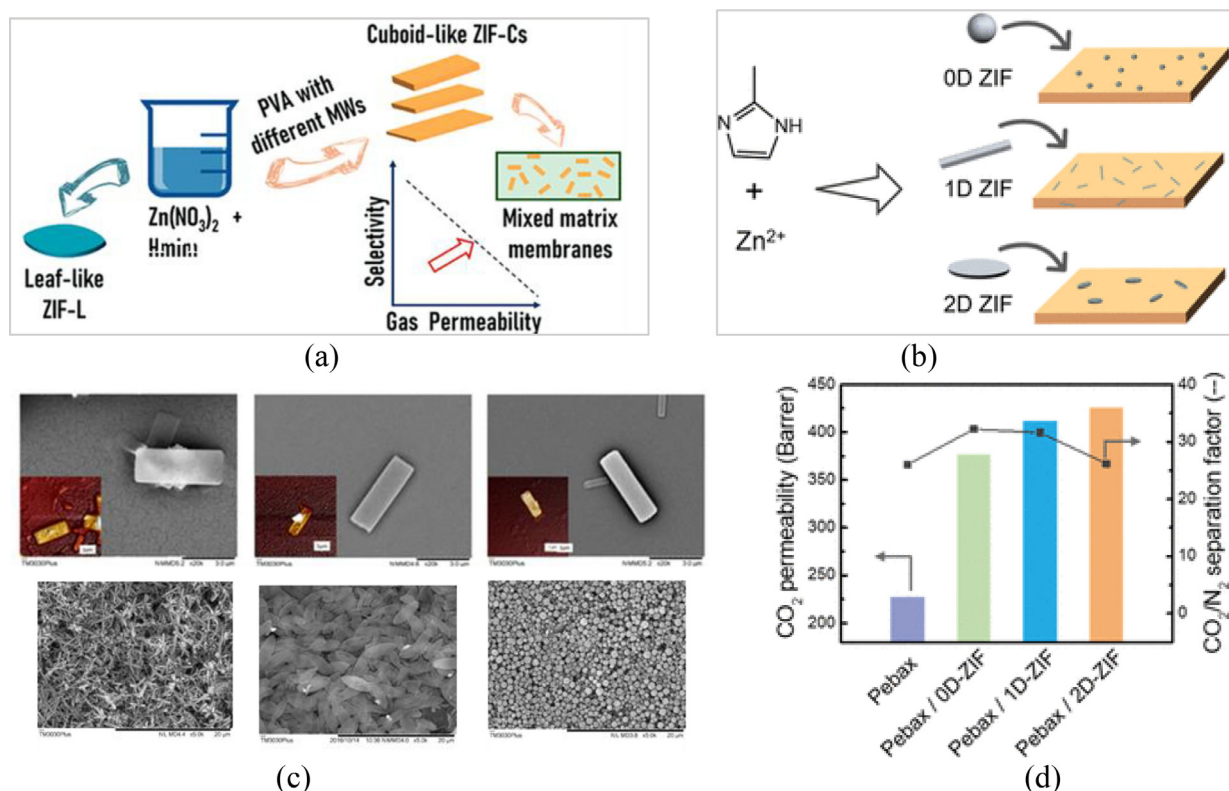


Fig. 6. (a) Synthesis ZIF of different shapes using PVA of different molecular weights, (b) membranes embedded with different shapes of ZIF, (c) SEM images of the ZIFs in different shapes and sizes, and (d) the effect of the shapes on the separation performances (Deng et al., 2020; Deng et al., 2020).

transfer is dominated by the molecular sieving transport mechanism, promoting the transport of dimensionally smaller molecules of gas pairs. MEMFO has a long history in CSM research, dating back to the early 2000s. Carbon membranes can be obtained from a variety of different classes of polymers/precursor materials. In the research performed at MEMFO, carbon membranes fabricated in both flat sheet and hollow fiber configurations have been investigated. Due to the superior packing density, carbon hollow fibers have received the most attention in MEMFO during recent years.

