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**NANYANG
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UNIVERSITY**

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**DEVELOPMENT OF NOVEL COMPOSITE HOLLOW
FIBER MEMBRANES FOR CO₂ REMOVAL FROM BIOGAS
USING MEMBRANE CONTACTOR**

XU YILIN

**Interdisciplinary Graduate School
Nanyang Environment and Water Research Institute
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A thesis submitted to the Nanyang Technological University in partial
fulfilment of the requirement for the degree of
Doctor of Philosophy

2018

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research, is free of plagiarised materials, and has not been submitted for a higher degree to any other University or Institution.

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Supervisor Declaration Statement

I have reviewed the content and presentation style of this thesis and declare it is free of plagiarism and of sufficient grammatical clarity to be examined. To the best of my knowledge, the research and writing are those of the candidate except as acknowledged in the Author Attribution Statement. I confirm that the investigations were conducted in accord with the ethics policies and integrity standards of Nanyang Technological University and that the research data are presented honestly and without prejudice.

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Prof Wang Rong

Authorship Attribution Statement

This thesis contains material from two papers published in the following peer-reviewed journals where I was the first author.

Chapter 4 is published as Y. Xu, Y. Lin, M. Lee, C. Malde, and R. Wang. Development of low mass-transfer-resistance fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membrane used for biogas upgrading in gas-liquid membrane contactor, *Journal of Membrane Science*, **552**, 253-264 (2018). DOI: 10.1016/j.memsci.2018.02.016.

The contributions of the co-authors are as follows:

- Prof Wang provided the initial project direction, provided guidance in the experimental design, provided supports during the whole work, and revised and edited the manuscript.
- I prepared the manuscript drafts together with Dr Lin. And Dr Lin was a co-first author in this paper.
- I co-designed the experiments together with Dr Lin and performed all the laboratory work at the Singapore Membrane Technology Centre.
- Preparation of composite hollow fiber membranes, membrane modules, solutions and samples, characterization of hollow fiber membranes, and operation of membrane contacting setup, were mostly conducted by me. I also analyzed the data.
- Dr Lin shared some laboratory works, such as conducting a field emission scanning electron microscope, an electron dispersive X-ray spectroscopy, and a goniometer and assisting in the preparation of composite hollow fiber membranes.
- Dr Lee assisted in the drawing of a schematic illustration and revised the manuscript.
- Dr Malde provided guidance in the experimental design and manuscript construction and revised the manuscript.

- I revised the manuscript according to the reviewer's comments from Journal of Membrane Science.

Chapter 5 is published as Y. Xu, Y. Lin, N. Chew, C. Malde, R. Wang, Biocatalytic PVDF composite hollow fiber membranes for CO₂ removal in gas-liquid membrane contactor, *Journal of Membrane Science*, **572**, 532-544 (2019). DOI: 10.1016/j.memsci.2018.11.043.

The contributions of the co-authors are as follows:

- Prof Wang provided the initial project direction, provided guidance in the experimental design, provided supports during the whole work, and revised and edited the manuscript.
- I wrote the drafts of the manuscript.
- I designed the experiments and performed all the laboratory work at the Singapore Membrane Technology Centre.
- I performed all the enzyme immobilization, enzyme characterization, membrane fabrication, membrane characterization and membrane contactor operation, and conducted data analysis.
- Dr Lin conducted a field emission scanning electron microscope and an electron dispersive X-ray spectroscopy, and revised the manuscript.
- Dr Chew provided guidance in PDA/PEI co-deposition, and revised the manuscript.
- Dr Malde provided guidance in the manuscript construction and revised the manuscript.
- I revised the manuscript according to the reviewer's comments from Journal of Membrane Science.

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LIST OF PUBLICATIONS

➤ *Journals:*

1. **Y. Xu**, Y. Lin, M. Lee, C. Malde, R. Wang, Development of low mass-transfer-resistance fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membrane used for biogas upgrading in gas-liquid membrane contactor, **J. Membr. Sci.**, 552 (2018) 253-264.
2. **Y. Xu**, Y. Lin, N. Chew, C. Malde, R. Wang, Biocatalytic PVDF composite hollow fiber membranes for CO₂ removal in gas-liquid membrane contactor, **J. Membr. Sci.**, 572 (2019) 532-544.
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➤ *Conferences:*

1. **Y. Xu**, Y. Lin, C. Malde, R. Wang, High-flux and chemical resistant fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membranes in gas-liquid membrane contactor for CO₂ removal from biogas, **Engineering with Membranes Conference 2017**, Singapore, 26th – 28th April 2017 (Poster Presentation)

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TABLE OF CONTENTS

ACKNOWLEDGEMENTS	i
LIST OF PUBLICATIONS	v
TABLE OF CONTENTS	vii
LIST OF TABLES	xi
LIST OF FIGURES	xiii
LIST OF ABBREVIATIONS	xvii
LIST OF SYMBOLS	xix
SUMMARY	xxi
Chapter 1 Introduction	1
1.1. Background	1
1.2. Challenges	5
1.3. Research objectives	9
1.4. Thesis outline	10
Chapter 2 Literature Review	13
2.1. Introduction of GLMC	13
2.1.1. GLMC configurations	13
2.1.2. Mass transfer in GLMC	15
2.1.3. Liquid absorbents in GLMC	18
2.1.4. Membranes in GLMC	20
2.2. Membrane wetting	29
2.3. Wetting prevention	32
2.3.1. Absorbent selection	33
2.3.2. Optimization of operation conditions	33
2.3.3. Membrane surface modification	34
2.3.4. Dense membranes	37
Chapter 3 Materials and Methods	41
3.1. Materials and chemicals	41
3.2. Characterizations of membranes	43
3.3. CO ₂ absorption performance in GLMC tests	45
3.4. Long-term performance	47
Chapter 4 Development of Low Mass-Transfer-Resistance Fluorinated TiO ₂ - SiO ₂ /PVDF Composite Hollow Fiber Membrane Used for Biogas Upgrading in Gas-liquid Membrane Contactor	49

4.1. Introduction	49
4.2. Experimental	51
4.2.1. PVDF surface hydroxylation.....	51
4.2.2. Preparation of a fTiO ₂ -SiO ₂ /PVDF composite hollow fiber membrane	51
4.2.3. Membrane characterizations	52
4.2.4. CO ₂ absorption and long-term performances in GLMC	53
4.3. Results and discussion.....	53
4.3.1. Surface hydroxylation of PVDF substrates by alkali treatment	53
4.3.2. Membrane Characterization	56
4.3.3. Performance of fTiO ₂ -SiO ₂ /PVDF composite hollow fiber membranes in the GLMC application	63
4.3.4. CO ₂ flux comparison in various membranes for GLMC	69
4.5. Conclusions	71
Chapter 5 Biocatalytic PVDF Composite Hollow Fiber Membranes for CO ₂	
Removal in Gas-liquid Membrane Contactor	73
5.1. Introduction	73
5.2. Experimental	75
5.2.1. Preparation of an amine-functionalized membrane support.....	75
5.2.2. Fabrication of a biocatalytic composite hollow fiber membrane	76
5.2.3. Enzyme activity assay and loading efficiency	76
5.2.4. Membrane characterizations	77
5.2.5. CO ₂ absorption performance in GLMC	78
5.2.6. Long-term stability of the biocatalytic composite membranes	78
5.3. Results and discussion.....	78
5.3.1. Amine-functionalized PVDF hollow fiber membranes	78
5.3.2. Biocatalytic CA-m-PVDF hollow fiber membranes	82
5.3.3. Membrane characterizations	86
5.3.4. CO ₂ absorption performance of the biocatalytic composite membrane in GLMC	93
5.3.5. Long-term stability of the biocatalytic composite membrane.....	95
5.3.6. CO ₂ absorption performance comparison with various membranes for GLMC	96
5.4. Conclusions	99
Chapter 6 Synthesis of ZIF-8 Based Composite Hollow Fiber Membrane with a	
Dense Skin Layer for Facilitated Biogas Upgrading in Gas-Liquid	
Membrane Contactor	101
6.1. Introduction	101
6.2. Experimental	103
6.2.1. Synthesis of ZIF-8 and modified ZIF-8 nanocrystals	103
6.2.2. Fabrication of a mZIF-8 based composite hollow fiber membrane	104

6.2.3. Characterizations of ZIF-8/mZIF-8 nanocrystals and composite membranes.....	105
6.2.4. CO ₂ absorption and long-term performances in GLMC.....	106
6.3. Results and discussion	107
6.3.1. Aminosilane-modification of ZIF-8 nanocrystals.....	107
6.3.2. mZIF-8 based composite hollow fiber membranes	112
6.3.3. Biogas upgrading performance in GLMC	120
6.3.4. Long-term performance	121
6.3.5. Comparison of CO ₂ absorption fluxes of various membranes	122
6.4. Conclusions.....	124
Chapter 7 Conclusions and Recommendations.....	127
7.1. Overall conclusions.....	127
7.2. Recommendations for future research	132
References.....	135

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LIST OF TABLES

Table 1-1. Comparisons of conventional technologies for CO ₂ removal [10, 11].	2
Table 2-1. Solubility of gases relative to CO ₂ in physical solvents absorption [90]. ...	19
Table 2-2. Summary of the features of different membranes/materials in GLMC.....	27
Table 2-3. CO ₂ absorption performance of various dense membranes in GLMC processes.	38
Table 3-1. Properties of the PVDF hollow fiber substrates.	41
Table 3-2. Chemical reagents used for experiments.....	42
Table 3-3. Characteristics of membrane modules and operation conditions in GLMC processes.....	47
Table 4-1. Compositions of precursor solutions for preparation of TiO ₂ - SiO ₂ /PVDF composite hollow fiber membranes.	51
Table 4-2. Overall comparison of CO ₂ absorption flux on various membranes in GLMC	70
Table 5-1. Surface roughness parameters, mechanical properties and contact angles of the PVDF, m-PVDF and CA-m-PVDF hollow fiber membranes.	89
Table 5-2. Elemental composition (%) of the outer/inner surfaces of the PVDF, m(5h)-PVDF and CA(600)-m(5h)-PVDF membranes.	92
Table 5-3. Comparison of CO ₂ absorption flux of the various microporous hollow fiber membranes in GLMC.	98
Table 6-1. Elemental composition (%) of the powder ZIF-8 and m(12h)ZIF-8 nanocrystals.....	108
Table 6-2. Calculated average crystallite sizes and zeta potentials of ZIF-8 and m(6—24h)ZIF-8 nanocrystals.	110
Table 6-3. Surface roughness parameters of the PVDF, Pp, Z-Pp and mZ-Pp hollow fiber membranes.	115
Table 6-4. Elemental composition (%) of the outer/inner surfaces of the PVDF substrate, Pp, Z-Pp and mZ-Pp membranes.....	118
Table 6-5. Comparison of CO ₂ absorption flux of the various hollow fiber membranes in GLMC.	123
Table 7-1. Summary of advantages/disadvantages and economic analysis for various membranes in GLMC applications.	131

