



CO₂ facilitated transport membrane promoted by mimic enzyme

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ABSTRACT

A mimic enzyme promoted facilitated transport membrane was developed and optimized for post-combustion CO₂ capture. This composite membrane has a thin dense polyvinyl alcohol (PVA) selective layer containing a low molecular weight mimic enzyme and a polysulfone (PSf) ultrafiltration porous support. The selected mimic enzyme (i.e., Zn-cyclen) was characterized by HNMR¹, ESI-MS and dissociation constant (pKa). The membrane morphology was studied by scanning electron microscope (SEM). The effect of mimic enzyme loading and the pH value of the membrane casting solution was investigated. The optimal Zn-cyclen loading of 5 μmol/g PVA and a pH value of 9 were determined. The influence of humidity on the performance of the membrane was also studied by conducting experiments at variable relative humidity levels (i.e., 50–100%). This membrane showed a CO₂ permeance of 0.69 [m³(STP)/(m² bar h)] and a CO₂/N₂ selectivity of 107, which is significantly higher than that of a PVA membrane without mimic enzyme operating under the same conditions.

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1. Introduction

The combustion of fossil fuels in power plants is the largest point source contributor to CO₂ emissions. The CO₂ concentration in natural gas-fired power plants varies between 4% and 10%, which increases for coal-based power plants (up to 13.5% CO₂). Several technologies have been investigated for CO₂ capture but high capital investment and operational costs are major hindrances in their large scale industrial application [1,2]. Currently, amine-based absorption is the leading technology for CO₂ separation. However, amine absorption is energy intensive and has associated pollution risks due to solvent emission.

Membrane technology is well recognized to be environmentally friendly and less energy intensive. It has been actively practiced for many years for CO₂ separation, but with a very small share in the market. This is mainly because the cost of the separation using current commercial membranes is much higher than the amine-based absorption. Innovative membrane materials may be the solution to significantly reduce CO₂ separation costs. However, such membranes should ideally have both high selectivity and CO₂ permeance that is above the so-called Robeson upper bound [3].

Facilitated transport membranes for CO₂ separation exhibit a potential to achieve both high selectivity and CO₂ permeance. In a CO₂ facilitated transport membrane, CO₂ transports mainly by

means of a reversible reaction of CO₂ with complexing agents (carriers) in the membrane, while nonreactive gases such as N₂ and CH₄ permeate only by the solution–diffusion mechanism. The first studied facilitated transport membranes for gas separation were supported liquid membranes (SLMs) with mobile carriers, in which carrier solutions were impregnated in the pores of a microporous support. SLMs have serious degradation problems. The loss of carrier solution due to evaporation or entrainment with the gas stream, or the deactivation of the complexing agent makes these types of membranes unstable and therefore not suitable for large scale applications.

Fixed-site-carrier (FSC) membranes were introduced to overcome the above limitations and contained carriers covalently bonded to the polymer backbones (e.g. amino groups). In FSC membranes the carriers have restricted mobility, hence the stability is no longer an issue, but the gas diffusivity (and thus permeability) in these membranes is 2–3 orders of magnitude lower than that in a mobile carrier membrane [4–9]. Several different mechanisms had been proposed to explain the reversible reaction involved in the CO₂ facilitated transport in a FSC membrane. Deng et al. proposed that the reversible reaction in a polyvinyl amine based membrane is the CO₂ hydration catalysed by the amino groups (so-called “carriers”), in a weak basic environment. The real “carrier” is actually water. When an FSC membrane works in a water swollen state, the separation performance significantly increases, not only due to the increased gas diffusivity, but also because that the presence of water enhances the CO₂ hydration and hence the facilitated transport effect [10]. Thus, as the presence of moisture in the feed gas stream can swell the membrane, it favors

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the CO₂ facilitated transport [11–15].

As a special type of facilitated transport, the use of immobilized carbonic anhydrase (CA) in water swollen membranes to mimic the mechanism of the mammalian respiratory system allows a dramatic increase in CO₂ selectivity over other gases, even at low partial pressures [16]. Carbonic anhydrase, naturally occurring in human body, has a fast and reversible reaction with CO₂ while having minimal heat of reaction. The CA enzyme can speed up the hydration of CO₂ to bicarbonate and the reverse bicarbonate dehydration; CA has the ability to catalyze the hydration of 600,000 molecules of CO₂ per molecule of CA per second, 4000 times faster than MEA in terms of catalytic activity whereas its energy consumption is almost 7 times less [16–18]. Very high selectivity at very low CO₂ concentrations (1–0.1%) was documented in a membrane with immobilized CA by Yang et al. [17]. A liquid membrane system catalyzed by CA has been developed by Carbozyme Inc. through a NETL project (US), and preliminary results show potential for significant decreases in energy penalties and costs [18]. The immobilization of CA has been extensively investigated [19], such as to cross-link enzymes and form a gel. Carbonic anhydrase can also be covalently attached or encapsulated within polymeric membranes. However, the lack of long-term stability (a life time of around 6 months) and the permanent loss of enzyme activity due to slight changes in pH and temperature have become the major drawbacks of this type of membrane. In addition, the enzymes are very costly and hence not suitable for large-scale applications.

In this work, a synthetic zinc complex resembling the active site of CA enzymes is used to mimic the bio-catalytic process and replace CA enzymes. A number of macrocyclic and tripodal complexes of zinc (II) and other metals have been reported to mimic the activity and the catalytic mechanism of CA in the CO₂/HCO₃[−] reaction cycle [20,21]. The mimic enzyme acts as a catalyst in the hydration of CO₂ in the same fashion as the bio-enzyme, i.e., CA [22]. A zinc based mimic enzyme is much more stable to impurities, is effective over a wide pH range and has high thermal stability (it is usually stable over 200 °C). The low molecular weight of the mimic enzyme leads to an additional benefit of a higher number of active sites per unit mass of compound, showing fast reaction rates comparable with the CA enzymes in terms of weight, hence providing cost-effective and more durable/stable substitutes for the CA enzymes [20].

Among many different “mimic enzymes” reported in the literature, Zn–cyclen was selected for study in this work based on its small cyclic structure, the highly hydrophilic nature of its ligands, its high kinetic rate constant and appreciably low heat of reaction [20,21].

