In Situ Layer-by-Layer Assembled Carbonic Anhydrase-Coated
Hollow Fiber Membrane Contactor for Rapid CO₂ Absorption

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Abstract:

The use of potassium carbonate as a solvent for the absorption of carbon dioxide is constrained by slow absorption kinetics, which hinders the overall rate of mass transfer. In this work, the reaction rate is promoted by the electrostatic adsorption of carbonic anhydrase (CA) onto the surface of both a porous polypropylene (PP) and a non-porous polydimethoxysilane (PDMS) hollow fiber membrane via layer-by-layer (LbL) assembly. The rate of CO$_2$ absorption into K$_2$CO$_3$ is increased approximately threefold when CA is adsorbed onto the PP membrane surface, while the absorption rate of the modified PDMS membrane was slightly lower, within 70 to 90% of the PP values. The results show that the ultrathin CA films are assembled mainly on the surface of the membranes and do not penetrate into the depth of the membrane pores. The CO$_2$ hydration is enhanced in all cases, and the wetting of the porous PP membranes is reduced significantly by the pore blockage induced by the LbL adsorption of the polyelectrolytes.

Key words: Carbonic anhydrase, hollow fiber membranes, membrane contactor
1) Introduction

Membrane gas absorption (MGA) has been investigated as an alternative to conventional packed towers which use solvent absorption for the capture of CO₂ from the flue gas streams produced by fossil fuel-fired power plants. This approach provides higher surface-to-volume ratios and thus a smaller equipment footprint [1]. These contactors also provide a better mass transfer efficiency in comparison to the absorption towers [2, 3]. The material requirements for the construction of membrane modules are also significantly less [4].

In a membrane-based gas-liquid contactor process, a hydrophobic membrane material acts as a barrier between the incoming flue gas and the absorption solvent [5]. This membrane prevents the solvent from entering the gas phase while allowing the gas to permeate through the membrane and be absorbed into the solvent. At the industrial scale, the solvents that are most commonly used for absorption are alkanolamines such as monoethanolamine (MEA) or diethanolamine (DEA) [6]. However, these alkanolamines are highly corrosive [6, 7] and are readily degraded in the presence of oxygen [8], so that their absorption capacity will decrease over time. Moreover, the thermodynamic stability of the carbamates also dictates that the desorption of CO₂ from the solvent for solvent reuse and CO₂ storage will require an extremely high energy penalty [9].

To reduce the energy penalty from the desorption process, alternative solvents such as potassium carbonate (K₂CO₃) may be used, as has been demonstrated in the case of the Benfield absorption process [10]. However, the absorption kinetics for K₂CO₃ are far slower than that of MEA or DEA [1, 11]. Increased CO₂ absorption kinetics within carbonate or bicarbonate solvents may be observed upon the addition of natural enzymes such as carbonic anhydrase (CA) into the solvent [12], as this enzyme is known to catalyze the conversion of CO₂ into HCO₃⁻ extremely rapidly [13].

CA has been shown to retain its activity upon covalent immobilization onto the surface of a membrane [14]. While such immobilization may provide good protein stability [15], it is a time consuming process that requires multiple reaction steps and makes use of toxic chemicals [14, 16]. In comparison, the electrostatic adsorption of enzymes onto membrane surfaces via the deposition of alternatively charged polyelectrolytes, a process referred to as layer-by-layer (LbL) technology, proceeds relatively rapidly, makes use of much less toxic substances and also makes use of small quantities of enzyme (10 to 1000 µg m⁻²) in film fabrication [17]. The mass production of enzymes from recombinant cell lines at
moderate cost [18] would then further aid in the development of immobilized enzyme hollow fiber membrane contactors for CO₂ capture, given that only relatively small quantities of free enzyme are required to improve the absorption rates of CO₂ into K₂CO₃ [19].

The immobilization of proteins onto flat sheet microporous membranes via LbL technology has been investigated previously [17, 20, 21]. However, these membranes have been used mainly for catalyzing reactions that occurred within a singular liquid phase, not in a biphasic gas-liquid absorption system. In a membrane-based gas-liquid absorption system, the key to maintaining an effective mass transfer rate lies in ensuring that the pores remain filled with gas rather than solvent. Wetted pores can contribute approximately 30% of the overall mass transfer resistance [22]. A degree of wetting as little as 5% can reduce the overall mass transfer rates by as much as 20% [23]. The ability of a membrane to withstand the breakthrough of a liquid through its pores is quantified by a parameter known as the liquid breakthrough pressure (LBP), which is the pressure that is required to force a liquid through the pores of the membrane. The Laplace-Young equation (Equation 1) relates the LBP of a membrane to the hydrophobicity and the pore size of the membrane [24]:

\[
LBP = \frac{4\gamma_{sl} \cos \theta}{d_p}
\]  

where \(\gamma_{sl}\) is the surface tension of the liquid against the membrane, \(\theta\) is the contact angle of the membrane and \(d_p\) is the maximum pore diameter of the membrane. \(\alpha\) is a pore characteristic value, where membranes with cylindrical pores have an \(\alpha\) value of 1 and \(0 < \alpha < 1\) if the pores are not cylindrical. For a membrane with a fixed pore size, it is evident that a reduced contact angle causes a reduction in the LBP, which therefore allows the solvent to penetrate into the membrane more easily.