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LIST OF FIGURES

Fig. 1-1. CO ₂ capture technologies category. Adapted from ref. [8].	2
Fig. 1-2. The growth of biogas upgrading plants with increasing years. Adapted from ref. [9].	3
Fig. 1-3. The CO ₂ absorption process in a porous hollow fiber gas-liquid membrane contactor. Adapted from ref. [23].	5
Fig. 2-1. (a) a schematic diagram of a parallel-flow hollow fiber membrane contactor module (counter current flow) and (b-d) schematic diagrams of cross-flow hollow fiber membrane contactor modules [83, 85, 86].	15
Fig. 2-2. A schematic of mass transfer and resistances in microporous GLMC [43].	16
Fig. 2-3. A schematic diagram of CO ₂ absorption in a dense membrane contactor.	24
Fig. 2-4. Three types of membrane structures of non-porous membrane for GLMC processes: (a) dense membrane, (b) asymmetric membrane and (c) composite membrane.	25
Fig. 2-5. Three operation modes in GLMC processes: (a) non-wetting mode, (b) overall-wetting and (c) partial-wetting mode [139].	30
Fig. 2-6. The relationship between breakthrough pressures with surface tension of liquid absorbents (experimental data was based on hydrophobic microporous PTFE membrane) [46].	32
Fig. 2-7. FE-SEM images (magnification at 1000×) for the outer surface morphologies of PVDF-HFP membrane: before (a) and after surface modification (b); CO ₂ flux as a function of liquid velocity for both original and modified membrane(c) [144].	35
Fig. 2-8. (a) FE-SEM images of PEIm-A (traditional fabrication process), PEIm-B (triple-orifice spinneret fabrication process), and PEIm-A-fSiO ₂ and PEIm-B-fSiO ₂ membranes after hydrophobic silica modification. (b) CO ₂ fluxes as the function of water and 2M sodium taurinate (ST) velocities for both hydrophobic silica particles modified PEIm membranes [79].	37
Fig. 3-1. Schematic diagram of CO ₂ absorption in the GLMC process.	46
Fig. 4-1. Schematic illustration of the fTiO ₂ -SiO ₂ /PVDF composite hollow fiber membrane and CO ₂ removal in the GLMC application.	50
Fig. 4-2. Comparisons of (a) surface hydrophilicity, (b) mechanical property, and XPS spectra on (c) C 1s and (d) O 1s of PVDF substrate after surface hydroxylation with different hours of treatment.	54
Fig. 4-3. FE-SEM images of shell surfaces of PVDF substrate (a) before and (b) after the surface hydroxylation process for 6 h.	55
Fig. 4-4. Pore size and pore size distributions of PVDF substrate before and after the surface hydroxylation process for 6 h.	55

Fig. 4-5. FE-SEM images of shell surfaces of (a) fTiO ₂ -SiO ₂ -0/PVDF, (b) fTiO ₂ -SiO ₂ -0.5/PVDF, and (c) fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membranes.....	57
Fig. 4-6. Pore size and pore size distributions of fTiO ₂ -SiO ₂ -0/PVDF, fTiO ₂ -SiO ₂ -0.5/PVDF, and fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membranes, respectively.	57
Fig. 4-7. The cross-section images of (a) PVDF substrate, and (b) fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membrane, and (c) EDX line scan of Ti (red) and Si (blue) elements across the cross-section of fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membrane.....	59
Fig. 4-8. The XPS spectra of (a) Ti 2p, (c) Si 2p, and (e) C 1s on fTiO ₂ -SiO ₂ -1/PVDF membrane and PVDF substrate; and the corresponding curve fittings of (b) Ti 2p, (d) Si 2p, and (f) C 1s for fTiO ₂ -SiO ₂ -1/PVDF membrane.	60
Fig. 4-9. Surface hydrophobicity with different modification treatments and adhesion characterization after ultrasonication.	62
Fig. 4-10. FE-SEM images of (a) fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membrane without surface hydroxylation before and (b) after ultrasonication, (c) fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membrane with surface hydroxylation before and (d) after ultrasonication.	63
Fig. 4-11. (a) pure CO ₂ absorption flux and (b) synthetic biogas upgrading performance of various membranes with different modification treatments.	64
Fig. 4-12. Long-term performances of (a) CO ₂ absorption flux (at absorbent velocity of 0.25 m s ⁻¹) and (b) surface hydrophobicity of PVDF substrate and fTiO ₂ -SiO ₂ -1/PVDF composite hollow fiber membrane under the absorbents of MEA and ST over a period of 31 days.	67
Fig. 4-13. FE-SEM images and pore size distributions of PVDF support and fTiO ₂ -SiO ₂ -1/PVDF composite HF membranes (a1-b1) before and after 31-day operation in (a2-b2) MEA and (a3-b3) ST solution, respectively.....	68
Fig. 5-1. Schematic illustration of the biocatalytic composite hollow fiber membrane and CO ₂ absorption in the GLMC process.	75
Fig. 5-2. FE-SEM images of the outer surface morphologies and pore size distributions of the PVDF (a1 and a2), ultrasonicated m(3h)-PVDF (b1 and b2), m(5h)-PVDF (c1 and c2), and m(8h)-PVDF (d1 and d2) membranes.....	80
Fig. 5-3. ATR-FTIR spectra (a) and dynamic water contact angles (b) of the pristine PVDF, m(3h)-PVDF, m(5h)-PVDF and m(8h)-PVDF membranes.....	82
Fig. 5-4. Relative activity and enzyme activity recovery for biocatalytic CA-m-PVDF membranes at different (a) m-PVDF supports (0.67% GLU; 200 µg·mL ⁻¹ CA; pH 8.0; 25 °C; 24 h for enzyme immobilization), (b) pH values (m(5h)-PVDF; 0.67% GLU; 200 µg·mL ⁻¹ CA; 25 °C; 24 h), (c) temperatures (m(5h)-PVDF; 0.67% GLU; 200 µg·mL ⁻¹ CA; pH 8.0; 24	

h), (d) reaction times (m(5h)-PVDF; 0.67% GLU; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 25 $^{\circ}\text{C}$) for enzyme immobilization.....	84
Fig. 5-5. Relative activity and enzyme activity recovery for biocatalytic CA-m-PVDF membranes under different (a) concentrations of GLU (m(5h)-PVDF; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 25 $^{\circ}\text{C}$; 24 h for enzyme immobilization), (b) concentrations of CA (m(5h)-PVDF; 0.67% GLU; pH 8.0; 25 $^{\circ}\text{C}$; 24 h for enzyme immobilization).	86
Fig. 5-6. FE-SEM images of the outer surface (a and b) and cross-section (c and d), and pore size distributions (a) of the ultrasonicated CA(600)-m(5h)-PVDF membranes.	87
Fig. 5-7. (a1 and b1) the outer surface and cross-section images of biocatalytic CA(600)-m(5h)-PVDF composite membrane, and EDX mappings for (a2 and b2) C, (a3 and b3) N, (a4 and b4) O, (a5 and b5) Zn elements.....	88
Fig. 5-8. AFM images of the outer surface of (a) PVDF substrate, (b) m-PVDF membrane support, and (c) CA-m-PVDF composite hollow fiber membrane.....	89
Fig. 5-9. ATR-FTIR spectra of the shell surfaces of the PVDF, m(5h)-PVDF and biocatalytic CA(600)-m(5h)-PVDF membranes.....	90
Fig. 5-10. (a1, b1 and c1) XPS survey scan spectra, and high-resolution C 1s (a2, b2 and c2), N 1s (a3, b3 and c3) XPS spectra of the outer surfaces of the CA(600)-m(5h)-PVDF, m(5h)-PVDF and PVDF membranes.	92
Fig. 5-11. CO ₂ absorption flux of biocatalytic CA-m-PVDF composite membranes with different (a) CA loading concentrations (200—1000 $\mu\text{g}\cdot\text{mL}^{-1}$) and (b) liquid absorbents (water and 1M MEA).	95
Fig. 5-12. The long-term activities of biocatalytic membrane and free enzyme in absorbent of water over 40 days storage.	96
Fig. 6-1. Schematic illustration of a proposed MOF based composite hollow fiber membrane and CO ₂ removal in a GLMC process.	103
Fig. 6-2. Schematic illustration of construction of a mZIF-8 based composite hollow fiber membrane.	105
Fig. 6-3. XRD patterns (a) and ATR-FTIR spectra (b) of powder ZIF-8, m(6h)ZIF-8, m(12h)ZIF-8 and m(24h)ZIF-8 nanocrystals.	108
Fig. 6-4. FE-SEM images of (a) ZIF-8, (b) m(6h)ZIF-8, (c) m(12h)ZIF-8 and (d) m(24h)ZIF-8 nanocrystals.	109
Fig. 6-5. FE-TEM images of (a) ZIF-8, (b) m(6h)ZIF-8, (c) m(12h)ZIF-8 and (d) m(24h)ZIF-8 nanocrystals.	110
Fig. 6-6. (a) Hydrophobicity and (b) zeta potential of different composite hollow fiber membranes.....	111
Fig. 6-7. TGA and DTG curves (a) and XRD patterns (b) of ZIF-8 nanocrystals, mZIF-8 nanocrystals, PDMS, ZIF-8@PDMS and mZIF-8@PDMS mixed matrixes.....	113
Fig. 6-8. FE-SEM images of the outer surface of (a)—(f) mZ-Pp composite membranes with mZIF-8 loading of 0, 2.5, 5, 10, 15 and 20 wt.%, respectively, (g) PVDF substrate and (h) Z-Pp composite membrane (5 wt.% ZIF-8 loading).....	114

Fig. 6-9. FE-SEM images for cross-section of (a) PVDF substrate, (b) Pp, (c) Z-Pp and (d) mZ-Pp hollow fiber membranes (the loading of mZIF-8 is 5 wt.% as example), of which the EDX mappings for F, Si and Zn elements.....	116
Fig. 6-10. (a) ATR-FTIR spectra and (b) XPS survey scan spectra of the outer surfaces of PVDF substrate, Pp, Z-Pp and mZ-Pp membranes.....	117
Fig. 6-11. High-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Si 2p, and (d) Zn 2p on the outer surface of the mZ-Pp membrane.	118
Fig. 6-12. Dynamic water contact angles of PVDF substrate, Pp, Z(5%)-Pp and mZ(2.5—20%)-Pp membranes.	119
Fig. 6-13. CO ₂ absorption fluxes of Pp, Z-Pp and mZ-Pp membranes (a), of mZIF-8 based composite hollow fiber membranes (b) with different mZIF-8 loadings and (c) using different liquid absorbents.	121
Fig. 6-14. Long-term performance of mZIF-8 based composite hollow fiber membrane over 15-day operation.....	122

LIST OF ABBREVIATIONS

Abbreviation	Description
AFM	Atomic force microscope
Al ₂ O ₃	Alumina
APTES	(3-aminopropyl)triethoxysilane
ATR-FTIR	Fourier transform infrared spectroscopy via attenuated total reflectance
CA	Carbonic anhydrase
CH ₄	Methane
CO ₂	Carbon dioxide
DA	Dopamine hydrochloride
DEA	Diethanolamine
DEPG	Dimethyl ether of polyethylene glycol
DLS	Dynamic light scattering
DTG	Differential thermal gravimetric
EDX	Electron dispersive X-ray
EtOH	Ethanol
FE-SEM	Field emission scanning electron microscope
FE-TEM	Field emission transmission electron microscopy
FS10	Fluorolink [®] S10
GLMC	Gas-liquid membrane contactor
GLU	Glutaraldehyde
H ₂ O	Water
H ₂ S	Hydrogen sulfide
HCl	Hydrochloric acid
HCO ₃ ⁻	Bicarbonate ion
HFMC	Hollow fiber membrane contactor
HFP	Hexafluoropropylene
Hmim	2-methylimidazole
IPA	Isopropyl alcohol
MDEA	Methyldiethanolamine
MEA	Monoethanolamine
MeOH	Methanol
MMM	Mixed matrix membrane
MOF	Metal-organic framework