The novelty of this work is the use of synthetic Zn²⁺ complexed organic compounds with an enzyme-like active site in membranes, and its catalytic effect to accelerate CO₂ hydration for CO₂ facilitated transport. In addition, a hydrophilic polymer is used as the membrane material to achieve a high degree of water swelling and hence provide sufficient water for CO₂ hydration. As this membrane works in a condition of being highly swollen with water, it combines the advantages of polymeric membranes and liquid membranes. Moreover, in this membrane the mimic enzyme (Zn²⁺ complex) is un-attached to the polymer and free to move inside the membrane, similar to mobile carriers in liquid membranes.

This paper presents a mimic enzyme promoted CO₂ facilitated transport membrane for CO₂ separation from postcombustion flue gas. A composite membrane with a thin dense polyvinyl alcohol (PVA) selective layer containing a low molecular weight mimic enzyme over a polysulfone (PSf) ultrafiltration porous support was prepared. The effects of mimic enzyme loading and the pH value of membrane casting solution were investigated to find the

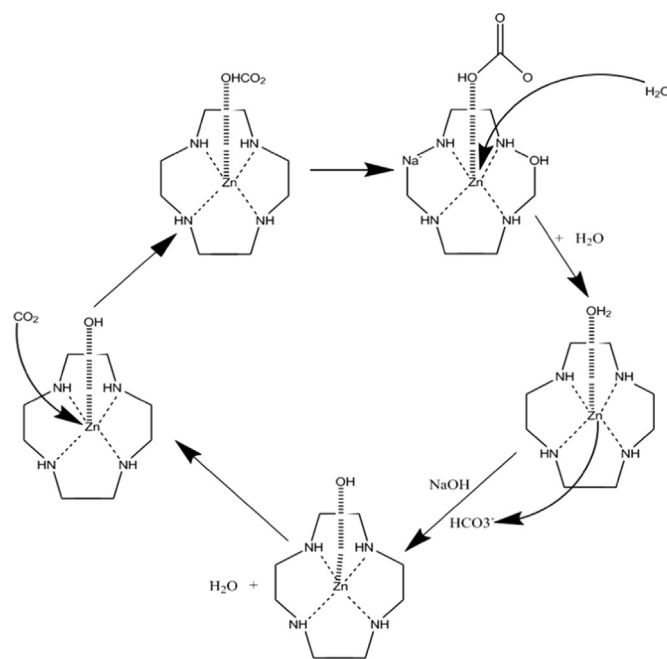
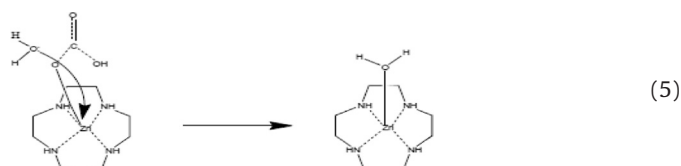
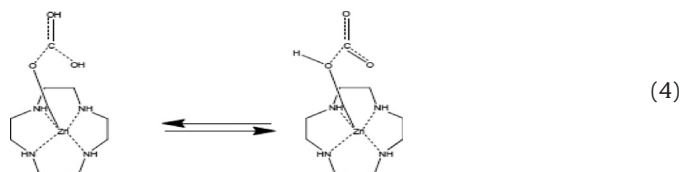
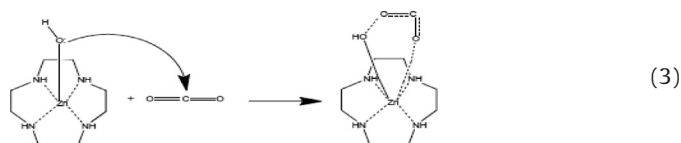


Fig. 1. CO₂ hydration promoted by Zn–cyclen mimic enzyme.

optimized membrane. The influence of feed gas humidity on the separation performance of the membrane was also studied. This membrane showed a significantly higher CO₂ separation performance than that of a PVA membrane without mimic enzyme operating under the same conditions.

1.1. Mimic enzyme

An illustration of the catalytic mechanism of CO₂ hydration promoted by Zn–cyclen (referred as “mimic enzyme” in this paper) can be seen in Fig. 1. A carbon dioxide molecule is attached to the Zn²⁺ active site to form a meta-stable complex. The complex is then attacked by a Lewis base (OH[−]) to produce bicarbonates (HCO₃[−]). In this two-step process, CO₂ is converted to HCO₃[−] and the active sites in the mimic enzyme are left unreacted. The mechanism is further elaborated in (Eqs. (1)–(5)) [20]



Since H_2O is involved in the $\text{CO}_2/\text{HCO}_3^-$ reaction cycle, polyvinyl alcohol (PVA) is used as the hydrophilic polymer membrane material in the selective layer to retain water. The membrane is designed to operate in a state that is highly swollen with water to achieve the best separation. The CO_2 diffusion in water swollen membranes is mainly in the form of HCO_3^- [10,23], more like ion transport through liquid, which could be two orders of magnitude higher than that of gases through solid polymers.

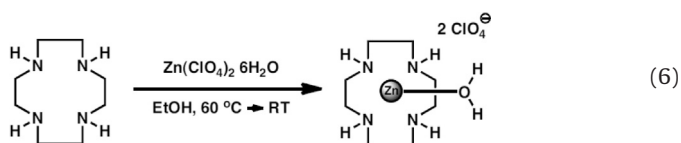
From Eq. (3) it can be seen that the mimic enzyme catalyzes the hydration reaction only when it is in a protonated state. For this purpose an excessive number of OH^- ions should be available in the membrane. Deionized water has a pH of around 7 and does not provide enough hydroxyl ions to protonate the mimic enzyme. It is critical to determine the dissociation constant (pK_a) of the mimic enzyme and maintain a pH higher than the pK_a to ensure an excess supply of OH^- ions.

2. Experimental

Analytical grade zinc perchlorate hexahydrate (in crystalline form), 1,4,7,10-Tetraazacyclododecane (97% purity), absolute ethanol, D_2O (99.9%), and polyvinyl alcohol Mwt 89,000–99,000 (89% hydrolyzed) were purchased from SigmaAldrich, NaOH was purchased from VWR, and the PSf ultrafiltration membrane (MWCO 50,000) was supplied by Alfa Lava. All these chemicals were used without further purification.