The adsorption of polyelectrolytes such as polyallylamine hydrochloride (PAH) and polystyrene sulfonate (PSS) onto a porous ultrafiltration membrane surface has been shown to reduce the pore size of the membrane to that comparable to a nanofiltration membrane [25, 26]. Indeed, LbL film assembly has previously been used for converting ultrafiltration membranes into nanofiltration and forward osmosis membranes in both flat sheet [25] and hollow fiber configurations [27, 28]. The reduction in the overall pore size may be useful in reducing the effect of pore wetting on MGA operation. However, the increase in membrane hydrophilicity upon adsorption of these charged polyelectrolytes may provide a competing effect that reduces the LBP by reducing the contact angle of the membrane surface.

Our previous work has shown that the fabrication of CA-containing polyelectrolyte films via LbL assembly on a flat sheet polypropylene membrane was useful in increasing the
rate of CO₂ hydration into HCO₃⁻ and reducing pore wetting [21]. We found that enzyme immobilization did not affect the CA activity under these conditions. However, to the best of our knowledge, there have been no investigations of using LbL film assembly onto hollow fiber membranes for this purpose.

In this work, we focus on the assembly of ultrathin films incorporating CA onto the surface of microporous polypropylene (PP) or nonporous polydimethoxysilane (PDMS) hollow fiber membranes through the LbL assembly technique. We apply the films in situ, to the shell side surface, so that the CA resides at the greatest proximity to the gas-liquid interface of the absorption process. These modified membranes are then tested for their CO₂ separation capabilities. We show that the mass transfer coefficient approximately doubles even for a biologically inactive polyelectrolyte film, due to reductions in pore wetting. Upon the incorporation of CA into the film, the mass transfer coefficient increases further, for both the porous PP and the nonporous PDMS membranes.

2) Theory

The CO₂ flux, NCO₂, from the gas to the liquid side in a membrane contactor can be represented by:

\[ N_{CO_2} = K(C_G - C_G^*) \] (2)

where K is the overall mass transfer coefficient, C_G is the gas phase CO₂ concentration and C_G^* is the gas phase CO₂ concentration that is in equilibrium with the CO₂ concentration in the bulk liquid phase.

When the concentration of dissolved CO₂ in the liquid is small, C_G^* is small relative to C_G and can therefore be eliminated from Equation 2. The overall mass transfer coefficient can then be related directly to the feed gas pressure P based on the ideal gas law:

\[ K = \frac{N_{CO_2}RT}{P} \] (3)

where R is the gas constant and T is the absolute temperature.

The overall mass transfer coefficient K for the chemical absorption of CO₂ using a microporous membrane can then be described as a function of the liquid phase mass transfer coefficient k_L^o in the absence of any chemical reaction, the gas phase mass transfer coefficient k_G and the membrane mass transfer coefficient k_M:

\[ \frac{1}{K} = \frac{1}{k_G} + \frac{1}{k_M} + \frac{1}{mE k_L^o} \] (4)
where \( m \) and \( E \) are the Henry’s law constant and the enhancement factor contributed by the chemical reaction, respectively.

The value of \( E \) can be determined from the Hatta number (\( Ha \)) as per Equation 5. \( Ha \) relates the overall absorption rate to the physical absorption rate of \( CO_2 \) and is defined in Equation 6 for the absorption of \( CO_2 \) into \( K_2CO_3 \) [29]:

\[
E = \frac{Ha}{\tanh (Ha)} \tag{5}
\]

\[
Ha = \sqrt{\frac{kD_L K_e \left( 1 - x_0 \right)}{2 k_L^0 x_0}} \tag{6}
\]

where \( k \) is the second order chemical reaction rate constant between \( CO_2 \) and hydroxyl ions, \( D_L \) is the diffusivity of \( CO_2 \) in the liquid solvent, \( K_e \) is the equilibrium constant and \( x_0 \) is the solvent loading of \( CO_2 \), which is the ratio of \( HCO_3^- \) ions to \( K^+ \) ions in solution. The value of \( K_e \) as a function of temperature is reported by Savage et al. [29].

The determination of \( k \) for \( CO_2 \) in \( K_2CO_3 \) solutions has been found to follow a correlation that is dependent on temperature (\( T \)) and ionic strength (\( I \)), as shown in Equation 7 [30]:

\[
\log k = 13.635 - \frac{2895}{T} + 0.08I \tag{7}
\]

The Henry’s Law constant that is used in Equation 4, \( m \), is dimensionless and is defined by Equation 8:

\[
m = \frac{C_{Li}}{C_{Gi}} \tag{8}
\]

where \( C_{Gi} \) and \( C_{Li} \) are the gas and liquid concentrations at the interface.

Astarita et al. [30] developed a correlation to determine \( m \) at various temperatures and \( K_2CO_3 \) concentrations of up to 1.8 M (Equation 9):

\[
\log \left( \frac{m_{CO_2, K_2CO_3}}{m_{CO_2, H_2O}} \right) = 0.025n \tag{9}
\]

where \( n \) is the total concentration of carbonate and bicarbonate ions present in solution and the value of \( m \) for \( CO_2 \) in water is approximately 0.83 [31]. Knuutila et al. [32] also presented similar results for higher \( K_2CO_3 \) concentrations of up to 30 wt% (approximately 2.8 M).