N ₂	Nitrogen
NaOH	Sodium hydroxide
NIPS	Nonsolvent induced phase separation
NMP	N-methy-2-pyrrolidone
PC	Propylene carbonate
PDA	Polydopamine
PDMS	Polydimethylsiloxane
PE	Polyethylene
PEI	Polyethylenimine
PEIm	Polyetherimide
PFTS	1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane
p-NP	4-Nitrophenol
p-NPA	4-nitrophenyl acetate
PP	Polypropylene
PSf	Polysulfone
PTFE	Polytetrafluoroethylene
PTMSP	Poly(1-trimethylsilyl)-1-propyne
PVDF	Polyvinylidene fluoride
PVDF-HFP	Polyvinylidene fluoride-co-hexafluoropropylene
PVTMS	Poly-(vinyltrimethylsilane)
SiO ₂	Silica
ST	Sodium taurinate
TEOS	Tetraethyl orthosilicate
TIPS	Thermal induced phase separation
TGA	Thermal gravimetric analyzer
TiO ₂	Titania
Tris	Tris(hydroxymethyl)aminomethane
TTIP	Titanium isopropoxide
XPS	X-ray photoelectron spectroscopy
XRD	X-ray diffraction
ZIF-8	Zeolitic imidazolate framework-8
Zn(NO ₃) ₂ ·6H ₂ O	Zinc nitrate hexahydrate
ZrO ₂	Zirconia

LIST OF SYMBOLS

Nomenclature	Description
A	Gas-liquid contact area (m^2)
A_{TE}	Activity of total free enzyme ($\text{U} \cdot \text{mg}^{-1}$ enzyme)
A_{UE}	Activity of un-immobilized enzyme in solution ($\text{U} \cdot \text{mg}^{-1}$ enzyme)
AR	Enzyme activity recovery (%)
$C_{CH_4, F}$	Concentration of CH_4 in feed stream ($\text{mol} \cdot \text{mol}^{-1}$)
$C_{CH_4, R}$	Concentration of CH_4 in retentate stream ($\text{mol} \cdot \text{mol}^{-1}$)
$C_{CO_2, R}$	Concentration of CO_2 in retentate stream ($\text{mol} \cdot \text{mol}^{-1}$)
$C_{CO_2, F}$	Concentration of CO_2 in feed stream ($\text{mol} \cdot \text{mol}^{-1}$)
$C_{g,in}$	CO_2 concentration in gas phase at inlet ($\text{mol} \cdot \text{m}^{-3}$)
$C_{g,out}$	CO_2 concentration in gas phase at outlet ($\text{mol} \cdot \text{m}^{-3}$)
$C_{l,in}$	CO_2 concentration in liquid phase at inlet ($\text{mol} \cdot \text{m}^{-3}$)
$C_{l,out}$	CO_2 concentration in liquid phase at outlet ($\text{mol} \cdot \text{m}^{-3}$)
$C_{l,m}$	CO_2 concentration in liquid-membrane interface ($\text{mol} \cdot \text{m}^{-3}$)
$\Delta C_{l, m}$	Logarithmic mean driving force based on liquid phase concentration ($\text{mol} \cdot \text{m}^{-3}$)
D_p	Average crystallite size (nm)
$D_{g,eff}$	Effective diffusion coefficient of gas in the gas-filled pores ($\text{m}^2 \cdot \text{s}^{-1}$)
$D_{g,kn}$	Knudsen diffusion coefficient of gas ($\text{m}^2 \cdot \text{s}^{-1}$)
$D_{g,m}$	Bulk diffusion coefficient of gas ($\text{m}^2 \cdot \text{s}^{-1}$)
D_l	Diffusion coefficient of the gas in the liquid-filled pores ($\text{m}^2 \cdot \text{s}^{-1}$)
d_i	Inner diameter of the membrane (m)
d_o	Outer diameter of the membrane (m)
d_{ln}	Logarithmic mean diameters of the membrane (m)
d_{max}	Maximum pore diameter (m)
E	Enhancement factor
H	Henry's constant
J	CO_2 absorption flux ($\text{mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$)
K_g	Gas mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)
K_l	Liquid mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)
K_m	Membrane mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$)

K_{ol}	Overall mass transfer coefficient ($\text{m}\cdot\text{s}^{-1}$)
L	Module length (m)
l_m	Thickness of the membrane (m)
P	Operating pressure (mmHg or bar)
P_g	Gas partial pressure (Pa)
ΔP	Minimum pressure or breakthrough pressure (Pa)
Q_{in}	Volume flow rate of gas feed-in ($\text{m}^3\cdot\text{s}^{-1}$)
Q_{out}	Volume flow rate of gas feed-out ($\text{m}^3\cdot\text{s}^{-1}$)
Q_l	Liquid volume flow rate ($\text{m}^3\cdot\text{min}^{-1}$)
R	Ideal gas constant, $62.4 \text{ mmHg}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, $0.083 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$
Re	Reynolds number
r_{max}	Maximum pore radius of hollow fibers (m)
R_m	Mass transfer resistance in membrane ($\text{s}\cdot\text{m}^{-1}$)
R_l	Mass transfer resistance in liquid phase ($\text{s}\cdot\text{m}^{-1}$)
R_g	Mass transfer resistance in gas phase ($\text{s}\cdot\text{m}^{-1}$)
R_{total}	Overall mass transfer resistance ($\text{s}\cdot\text{m}^{-1}$)
Sc	Schmidt number
Sh	Sherwood number
T	Temperature (K)
V	Velocity ($\text{m}\cdot\text{s}^{-1}$)

Greek

α_{CO_2/CH_4}	CO_2/CH_4 selectivity
β	Line broadening in radians
λ	X-ray wavelength ($\text{\AA}$)
ε	Porosity of the membrane (%)
γ	Liquid surface tension (dyn/cm)
θ	Contact angle ($^\circ$)
θ_b	Bragg angle in XRD ($^\circ$)
τ_m	Tortuosity of membrane

Description

SUMMARY

Biogas is a clean and renewable energy source in a carbon-constrained world. Carbon dioxide (CO₂) capture is essential for upgrading biogas to increase energy density. The gas-liquid membrane contactor (GLMC) has been proposed and investigated as a promising alternative to conventional CO₂ absorption techniques such as packed towers and bubble columns. Owing to its desirable properties such as hydrophobicity, suitable pore size, high porosity, good mechanical strength, and high thermal stability, polyvinylidene fluoride (PVDF) membrane has been extensively used in GLMC processes. However, PVDF membrane is vulnerable to wetting, swelling and degradation by solvents under long-term operations, thus restricting its application for CO₂ removal in membrane contacting processes. Therefore, developing novel membranes to improve the durability in the GLMC process is of significant importance.

To achieve this goal, an inorganic-organic fluorinated titania-silica (fTiO₂-SiO₂)/PVDF composite membrane was fabricated via facile *in-situ* vapor-induced hydrolyzation method followed by hydrophobic modification. This low mass-transfer-resistance membrane, composing of a mesoporous layer deposited onto macroporous substrate, was designed for biogas upgrading in GLMC application. Surface hydroxylation was introduced to facilitate the bridging of TiO₂-SiO₂ nanoparticles and PVDF substrate, which resulted in a more coherent deposition of fTiO₂-SiO₂ layer onto the substrate. The surface microstructure was fine-tuned by controlling the amount of doped Si precursor, forming an integrated mesoporous fTiO₂-SiO₂ layer. The resultant fTiO₂-SiO₂/PVDF composite hollow fiber membrane exhibited a tighter pore size of ~25 nm and a desired water contact angle of ~124°, which effectively prevented membrane wetting. The high CO₂ absorption fluxes were achieved due to lower mass transfer resistance, by using 1 M of monoethanolamine (MEA) and sodium taurinate as

absorbents, respectively. The long-term stability test showed a good integrity between the fTiO₂-SiO₂ layer and the PVDF substrate after 31 days of GLMC operation. The main benefit is the robust fluorinated inorganic layer that exhibited strong chemical resistance and high hydrophobicity, thus preventing membrane damage and pore wetting. This study provides an insight into the preparation of high-performance inorganic/organic composite hollow fiber membranes for CO₂ removal in GLMC applications.

Considering the high corrosion and energy-intensity of using traditional amine-based absorbents for CO₂ capture in GLMC processes, it is more appropriate to use environmentally-benign solvents for CO₂ capture. A highly efficient biocatalytic carbonic anhydrase (CA)-polydopamine (PDA)/polyethylenimine (PEI)-PVDF composite membrane was designed and fabricated for CO₂ conversion and capture using water as absorbent. The co-deposition of PDA/PEI with amino functional groups was employed to amine-functionalize a PVDF substrate as support for subsequent *in-situ* CA immobilization by cross-linking with glutaraldehyde. This enhances the enzyme stability and prolongs its lifespan, thus facilitating CO₂ removal efficiency in the GLMC process due to the superb catalysis of CA enzyme for CO₂ hydration. By using water as absorbent with a liquid velocity of 0.25 m·s⁻¹ in a bench-scale GLMC setup, a high-efficiency CO₂ absorption flux (2.5×10^{-3} mol·m⁻²·s⁻¹) of the proposed biocatalytic membrane was obtained, which was ~165% higher than that of the non-biocatalytic membrane. A good long-term stability in terms of enzyme activity for CO₂ hydration of the biocatalytic composite membranes was also achieved during 40 days of test duration. Overall, the results achieved in this work could provide promising insights into the development of biocatalytic membranes for extended GLMC applications using environmentally-benign absorbents to achieve a high-efficiency CO₂ removal.

Inspired by better gas selectivity along with tunable pore size and facile functionalization of metal-organic frameworks (MOFs), a highly efficient aminosilane-modified zeolitic imidazolate framework-8 (mZIF-8) based composite hollow fiber membrane with a dense skin layer was successfully fabricated for biogas upgrading in the GLMC process by dispersing mZIF-8 into dense polydimethylsiloxane (PDMS) matrix and depositing on a porous PVDF substrate. (3-aminopropyl)triethoxysilane was introduced to modify the ZIF-8 nanocrystals in order to cross-link with PDMS chains for further hydrophobicity enhancement. Compared with the pristine PVDF membrane, the newly developed composite membranes with a dense skin exhibited competitive hydrophobicity with a contact angle of 130° , ensuring its anti-wetting ability. The mZIF-8 based composite membrane realized a higher CO_2 mass transfer efficiency as well as a higher selectivity of CO_2/CH_4 using water or aqueous amine absorbents in GLMC processes. A robust long-term stability of mZIF-8 based composite membrane was also achieved in a 15-day operation. This work provides a new strategy to improve the biogas upgrading performance using dense composite membranes with modified MOFs in GLMC applications.