2.1. Synthesis of Zn–cyclen (mimic enzyme)

The synthesis of Zn–cyclen involves the treatment of the azamacrocyclic scaffold with the perchlorate salt of the metal, and heating the mixture at 50–60 °C. All the raw materials for the catalysts are soluble in ethanol, but the catalyst is insoluble in ethanol. 5 ml solution of cyclen in ethanol was added with 10 ml of $\text{Zn}(\text{ClO}_4)_2$ solutions in ethanol over a period of 1.5 h [24,25]. Both reactants were added in a molar ratio of 1:1. The reactions involved in the synthesis of Zn–cyclen are presented in Eq. (6) [21]



At the end of the reaction the product was separated from the solution using vacuum filtration and then washed several times with absolute ethanol. ^1H NMR 400 and MS were used to verify the completion of the reaction.

2.2. Characterization of the mimic enzymes

The $1\text{D } ^1\text{H}$ NMR spectra of Zn–cyclen in D_2O were recorded on a Bruker Avance DPX 400 MHz NMR spectrometer at 25 °C. The samples were prepared by dissolving the mimic enzymes in D_2O at room temperature. The solutions were then placed in NMR tubes and subjected to ultrasonic mixing to ensure that the composition of the sample was constant throughout the sample. The data recorded by NMR were analyzed using TopSpin™ software.

Furthermore, mass spectroscopy was conducted to determine the molecular composition of the produced mimic enzymes and their molecular weight experimentally.

2.3. Dissociation experiment

Potentiometric measurements were carried out in a Mettler Toledo G20 compact titrator equipped with a pH-electrode DSC-

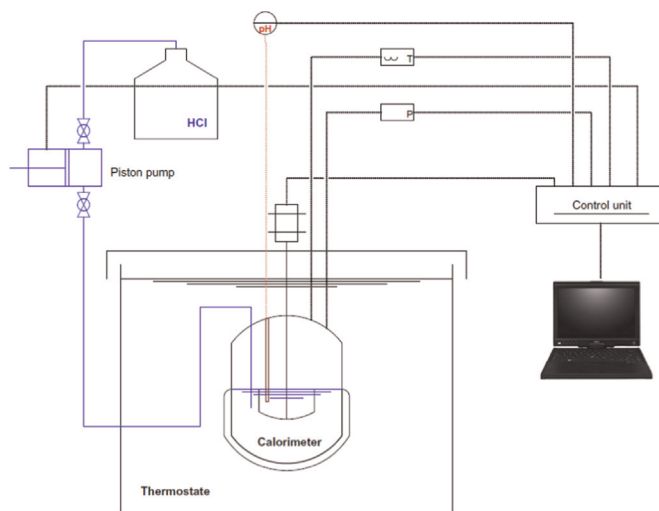


Fig. 2. Titration setup for the protonation experiment.

115 (uncertainty ± 0.02 pH) and temperature sensor DT100 (uncertainty ± 0.1 °C). The temperature in the jacketed glass vessel (100 ml volume) used for titration was controlled using a Julabo M4 heating circulator (temperature stability ± 0.1 °C). Dow 10 cSt silicone oil was used as a heat transfer medium. The calibration of the glass pH-electrode was performed at a temperature of 25 °C using buffer solutions supplied by the National Bureau of Standards (pH 2.01, 7.00, 9.21, and 11.00 from Mettler Toledo).

About 30 g of the mimic enzyme solution (10 mg/30 g- H_2O) was titrated with 0.1 M NaOH solution. The optimum titrant addition rate was selected in order to keep the temperature constant within ± 0.1 °C in the titration vessel. All the measurements were carried out in duplicate and the average values were reported. The titration procedure was computer controlled. All the data were recorded using the LabX 3.1 software provided by Mettler Toledo. A schematic diagram of the experimental setup is presented in Fig. 2.

The pK_a values were calculated in the software as a pH at half-equivalence. Uncertainties in the experimental data were mainly determined by the uncertainty of the electrode used, which is 0.02 pH.

2.4. Membrane preparation

A thin dense layer of polyvinyl alcohol (PVA) containing mimic enzyme was cast over a PSf support membrane using a dip-coating procedure. A calculated amount of PVA powder was added in deionized water to produce a 10 wt% mixture. The mixture was kept at 90 °C for 1.5 h to get a transparent, clear solution, and then left for rolling overnight at room temperature. This PVA solution was then diluted with the mimic enzyme solution and water, and then 0.1 M NaOH solution to adjust the pH value.

All the membranes were produced by using a dip-coating technique. A flat sheet PSf ultrafiltration membrane washed with deionized water was masked onto a glass slab. This support membrane was then dipped into the coating solution for 30 s. After lifting the membrane above the coating bath, it was held nearly vertically to allow the extra solution to flow off evenly and form a homogeneous and continuous film. The coated membrane was kept in a dust-free environment to dry in an ambient condition for 3 h and then recoated following the same procedure. Every membrane was coated twice to ensure that the entire membrane surface was evenly coated and to eliminate possible defects. The twice coated membrane was left in the dust-free space overnight, and then to dry in a convection oven at 45 °C for 3 h.

2.5. Membrane morphology

The cross-section and surface of the membranes were examined using field emission scanning electron microscopy (FESEM, Zeiss Ultra 55 Limited Edition). The cross-sectional samples were prepared by fracturing the membranes in liquid nitrogen. The samples were coated with gold before observation.

2.6. Swelling test

The swelling behavior of the membrane materials under humid conditions at room temperature was measured. The samples (polymer films) were vacuum dried for 3 h prior to the tests, and then placed in a closed container saturated with water vapor. Samples were weighed after regular intervals to determine the uptake of water by the membrane from the water vapor saturated air. The degree of swelling was calculated based on a gravimetric analysis of samples. Eq. (7) for the calculation of the degree of swelling is presented below

$$\% \text{Swell} = \frac{W_s - W_d}{W_d} \times 100 \quad (7)$$

where W_s and W_d are the masses of the swollen and dry membranes, respectively.

2.7. Permeation test

The separation performances of the membranes were tested in a specially designed gas permeation rig with humidifiers [26]. The feed gases were supplied from a premixed gas cylinder (10 vol% of CO_2 in CO_2/N_2 gas mixture, AGA AS). A flat sheet type membrane module was mounted in a thermostatic cabinet with a temperature control system. A membrane (diameter of 50 mm) was sandwiched between the permeate chamber and the feed gas chamber, supported by a porous metal disk and sealed with rubber O-rings. Both the feed gas and sweep gas were saturated with water vapor by bubbling through their respective humidifiers. A bypass line with a precise valve paralleling with the upstream humidifier was attached to adjust the humidity of the feed gas. The flow rate and pressure were recorded and controlled by a flow controller, flow indicator and pressure transmitters (MKS) respectively and logged directly into a computer (by Labview). The relative humidity of the feed gas was measured online by using a humidity analyzer.