For a pure \( CO_2 \) feed, there is no gas phase resistance and so the overall mass transfer coefficient expression can be simplified further to be solely dependent on \( k_L^0 \) and \( k_M \), assuming that there is no liquid in the membrane pores:
\[
\frac{1}{K} \approx \frac{1}{mk_L^\circ} + \frac{1}{k_M}
\]  

The value of \( k_L^\circ \) can be determined from shell-side correlations relating the Sherwood number (Sh) to the Reynolds number (Re) and the Schmidt number (Sc). In this study, the correlation developed by Costello et al. [33] for Re < 350 was used (Equations 11 – 13).

\[
Sh = \frac{k_L^\circ D_L}{d_H} = (0.53 - 0.58\varphi)Re^{0.53}Sc^{0.33}
\]  

\[
Re = \frac{\rho v d_H}{\eta}
\]  

\[
Sc = \frac{\eta}{\rho D_L}
\]

where \( d_H \) is the hydraulic diameter of the membrane module, \( D_L \) is the diffusivity of the gas in the liquid, \( \varphi \) is the packing density, \( \eta \) is the liquid dynamic viscosity, \( v \) is the liquid flow velocity and \( \rho \) is the liquid density. The value of \( d_H \) can be calculated as per Equation 13 [34]:

\[
d_H = \frac{4 \times \text{cross-sectional area of flow}}{\text{total fibre circumference}} = \frac{d_{cin}^2 - nd_{out}^2}{nd_{out}}
\]

For partially wetted pores, \( k_M \) can be deconstructed into the contribution from the wetted pores and the contribution from the non-wetted pores [1]:

\[
\frac{1}{k_M} = \frac{\delta_w \tau}{mED_L \varepsilon} + \frac{\delta_{nw} \tau}{D_G \varepsilon}
\]

where \( \delta_w \) and \( \delta_{nw} \) refer to the length of wetted and non-wetted pores, respectively, \( D_G \) is the diffusivity of CO\(_2\) in the gas phase, respectively, \( \tau \) is the tortuosity of the membrane and \( \varepsilon \) is the porosity of the membrane. However, as reaction enhancement now occurs within the wetted segment of the pores, Equation 10 must be modified to Equation 16:

\[
\frac{1}{K} = \frac{1}{k_M} + \frac{1}{mk_L^\circ}
\]

The degree of pore wetting can then be taken to be [1]:

\[
Pore\ \text{wetting} = \frac{\delta_w}{\delta_w + \delta_{nw}}
\]
3) **Materials and Methods**

3.1 **Materials**

Polyethyleneimine (PEI, 25 kDa), polystyrene sulfonate (PSS, 70 kDa) and polyallylamine hydrochloride (PAH, 10 kDa) were obtained from Sigma-Aldrich (Castle Hill, NSW, Australia). Hydrochloric acid (HCl, 37%) and sulfuric acid (H₂SO₄, 98%) were purchased from Scharlau (Gillman, SA, Australia). Trishydroxymethylaminomethane (Tris) was obtained from ChemSupply (Gillman, SA, Australia). All chemicals were used as purchased unless otherwise stated. Ultrapure water was obtained from a Milli-Q purification system (Merck Millipore, Kilsyth, VIC, Australia) with a resistivity greater than 18.2 MΩ cm, while purified water was obtained from an Elix purification system (Merck Millipore, Kilsyth, VIC, Australia) with a resistivity greater than 5.0 MΩ cm. Tris buffer (50 mM, pH 7.2) was prepared in ultrapure water and the pH was adjusted by dropwise addition of hydrochloric acid (1 M). The polyelectrolyte (PEI, PSS, and PAH) solutions were all prepared in Tris buffer at a concentration of 1 mg mL⁻¹.

The CA that was used was a thermostable microbial CA (NCA) produced by Novozymes A/S (Bagsværd, Denmark) via a fermentation process. The enzyme solution was stored as received at -4°C and only thawed to room temperature when required for use. This solution was then diluted to 2% (v/v) with Tris buffer (pH 7.2) prior to LbL adsorption.

Potassium carbonate (K₂CO₃, ≥ 99%) was obtained from Thasco Chemical Co. Ltd (Bangkok, Thailand) and dissolved in tap water to prepare a 30 wt% solution. Table 1 indicates the relevant parameters for this solvent at 25°C, 35°C and 50°C. In some experiments, 0.05 or 0.2% NCA (v/v) was dissolved within the 30 wt% K₂CO₃ solvent.

**Table 1.** Operating Parameters for the Potassium Carbonate (30 wt%) Solvent

<table>
<thead>
<tr>
<th>Solvent Parameters</th>
<th>25°C</th>
<th>35°C</th>
<th>50°C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density (kg m⁻³)</td>
<td>1287</td>
<td>1282</td>
<td>1267</td>
</tr>
<tr>
<td>CO₂ Diffusivity (m² s⁻¹)</td>
<td>9.2 × 10⁻¹⁰</td>
<td>1.19 × 10⁻⁹</td>
<td>1.57 × 10⁻⁹</td>
</tr>
<tr>
<td>Viscosity (mPa s)</td>
<td>2.26</td>
<td>1.78</td>
<td>1.37</td>
</tr>
</tbody>
</table>

Porous PP hollow fiber membranes were obtained from Memtec Australia and nonporous polysulfone (PS) hollow fiber membranes that were coated with a 0.5 μm layer of
polydimethoxysilane (PDMS) were supplied by Airrane Co. Ltd. (Daejeon, Korea). The parameters for these hollow fibers are shown in Table 2.