Cellulose and its derivatives have long been the major precursor in carbon membranes in MEMFO (Lie and Hägg, 2005; Lie and Hägg, 2006; Lei et al., 2019). The main advantage of cellulose acetate (CA) materials as precursors is that they are derived from natural sources as abundant green materials. However, this type of carbon membrane showed a low permeance due to the thick wall (ca. 25–30  $\mu m$ ) with a symmetric wall structure. Carbon membranes based on this approach were somewhat successfully upscaled into pilot-sized membrane modules, and, as an outcome, a spin-off company, MemfoACT AS (now closed), was established. Detailed technical information of the scaled-up production process in MemfoACT, from making a spinnable dope of cellulose acetate, winding fibers next to each other in a detachable collection device, washing, reacting (deacetylation) the fibers, drying fibers, to quality control of fibers were published (Haider et al., 2018; Haider et al., 2018) after the company is closed. Information also covers the carbonization oven loading, carbonizing of up to 7000 fibers in one batch, and yield /quality analysis of produced carbon membranes. The unavoidable time gap between production, module making, and the produced carbon varies, posing a challenge in the aging of the fibers once exposed to oxygen and water vapor in the air. How we dealing with this challenge was reported (Haider et al., 2019). One of the strengths of carbon membranes, in general, is that they are not damaged by high partial pressures of  $CO_2$  or high feed pressures; this gives, together with the inherent high  $CO_2/CH_4$ , an advantage in biogas upgrading to fuel quality

biomethane (Haider et al., 2016). The company got a pilot demonstration unit built at a municipal waste handling site in Norway, and after some initial challenges, it managed to upgrade a significant amount of biogas into biomethane in a reasonable time (Haider et al., 2018).

Carbon membrane fibers were also produced with deacetylation of cellulose acetate as precursors, which has one advantage (it is easy to find a proper solvent for dissolving the CA, i.e., NMP or DMSO) and at least two disadvantages: the fibers get very weak and soft during the deacetylation procedure, and the deacetylation erases porosity in the precursor fiber, yielding a homogenous dense carbon after carbonization. One obvious solution is to dissolve cellulose directly in any “benign” solvent, which is however hard to find. After a thorough screening of possible solvents and spinning parameters, the 1-ethyl-3-methylimidazolium acetate ([Emim]AC) in combination with DMSO was used to dissolve cellulose, spinning, and making cellulose hollow fibers (Lei et al., 2021), which was subsequently carbonized to produce high-performance carbon hollow fiber membranes later also with porosity gradients in the wall (Lei et al., 2020). The asymmetric carbon hollow fiber membranes were measured with an  $H_2$  permeance of 148.2 GPU and an  $H_2/CO_2$  selectivity of 83.9 at 130 °C (Lei et al., 2021). Very recently, CSM based on a new polymer precursor, a Tröger’s base polymer, has also been explored (Dai et al., 2023). This membrane exhibited a surprisingly high  $H_2$  permeability (up to 1135 Barrer) with an  $H_2/CH_4$  selectivity of 1170. The  $H_2/CO_2$  and  $CO_2/CH_4$  separation performances also substantially exceed the Robeson upper bound.

### 3.5. Membrane absorption

As a joint activity with the absorption group in the same department, MEMFO integrates the expertise of two groups to combine the advantages of two technologies, e.g., the high selectivity of chemical absorption and the small footprints and modularity of membrane separation (Zhao et al., 2016; Shiravi et al., 2024). MEMFO’s research on mem-