The composition of the permeate gas was analyzed online by using a gas chromatograph equipped with a thermal conductivity detector (MicroGC3000). Some operation conditions, such as the feed gas flow rate, relative humidity, and feed pressure were varied to investigate their respective effects on the membrane performance. A sweep gas was used on the permeate side for a better recording of fluxes and gas compositions. Permeance of a species i (given the symbol P_i) was defined as the flux divided by the partial pressure differences between the upstream and downstream of the membrane, and reported in units of $[\text{m}^3(\text{STP})/(\text{m}^2 \text{ bar h})]$. The selectivity (α) was calculated from the permeance of CO_2 (P_{CO_2}) and N_2 (P_{N_2}), as expressed in Eq. (8) [27]

$$\alpha = \frac{P_{\text{CO}_2}}{P_{\text{N}_2}} \quad (8)$$

CO_2 - N_2 (10 vol% CO_2) mixed gas was used as the feed gas. The permeation experiments were carried out at 25 °C with a feed pressure varying from 1 bar to 3 bar, and the separation performance was recorded when the system had been stabilized.

3. Results and discussion

3.1. Characterization and evaluation of the mimic enzyme

The selected mimic enzyme (Zn-cyclen) synthesized for this work was tested using ^1H NMR and mass spectroscopy to validate the completion of the reaction. The results from the NMR verify the existence of mimic enzymes and agree well with the literature [25,28]. An elemental analysis in ESI-MS validated the structure and molecular weight of the synthesized compound.

It is evident from (Eqs. (3)–5) that either water molecule or OH^- ion can be attached to the active site of the mimic enzyme. However, the hydration reaction involves an activated mimic enzyme (OH^- attached to Zn). In order to efficiently use the full potential of the mimic enzyme, the pH value of the membrane casting solution should be maintained to ensure the excessive supply of OH^- . The dissociation constant (pK_a) is defined as the pH value at which 90% of the mimic enzyme is activated. Hence it is important to know the pK_a of mimic enzyme to maintain the membrane at a higher pH value than the pK_a value to ensure a sufficient supply of OH^- ions.

Fig. 3 presents the titration curve of an infinitely dilute mimic enzyme solution with NaOH at 25 °C. The sharp peak in the first derivative of the pH with respect to the volume of NaOH marks the end point of reaction, which is further used to calculate the pK_a as explained by Hartono et al. [30]. The dissociation constant calculated from experimental results are compared with literature in Table 1. The results from experimentation are in good agreement with the literature. These values indicate that the mimic enzyme activates at a pH of over 7 (neutral). A slightly basic environment must be maintained to ensure the activation of the mimic enzyme. Satcher et al. [21] studied the kinetics of CO_2 hydration with mimic enzyme at a pH range of 7.5–9.8 and concluded that the kinetic rate constant for CO_2 hydration increases appreciably with respect to an increase in pH. William et al. [28] evaluated the influence of mimic enzyme concentration, pH of solution and temperature on kinetic rate constant of CO_2 hydration and suggested that the mimic enzyme functions more efficiently at low bicarbonate (HCO_3^-) concentrations.

3.2. Membrane preparation and swelling test

A SEM image of the cross-section of a PVA membrane coated for this study is shown in Fig. 4. The membrane was prepared following the dip-coating procedure, and the thickness of the

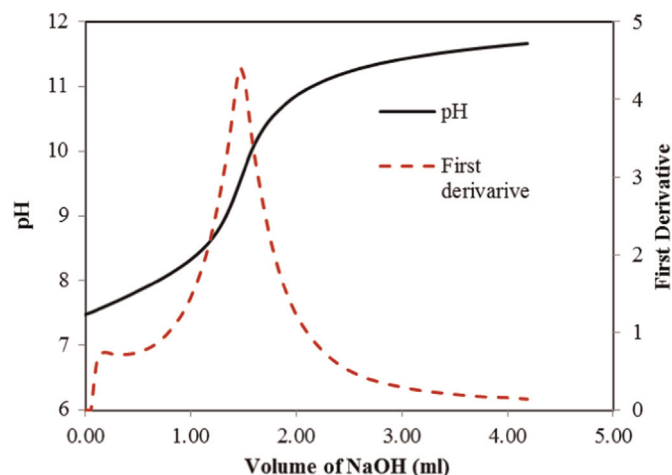


Fig. 3. Titration of Zn-cyclen against NaOH to determine dissociation constant (pK_a).

Table 1
Dissociation constant of the mimic enzymes.

Mimic enzyme	pKa	Reference
Zn-cyclen	7.9	[24]
Zn-cyclen	8.1	[20]
Zn-cyclen	8.02	[29]
Zn-cyclen	7.98 ± 0.05	This work

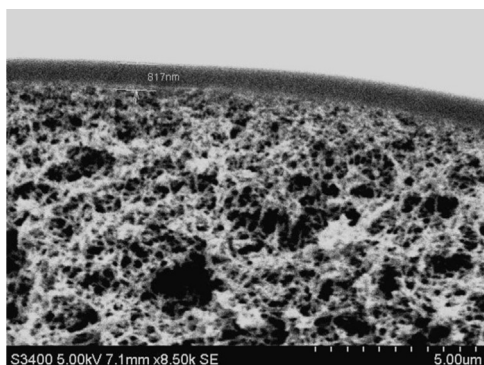


Fig. 4. SEM picture of the PVA membrane on PSf support.

coating can be controlled by adjusting the polymer concentration of the casting solutions. 2 wt% PVA solution was used to cast the membrane shown in Fig. 4. All the membranes presented in this work were cast with 2 wt% PVA, and the thickness of the membranes was in the range of 760–850 nm.

Membranes of different thicknesses were also casted by coating the PSf support with different concentrations of PVA solutions while keeping other parameters unchanged (e.g., temperature, withdrawing velocity, pre-treatment of the support membranes), to investigate the influence of casting solution on the membrane thickness. The thicknesses of selective layer were measure from SEM images. Thickness of a membrane as a function of coating solution concentration using the same procedure is presented in Fig. 5. Multiple samples were examined and a 3% average deviation in thickness of selective film was noted. It shows that a thinner or thicker defect-free coating layer (e.g., 0.3–8 μm) can be readily prepared by adjusting the PVA concentration in the casting solution.