Table 2. Membrane Module Operating Parameters

<table>
<thead>
<tr>
<th>Membrane Parameter</th>
<th>PP</th>
<th>PDMS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore Diameter (μm)</td>
<td>0.2</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Fiber Internal Diameter $d_{in}$ (mm)</td>
<td>0.24$^a$</td>
<td>0.30$^a$</td>
</tr>
<tr>
<td>Fiber External Diameter $d_{out}$ (mm)</td>
<td>0.52$^a$</td>
<td>0.45$^a$</td>
</tr>
<tr>
<td>Module Hydraulic Diameter $d_H$ (mm)</td>
<td>0.59</td>
<td>0.81</td>
</tr>
<tr>
<td>Porosity</td>
<td>0.65 [36]</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>2.5 [36]</td>
<td>Nonporous</td>
</tr>
<tr>
<td>Packing Density (%)</td>
<td>40</td>
<td>30</td>
</tr>
</tbody>
</table>

$^a$These values were obtained from cross-sectional scanning electron microscopy (SEM) images.

These membranes were packed into a membrane module housing (internal diameter 0.37 cm) with an effective length of 20.5 cm in bundles of 20. The ends of the module housing were sealed with an epoxy adhesive (Selleys Araldite Super Strength Epoxy Adhesive, Selleys Pty Ltd, NSW, Australia) and left to dry for at least 24 hours before conducting any experiments.

3.2 Layer-by-Layer Electrostatic Adsorption on Hollow Fiber Membrane Contactors

For some modules, polyelectrolyte solutions were pumped through the shell side of the hollow fiber membrane modules using a peristaltic pump (pump through mode) at an ambient air temperature of 20°C. The solutions were continuously circulated through the membrane module for a specified time, followed by a wash step with ultrapure water for 10 minutes before the next polyelectrolyte solution was pumped through the module at the same flow rate and for the same time. A film was fabricated onto the hollow fibers from the adsorbed polyelectrolytes in the form of a PEI/PSS/PAH/[PSS/PAH/NCA]$_x$ film, where $x$ refers to the number of [PSS/PAH/NCA] trilayers deposited for film fabrication. The flow rate of the polyelectrolyte solutions and the contact time with the membrane were varied for optimization purposes. Two membrane modules were prepared for each condition to allow reproducibility to be determined. Other membrane modules were also prepared with adsorbed PEI/[PSS/PAH]$_2$ or PEI/[PSS/PAH]$_4$ polyelectrolyte films in a similar manner but without any NCA as control systems.
Other hollow fiber modules were prepared by pumping polyelectrolyte solution into the module chamber until the chamber was filled. The solution was then allowed to remain in contact with the hollow fibers for 5 min (static mode) before washing with Milli-Q water at 20 mL/min for 10 min.

Other PP modules were also prepared by forcing polyelectrolyte solution across the membrane into the lumen side (permeation mode). This was achieved by using a needle valve to restrict the flow of the polyelectrolyte solution out of the shell side exit, which increased the transmembrane pressure to a point where the solution could penetrate the membrane structure and cause complete wetting.

Most modules were used directly for contactor experiments after the final wash step. Where indicated, some modules were dried before use by passing nitrogen gas through the lumen side of the hollow fibers at a flow rate of 1 L/min for 2 h.

### 3.3 Operation of Hollow Fiber Membrane Contactors

A pilot plant gas absorption unit described previously [1] was utilized for these experiments. Pure gaseous CO₂ (99%, Coregas, Thomastown, VIC, Australia) at 1.0-1.5 bar was used as feed to the lumen side of the hollow fibers, with the feed gas flowrate measured by a gas rotameter from Kytola (Muurame, Finland) and the retentate flowrate measured by a gas meter (Ampy Email metering Model 750). The potassium carbonate solvent was pumped through the shell side of the fibers (Micropump with an Ismatec controller) at a pressure differential of 0.1 bar above the gas pressure to prevent bubble formation within the solvent for the microporous membranes. The flowrate was measured by another Kytola rotameter and controlled by the pump speed. The solvent flowrate was maintained for 1 h to ensure that steady state was reached before measurements were taken.

### 3.4 Analysis

Samples of spent solvent exiting the contactor were analyzed for their K₂CO₃ and KHCO₃ concentrations via titration with a Metrohm–Titrando 809 (Switzerland) auto-titrator coupled with a pH probe. Approximately 5 mL of solvent was diluted with 60 mL of RO water using a set volume liquid dispenser (Eppendorf, Varispencer, Germany). This mixture was then auto-titrated against a 0.4 M sulfuric acid solution to determine the HCO₃⁻ and the H₂CO₃ equivalence points. The bicarbonate concentration was then used to determine the CO₂ flux \( N_{CO2} \) through the hollow fiber membranes, based on the CO₂-K₂CO₃ reaction stoichiometry (Equation 18):
Segments of the hollow fiber membranes were dried under a nitrogen stream, sputter-coated with gold and analyzed using a Phillips XL30 FEG field emission scanning electron microscope (FESEM) at a voltage of 2.0 kV to determine the surface morphology. Wetted hollow fiber samples were immersed in liquid nitrogen for 5 min and then fractured to analyze the cross-sections of the membranes.