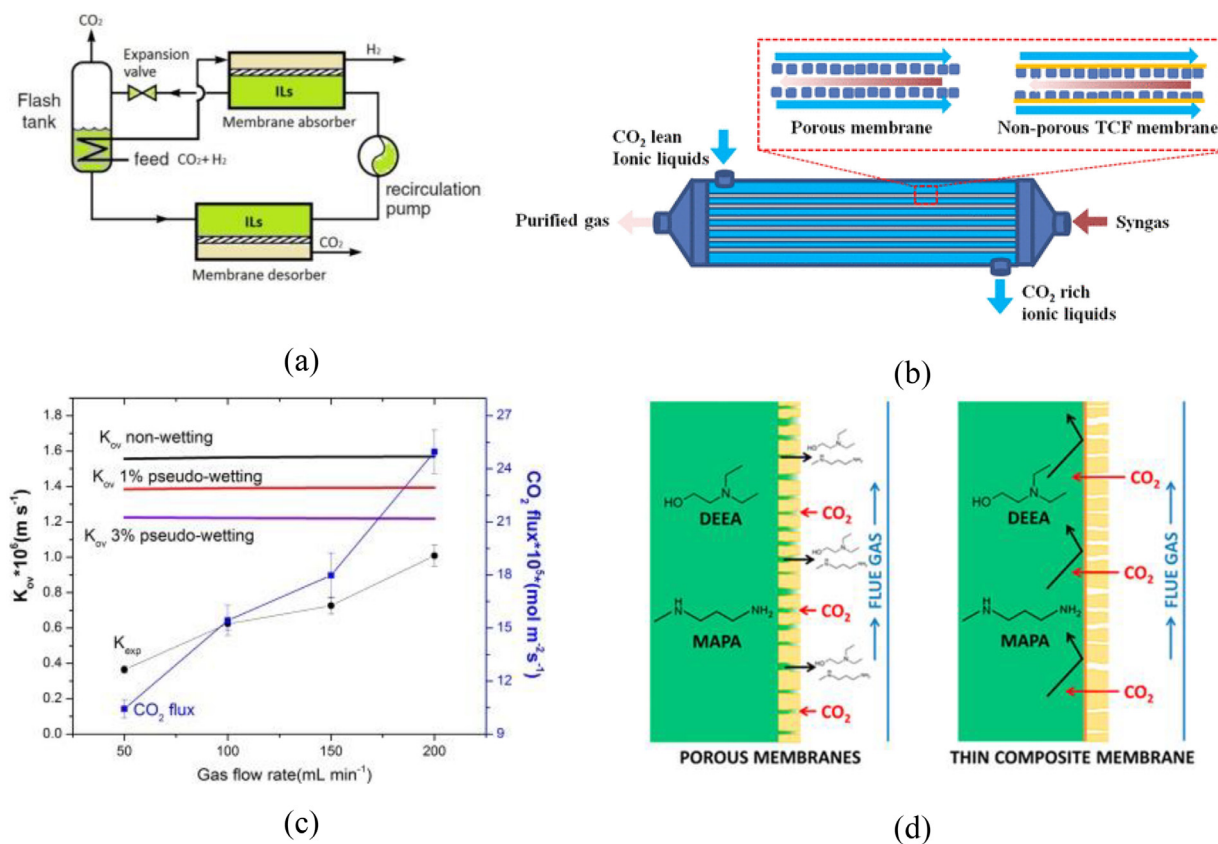


Fig. 7. (a) Closed loop pressure swing membrane contactor using ILs (Dai and Deng, 2016), (b) Comparison of porous and non-porous membrane contactors (Dai et al., 2016), (c) Comparison of mass transport resistances with or without pore wetting in membrane contactors, and (d) CO<sub>2</sub> and amine permeation through porous and non-porous TFC membrane contactors, showing amine evaporation prevention (Ansaroni et al., 2017).

brane absorption has focused on designing and optimizing the membrane phase for selected solvents of unique properties. Long-term stability and good interface compatibility are the critical aspects to ensure the high performance of the process (Gao et al., 2022). A few special solvents under investigation in MEMFO were selected because that an additional membrane as interface can prevent the emission of volatile solvents and enable pressure swing desorption when non-volatile solvents are used. We have also tried mimicking enzymes in aqueous monoethanolamine (MEA) or other alkaline solutions to promote CO<sub>2</sub> absorption in membrane contactors (Saeed and Deng, 2016).