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Chapter 1 Introduction

1.1. Background

The global energy demand is continuously increasing with an expected 30% rise by 2040, as reported in World Energy Outlook 2016 [1]. The heavy reliance on fossil energy produces high levels of greenhouse gases leading to global warming, where carbon dioxide (CO_2) is one of the major greenhouse gases. While historical trends indicate gradual decarbonization of fuel sources over time, there is an increasing interest in clean and renewable energy resources such as biogas for mitigating CO_2 emissions [2, 3]. Biogas, also known as biomethane, can be generated through anaerobic digestion of organic materials, thermal gasification of organic residuals or lignocellulosic biomass feedstock, or capture from landfill gas, which has been used for electricity generation, vehicle fuel and injection into gas grid after purification.[4]. The components of raw biogas are 55~75 % methane (CH_4), 30~45% CO_2 , and other traces of gases such as nitrogen (N_2), hydrogen sulfide (H_2S), and water vapor (H_2O) [5]. Among them, CO_2 is one of the major acid gas impurities in raw biogas which can lead to pipeline corrosion, energy content reduction, and occupation of pipeline volume during transportation [6]. Generally, the purity of CH_4 used in fuel should be above 95% [6]. Therefore, biogas upgrading by removal of CO_2 from biogas is of great importance for its practical utilization.

Currently, CO_2 capture has been commercially implemented with a variety of process technologies, such as pressurized water scrubbing, physical/chemical absorption, pressure/temperature swing adsorption (PSA/TSA), cryogenic separation, and membrane technology, as shown in Fig. 1-1 [7, 8]. Their main advantages and disadvantages are summarized in Table 1-1. The market developments of the various biogas upgrading

technologies are shown in Fig. 1-2. Water scrubbing, PSA, and amine scrubbing still has been the predominant today. Compared with absorption and adsorption processes, membrane technology for biogas upgrading is less mature, but has rapidly gained interest and market shares. The main challenge for membrane-based upgrading equipment is the stable operation for a long term and economic feasibility for large installations. Some novel membranes have not been pilot-plant tested in operation for over a few years, thus lead to an uncertain lifetime [9].

Fig. 1-1. CO₂ capture technologies category. Adapted from ref. [8].

Table 1-1. Comparisons of conventional technologies for CO₂ removal [10, 11].

Technology	Advantages	Disadvantages	References
Physical absorption	<ul style="list-style-type: none"> • Widely used and mature technology • Absorbent can be regenerated by pressure reduction and/or heating • High absorption efficiency 	<ul style="list-style-type: none"> • Need high CO₂ concentration as feed gas • Need high pressure in absorption processes 	[9, 12]
Chemical absorption	<ul style="list-style-type: none"> • Insensitive to pressure for aqueous amine • High absorption efficiency • Absorbent can be regenerated by heating 	<ul style="list-style-type: none"> • Consume high-energy to regenerate the absorbent • Environmental issue of discharge of waste chemical 	[13, 14]
Adsorption	<ul style="list-style-type: none"> • Adsorbent can be recycle used • Process is reversible 	<ul style="list-style-type: none"> • High temperature required • High energy consumption 	[11, 15]

	<ul style="list-style-type: none"> • High adsorption efficiency 		
Cryogenic	<ul style="list-style-type: none"> • High CO₂ recovery 	<ul style="list-style-type: none"> • Need very high CO₂ concentration 	[16]
Membrane separation	<ul style="list-style-type: none"> • Can be adopted for multiple gases separation • Low capital and operation costs • High gas recovery • Small space requirement • Less environmental concern 	<ul style="list-style-type: none"> • Highly energy intensive • Low flux • Selectivity and permeability are sensitive for separation efficiency • Require recompression of permeate gas 	[17, 18]

Fig. 1-2. The growth of biogas upgrading plants with increasing years. Adapted from ref. [9].

Most of above conventional technologies are usually energy-intensive and require large infrastructure, high capital investment, and high operation cost. In spite of the absorption process being considered as one of the most mature technologies, the gas-liquid contacting process frequently leads to problems such as foaming, channelling, flooding, weeping, excessive loading, and entrainment [19]. Membrane separation technology has attracted widespread attention in CO₂ capture processes due to its low energy consumption,

low capital and operation costs as well as small plant footprint. However, it is still facing the challenges of unsatisfactory selectivity and limited permeability for targeted gas. To overcome the above-mentioned challenges, gas-liquid membrane contactor (GLMC) has been proposed as a promising alternative to conventional absorption processes [19]. In a typical GLMC for CO₂ capture, gas diffuses from the bulk gas phase to the membrane surface and passes through the membrane pores before transferring from the gas-liquid interface to the bulk liquid followed by liquid phase physical diffusion and/or chemical reaction. Its main operational and economical advantages include high surface area for mass transfer per unit volume, individual flow of gas and absorbent flues, easier prediction, linear scale-up and ease of operation, convenient start-up and shut-down, small plant footprint, low cost, and low energy consumption [20, 21]. Falk-Pedersen *et al.* reported [22] that their applied polytetrafluoroethylene (PTFE) membrane contactors provided much larger interfacial area thus resulting in a 65–75% reduction in weight and size compared to conventional absorbers, which were used for natural gas upgrading, dehydration as well as CO₂ removal from exhaust gas. An offshore installation of GLMC unit was employed for CO₂ removal from the exhaust gas of a LM 2500 marine gas turbine using conventional aqueous amine solution of 30 wt.% MEA, presenting the benefits of: 1) saving operating cost of 38–42%; 2) reducing dry equipment weight of 32–37%; 3) reducing operating equipment weight of 34–40%; 4) reducing footprint requirement by 40–50%; 5) reducing capital cost of 35–40%. These membrane contactors can be supplied by hollow fiber, tubular, flat sheet, and spiral wound membrane modules. Among different types of configuration, porous hollow fiber membrane contactor is widely studied due to its significantly high packing density [20] as illustrated in Fig. 1-3 [23].

Fig. 1-3. The CO₂ absorption process in a porous hollow fiber gas-liquid membrane contactor. Adapted from ref. [23].

1.2. Challenges

Normally, membranes in GLMC act as non-selective interfacial barrier between the liquid and gas phases to provide a large gas-liquid contact area without dispersing one phase into the other. Therefore, CO₂ selectivity is determined by the loading capacity of the liquid absorbent, rather than the membrane itself [24, 25]. It is preferable to run the process with non-wetted mode, *i.e.*, the membrane pores are always filled with gas. When the pores are partially or totally liquid-filled over prolonged periods of operation, the mass transfer flux can be significantly reduced due to lower CO₂ diffusion rate in the liquid [26, 27]. Therefore, minimizing pore wetting of porous membranes has proven to be a main challenge in GLMC processes.

Hydrophobic membranes with lower surface energies are less prone to wetting. Therefore, most of the current traditional membranes applied in GLMC are made from hydrophobic polymeric materials such as PTFE, polypropylene (PP), polyethylene (PE),

polyvinylidene fluoride (PVDF), polysulfone (PSf), and polyetherimide (PEIm), *etc.* [23, 28-30]. However, most of the polymeric membranes applied in GLMC are still vulnerable to membrane wetting over prolonged periods of operation, leading to significant restriction of the gas mass-transfer efficiency and the long-term performance [23, 31-34]. Three main alternative techniques have been proposed to prevent membrane wetting by solvents: (i) surface modification (membrane surface energy); (ii) tuning of membrane structural parameters (pore size distribution and porosity of membrane); and (iii) adjustment of operating conditions [31, 35, 36]. Among these, surface modification techniques such as coating, grafting, and plasma polymerization are cost-effective and have been widely employed to deposit a layer of low surface energy materials on porous membrane substrates to enhance the hydrophobicity of membrane surfaces [37, 38].

In addition, membrane wettability is also influenced by pore size and porosity. According to the Young-Laplace equation, the critical liquid entry pressure is higher for membranes with smaller pores, and thus they are less prone to wetting [39, 40]. To date, the pore sizes of most hollow fiber membranes employed in GLMC applications are less than 200 nm to prevent the penetration of adsorbents, thus reducing mass transfer resistance [31, 32, 41, 42]. On the other hand, although tight pore structure is beneficial to improving wetting resistance, the gas phase transportation in tight pores might also be retarded, resulting in lower CO₂ flux. Ideally, the membrane itself should possess a hydrophobic layer with a small pore size deposited on a highly porous substrate with large pores for highly efficient CO₂ removal in GLMC processes [24, 43]. However, preparation of such composite membranes is still in the proof-of-concept stage. A challenge impeding the development is the difficulty in depositing an integrated hydrophobic layer onto porous substrates with large pores. The top mesoporous layer should be as thin as possible, meanwhile covering the macro-pores of the substrate to prevent membrane wetting.

Besides the membrane hydrophobicity and pore size, membrane wetting can also be induced by using highly corrosive amine-based aqueous absorbents, such as MEA, DEA, and MDEA, which are commonly used in CO₂ absorption processes [44-46]. It is widely accepted that organic membranes in GLMC are easily swelled and degraded by amine aqueous solvents [31, 36], which in turn leads to membrane wetting and consequently significant CO₂ mass-transfer reduction. Therefore, to prevent organic membrane degradation and wetting, developing membranes with excellent chemical resistance is of great importance for feasible GLMC operations. Inorganic membranes, such as ceramic membranes, have received much attention due to their excellent chemical resistance, thermal stability, and mechanical properties under harsh conditions [47-49]. By fabricating an inorganic layer on a porous organic substrate, it is possible to construct membranes with combined merits of both materials to broaden their applications. However, the design of inorganic top layer with desired microstructure on a porous polymeric substrate is most commonly achieved by the atomic layer deposition method, which involves hundreds of preparation cycles of “pulse-exposure-purge” to form a uniform and defect-free inorganic layer [29]. The complicated process makes it unviable to prepare integrated inorganic/organic composite membranes in hollow fiber configuration for GLMC.

Meanwhile, the properties of absorbent itself also affect the CO₂ absorption performance in GLMC processes. Amine-based solvents such as MEA and DEA are often consumed in large quantities and easily degraded by oxygen, resulting in reduction of their CO₂ loading capacities [50]. In addition, the recovery of amine-based solvents or desorption of CO₂ consumes huge amounts of energy [51]. Therefore, it is desirable to use environmentally-benign solvents for CO₂ capture since it can decrease the consumption penalties of energy and investment for CO₂ capture in GLMC applications [52]. However, most benign solvents have much lower CO₂ loading capacities than that of amine-based absorbents, that is caused by their lower CO₂ hydration kinetics. In order to address the

rate-limiting problem of CO₂ capture, a biocatalysis approach by using enzymes such as carbonic anhydrase (CA, E.C.4.2.1.1) as catalyst for CO₂ hydration has received much attention [52, 53]. In literature, enzymatic CO₂ capture has been widely studied for facilitating the CO₂ conversion in absorption, sorbent adsorption, and sequestration [54]. Various supports such as TiO₂ nanoparticles, mesoporous silica SBA-15 and Fe₃O₄ magnetic microspheres [55-59] have been applied for CA immobilization. However, the immobilization of enzyme on pure polymeric membranes used for CO₂ capture in GLMC has been rarely reported in literature.