4) Results and Discussion

4.1 SEM Microscopy of the Hollow Fiber Membranes

In our previous work, we showed that it was possible to obtain uniform coverage of a flat sheet PP membrane with a PEI/PSS/PAH/[PSS/PAH/NCA]₃ coating applied using a simple paintbrush [21]. In this work, SEM images of the PDMS membrane before and after adsorption (Figures 1a and 1b) indicate that the surface of the PDMS layer is evenly coated with the polyelectrolyte solution, probably because it was already smooth and non-porous prior to adsorption. However, the coating of the PP hollow fiber membranes in situ was less successful (Figures 1c-1f), with some defects in the film clearly evident. These defects may reflect the greater pore size of these PP membranes (0.2 µm versus 0.1 µm) or the more indirect coating method that was utilized.

A close inspection of the SEM images from the PP membranes coated in a pump through mode indicated that better coverage was achieved through longer adsorption times and lower adsorption flowrates. However, the three approaches to coating in general (pump through mode, static mode, permeation mode) appeared to give comparable coatings, with some evidence of a slightly more complete coating with the permeation mode (Figure 1e).

Figure 2 shows that there is little difference in the cross-sectional morphology of the untreated PP or PDMS membranes (Figures 2a and 2d) in comparison with membranes that have been coated with multiple layers of polyelectrolytes (Figures 2b, 2c and 2e). There is no evidence of polyelectrolyte permeation into the bulk of the hollow fiber membranes with all the enzyme activity concentrated at the membrane surface. There is no evidence of a thick dense polyelectrolyte layer building up on the surface of the membrane, which shows that the films are extremely thin and will not contribute significantly to an increased membrane mass transfer resistance (Figures 2b and 2e). The porosity of the substructure also appears to be relatively unchanged, providing little resistance to CO₂ mass transfer. The cross section image of the PP membrane in permeate mode shows a polyelectrolyte layer of less than 1 µm
thickness (Figure 2c), which is consistent with our previous observations of polyelectrolyte film thickness when coated onto planar membrane coupons [21].

4.2 The Influence of Polyelectrolyte Layer Buildup onto PP Fibers on the Absorption of CO₂

The overall mass transfer coefficients for CO₂ absorption through PP hollow fibers into 30 wt% K₂CO₃ can be calculated from Equation 3. For an unmodified contactor, this mass transfer coefficient does not vary significantly with the Reynolds number, with a value of approximately 1.7 × 10⁻⁵ m s⁻¹ (Figure 3). The lack of dependence on Reynolds number suggests that the liquid phase is not rate controlling, but rather, membrane wetting contributes significantly to the membrane mass transfer coefficient.

The addition of pure polyelectrolyte films containing no enzyme in pump through mode leads to a significant increase in the mass transfer rate (Figure 3). The addition of four trilayers (PEI/[PSS/PAH]₄) is more effective than the additions of two trilayers (PEI/[PSS/PAH]₂), with the mass transfer coefficient approximately doubling in this case to between 2 and 4 × 10⁻⁵ m s⁻¹. This increase in the mass transfer coefficient suggests that the successive addition of LbL films is restricting membrane wetting by reducing the pore size at the surface. Even though the adsorption of the film onto the membrane surface causes the membrane surface to become more hydrophilic [21], the coating is able to reduce liquid penetration into the pores. The increased dependence of the mass transfer coefficient on the Reynolds number also suggests that the role of membrane resistance is declining relative to the liquid phase resistance.

This reduction in pore wetting can be confirmed by application of Equations 4 to 17. For PP fibers that were not coated, the reaction enhancement factor is calculated to be 1.06 (Equations 5-7), which is in good agreement with results published elsewhere [1]. With this enhancement factor known, the pore wetting can be estimated as 4% for these unmodified PP fibers (Equations 11-17). Upon the application of the PEI/[PSS/PAH]₂ film, the pore wetting reduces to 2.3%, while the addition of four trilayers (PEI/[PSS/PAH]₄) reduces it further to 0.5% (see Table 4).

However, the adsorption of a single trilayer of NCA within these polyelectrolyte films increases the mass transfer coefficient to a much greater extent throughout the range of solvent flow rates (Reynolds numbers) that were investigated, as shown in Figure 3. The adsorption of more than one trilayer onto the membrane causes a further minor increase in the overall mass transfer coefficient. This increased mass transfer coefficient reflects both a higher NCA loading and an increase in the surface coverage of the membrane.
The pore wetting factors determined in the absence of any enzyme, can now be used to calculate the enhancement factors for these enzyme containing systems, again using Equations 11 to 17 (Table 4). There is a clear increase in the enhancement factor when the number of NCA deposition cycles is increased from 1.9 with one trilayer to 6.9 with three trilayers containing NCA (Table 4). This increased enhancement factor confirms that the addition of more enzyme layers is both increasing reaction rates as well as reducing pore wetting.