### 3.5.1. Membrane contactor using ionic liquids-based solvents

The unique features ionic liquids can offer as non-volatile and highly CO<sub>2</sub>-selective solvents make them perfect for use in membrane contactors based on pressure-swing adsorption-desorption. MEMFO researchers have demonstrated the potential of applying ionic liquids in a membrane contactor for pre-combustion CO<sub>2</sub> capture at elevated temperatures (303–393 K) and pressures (20 bar) by applying pressure swing absorption and desorption in a closed loop. This concept was patented and later employed in a subsea natural gas processing process (Fig. 7a) (Dalane et al., 2018; Dalane et al., 2019; Dalane et al., 2019; Dalane et al., 2017). After the screening, Butyl-3-methylimidazolium tricyanomethanide ([Bmim][TCM]) and PEG/IL blend solvents were selected as CO<sub>2</sub> absorbents due to their high thermal stability, moderate viscosity, and high CO<sub>2</sub> absorption capacity (Dai and Deng, 2016; Dai et al., 2016; Li et al., 2016). The effects of the operating parameters on the CO<sub>2</sub> capture performance in a tubular glass membrane contactor (with small and uniform pores) were systematically investigated. Later, non-porous polymeric composite membranes were also applied (Fig. 7b). The compatibility and stability of six different poly-

meric membranes were evaluated, while the porous polytetrafluoroethylene (PTFE) membrane and non-porous Teflon/polypropylene (PP) composite membrane were found the most suitable, showing comparable separation performances of CO<sub>2</sub> flux values. Modeling of gas transport was conducted in the pressure-swing membrane absorption process. The mass transfer coefficient ( $K_{exp}$ ) in the glass membrane contactor obtained from the experimental characterization was compared with the  $K_{ov}$  estimated from the resistance-in-series model (Dai and Deng, 2016; Dai et al., 2016), indicating that the liquid phase resistance contributes to 67 % and 44 % of the total mass transfer resistance for non-wetted and wetted modes of the membrane, respectively (Fig. 7c). Similar results were reported by Yuan et al., showing that wetting increases the mass transfer resistance significantly (Yuan et al., 2022). Models for non-porous, polymeric hollow fiber membrane contactors were also validated experimentally (Usman et al., 2017; Usman et al., 2016; Usman et al., 2018). It is found that the liquid phase mass transfer dominated the overall mass transfer. Membranes with high porosity and small thickness (dense layer) could apparently reduce the membrane resistance and thus increase the separation efficiency. On the other hand, the influence of tubular diameter and length of the membrane is relatively small within the operation range (Dai et al., 2016).

### 3.5.2. Membrane contactor using volatile amine-based solvents

In amine-based absorption, the development of more cost-effective solvents is required in order to make the process more economically feasible. Blends of primary/secondary amines with tertiary amines, e.g., diethyl-ethanolamine (DEEA) /3-methylamino-propylamine (MAPA), named as the “3rd generation (3 G) solvents”, possess these features, but their implementation is limited due to the much higher amine evaporation rate compared to traditional solvents, such as MEA. Non-porous

membrane contactors were designed in order to prevent amine evaporation while minimizing its impact on the CO<sub>2</sub> mass transfer coefficient, as shown in Fig. 7d.