Increasing the CO₂ transfer efficiency is another challenge in GLMC processes. The porous membranes are subjected to a trade-off limitation between high CO₂ transfer efficiency and anti-wetting properties, which passively influences their utilization on a large scale. Dense polymeric membranes have also been proposed for CO₂ removal in GLMC processes [60-63], which indeed offer a remarkable wetting protection effect due to no pores present. In this situation, the dense membrane acts as a selective barrier, which controls CO₂ transfer by the selectivity and permeability of CO₂/CH₄ [64]. However, it triggers a high membrane mass transfer resistance thus resulting in low CO₂ flux, although operated under high transmembrane pressure [65, 66]. Currently, incorporating nanofillers into polymers to fabricate mixed matrix membranes (MMMs) has been proven to be an efficient approach via combination of the advantages of these two phases [67-69]. Among a series of nanofillers, metal-organic frameworks (MOFs) have emerged as a promising alternative to enhance the gas selectivity as well as permeability due to their high surface area, large porosity and pore volume, tunable pore size and shape, and facile functionalization [70, 71]. The intrinsic organic moiety of MOFs can provide good compatibility with polymer matrix by multiple kinds of interactions, such as weak intermolecular interaction, hydrogen-bonding interaction, covalent bonding interaction, *etc.* [72]. The presence of MOFs in MMMs can provide additional channels for gas penetration.

Meanwhile, the hydrophilicity/hydrophobicity of MOFs can be adjusted based on its application. Therefore, development of a MOFs-based composite membrane with a dense skin layer can be considered as a promising alternative for enhancement of CO₂ mass transfer as well as wetting prevention in GLMC, although it is rarely reported in literature [73]. In this research area, synthesizing a uniform, defect-free and hydrophobic MOF-based composite dense membrane for CO₂ absorption is still challenging [74]. 成本

1.3. Research objectives

This study aims to develop highly efficient composite hollow fiber membranes for CO₂ removal from biogas in GLMC processes via a series of surface modification methods, which mainly focuses on overcoming the traditional challenges mentioned above. The main research objectives are to:

- design and fabricate an inorganic/organic composite hollow fiber membrane via facile *in-situ* vapor-induced hydrolyzation method followed by hydrophobic modification to achieve highly efficient CO₂ mass transfer as well as anti-wetting performance;
- design and fabricate a novel biocatalytic composite membrane via two-step co-deposition and cross-linking method to significantly enhance CO₂ conversion and capture using water as absorbent;
- design and fabricate a MOFs based composite hollow fiber membrane with a dense skin layer for facilitated biogas upgrading in the GLMC application; and
- investigate the mechanisms of surface modification and composite membranes formation processes through exploring the involved chemical reactions and evaluate the CO₂ absorption and long-term operation performances of proposed composite membranes in the GLMC process.

1.4. Thesis outline

This thesis encompasses seven chapters, which are highlighted as follows:

Chapter 1: Introduction – Background information on GLMC, challenges statement, and research objectives are summarized in this chapter.

Chapter 2: Literature review – This is a critical review of the available literature on the different GLMC configurations, mass transfer, liquid absorbents and membranes in GLMC, membrane wetting, and wetting prevention in GLMC to better appreciate the different topics covered in this thesis.

Chapter 3: Materials and methods – This chapter outlines the materials and methods used. The first section summarizes all materials and chemicals; the second section introduces the characterizations of membranes; and the third and fourth sections describe the CO₂ absorption experiments in the lab-scale GLMC setup and the long-term performance tests, respectively.

Chapter 4: Development of low mass-transfer-resistance fluorinated TiO₂-SiO₂/PVDF composite hollow fiber membrane used for biogas upgrading in gas-liquid membrane contactor – This chapter proposes a facile method for preparing inorganic/organic composite hollow fibers membrane. Surface hydroxylation improves the integrity between inorganic and organic layers. Macro-pores of membrane can be tuned by controlling of Si precursors. The fluorinated TiO₂-SiO₂ layer improves hydrophobicity and chemical resistance in GLMC. The proposed membranes show an excellent long-term performance towards amine-based and amino acid salts absorbents.

Chapter 5: Biocatalytic PVDF composite hollow fiber membranes for CO₂ removal in gas-liquid membrane contactor – The previous proposed inorganic/organic composite membrane discussed in Chapter 4 could survive in amine alkali solutions. Hence, the focus is shifted towards achieving high-efficiency CO₂ capture performance with benign solvent. It is firstly reported on design and fabrication of a highly efficient biocatalytic composite hollow fiber membranes for CO₂ conversion and capture in GLMC via two-step co-deposition and cross-linking method. Polydopamine (PDA)/polyethylenimine (PEI) layer with amino functional groups is co-deposited to amine-functionalize a PVDF substrate. Subsequent *in-situ* CA immobilization was conducted by cross-linking. The resultant membrane shows a high CO₂ absorption flux using water as absorbent.

Chapter 6: Design of novel ZIF-8 based composite hollow fiber membrane with a dense skin layer for facilitated biogas upgrading in gas-liquid membrane contactor – The previous studies in Chapters 4 and 5 mainly focus on the developments of highly efficient microporous composite membranes, but membrane wetting problem is still a concern. This chapter proposes an aminosilane-modified ZIF-8 based composite hollow fiber membrane for mass-transfer-enhanced CO₂ removal from biogas. Aminosilane-modified ZIF-8 nanocrystals are embedded in polydimethylsiloxane (PDMS) matrix deposited on a PVDF substrate, which improves the CO₂ mass-transfer through non-porous PDMS coated layer. The ZIF-8 based composite hollow fiber membrane shows significant hydrophobicity enhancement and anti-wetting property in GLMC. High CO₂ removal flux from biogas and long-term stability are achieved.

Chapter 7: Conclusions and recommendations – The important findings from Chapters 4, 5, and 6 and recommendations for future work are presented in this chapter.

Chapter 2 Literature Review

This chapter provides a review on the current status and development of GLMC technology. Several basic aspects such as configurations, mass transfer, liquid absorbents and membranes in the GLMC technology will be firstly presented. Then, membrane wetting, as the most important technical challenge in GLMC processes, will be comprehensively reviewed, especially on wetting causes and wetting preventions. Meanwhile, the fundamental mechanisms of membrane wetting and different approaches to prevent membrane wetting will also be discussed. Finally, the state-of-the-art of membrane development for GLMC applications will be summarized.

2.1. Introduction of GLMC

2.1.1. GLMC configurations

The module configuration of GLMC is important for determining the performance of CO₂ absorption and operation of the process. The membrane module in GLMC should provide an efficient gas–liquid interface contact area and eliminate convective flow of fluids through the membrane. A number of different membrane module configurations such as flat sheet [56, 60], spiral-wound [75], tubular [76, 77], and hollow fiber [20, 42, 78, 79] have been used in GLMC. Among them, the hollow fiber membrane module typically packed with a bundle of hollow fibers can offer superbly high interfacial area, which is around 30 times higher than that of conventional absorbers [21, 80, 81]. Two main kinds of hollow fiber membrane contactor modules, longitudinal flow (or parallel-flow) and cross-flow, have been extensively applied for CO₂ absorption in GLMC processes [45].

A schematic diagram of a longitudinal flow module is shown in Fig. 2-1(a). The gas and liquid fluids flow either counter-currently or concurrently in parallel to each other

on opposite sides of the hollow fibers [20, 45]. deMontigny *et al.* [82] studied both counter-current and concurrent flow in a GLMC process and found that the mass transfer efficiency in counter-current mode was 20% higher than that in concurrent mode. Owing to its simplicity in manufacture, most lab-scale studies have been carried out using longitudinal flow module design [83]. However, compared with the cross-flow module, the longitudinal flow module generally offers a mediocre efficiency in mass transfer, caused by the channelling, bypassing, and pressure drop of fluid on the shell side [84].

The most well-known cross-flow module designed for GLMC is the Liquid-Cel[®] Extra-Flow module (CELGARD LLC, Charlotte, NC, USA) containing a central shell side baffle, of which the schematic diagram is shown in Fig. 2-1(b). The baffle offers two main advantages in improving the mass transfer efficiency by minimizing bypass on the shell side and providing a component of velocity normal to the membrane surface, thereby resulting in an outperformance for mass transfer compared with parallel-flow modules [20]. Two types of complicated cross-flow modules had been patented by K.A. Hoff [85] and TNO of the Netherlands [81], which can offer good mass-transfer characteristics and scale-up potential as schematically shown in Fig. 2-1(c-d), respectively.

Fig. 2-1. (a) a schematic diagram of a parallel-flow hollow fiber membrane contactor module (counter current flow) and (b-d) schematic diagrams of cross-flow hollow fiber membrane contactor modules [83, 85, 86].

The fluids of gas and liquid have two possible flow directions, which are liquid inside (liquid absorbent flow in the lumen side and gas flow through on the shell side) and liquid outside (liquid absorbent flow through on the shell side and gas flow in the lumen side) [87]. The liquid inside configuration is beneficial to industrial applications, because of its larger cross-section area for dense gas flow. However, it is more prone to membrane wetting due to the high lumen-side pressure induced by the restrained liquid flow. The liquid outside configuration with lower liquid resistance in the shell side offers a larger gas–liquid interfacial area, while increases a pressure drop of gas in lumen side [83].

2.1.2. Mass transfer in GLMC

Mass transfer in the GLMC process refers to gas movement through membrane from gas phase to liquid phase. Typically, three continuous steps are involved in mass transfer in GLMC illustrated in Fig. 1-3: firstly, the bulk of gas diffuses to the membrane surface; secondly, the gas diffuses through the pores of membrane; thirdly, the gas contacts with liquid at gas-liquid interface followed by diffusion into the bulk liquid and/or directly reaction [23].

A well-known resistance-in-series model is shown in Fig. 2-2. Three individual mass transfer coefficients (K_l , K_m , and K_g) are associated with the process in liquid phase, microporous membrane, and gas phase, respectively.

Fig. 2-2. A schematic of mass transfer and resistances in microporous GLMC [43].

The overall resistance, R_t , can be expressed as follows for a non-wetted GLMC [20]:

$$R_t = R_l + R_m + R_g \quad (2-1)$$

$$\frac{1}{K_{ol}} = \frac{1}{Ek_l} + \frac{Hd_o}{k_m d_{ln}} + \frac{Hd_o}{k_g d_i} \quad (\text{Liquid inside}) \quad (2-2)$$

$$\frac{1}{K_{ol}} = \frac{1}{Ek_l} + \frac{Hd_i}{k_m d_{ln}} + \frac{Hd_i}{k_g d_o} \quad (\text{Liquid outside}) \quad (2-3)$$

$$C_{l,m} = HP_g \quad (2-4)$$

where K_{ol} is the overall mass transfer coefficient ($\text{m} \cdot \text{s}^{-1}$); E is the enhancement factor; H is the Henry's law constant; d_o is the outer diameter of membrane (m); d_i is the inner diameter of membrane (m); d_{ln} is the logarithmic mean diameter of membrane (m); $C_{l,m}$ is the CO_2 concentration in liquid-membrane interface ($\text{mol} \cdot \text{m}^{-3}$); P_g is gas partial pressure (Pa).