Self-supported sample membranes prepared from PVA casting solutions without pH adjustment, and at pH values of 9 and 12, were prepared for the swelling capacity tests. They were placed in

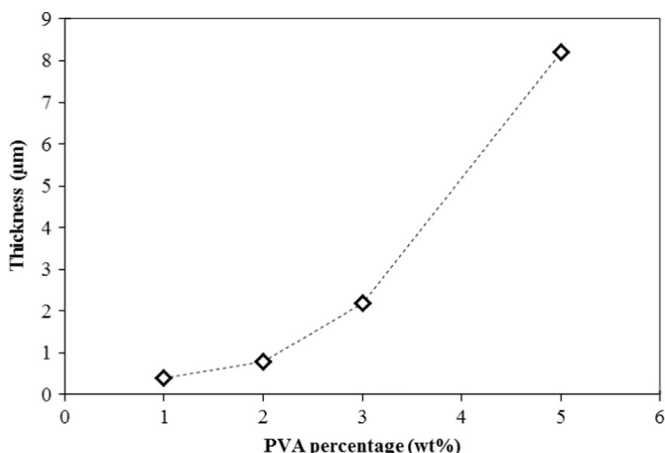


Fig. 5. Effect of the casting solution PVA concentration on the thickness of the selective layer.

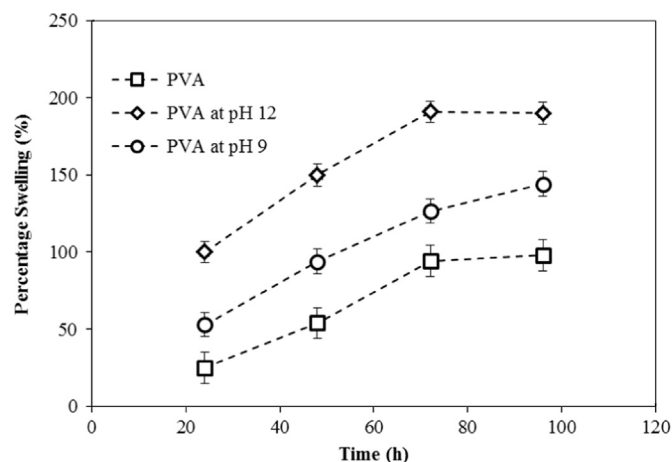


Fig. 6. Swelling behavior of membranes under humid conditions.

a humidification chamber at room temperature for several days, while a gravimetric analysis was performed periodically based on the weight gain to calculate the degree of swelling. As presented in Fig. 6, it can be seen that the PVA membrane becomes more swollen with the increase in the pH value of the membrane casting solutions.

3.3. Effect of the preparation parameters on CO₂ permeation

Membrane gas separation is a non-equilibrium thermodynamic process. Mimic enzyme in a water swollen membrane can promote CO₂ transport by introducing catalytic effect and accelerating the CO₂ hydration rate, and water plays an important role in this process. CO₂ transport through this type of membrane may involve three steps: (1) CO₂ from the feed gas is hydrated in the presence of mimic enzyme, (2) the produced HCO₃[−] diffuses through the membrane due to its concentration gradient, and (3) CO₂ is continuously dissociated and removed from the permeate side of the membrane. Therefore, the mimic enzyme PVA membrane was subjected to testing under humidified conditions.

Experiments were conducted to study the effect of the addition of mimic enzyme on separation performance of the PVA membrane prepared using casting solution at various pH values. PVA is a hydrophilic material with excellent film forming abilities. An aqueous solution of PVA is acidic in nature (pH 5–6). In this work NaOH was added to the membrane casting solution to adjust the pH value.

The experimental results presented in Fig. 7 compares the performance of membranes with and without mimic enzyme prepared with casting solution at various pH values. It is evident that the CO₂ permeance of the PVA membrane without the addition of mimic enzyme increases with increase in the pH value, whereas the CO₂/N₂ selectivity remains nearly consistent at around 60. The selectivity of CO₂/N₂ in water is approx. 55 based on Henry's law constant. These results suggest that by increasing the pH value of membrane casting solution, the amorphous domains in the polymer network may swell more water, and hence become more open and more gas permeable. However, the addition of NaOH does not lead to CO₂ facilitated transport, as the CO₂ hydration reaction is not accelerated by the presence of NaOH.

The PVA membranes containing mimic enzyme prepared at different pH values perform differently. The highest CO₂ permeance in mimic enzyme membranes (i.e., 0.69 ± 0.02 m³(STP)/(m² bar h)) was documented at pH value of 9, which is appreciable as compared to CO₂ permeance in pure PVA membrane. Similarly CO₂/N₂ selectivity of the PVA membrane containing mimic enzyme is 107 ± 5 , which is also higher than that of the pure PVA

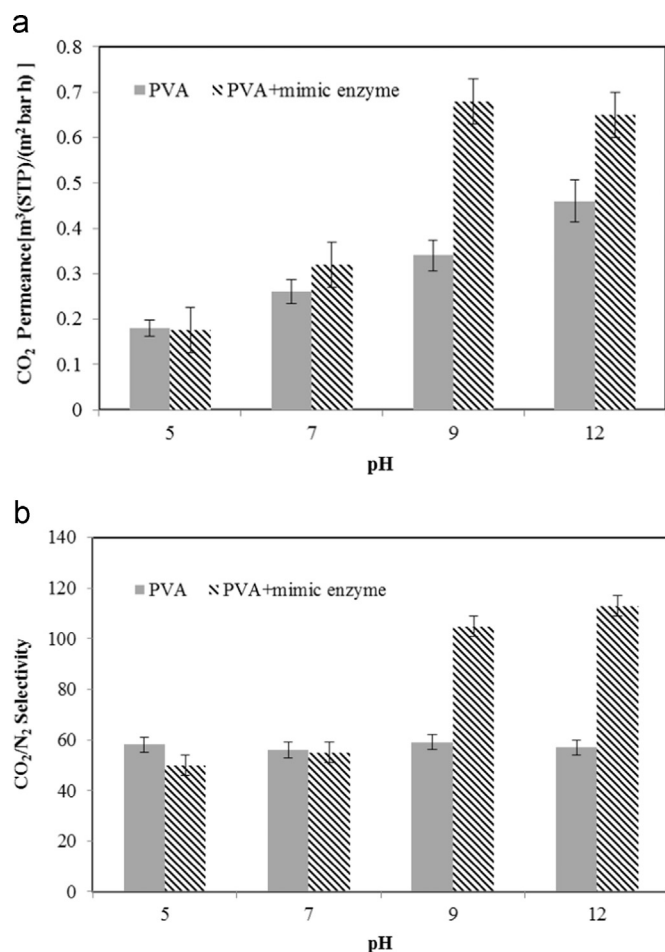


Fig. 7. Comparison of (a) CO₂ permeance and (b) CO₂/N₂ selectivity in membrane with and without mimic enzyme, at room temperature, 1.2 bara. Membrane casting solution at pH 5, 7, 9 and 12.