Due to the aggressive nature of amine chemistry, ensuring the durability and compatibility of the membrane in contact with the 3 G solvent is of utmost importance. Fluorinated polymers were found to be highly stable and able to provide necessary compatibility with a large variety of advanced solvents. Since only a thin, dense layer is in contact with the amines, it is possible to avoid using the expensive fluoropolymer as the porous support. A cheaper alternative, porous PP, was tested in extremely harsh conditions and found suitable for the application (Ansaloni et al., 2016). This combination was later introduced to a subsea membrane process to ensure a long lifetime of the membranes for subsea natural gas treatment (Ahmadi et al., 2021; Ahmadi et al., 2021). To properly compare the amine evaporation in membrane contactors and in absorption columns, the amine mass transfer coefficient needs to be identified. Therefore, the permeation of aqueous solutions of various amines (MEA, DEEA, and MAPA) was tested by means of pervaporation experiments. In the case of high volatile absorbents (DEEA-MAPA blends), the membrane contactor is able to limit the amine emissions to a significant extent (up to 80 %), but if low volatile absorbents (e.g., 5 M MEA) are considered, the evaporation prevention becomes negligible (Ansaloni et al., 2017). Membrane contactor tests were also performed using a thin composite membrane where a thin (2 µm) layer of AF2400 was coated on porous PP support in either flat sheet or hollow fiber configurations (Ansaloni et al., 2019). Despite the better performance expected for by applying advanced amine solvents, the CO<sub>2</sub> mass transfer coefficient was found to be lower compared to the benchmark of 5 M MEA. An increase in temperature reduced the gap in performances, suggesting it was the higher viscosity of the 3 G solvents that resulted in the unexpected performance loss. The resistance-in-series model indicated the main resistance was to be found at the liquid boundary layer, where the CO<sub>2</sub> diffusion was significantly hindered.

The membrane contactor materials have also been applied in a dissolved oxygen removal apparatus developed by TNO (Figueiredo et al., 2021). In this case, the selective layer is intended to allow the permeation of the dissolved O<sub>2</sub> in the rich solvent while preventing the amine permeation and the wetting of the membrane pores. Tests performed at TNO clearly showed that non-porous membrane contactors are the most promising approach to ensure operation stability of the apparatus. The technology is amongst the most promising solvent management approach, and it is expected to prevent oxidative degradation phenomena of amines, lowering the overall OPEX of amine capture plants.

### 3.6. Process design and optimization

Considering the significant differences between process size and conditions and different requirements of the final products, it is critical to select suitable technologies with sufficient economic and technical benefits to motivate the industry to implement CCUS solutions. Although membrane processes for CO<sub>2</sub> capture or separation are known for their small footprint, low environmental impact, and high energy efficacy, to realize these advantages, the process design must be on a case by case basis, and the operation is the best under optimal conditions (Dai and Deng, 2024). MEMFO researchers have, therefore, paid particular attention to the membrane system design and optimization, and assessment of the membranes we developed for intended applications. Prior to the time period reported here, MEMFO alumni members developed a membrane simulation unit operation integrated in Aspen Hysys®, called “ChemBrane” (Grainger and Hägg, 2008; Grainger and Hägg, 2008), which is able to interface with the Adjust function to manipulate membrane area or operating pressure to achieve desired product recovery and/or purity, allowing more realistic energy consumption data and the use of complex recirculation flow scheme. ChemBrane also allows the driving force to be integrated according to a co-current flow pattern, mixed flow pattern (cross flow, plug-flow model in feed to retentate,

complete mixing on sweep permeate side), or counter-current flow pattern.

Process design based on FSC membranes and carbon membranes with tailored properties has been extensively studied in MEMFO for CO<sub>2</sub> separation from different sources of gas mixtures at their specific process conditions, such as powerplant flue gas, biogas, and natural gas, where the operating temperatures and pressures differ significantly, all with gas streams saturated with water vapor. Through many case studies, simulation results indicate that implementing membrane systems for CO<sub>2</sub> capture with a relatively smaller gas volume is beneficial compared to large-scale power plants (Hong, 2022; Janakiram et al., 2022; Xu et al., 2023). For a small to medium process, the threshold for establishing a membrane process is much lower compared to other technologies, which requires much less investment and space and is much easier to scale up and maintain. Moreover, membrane systems are more economical if they aim at a moderate CO<sub>2</sub> capture ratio, such as <80 %. When high-purity gas flows and/or high recovery rates are required, multi-stage membrane processes should be applied, and in most cases, with recycle flows. However, setting up a membrane process with more than two stages significantly increases the capital cost and the operational complexity. Based on process simulations, we found that it is more economical to apply hybrid processes when high-purity gases are desired; this concept is to be implemented through an ongoing research project by setting a CO<sub>2</sub> liquefaction step to replace the final membrane stages or combining the membrane with the adsorption process. Similar ideas have been reported by Li et al. (2022) and Soeptyan et al. (2024).