The overall mass transfer coefficient K_{ol} can be calculated by the following equation:

$$K_{ol} = \frac{Q_l}{A} \cdot \frac{C_{l,out} - C_{l,in}}{\Delta C_{l,m}} \quad (2-5)$$

$$\Delta C_{l,m} = \frac{(HC_{g,in} - C_{l,out}) - (HC_{g,out} - C_{l,in})}{\ln(HC_{g,in} - C_{l,out}) / (HC_{g,out} - C_{l,in})} \quad (2-6)$$

where the Henry's constants (H) for water and 1 M MEA solution are 0.831 [43] and 0.665 [88], respectively; Q_l represents the liquid flow rate ($\text{m}^3 \cdot \text{min}^{-1}$); $C_{l,out}$ and $C_{l,in}$ are the CO_2 outlet and inlet concentration in liquid phase ($\text{mol} \cdot \text{m}^{-3}$); $\Delta C_{l,m}$ is Logarithmic mean driving force based on liquid phase concentration ($\text{mol} \cdot \text{m}^{-3}$); A is the gas-liquid contact area (m^2); $C_{g,out}$ and $C_{g,in}$ are the CO_2 outlet and inlet concentration in gas phase, respectively ($\text{mol} \cdot \text{m}^{-3}$).

The shell side mass transfer coefficient can be calculated by the Lvque's correlation equation [20, 89]:

$$Sh = 1.62 \left(\frac{d_t^2 V}{LD} \right)^{1/3} \quad (2-7)$$

where Sh is Sherwood number; V is fluid velocity in the shell side ($\text{m} \cdot \text{s}^{-1}$); L is the module length (m); and D is the fluid diffusion coefficient.

The Sherwood number can also be expressed by:

$$Sh = a Re^\alpha Sc^\beta \quad (2-8)$$

where Re is Reyonlds number, and Sc is Schmidt number.

If the liquid flow in the shell side of membrane, the liquid mass transfer coefficient can be expressed by:

$$k_l = C_l V^\alpha \quad (2-9)$$

For non-wetted membrane, the membrane mass transfer coefficient can be determined by:

$$k_m = \frac{D_{g,eff}\varepsilon_m}{\tau_m l_m} \quad (2-10)$$

where $D_{g,eff}$ is the gas effective diffusion coefficient in membrane's pores ($\text{m}^2 \cdot \text{s}^{-1}$), which is the combination of gas molecular self-diffusion coefficient and the diffusion coefficient of the interaction between gas molecules and membrane pores; ε_m is the porosity of the membrane (%); τ_m and l_m are the tortuosity and thickness (m) of the membrane, respectively.

2.1.3. Liquid absorbents in GLMC

Generally, the absorbents used in conventional absorption processes can also be applied in GLMC processes. The absorbents can be mainly divided into physical absorbents and chemical absorbents. For physical absorbents, the suitability of a solvent for CO_2 removal from biogas is decided by the solubility difference between CO_2 and CH_4 in that solvent [13]. Water is most widely used for physical absorption of CO_2 in GLMC. The solubility of CO_2 and CH_4 in water (25 °C) is 340 and 13.2 $\text{mmol} \cdot \text{kg}^{-1} \cdot \text{MPa}^{-1}$, respectively, under 0.1 MPa gas partial pressure [5]. Moreover, organic solvents such as dimethyl ether of polyethylene glycol (DEPG, Selexol®), propylene carbonate (PC, Fluor process), N-methyl-2-pyrrolidone (NMP, Purisol process) and methanol (MeOH, Rectisol process) [90] can be also applied in CO_2 physical absorption processes. Other compounds such as H_2S , H_2O , O_2 , and N_2 can be removed together with CO_2 . Solubility of gases in physical solvents relative to CO_2 are shown in the Table 2-1.

Table 2-1. Solubility of gases relative to CO₂ in physical solvents absorption [90].

Gas Component	DEPG at 25°C	PC at 25°C	NMP at 25°C	MeOH at -25°C
CO ₂	1.0	1.0	1.0	1.0
H ₂	0.013	0.0078	0.0064	0.0054
N ₂	0.020	0.0084	–	0.012
CO	0.028	0.021	0.021	0.020
CH ₄	0.066	0.038	0.072	0.051
H ₂ S	8.82	3.29	10.2	7.06
H ₂ O	730	300	4000	–

CO₂ capture can also be realized with various chemical absorbents including caustic/alkaline solvents (NaOH, KOH, K₂CO₃, NaHCO₃, NH₃, *etc.*) [91], amines (MEA, DEA, MDEA, TEA, 2-amino-2-methyl-1-propanol (AMP), *etc.*) [45], and amino acid salts (sodium/potassium salts of taurine, glycine, sarcosine, proline, alanine, serine and α -aminobutyric acid, *etc.*) [13, 46, 92]. Amine-based aqueous solutions are the most investigated chemical absorbents for CO₂ capture. An amine can be derived from NH₃, where one or more hydrogen atoms have been substituted with an alkyl or aromatic group forming primary, secondary, and ternary amines, respectively. The amine functional group of the absorbents provides a weak base to react with acid gases. The reactivity of amines to CO₂ can be ordered as: primary > secondary > ternary amines [93]. MEA as primary amine is the most commonly used commercial absorbent for CO₂ capture. Therefore, MEA was chosen as an amine absorbent in this study. The reaction between MEA and CO₂ can be changed with the increase in CO₂ loading [94].

At low CO₂ loading, the fast-exothermic reaction of MEA with CO₂ can be described by zwitterion mechanism in two steps. The alkanolamine is first reacted with CO₂ forming intermediate zwitterion, and then the zwitterion is instantaneously deprotonated by the base in solution (amine, OH⁻, or H₂O) forming a carbamate [95, 96].

At high CO₂ loading, the kinetic of chemical reaction is not very high while the hydration reaction is developed. The intermediate products of HCO₃⁻ and CO₃²⁻ will react with amine forming carbamate. The carbamate can also react with H⁺ forming bicarbonate.

When the CO₂ loading is very high or the concentration of MEA is low enough, the reaction kinetics of MEA with CO₂ will be suppressed. The carbamate will become unstable and decompose to HCO₃⁻ or CO₃²⁻ by H⁺ [94]. Thus, CO₂ concentration or CO₂ partial pressure is a key factor for efficient CO₂ absorption.

2.1.4. Membranes in GLMC

2.1.4.1. Hydrophobic microporous polymeric membranes

In a GLMC, membranes play an important role to provide the gas-liquid interfacial surface for CO₂ absorption. Typically, GLMC is equipped with microporous hydrophobic hollow fiber membranes. According to Fig. 1-3, desirable properties of porous hollow fiber membrane in GLMC should be outstanding hydrophobicity, high porosity, and excellent chemical and thermal resistance to prevent the penetration of absorbent into the membrane and maintain the microstructure of membrane contact surface [97].

Various porous hydrophobic polymeric hollow fibers, such as PP, PE, PTFE, and PVDF have been widely applied in GLMC [97]. PP and PE are traditionally used for

hydrophobic membrane fabrication due to their low cost. PTFE shows high hydrophobicity and excellent resistance to chemical attack due to its entire carbon-fluorine structure. However, due to the lack of proper solvent to dissolve the polymers, PP, PE, and PTFE membrane are generally fabricated through stretching and thermal methods, which result in the low porosity of obtained membranes [23]. PVDF with two hydrogen atoms substituted by fluorine atoms offers a good chemical resistance towards many solutions. PVDF can dissolve in many organic solvents such as N,N-dimethylformamide, N,N-dimethylacetamide, N-methylpyrrolidone, and dimethylsulfoxide *etc.* [98], which can be fabricated by nonsolvent induced phase separation (NIPS) and thermal induced phase separation (TIPS) processes, offering possibility to control the membrane pore structures and achieve high porosity [43, 99, 100]. The performance of PTFE, PVDF, and PP membranes for CO₂ absorption in GLMC was studied by Khaisri *et al.*, which could be ranked as PTFE > PVDF > PP [101]. Some less hydrophobic membranes such as PSf, PEIm, and polyamide-imide (PAI) were also investigated for CO₂ absorption in GLMC [102-105]. However, the performance stabilities under long-term operation still require further improvement.

2.1.4.2. Inorganic membranes

Inorganic membranes have been proposed as an alternative which can offer excellent chemical and thermal resistance as well as high mechanical strength. Oxide ceramics such as titania (TiO₂), alumina (Al₂O₃), silica (SiO₂), and zirconia (ZrO₂) are the most commonly used ceramic materials for inorganic membranes, which have great potential for gas absorption in GLMC. Due to their intrinsic hydrophobic properties, most ceramic membranes used for GLMC are decorated to be hydrophobic to prevent wetting. A traditional modification technique is the grafting of hydrophobic substances such as perfluoroalkylsilanes onto pre-treated membrane surface with active sites such as hydroxyl

(–OH) groups on the membranes surface [78, 106, 107]. Kujawa *et al.* [108, 109] successively constructed the fluorinated Al₂O₃, TiO₂, and ZrO₂ ceramic membranes modified by different perfluoroalkylsilanes, and tuned their hydrophilic nature to superb hydrophobic surfaces improving the contact angle to ~140°. Yu *et al.* [110] modified Al₂O₃ tubular membranes with fluorinated ZrO₂ layer for membrane contactor, generating superhydrophobic surface that led to good long-term operation stability. Sirichai *et al.* [111] applied hydrophobically modified Al₂O₃ membranes in GLMC system for CO₂ stripping using MEA solution and found that the inorganic Al₂O₃ membranes presented better thermal stability compared to polymeric membranes.

2.1.4.3. Novel biocatalytic membranes

Recently, novel enzyme-catalysed approach with CA enzyme as catalyst has attracted attention for CO₂ capture processes [52, 53]. The CA enzyme is a metalloenzyme involving zinc ion (Zn²⁺), which has been widely studied due to its specific functionality of catalysing reversible hydration CO₂ to bicarbonate ion (HCO₃[–]) and proton [112]. Moreover, CA has a high turnover number of up to 10⁶ mol CO₂·mol^{–1} CA·s^{–1}, rendering it the fastest catalyst for CO₂ hydration [113]. The CA enzyme reaction of the CO₂ hydration process can be expressed as:

In literature, enzymatic CO₂ capture has been widely studied for facilitating the CO₂ conversion in absorption, adsorption and sequestration [54]. However, the drawbacks of free enzyme such as short lifetime and low stability under harsh operating conditions restrict its practical applications in CO₂ capture. To address these concerns, the preparation

of biocatalytic materials based on enzyme immobilization has been proposed as a solution to improve the stability of the enzyme, thus increasing the possibility of enzyme recovery and reuse [55, 57-59]. While the choice of immobilization strategies plays a crucial role in determining the biocatalytic material performance, various immobilization carriers with different chemical structure properties should also be taken into consideration. Carriers with functional groups such as amine, epoxy, carboxyl, sulfhydryl, hydroxyl, imidazole, indole, *etc.*, could be involved in the bindings [114, 115]. Moreover, various supports, such as nanoparticles [52, 55, 56], mesoporous silica SBA-15 [57, 58] and Fe₃O₄ magnetic microspheres [21], have also been applied for CA immobilization after their amine-, epoxy-, or carboxyl-functionalization. However, due to the drawbacks of low enzyme activity recovery, poor enzyme stability, and membrane wetting, the immobilization of enzyme on pure polymeric membranes used for CO₂ capture are rarely reported in literature. Yong *et al.* [116] as pioneer designed the PP and PSf-PDMS based biocatalytic membranes via layer-by-layer coating with mesoporous silica, PEI, polystyrene sulfonate, polyallylamine hydrochloride and CA applied in GLMC processes for CO₂ hydration. Similarly, Hou *et al.* [52] developed a TiO₂ based biocatalytic PVDF membrane for CO₂ hydration, with a sequential immobilization process of post functionalized by modifying (3-aminopropyl)triethoxysilane (APTES) and then glutaraldehyde (GLU), then covalent bound with CA enzyme. The results suggest that the immobilization of CA on polymeric membranes can exhibit enhanced stability relative to their free states while maintaining their activity within the film for longer periods.