Figure 4 indicates that there is also a clear increase in the mass transfer coefficient when the polyelectrolyte solutions are pumped through the module for longer periods. There is also a slight increase in the overall mass transfer coefficient when the flow rate that is used for adsorption is lower, which can be attributed to a reduced shear rate that is experienced by the polyelectrolytes (Figure 5). A reduced liquid shear rate on the membrane surface allows for better dynamic adsorption of the polyelectrolytes, as is evidenced in research regarding the adsorption of foulants onto a membrane surface [37]. A static adsorption, where there was no flow during the 5 minute adsorption period and thus no shear, provided the greatest increase in the mass transfer coefficient (Figure 5). Similar increases in the enhancement factor are also observed (Table 4).
**Table 4.** Enhancement factors and wettability of various membrane modules at 25°C and a Reynolds Number of 35

<table>
<thead>
<tr>
<th>Membrane Coating</th>
<th>Adsorption Mode</th>
<th>Enhancement Factor</th>
<th>Pore Wetting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>None</td>
<td>1.06</td>
<td>4</td>
</tr>
<tr>
<td>PDMS</td>
<td>None</td>
<td>1.06</td>
<td>-</td>
</tr>
<tr>
<td>PP</td>
<td>0.2 vol% NCA in solution</td>
<td>None</td>
<td>12</td>
</tr>
<tr>
<td>PP</td>
<td>0.05 vol% NCA in solution</td>
<td>None</td>
<td>8.4</td>
</tr>
<tr>
<td>PP</td>
<td>PEI/[PSS/PAH]$_2$ (no NCA)</td>
<td>Pump through</td>
<td>1.06</td>
</tr>
<tr>
<td>PP</td>
<td>PEI/[PSS/PAH]/[PSS/PAH/NCA]$_x$ film</td>
<td>Pump through</td>
<td>1.06</td>
</tr>
</tbody>
</table>

**PEI/PSS/PAH/[PSS/PAH/NCA]$_x$ film**

<table>
<thead>
<tr>
<th>Polyelectrolyte flow rate (mL/min)</th>
<th>Adsorption time per layer (min)</th>
<th>NCA deposition cycles (x)</th>
<th>Adsorption Mode</th>
<th>Enhancement Factor</th>
<th>Pore Wetting (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PP</td>
<td>120</td>
<td>5</td>
<td>1</td>
<td>Pump through</td>
<td>1.9</td>
</tr>
<tr>
<td>PP</td>
<td>120</td>
<td>5</td>
<td>2</td>
<td>Pump through</td>
<td>4.7</td>
</tr>
<tr>
<td>PP</td>
<td>120</td>
<td>5</td>
<td>3</td>
<td>Pump through</td>
<td>6.9</td>
</tr>
<tr>
<td>PP</td>
<td>50</td>
<td>5</td>
<td>2</td>
<td>Pump through</td>
<td>4.9</td>
</tr>
<tr>
<td>PP</td>
<td>20</td>
<td>5</td>
<td>2</td>
<td>Pump through</td>
<td>4.9</td>
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<tr>
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<td>Static</td>
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4.3 Investigating the Effects of Membrane Drying on the Mass Transfer Performance

It can be observed that the fibers dried with N$_2$ after static adsorption prior to conducting the solvent absorption experiments behaved in a comparable manner to those that had not been dried (Figure 6). These comparable mass transfer coefficients indicate that the polyelectrolyte adsorption process did not itself wet the membrane pores and also that the NCA activity is only slightly reduced after this drying process. In contrast, when the polyelectrolyte solutions are forced to permeate through the membrane pores, the overall mass transfer coefficients fall to 59 ± 3% of the static mode values, even after drying with N$_2$.

The lower mass transfer coefficients arising from coating in permeation mode could arise because a thicker film is formed (Figure 2c); because the film itself blocks some of the pores; or because the passage of the polyelectrolyte solution through the pores renders them
more hydrophilic and hence more susceptible to wetting even after drying with N\textsubscript{2}. The fabrication of polyelectrolyte films onto hollow fiber membranes in a similar permeation mode was reported by Menne \textit{et al.} [28] to lead to a more uniform film with reduced pore size relative to the pump through mode, consistent with the present results. In the case of the membrane contactors that were investigated in this study, the fibers that were coated in permeation mode were still found to provide higher mass transfer rates than the unmodified membrane (Figure 6) because of adsorbed NCA providing an enhanced chemical reaction rate.

4.4 A Comparison of the Free Enzyme with the Immobilized Enzyme

The performance of a PP membrane contactor where the fibers had been coated with two CA tri layers was also compared with the use of free CA in the potassium carbonate solvent (Figure 7). Two concentrations of free CA were evaluated, 0.05% v/v and 0.2% v/v, corresponding to a total enzyme mass within the module at any time of 0.1 mg and 0.4 mg, which corresponds to enzyme concentrations of 75 mg/L or 300 mg/L in the module. The quantity of CA immobilized via static adsorption in 2 trilayers within the hollow fiber module can also be estimated to be approximately 0.1 mg, based on the activity and adsorption data provided in our previous work [21]. It can be observed that the overall mass transfer coefficient is approximately the same for the two cases where 0.1 mg of enzyme was used whether it was free or immobilized.