membrane. It is believed that mimic enzyme catalyzes the hydration reaction of CO₂ and enhances the formation of HCO₃[−] ions, which diffuse through the membrane much faster than CO₂ and N₂ gas molecules. In addition, this increase in membrane performance is noticed only at pH value of 9 and 12 (pH > pK_a of the mimic enzyme), which clearly indicates that only activated mimic enzyme facilitates the CO₂ transport, and the pH value of membrane casting solution must be higher than the pK_a of the mimic enzyme to ensure a sufficient amount of OH[−] ions in membrane. This phenomenon is in agreement with the observations reported by Satcher et al. [21] and William et al. [28]. They investigated the effects of pH value on the performance of mimic enzyme and concluded that mimic enzyme activates at pH > pK_a, and requires excess OH[−] ions to have an effective catalytic function.

Table 2
Comparison of CO₂ separation performance.

Membrane	Feed gas		CO ₂ /N ₂ selectivity	CO ₂ permeance	Reference
	Composition CO ₂ /N ₂ (%)	Pressure (kPa)	α	m ³ (STP)/m ² bar h	
PVAm/PVA	10	200–1000	174–66	0.58–0.13	[23]
PVAm/PPO	10	200–1000	60–120	0.998–0.10	[31]
DNMDAM–TMC/PS	20	200–1000	70–56	0.47–0.27	[32]
PVI–Zn complex 1	15	200–1600	75–50	1.23–0.82	[33]
PVI–Zn complex 2	15	200–1600	65–40	0.95–0.41	[33]
PVA/mimic enzyme	10	100–300	107–79	0.69–0.49	This study
PVA	10	100–500	58–48	0.18–0.15	This study

According to Fig. 7, a mimic enzyme PVA membrane prepared at pH 12 does not show a significant difference in terms of CO₂/N₂ selectivity to a mimic enzyme PVA membrane prepared at pH 9, while its CO₂ permeance is only slightly higher. Compared to the membrane of the casting solution at pH 9, the main difference in membrane with a pH of 12 may be the concentration of OH[−] ions. Although mimic enzyme is the facilitator that requires excess OH[−] ions to function, it seems that excessive amount of OH[−] does not show significant effect on performance of mimic enzyme once the pH is over its pK_a. The slightly increased CO₂ permeance can be attributed to the increase in the degree of swelling of the PVA membrane at a higher pH value, maybe due to the osmotic effect of NaOH.

A small quantity of mimic enzyme in a PVA membrane has shown a considerable increase in the CO₂ separation performance as compared to a PVA membrane without mimic enzyme, and also shows a comparable CO₂/N₂ separation performance to some high performance membranes reported in recent years. A comparison of the separation performance of the PVA-mimic enzyme membrane with that of some state-of-the-art CO₂ facilitated transport membranes is presented in Table 2.

CO₂ facilitated membrane with enzymatic functions of synthetic metal–organic compounds has rarely been reported. The only publication we found was on a PVI–Zinc complex membrane reported by Yao et al. [33]. Although the catalytic sites for the transport of CO₂ in their membrane are also Zn-complexes, the facilitation mechanism in their membrane is quite different. The PVI–Zn complex membrane operates with dry gas. Water is not involved in the reversible CO₂ facilitation reaction. The mimic enzyme membrane in the current work, however, works only under humidified conditions and requires a basic environment at a pH value more than the pK_a of the mimic enzyme used. The CO₂/N₂ selectivity of the mimic enzyme PVA membrane is higher than that of the PVI/Zn membrane, but the reported CO₂ permeance of the PVI–Zn complex membrane is slightly higher. This is believed to be mainly due to the much thinner selective layer thickness in the PVI–Zn membrane (approx. 200 nm) compared to that in the mimic enzyme PVA membrane in this study (approx. 800 nm), as gas permeance is usually inversely proportional to the thickness of the membrane selective layer in similar membranes.

The effect of mimic enzyme concentration on the performance of a membrane was studied by adjusting its concentration in the casting solution. Six different concentrations of mimic enzyme (0.0025–1 mmol/g PVA) were tested. Fig. 7 compares the performance of these membranes based on their CO₂ permeance and CO₂/N₂ selectivity. A decline in membrane separation performance with increasing the mimic enzyme concentration is observed although the total number of catalytic sites is increased. Similar trends have been reported in the literature for PVI–Zn complex membrane [33]. Although a few milli-moles of mimic enzyme is a small quantity of catalyst in the casting solution, its concentration rises appreciably, as the mimic enzyme in the coated swollen

membrane is much more concentrated than in the casting solution. The concentration of mimic enzyme in the selective layer could be several moles per gram of water in membrane depending on the degree of swelling. A higher concentration of mimic enzyme in the membrane may affect the membrane performance in several ways. Firstly, the high concentration of mimic enzyme leads to a higher pKa value. In addition, when a higher concentration of mimic enzyme exists which exhausts more OH^- , the OH^- ions resulting from pH adjustment becomes scarce. Moreover, although the HCO_3^- ions produced by the hydration reaction are supposed to be removed from membrane at the permeate side by the CO_2 dissociation and releasing, the existence of HCO_3^- in the membrane is unavoidable, due to the equilibrium of the CO_2 hydration reaction and that the HCO_3^- concentration is higher when more mimic enzyme is presented because of the competition between the CO_2 hydration reaction and HCO_3^- diffusion. As the catalytic sites in mimic enzyme deactivate in the presence of HCO_3^- ions [28], the excess production of HCO_3^- ions deactivates the catalyst, and hence suppress the catalytic function of the mimic enzyme. Another reason is that mimic enzyme is an amorphous solid with high solubility in water. However, its solubility has a limitation. As shown in Fig. 8(a), CO_2 permeance of membrane with 1 mmol mimic enzyme is less than its counterpart PVA membrane without mimic enzyme. This shows that the water filled amorphous domains of polymer membrane have become less available for the CO_2 transport if the mimic enzyme concentration is higher than it can be dissolved in the amount of water swollen in the membrane. The mimic enzyme becomes solidified due to a high concentration in membrane. The solidified salt may fill up these domains and result in a lower gas diffusion rate. The selectivity of CO_2/N_2 in this membrane shows a similar