#### 3.6.1. CO<sub>2</sub> capture from flue gas

A major source of CO<sub>2</sub> emission is fossil fuel-based power plants, flue gas, or energy generation in other energy-intensive industries. A low specific cost of <20 \$/tonne CO<sub>2</sub> captured from flue gases containing CO<sub>2</sub> of >13 vol.% was reported for both Polaris and PolyActive membranes (Han and Ho, 2021). Facilitated transport membranes are also known for excellent CO<sub>2</sub> separation performance. Several membranes developed in MEMFO have been demonstrated at pilot scales for carbon capture from flue gas in cement factories and fossil fuel-fired power plants, enabling a realistic basis for more accurate process simulation with sufficient onsite data.

Design and optimization of processes using FSC membranes developed by MEMFO have been studied for CO<sub>2</sub> capture from flue gas. The process simulation of FSC membranes has a particular challenge, i.e., water is a facilitator in the reaction and causes the membrane material to swell. This dual CO<sub>2</sub> transport pathway through the membrane also means that there are two parallel terms in Fick’s law, one for free CO<sub>2</sub> and one for site-associated CO<sub>2</sub>. Currently, not enough relations/measurements are known to be able to solve this analytically (or numerically). The second-best option is to measure the actual module performance (using a module closely resembling actual length and fiber dimensions and operating it at a reasonable pressure drop, pressure ratio, and temperature). Once this is done, we treat the module like a “black box” and, via trial and error, adjust all permeances to obtain “apparent permeances”, i.e., permeances that, by applying “one driving force” based on Fick’s law, will yield the measured simultaneous retentate and permeate purities. Those “apparent permeances” can then be used as a basis for high-level cost and size simulation of “real” flue gas capture (Janakiram et al., 2022).

#### 3.6.2. Biogas upgrading

Using ChemBrane to simulate carbon membranes for biogas upgrading is found to be relatively straightforward and yielded similar or, in some cases, slightly better field results than those simulated (Haider et al., 2016). ChemBrane has also been used to compare and evaluate carbon membranes relative to traditional polyimides for biogas upgrading. It was found that even though the carbon membrane has a significantly higher material cost, this is canceled out by superior pressure stability and elevated CO<sub>2</sub> partial pressure tolerance [92]. Biogas

upgrading is also an attractive market for the FSC membrane, considering the high water content in the raw gas, favoring facilitated transport of CO<sub>2</sub>. Since the separation performances of FSC membranes are sensitive to the process pressure, the membranes intended for the process were tested under various operating pressures to provide a more reliable basis for the process analysis. A two-stage membrane process with a recycle flow was the most efficient, enabling the purification of 98 % CH<sub>4</sub> with a 98 % recovery rate of CH<sub>4</sub> (Deng and Hägg, 2010).