2.1.4.4. Dense polymeric membranes

Dense (non-porous) membranes have been proposed to be applied in GLMC processes [62, 64, 117-120], as illustrated in Fig. 2-3. Compared with microporous membrane in GLMC processes, the dense membrane presents the advantage of lower

wetting tendency. However, the dense membrane with selectivity of specific gases offers a significant membrane resistance, which will restrict gas mass transfer efficiency. Moreover, for certain conditions, the dense membrane may be operated in cases where the gas streams are emitted at high pressure. Therefore, to minimize the membrane mass transfer resistance, the dense membrane should be as thin as possible to maintain its high CO₂ permeability as well as highly chemical, thermal, and pressure resistances [60].

Fig. 2-3. A schematic diagram of CO₂ absorption in a dense membrane contactor.

Typically, there are three main types of dense membrane configurations, which are dense, asymmetric, and composite membranes as shown in Fig. 2-4. For dense membrane, it has a single, uniform and dense film which can bring a significant mass transfer resistance [64]. For asymmetric membrane, the structure of membrane is not uniform composing of a thin dense top layer and a porous substrate, can significantly reduce membrane mass transfer resistance due to its thin dense layer and high permeance of the porous substrate [6]. Chen *et al.* [121] studied the wetting resistance of both symmetric and asymmetric PTFE membranes using amine-based absorbent. As a result, the asymmetric PTFE membrane showed a lower wettability in comparison to the symmetric one, mainly because

absorbents hardly tend to intrude the dense top layer of the asymmetric membrane. Composite membrane, also called as dual-layer membrane, is fabricated by coating a dense skin layer on a microporous substrate with different polymeric materials. The major advantage of composite membrane is the cost reduction. A high hydrophobic and chemical stable but expensive polymer for the CO₂ absorption process is only required for the thin dense layer while an economic polymer can be fabricated as the porous substrate [6]. The membranes such as PDMS, poly-(vinyltrimethylsilane) (PVTMS), and poly(1-trimethylsilyl)-1-propyne (PTMSP) are the most popular materials for dense membrane fabrication [63, 118, 119].

Fig. 2-4. Three types of membrane structures of non-porous membrane for GLMC processes: (a) dense membrane, (b) asymmetric membrane and (c) composite membrane.

The key features of different membranes/materials in GLMC applications were summarized in Table 2-2. Although most polymer membrane materials were low cost and anti-wetting, their undesired mechanical properties would affect the long-term stability in harsh conditions. With the addition of various inorganic top layers (*e.g.*, TiO₂, ZrO₂, SiO₂), the chemical stability and mechanical property of composite membranes were improved [78]. However, due to their nature hydrophilicities, a fluorinated modification was necessary for improving their hydrophobicities [106]. Incorporating MOFs into polymeric

membranes, the CO₂ permeability and separation performance were ameliorated due to unique affinity between MOFs and CO₂, although the cost should be considered [122]. Besides, enzyme such as CA could highly accelerate CO₂ hydration [113]. In this thesis, enzyme and MOFs were introduced into the composite membrane system for achieving highly efficient CO₂ removal in the GLMC process.

Table 2-2. Summary of the features of different membranes/materials in GLMC.

Materials	Application	Chemical stability	Wettability	Mechanical property	Cost	Key features	Ref.
PTFE/ Teflon	Porous/non-porous membrane, additive, top layer	+++++	—	+++++	+++++	High hydrophobicity; Low porosity; Weak modifiability	[29, 62]
PP	Porous membrane	++++	++	++++	+	Low porosity; Weak modifiability	[31]
PVDF	Porous membrane	++++	++	+++	+++	High porosity; Modifiability	[123, 124]
PSf	Porous membrane	++++	++	+++	+++	High porosity; High Modifiability	[32, 103]
PEIm	Porous membrane	+++	++++	++	++	Less hydrophobicity; High porosity; High Modifiability	[125]
PDMS	Non-porous membrane, Additive, top layer	++++	—	+++	++	High flexibility	[64, 126]
TiO ₂	Ceramic membrane, additive, top layer, nano-filler	+++++	+++++	+++++	+++++	High Modifiability; Requirement of hydrophobic modification	[78]
ZrO ₂	Ceramic membrane, additive, top layer, nano-filler	+++++	+++++	+++++	+++++	High Modifiability; Requirement of hydrophobic modification	[127]
SiO ₂	Ceramic membrane, additive, top layer, nano-filler	+++++	+++++	+++++	++++	High Modifiability; Requirement of hydrophobic modification; Improving surface roughness	[128, 129]
Zeolite	Inorganic membrane, additive, top layer, nano-filler	+++++	+++++	+++++	++++	High porosity; High Modifiability	[130]

MOFs	Additive, top layer, nano-filler	+++	+++	++++	+++++	Multiple pore channels; CO ₂ affinity	[131, 132]
Enzyme	Top layer, absorbent	++	+++++		+++++	High CO ₂ hydration catalysis; Requirement of immobilization	[52]

Note: ‘+’ represents for the impact intensity; ‘+++++’ means the maximum impact intensity; ‘–’ means non-wettability.

2.2. Membrane wetting

To develop a high-performance membrane contactor, minimizing overall mass transfer resistance is the main challenge for CO₂ absorption in GLMC. It has been confirmed that the mass transfer resistance would increase significantly once the membrane is wetted [31, 133]. The liquid would enter into the pores of membrane and hard to achieve mass transfer. Even marginal wetting could lead to a significant resistance to diffusion in the hollow fiber phase, as high as 60~80% of the total mass transfer resistance [134, 135]. This wetting phenomenon also occurred in membrane distillation (MD) process, which shared the similar wetting mechanism. Once the membrane got wetted due to less hydrophobicity of membrane or amphiphilic molecules of feed water altering the properties of membrane walls, the feed water would directly permeate into the distillate stream and significantly undermine salt rejection rate [136, 137]. In the case of full wetting, the MD process no longer acts as a barrier, resulting in a viscous flow of liquid water through membrane pores, incapacitating the MD process [138]. However, in GLMC processes, membrane wetting will also be induced by the corrosion of absorbent on membrane structure, which will be discussed in the following section.

The operation of the microporous GLMC can be classified into three modes: non-wetted mode, overall-wetted mode, and partial-wetted mode, as shown in Fig. 2-5. At two theoretical extreme conditions, the membrane pores are either fully filled up with liquid absorbent or fully filled up with gas, which correspond to the overall-wetted mode and non-wetted mode, respectively. For non-wetted operation mode (Fig. 2-5(a)), the membranes are hydrophobic, which prevent the liquid from penetrating into the pores (or wetted); while hydrophilic membrane will result in overall-wetted mode (Fig. 2-5(b)). Both theoretical simulation and experiment data have proven that the non-wetting mode will offer higher CO₂ gas flux from bulk gas phase to bulk liquid phase, and thus result in higher absorption

efficiency, which is preferred for CO₂ capture in membrane contactors. In contrast, if the membrane pores are fully occupied by the liquid, the CO₂ flux will be significantly suffered. Wang *et al.* [31] presented a simulation result showing that the CO₂ flux for a non-wetted membrane contactor was about six times higher than that of overall wetted membrane contactors.

Fig. 2-5. Three operation modes in GLMC processes: (a) non-wetting mode, (b) overall-wetting and (c) partial-wetting mode [139].

Therefore, for CO₂ absorption in the microporous GLMC, the non-wetted operation mode with highly hydrophobic membrane materials is always preferred. However, in real operation condition, liquid absorbents could partially penetrate into the hydrophobic membrane pores, especially during long-term operation in GLMC processes. It is regarded as membrane wetting which can refer to the partial-wetting mode (Fig. 2-5(c)). It has been well recognized that membrane wetting could lead to an increase in total mass transfer resistance, and downgrade long-term membrane performance due to stagnant liquid within the membrane pores. The theoretical modelling done by Wang *et al.* showed that with only 5% wetting, the total mass transfer resistance would increase 20% [31].

To develop membrane with anti-wetting property is one of the key research interest in membrane contactors. The ability of membrane to resist wetting by liquid is usually characterized by breakthrough pressure, ΔP , which is determined by the Young-Laplace equation [140]:

$$\Delta P = -\frac{2\gamma \cos \theta}{r_{max}} \quad (2-21)$$

where γ is the liquid surface tension; θ is the membrane's contact angle in liquid; and r_{max} is the maximum radius of membrane pores. The breakthrough pressure characterizes the minimum pressure on the liquid side that will result in liquid penetration into the membrane pores. From this equation, it can be clearly concluded that the anti-wetting property of membrane depends on the liquid surface tension, hydrophobicity of the membrane, as well as the porous structure of the membrane. However, the pores of most membranes are not cylindrical. To consider the irregular structure of pores, Franken *et al.* [140] developed a geometric pore coefficient B in the Young-Laplace equation:

$$\Delta P = -\frac{2B\gamma \cos \theta}{r_{max}} \quad (2-22)$$

where $B = 1$ for cylindrical pores, and $0 < B < 1$ for irregular pores.

Besides hydrophobicity, chemical attack by liquid absorbents such as amines also triggers membrane wetting, which results in both morphology and property changes of the membrane surface. Wang *et al.* studied the wetting behaviour of commercial PP (Celgard X40-200 and Celgard X50-215) resulted from DEA exposure. The porous structure of the membrane was significantly altered after immersing in DEA solution for several days. The uniformly slit-like pores became elliptical in shape with enlarged pore radius [19]. Such enlargement of the membrane pores will lead to a lower breakthrough pressure according to the Young-Laplace equation, which aggravates the tendency for the membrane to be wetted. In addition, they also observed that the water contact angle after 10 days of DEA immersion decreased from 108.5° to 97.5° . Their study provided direct observation of impact of chemical attack on membrane properties. Therefore, it is also important to develop membranes with strong chemical stability.

Kumar *et al.* [46] investigated the relationship between the breakthrough pressure with the surface tension of various liquid adsorbents based on experimental studies and the

Young-Laplace equation. As shown in Fig. 2-6, a positive linear relationship was obtained. It is worth mentioning here that although pure water has a relatively large surface tension, which will lead to a higher breakthrough pressure, its low CO₂ absorption capacity based on physical dissolution may decrease the overall CO₂ absorption efficiency. In contrast, amine solutions have high CO₂ absorption capacity based on reversible chemical reactions. As a result, despite the fact that amine solutions (DEA, MEA, DMEA, *etc.*) normally are with low surface tension as well as chemical corrosion to membrane materials, they are still extensively researched and used as liquid absorbents for membrane contactors due to their high CO₂ absorption capacities. Therefore, it is of paramount importance to develop membranes with high hydrophobicity and good chemical stability.

Fig. 2-6. The relationship between breakthrough pressures with surface tension of liquid absorbents (experimental data was based on hydrophobic microporous PTFE membrane) [46].

2.3. Wetting prevention

In order to minimize membrane wetting, different methods have been suggested including effective selection of absorbents, optimization of operation conditions, surface modification of membranes, and development of dense membranes.