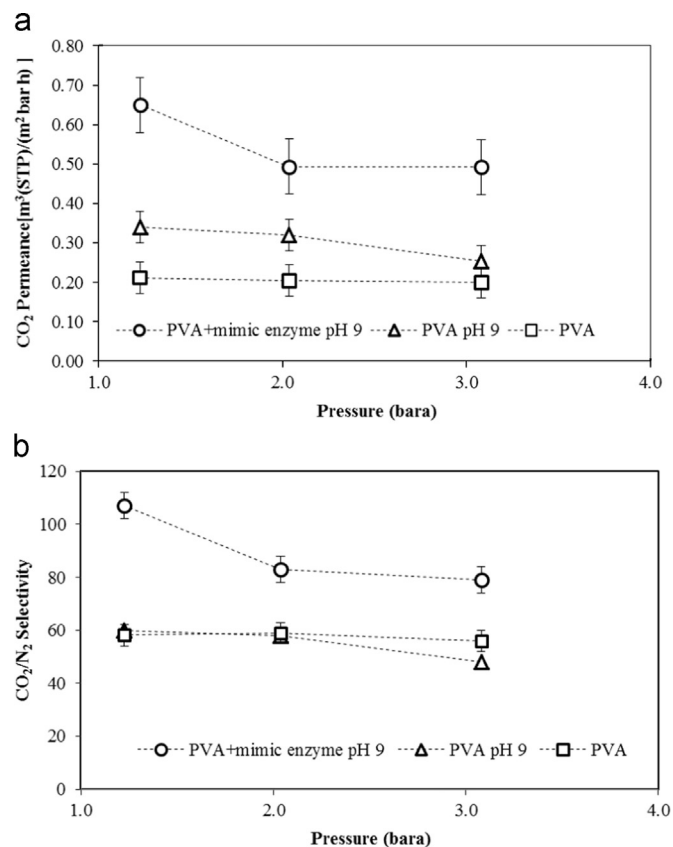


Fig. 9. Effect of feed pressure on (a) CO_2 permeance and (b) CO_2/N_2 selectivity, at room temperature.

trend.

3.4. Effect of operating conditions

To further evaluate the effect of driving force on membrane performance, experiments were conducted at different pressures (1.2, 2 and 3 bara) with a constant methane sweep flow at atmospheric pressure at the permeate side. Fig. 9 presents the effect of pressure on the performance of a mimic enzyme membrane and its comparison with its counterpart without the mimic enzyme.

The effect of CO_2 partial pressure on the CO_2/N_2 separation performance of the membrane was studied by operating the membrane at feed pressures from 1.2 to 3 bar under humidified conditions, as shown in Fig. 9. A decline in both CO_2 permeance and CO_2/N_2 selectivity was observed with increasing in feed pressure. This is a typical behavior of a facilitated transport membrane. CO_2 transport in mimic enzyme membrane is believed to take place by two parallel mechanisms: the diffusion of CO_2 molecules through the amorphous regions of the polymer network, and the diffusion of HCO_3^- ions produced by the CO_2 hydration catalyzed through the water phase in the PVA network. At 1.2 bara feed pressure, partial pressure of CO_2 in gas stream is 0.12 bar. At this partial pressure, the feed side CO_2 concentration is low, and CO_2 transport through membrane mainly in the form of HCO_3^- due to efficient CO_2 hydration. With an increase in the feed gas pressure and hence the CO_2 partial pressure, however, the CO_2 concentration increases. When it increase to a certain extent, water (the “carriers”) becomes not sufficient to ensure a full CO_2 hydration reaction. Therefore, the CO_2 molecule diffusion increases when a certain CO_2 partial pressure is reached, and HCO_3^- diffusion decreases, which results in a decline in CO_2/N_2 selectivity. Similar trends have often been reported in literature in facilitated

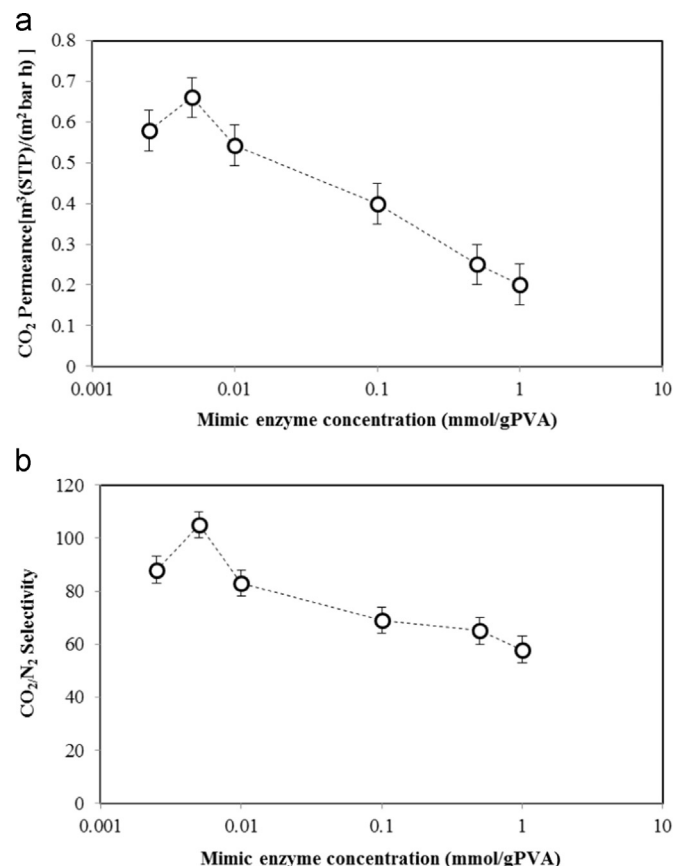


Fig. 8. Effect of mimic enzyme concentration in membrane on (a) CO_2 permeance and (b) CO_2/N_2 selectivity, at room temperature, 1.2 bara.