### 3.6.3. H<sub>2</sub> purification

As energy generation from fossil fuels is the major source of CO<sub>2</sub> emission, shifting the energy structure to non-carbon-based fuels is a strategic pathway to avoid increasing CO<sub>2</sub> emissions. MEMFO researchers have investigated the use of membranes in hydrogen purification (Lei et al., 2021; Grainger and Hägg, 2008). As hydrogen production involves the purification of the mixture streams from reactors (e.g., IGCC and dark fermentation) that contain a large amount of CO<sub>2</sub> and are saturated with water (Lee et al., 2011), purifying H<sub>2</sub> from the water-saturated CO<sub>2</sub>/H<sub>2</sub> mixture is challenging. Since the molecular size of H<sub>2</sub> (2.9 Å) is significantly smaller than that of CO<sub>2</sub> (3.3 Å) (Pal and Agarwal, 2021), membranes used for CO<sub>2</sub> and H<sub>2</sub> separation may be H<sub>2</sub>-selective membranes or CO<sub>2</sub>-selective membranes. MEMFO researchers have contributed to the process assessments using their developed membranes. Lei et al. reported a process using an H<sub>2</sub>-selective carbon membrane for CO<sub>2</sub> and H<sub>2</sub> separation from an IGCC plant (Lei et al., 2021). Later, He et al. studied the use of the same H<sub>2</sub>-selective carbon membrane on biohydrogen recovery from dark fermentation (Chen et al., 2023). A membrane process using CO<sub>2</sub> selective FSC membrane for dark fermentation biohydrogen purification has also been designed and optimized to achieve simultaneous CO<sub>2</sub> removal. A CO<sub>2</sub>-selective PVAm-based nanocomposite membrane was selected considering the membrane's high CO<sub>2</sub>/H<sub>2</sub> separation performance and unique features (e.g., water vapor favorable) suitable for the process conditions. A two-stage process with a recycle stream is determined for the optimal performance, and an alternative design to simultaneously capture CO<sub>2</sub> by introducing a 3rd-stage using the same CO<sub>2</sub>-selective membrane or an alternative H<sub>2</sub>-selective CMSM membrane were investigated. Adding the 3rd-stage can capture and purify CO<sub>2</sub> as a side product of various purities for storage or utilization, which further decreases the H<sub>2</sub> loss, leading to additional economic benefits.

## 4. Conclusions and outlook

MEMFO's research on CO<sub>2</sub> separation membranes has primarily focused on facilitated transport membranes. Our research also involves several mainstream membrane materials, including CO<sub>2</sub>-philic polymeric membranes, hybrid membranes, and carbon membranes. Each of these membrane types has its unique advantages and drawbacks. It is beneficial to find suitable membranes for specific applications and process conditions.

In general, polymeric membranes are easier to upscale and cheaper to implement compared to hybrid membranes and carbon membranes. Hybrid membranes, by introducing fillers, possess desired features for CO<sub>2</sub> separation in addition to those offered by polymeric membranes. Carbon membranes are not subjected to the trade-offs that limit most polymeric membranes. However, their fabrication and installation are more challenging, and water or other impurities may somehow deteriorate their performance. Facilitated transport membranes have all the inherent advantages of polymeric membrane and the mechanism to break through the performance trade-offs. The presence of water in most CO<sub>2</sub>-containing mixed gases favors CO<sub>2</sub> transport in facilitated transport membranes. However, most facilitated membranes are water-swollen with sacrificed mechanical strength that must be compensated, and it is critical to maintain an optimal water profile inside the membrane modules to sustain its high performance.

Based on our experience, polymer-based membranes, particularly facilitated transport membranes, will remain the most promising for industrial applications in the future. We believe that unanticipated new technologies, such as artificial intelligence (AI) aided approaches, could enhance our understanding of membrane transport mechanisms, while emerging materials, such as new 2D and 3D nanostructured materials, may enable the polymeric membranes with better structure-specified properties to overcome the performance trade-offs. Therefore, keeping a close eye on cutting-edge technologies and emerging materials and adopting innovative approaches to membranes and membrane processes will be certainly our strategies in future work.

MEMFO's mission of advancing membrane-based CO<sub>2</sub> separation technologies will, of course, remain as our current research activities, but in future studies, our focus may shift slightly toward industrial applications to promote the implementation of our membrane in CO<sub>2</sub> separation membrane processes, particularly for the now neglected CO<sub>2</sub> emission sources. It emphasizes supporting the industry in jointly solving problems on the road to commercialization and meeting the real needs of the "customized" applications.

Looking back, MEMFO's efforts have been worthwhile; our research on CO<sub>2</sub> separation membrane materials, processes, and upscaling through innovative approaches to combining emerging new materials and technologies in the past few decades has become one of the bricks paving the road of CO<sub>2</sub> membranes towards industrial applications. We hope that one day, with the combined efforts of the membrane community, revolutionary CO<sub>2</sub> separation membrane concepts can be developed, making membrane technology a much more dominant competitor in the CCSU market.

### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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