However, the module with free CA also suffers from greater pore wetting as discussed above. The enhancement factor is actually greater for the free CA case, as it needs to counteract this increase in pore wetting to achieve the same mass transfer rate. Indeed, the enhancement factor for the 0.05% v/v solvent is calculated as 8.4, somewhat larger than that for the immobilized case of 5.3 (Table 4 and Figure 8). While possibly within the range of experimental error, this may suggest a slight loss in enzyme activity upon immobilization, although we observed no such loss in our previous work using planar membrane surfaces [21]. As shown in Figure 8, the enhancement factor increases with the enzyme loading but then plateaus at higher loadings for the free enzyme case. Similar limitations have been observed in earlier work by Thee \textit{et al.} [19], where high enzyme dosages of 9.1 \textmu M (approximately 270 mg/L) resulted in enzyme flocculation within the solvent and rendered the enzyme less effective. The enhancement factor with an unmodified PP membrane in the presence of free NCA (0.2% v/v) was the greatest recorded at 12.
4.5 A Comparison Between the PP and the PDMS Membrane Performance

The overall mass transfer coefficient of the unmodified PDMS membrane is comparable to that of the unmodified PP membrane, which implies that the impact of the dense non-porous PDMS layer is comparable to the impact that is provided by the membrane wetting in the PP system. This result is consistent with that reported by Wang et al. [23], who observed that a degree of wetting as little as 5% could reduce the overall mass transfer rates by 20%. Adding the pure PEI/[PSS/PAH]₄ polyelectrolyte film to the PP membrane reduces this wetting as described above, so that this system outperforms the PDMS membrane in the absence of enzyme. Under these circumstances, the resistance of the dense non-porous PDMS layer is greater than that of an applied polyelectrolyte film. Differences in the porous membrane support structure may also play a minor role in differentiating the performance of these two membrane systems.

For both the porous PP and the PDMS membrane contactors, the mass transfer coefficient increases with an increased absorption temperature as reported elsewhere [1, 38] (Figure 9). The mass transfer coefficient is observed to be higher for the CA-coated porous PP fibers than the CA-coated PDMS fibers at all temperatures. Furthermore, the dependence upon the Reynolds number is less for the PDMS fibers than it is for the PP fibers. These results reflect the fact that the non-porous PDMS layer adds an additional resistance that does not change with the Reynolds number [39].

However, these experiments were conducted over a short period of time (approximately 6 hours). The PP membrane is likely to become further wetted over a longer period of time. This wetting will cause the mass transfer coefficient for this module to decrease because of an increased membrane mass transfer resistance. It is thus quite likely that the PP module will end up performing less efficiently than the PDMS membrane. Such behavior has been shown in long-term experiments conducted by Chabanon et al. [40], who compared the performance of PP and PDMS membrane contactors over a period of 50 days. However, the overall mass transfer coefficients for this PDMS membrane are still much greater than the mass transfer coefficients exhibited by the unmodified membranes.

In contrast with the PP membranes, the PDMS membranes have a dense nonporous PDMS layer on the membrane surface and thus will not experience any wetting. In this case, the best estimate of the membrane mass transfer coefficient can be estimated for the known carbon dioxide permeability of PDMS in the presence of water at 4500 Barrer [41]. This leads to a membrane mass transfer coefficient of $7.5 \times 10^{-3}$ m s$^{-1}$ for a PDMS thickness of 0.5
µm. The resulting reaction enhancement is comparable to that achieved with the PP system (Table 4).

5) Conclusions

The coating of a polyelectrolyte film (with or without NCA) onto microporous PP membranes in a static or pump through mode results in a reduction in pore wetting even though the membrane surface has been made more hydrophilic. The adsorption of the film occurs mainly on the membrane surface and does not result in any significant internal pore blockage. The reduction in pore wetting is beneficial in increasing mass transfer rates. The inclusion of CA within the film further promotes the absorption of CO₂ for both porous PP and dense PDMS hollow fiber membranes, leading to a substantial increase in the reaction enhancement factor. Adsorption was found to be slightly more effective at lower adsorption flow rates and higher adsorption times, and NCA surface coverage was also found to be more effective with the adsorption of more polyelectrolyte layers. The overall mass transfer coefficient was found to be similar to that observed when an equivalent amount of free NCA was used in solution. However, after accounting for pore wetting, this suggested that immobilization had indeed caused a slight loss in enzyme activity. While the performance of the coated PP fibers was slightly better than that of the equivalent PDMS fibers, the mass transfer coefficient exhibited by the porous PP membranes will experience a decline over time because of longer term membrane pore wetting. From this perspective, the use of the non-porous PDMS system is likely to be the better option over long time frames.

The surface coverage of the film on the PP membrane surface was not completely uniform. The surface coverage appears to be better when the polyelectrolyte solution is forced to permeate through the membrane pores, which is in agreement with results that were reported elsewhere [28]. However, this latter permeation technique results in a reduced CO₂ mass transfer coefficient, which could arise either from pore blockage or because the resulting pore structure is more hydrophilic and hence more prone to membrane wetting.

Importantly, the film is applied in situ to fibers that have already been assembled within a membrane module, which allows the coating process to be readily and economically scaled up to a commercial level. This adsorption approach also allows for the re-application of fresh films over time during the life of the contactor. Further, the retention of the NCA as an immobilized film within the absorption contactor, avoids transfer into the desorption unit.
The desorption unit is typically operated at 120-140°C [8], which would be highly detrimental to the enzymatic activity.

The experiments that have been conducted in this work are short term studies (less than 1 day) that do not factor into account any enzyme deactivation kinetics, which will reduce the reaction enhancement over a longer period of time. The presence of toxic impurities such as sulfur dioxide (SO₂) and nitrogen dioxide (NO₂) in flue gases may further inhibit the enzyme activity [43]. These issues will be addressed in our ongoing work.
### List of Symbols

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<tr>
<th>Term</th>
<th>Symbolizes</th>
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Acknowledgements

The work was supported by the Australian Research Council Centre of Excellence in Convergent Bio-Nano Science and Technology (Project number CE140100036) and the Particulate Fluids Processing Centre (PFPC), a Special Research Centre of the Australian Research Council. Novozymes A/S kindly supplied the enzyme, NCA. These sources of support are gratefully acknowledged.