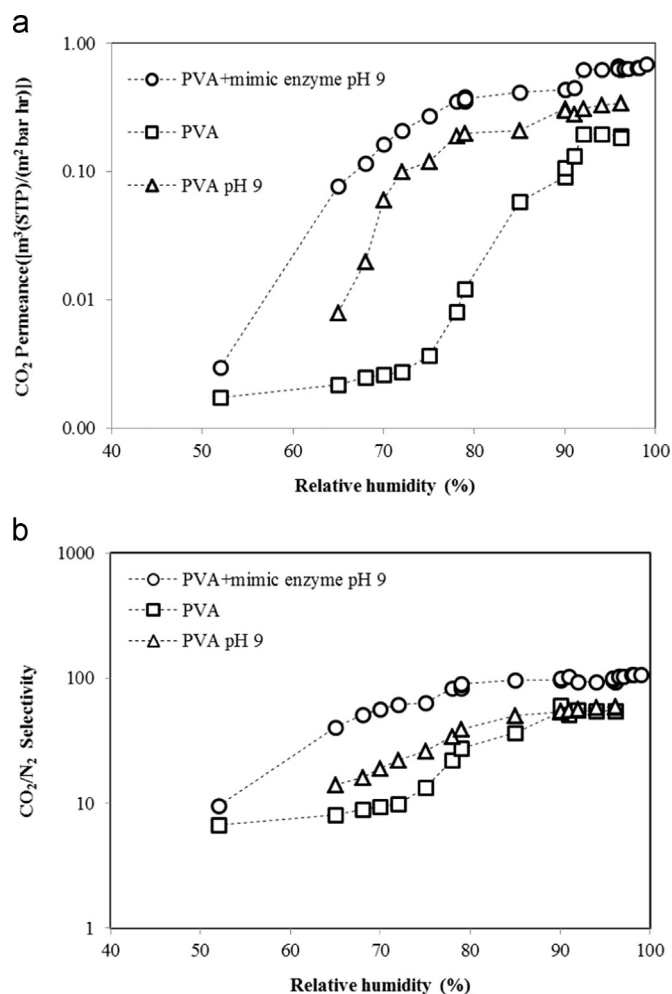


Fig. 10. Effect of humidity on performance of membrane with and without mimic enzyme on (a) CO₂ permeance and (b) CO₂/N₂ selectivity, at room temperature, 1.2 bara.

transport membranes.

Effect of relative humidity in feed gas on membrane performance was studied. PVA is a hydrophilic polymer and swells by absorbing moisture from a gas stream. Water in PVA helps to open up the amorphous domains of polymer for mass transfer. It is also necessary for the mimic enzyme to have aqueous environment to function well. Fig. 10 presents the CO₂/N₂ separation performance of membranes operating with feed gas under humidified conditions (relative humidity at 50–100%). In Fig. 10, both CO₂ permeance and CO₂/N₂ selectivity in all three membranes increase with the increase of relative humidity in the feed stream. All three membranes show significant increase in performance with gas humidity level of 80% or higher. However, at the same relative humidity, the membrane containing mimic enzyme have higher CO₂ permeance and CO₂/N₂ selectivity compared to those without mimic enzyme. Water in mimic enzyme based membrane swells polymer, which not only opens the polymer network and increases gas/ion diffusivity, but most importantly, also attaches to mimic enzyme as a temporary ligand to complete the hydration cycle. From Fig. 10 it is clear that relative humidity in feed gas has strong influence on the CO₂ separation performance, and the mimic enzyme based PVA membrane should be operated under humidified conditions to take the advantage of the catalytic function to CO₂ hydration and improve the CO₂/N₂ separation performance.

Dry polyvinyl alcohol is impermeable with regard to both CO₂ and N₂. Water swollen PVA membrane is more permeable as water

opens up the amorphous domains for mass transfer. With an increasing humidity level in gas stream, swelling degree of membrane increases and hence the membrane becomes more gas permeable. Most importantly, the presence of more water enhances the CO₂ hydration reaction for the CO₂ facilitated transport.

Fig. 10 shows that between relative humidity 50–70%, PVA membranes without pH adjustment has a much lower CO₂ permeance compared to the membrane prepared at pH 9 in casting solution. This suggests that the influence of relative humidity on the PVA membranes made of casting solutions at different pH levels is also different. This can be explained by the different swelling behaviors of the membranes shown in Fig. 6: with an increase in pH value in membrane casting solution, the swelling degree of the membrane increases.

4. Conclusions

A defect free composite membrane containing mimic enzyme in water swollen selective layer was developed. Compared to a PVA membrane, the mimic enzyme promoted PVA membrane shows much greater separation performance. The permeance of CO₂ in a mimic enzyme PVA membrane is 5 times greater as compared to that in a PVA membrane. The CO₂/N₂ selectivity is also doubled.

Mimic enzyme is a catalyst which hydrates CO₂ and promotes the formation of HCO₃[−]. Even a small quantity of mimic enzyme in a water swollen membrane could catalyze the hydration to a large extent so that CO₂ permeance increases from 0.18 to 0.69 m³(STP)/m² bar h. The pH value in the casting solution of membrane also affects the membrane separation performance. The dissociation constant (pKa) of the selected mimic enzyme Zn–cyclen is 7.9. Only mimic enzyme membrane with a pH value higher than the pKa of the mimic enzyme shows an appreciable separation performance. The optimal loading of the mimic enzyme in PVA was found to be 0.005 mmol/g and pH value of 9 in the casting solution. The factor that the mimic enzyme membranes tested at pH value lower than the pKa value did not show any facilitated transport effect indicates that although the mimic enzyme (Zn–cyclen) has abundant amine groups on its structure, these amine groups do not function as CO₂ facilitated transport carriers as in other amine-based facilitated transport membranes. In addition, the amount of mimic enzyme added was very small. With this amount the facilitated transport effect by the amino groups would not be so significant. In an earlier stage of this work, experiments were conducted with aqueous cyclen solutions (without the Zn²⁺ active site) to absorb and desorb CO₂. The results also showed that cyclen itself could not function as absorbent or facilitator for CO₂ capture.

PVA is a commercially available, low cost polymer with high tensile strength and excellent film forming properties. With the addition of a very small amount of mimic enzyme, the CO₂ separation permeance in a PVA membrane increases by many folds. Low cost, simple production procedure and high CO₂/N₂ separation performance are distinct advantages of this mimic enzyme based membrane. It can be a cost effective membrane for CO₂ capture with great potential for industrial scale applications, especially for CO₂ capture from post-combustion flue gas.

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