6) References


Figure Captions:

**Figure 1.** SEM images of hollow fiber membrane surfaces (a) unmodified PDMS, (b) PDMS after static LbL adsorption of a PEI/PSS/PAH/[PSS/PAH/NCA]_2 film, (c) unmodified PP, (d) PP after static LbL adsorption of a PEI/PSS/PAH/[PSS/PAH/NCA]_2 film, (e) PP after adsorption of a PEI/PSS/PAH/[PSS/PAH/NCA]_2 film in permeation mode, (f) PP with two NCA trilayers applied in pump through mode (pump flow rate 20 mL/min, adsorption time 5 min).

**Figure 2.** A cross section of PP hollow fiber membranes (a) before LbL treatment, (b) after LbL treatment in static mode, (c) after LbL treatment in permeation mode and PDMS hollow fiber membranes (d) before LbL treatment and (e) after LbL treatment. Scale bars = 2 µm.

**Figure 3.** Overall mass transfer coefficients as a function of the shell side Reynolds number during gas absorption at 25°C. Data is shown for an unmodified PP membrane and upon the adsorption of either a pure polyelectrolyte film (PEI/[PSS/PAH]_2 or PEI/[PSS/PAH]_4) or an enzyme film (PEI/PSS/PAH/[PSS/PAH/NCA]_x where x = 1, 2 or 3) in pump through mode. Adsorption flow rate = 120 mL min^{-1}, adsorption time = 5 min.

**Figure 4.** Overall mass transfer coefficients as a function of the shell side Reynolds number during gas absorption at 25°C; after the fabrication of a pure polyelectrolyte film(PEI/[PSS/PAH]_4) or an enzyme film (PEI/PSS/PAH/[PSS/PAH/NCA]_2) on a PP membrane contactor in pump through mode. The pump flow rate is 20 mL/min, while the adsorption time is varied as shown.

**Figure 5.** Overall mass transfer coefficients as a function of the shell side Reynolds number during gas absorption at 25°C; after the fabrication of a pure polyelectrolyte film(PEI/[PSS/PAH]_4) or an enzyme film (PEI/PSS/PAH/[PSS/PAH/NCA]_2) on a PP membrane contactor. The adsorption time is 5 minutes, while the pump circulation flowrate is varied from zero (static mode) to between 20 and 120 mL min^{-1} (pump through mode).

**Figure 6.** Overall mass transfer coefficients as a function of the shell side Reynolds number during gas absorption at 25°C after the fabrication of PEI/PSS/PAH/[PSS/PAH/NCA]_2 films
onto PP membranes, using different techniques. An unmodified PP module is included as a comparison.

**Figure 7.** Overall mass transfer coefficients as a function of the shell side Reynolds number during gas absorption at 25°C for (i) an unmodified PP contactor (ii) an unmodified PP contactor with the addition of 0.05 or 0.2 vol% free NCA and (iii) a PP contactor coated with a PEI/PSS/PAH/[PSS/PAH/NCA]₂ film in static mode with an adsorption time of 5 min per layer.

**Figure 8.** The influence of the mass of immobilized or free enzyme on the enhancement factor of the CO₂ hydration reaction. The lines that are drawn are solely for illustration purposes and may not reflect the enhancement factor trends.

**Figure 9.** Influence of temperature on the absorption of CO₂ into K₂CO₃ as a function of the solvent Reynolds number. The data shown is for PEI/PSS/PAH/[PSS/PAH/NCA]₂ films coated onto PP or PDMS hollow fibers in static mode with an adsorption time of 5 min per layer. Mass transfer data for the unmodified hollow fibers at 25°C is shown as a baseline scenario.
Figure 1
Figure 3

Overall Mass Transfer Coefficient ($\times 10^4$ m s$^{-1}$)

- ▲ 3 Trilayers NCA
- ◊ 2 Trilayers NCA
- ■ 1 Trilayer NCA
- × PEI/[PSS/PAH]$_4$ Film
- ○ PEI/[PSS/PAH]$_2$ Film
- ● Unmodified PP

Re
Figure 4

Overall Mass Transfer Coefficient ($\times 10^4$ m s$^{-1}$)

- ▲ 30 Minutes
- □ 15 Minutes
- ◇ 5 Minutes
- × PEI/[PSS/PAH]$_4$ Film

Re

0 20 40 60
Figure 5
Figure 6

Overall Mass Transfer Coefficient ($\times 10^4$ m s$^{-1}$)

- Static Adsorption
- Static Adsorption with Drying
- Permeation Mode with Drying
- Unmodified PP
Figure 7

Overall Mass Transfer Coefficient ($\times 10^4 \text{ m s}^{-1}$)

- Unmodified PP with 0.2% CA
- Unmodified PP with 0.05% CA
- Static Adsorption
- Unmodified PP Without CA

Re

0 20 40 60
Figure 8

A graph showing the relationship between enhancement factor and mass of enzyme in the contactor. The graph compares immobilized enzyme and free enzyme. The enhancement factor increases as the mass of enzyme in the contactor increases.
Figure 9
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