2.3.1. Absorbent selection

Firstly, an ideal absorbent should have a high absorption capacity (high solubility of CO₂ or high reactivity with CO₂). Secondly, a good chemical compatibility with the membrane material is also important for preventing swelling and degradation of membrane physically or chemically. Therefore, an absorbent with high surface tension and low corrosivity is generally preferred. Moreover, it can offer a high breakthrough pressure or liquid entry pressure for reducing wetting tendency. What's more, low vapor pressure and good thermal stability of absorbent should be considered, which will minimize solvent loss and thermal degradation during operation. In addition, if the absorbent is volatile, its vapor can diffuse then condense in the membrane pores and even penetrate through the membrane, thus inducing extra membrane mass transfer resistance [141]. Last but not least, the absorbent should preferably be non-toxic and easy to regenerate in consideration of environment-friendly and economy of the operation [36, 45, 83].

2.3.2. Optimization of operation conditions

Operating parameters such as temperature and pressure have been proven to affect membrane wetting and CO₂ absorption performance [36]. Lu *et al.* [139] reported that CO₂ absorption performance decreased about 59% by increasing the operating temperature from 288 K to 308 K due to changes in absorbent and membrane physical properties (solubility for CO₂, solvent viscosity, surface tension of solvent and membrane hydrophobicity). The liquid operating pressure ought to be higher than pressure of the gas phase in order to prevent bubbling that can lead to CH₄ loss and reduction in absorption efficiency [142]. In contrast, high liquid pressure can increase the wetting tendency due to easier liquid penetration into membrane pores.

2.3.3. Membrane surface modification

The ideal microporous membrane contactor should have characteristics such as high hydrophobicity, suitable pore size, low membrane resistance, good mechanical properties, and chemical resistance. The overall membrane performance is determined by intrinsic polymer properties, membrane structures, dopant effect, *etc.*. Therefore, developing new membrane materials always requires a series of studies of fabrication processes and optimization of various parameters. In contrast, membrane surface modification on pre-fabricated porous membrane substrate is relatively less complex to achieve the mentioned requirements for wetting prevention by endowing the membrane surface with enhanced hydrophobicity without changing the internal porous structure of the membrane. Several chemical and physical methods have been used for surface modification, such as chemical grafting, surface coating, solution casting, plasma and laser treatment, and other methods, to increase membrane surface hydrophobicity and roughness [36, 97]. Plasma treatment triggered the formation of coating layer with good adhesion on the polymeric surface [36]. Therefore, the duration of coating layer for long-term process should be satisfied. Similarly, a robust active layer also can be obtained by chemical grafting which involved the chemical attachment of compounds on reactive sites of membrane surface [143]. However, as compared with chemical grafting, plasma treatment process is expensive due to the need of vacuum environment [97], thereby limiting its scalability. Besides, although a uniform coating layer can be formed with solution casting method, this process is uneconomical (expensive solvents) and environmentally malignant [36]. Therefore, the scalability should be considered. Some case studies have been introduced for better understanding of the advantages of membrane modification.

As secondary bonding force between carbon-fluorine bonds requires minimum energy to break, the surface energy for a membrane surface with higher fluorine content

will have minimum surface energy and thus more hydrophobic. Therefore, the most applied strategy to develop new membrane with higher hydrophobicity is to increase the fluorine content. For example, porous PVDF-co-hexafluoropropylene (PVDF-HFP) hollow fiber membrane was modified with the mixture solution of Fluorolink[®]S10 (FS10) and tetraethyl orthosilicate (TEOS) [144]. After the dehydrofluorination process by alkaline treatment, hydroxyl groups can be attached on the main carbon chain. The hydroxyl groups can link to TEOS, which subsequently connected to FS10 through condensation reaction. After surface modification, the membrane structure was almost unchanged (Fig. 2-7(a—b)). However, the water contact angle increased significantly from 95.5° to 127.8°. In this study, it was shown that the modified PVDF-HFP membrane always had a higher CO₂ absorption flux than the unmodified membrane under different operation conditions, as shown in Fig. 2-7(c). This can be explained by the enhanced hydrophobicity inducing higher breakthrough pressure, thus preventing water penetrating into membrane pores. This will lead to an increase in total mass transfer coefficient, thereby enhancing the CO₂ absorption flux. Similarly, FS10 can also be employed to modify the surface of a hydrophilic PAI membrane to achieve a higher contact angle of 117° [104].

Fig. 2-7. FE-SEM images (magnification at 1000×) for the outer surface morphologies of PVDF-HFP membrane: before (a) and after surface modification (b); CO₂ flux as a function of liquid velocity for both original and modified membrane(c) [144].

It is worth mentioning that surface modification strategies for the above introduced work both observed a decrease in the mean pore diameters of the membrane. This might lead to the loss of CO₂ flux in some degree. In the gas-liquid CO₂ absorption process using

membrane contactor, the membrane itself provides a non-selective additional barrier for mass transport. Larger membrane pores could minimize such hindrance. Therefore, membranes with large pore sizes could improve the CO₂ absorption efficiency. However, enlarging the pore size will inevitably increase the membrane wetting tendency according to the Young-Laplace equation. Therefore, it is a challenge to develop membranes simultaneously with large pore sizes and anti-wetting property. To address this contradicting effect, a novel approach of incorporating hydrophobic inorganic nanoparticles to PEIm membrane was developed [79]. The PEIm substrate was fabricated through a novel triple-orifice spinneret in the hollow fiber spinning process. As a result, the as-fabricated PEIm membrane possessed a high surface porosity and large pore size compared with that from the normal process, as shown in Fig. 2-8(a). The increase in pore size could minimize the total membrane mass transfer resistance. Subsequently, by incorporating hydrophobic inorganic nanoparticles, the membrane surface can be made into highly hydrophobic and chemical resistant to prevent the membrane from wetting caused by its large pores. As a result, the CO₂ flux for the membrane with large pore diameter is always higher than that of the membrane with small pores under various liquid flow velocities (Fig. 2-8(b)). Besides, Lin *et al.* [78] developed a fluorinated TiO₂/PVDF composite hollow fiber membrane via an *in-situ* vapor induced hydrolyzation process incorporated with perfluoroalkylsilane grafting. The surface microstructure and pore size of the PVDF substrate could be tuned (100 nm to 25 nm) by controlling the Ti precursor doping amount. High CO₂ flux, high hydrophobicity, and excellent chemical resistance could be achieved and maintained using MEA solution as absorbent in a 21-day long-term operation.

Fig. 2-8. (a) FE-SEM images of PEIm-A (traditional fabrication process), PEIm-B (triple-orifice spinneret fabrication process), and PEIm-A-fSiO₂ and PEIm-B-fSiO₂ membranes after hydrophobic silica modification. (b) CO₂ fluxes as the function of water and 2M sodium taurinate (ST) velocities for both hydrophobic silica particles modified PEIm membranes [79].

2.3.4. Dense membranes

Dense membranes with lower wetting tendency and better chemical and thermal resistance have received attention. A series of works have devoted to comparing the CO₂ absorption performance between microporous and dense membrane contactors by mass-transfer and process simulations, which are important for practical application of GLMC. Several representative studies of dense membranes are summarized in Table 2-3.

Table 2-3. CO₂ absorption performance of various dense membranes in GLMC processes.

Membrane material	Membrane type	Dense layer thickness (μm)	Absorbent	Pressure (bar)	CO ₂ (%)	Remarks	Ref.
PDMS	Dense	165	Water/DEA	–	10(CO ₂ /N ₂)	The dense PDMS presented a lower CO ₂ removal efficiency than that of microporous membrane, due to the addition of membrane resistance. However, the PDMS membrane selectivity could compensate for the low permeation rate to an extent.	Al-Saffar <i>et al.</i> [64]
PDMS	Dense	165	Water/MEA /DEA	3.4~24	10(CO ₂ /N ₂)	Mass transfer coefficient in dense membrane is lower than of microporous membrane. Aqueous solutions can reduce the need to maintain a high pressure.	Ozturk <i>et al.</i> [117]
PDMS	Dense	35	Water	–	20~80(CO ₂ /CH ₄)	In the water absorption process, the membrane resistance is dominant. The CO ₂ /CH ₄ selectivity declined with an increase in liquid velocity.	Heile <i>et al.</i> [118]
PVTMS	Asymmetric	0.1	Water/MEA	0	53(CO ₂ /CH ₄)	It is one of the early stage studies of dense membrane contactor.	Shelekhin <i>et al.</i> [120]
PVTMS	Asymmetric	0.2	Water/ K ₂ CO ₃	–	100	The circulating mode can achieve higher gas permeance than flow through mode using water as absorbent. Increasing the conc. of K ₂ CO ₃ in a certain range can significantly improve the mass transfer coefficient.	Shalygin <i>et al.</i> [119]

PTMSP/PP Teflon AF2400/PP	Composite	1.1 1.9	MEA/DEA/ TEA	0.5~35	30(CO ₂ /N ₂)	The composite hollow fiber can provide a wetting protection effect without affecting the overall mass transfer coefficient.	Nguyen <i>et al.</i> [62]
Teflon AF1600/PP PTMSP/PP PIM-1 ^a /PP	Composite	12 2 2	Water/MEA	1.2	99.7	Compared with Teflon AF1600/PP membrane, PTMSP/PP and PIM-1/PP membranes provided the higher overall mass transfer coefficient due to thinner dense layers. However, the wetting problem still could be occurred in PTMSP/PP and PIM-1/PP, due to the presence of water and MEA vapor within the non-porous layer hindering the migration of CO ₂ through both membranes.	Scholes <i>et al.</i> [145]
PPO ^b /PolyActive TM ^c	Composite	1	Water	8	35(CO ₂ /CH ₄)	The process could recover 96.6% of CO ₂ and purify CH ₄ to 98%. The corresponding energy requirement is 20 to 35% lower than that reported for packed column-based processes. Due of the preponderant water side mass transfer resistance, gas selectivity is mainly controlled by the absorbent selectivity.	Belaissaoui <i>et al.</i> [146]

^a PIM-1: polymer of intrinsic microporosity;

^b PPO: commercial membrane of Parker P-240;

^c PolyActiveTM represents for poly(ethylene oxide) PEO (amorphous)–poly(butylene terephthalate) PBT (crystalline) block copolymer.

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Chapter 3 Materials and Methods

This chapter covers detailed information of the materials, chemicals and methodologies used in Chapters 4, 5 and 6. The first section summarizes all the materials and chemicals; the second section introduces the commonly used methods for membrane characterizations; and the third and fourth sections describe the CO₂ absorption experiments in the lab-scale GLMC setup and the long-term performance tests, respectively.

3.1. Materials and chemicals

PVDF hollow fiber membranes were selected as substrates for development of composite membrane contactors due to the desirable properties such as hydrophobicity, suitable pore size, high porosity, good mechanical strength, and high thermal stability for GLMC applications (see Table 3-1). All chemicals used for experiments in Chapters 4, 5 and 6 are summarized and listed in Table 3-2. In particular, ST solution [79] as absorbent for CO₂ absorption was prepared by taurine and NaOH. Deionized water (DI water, produced by Milli-Q system, Millipore, USA) was used for preparing solutions and as physical absorbent for CO₂ absorption.

Table 3-1. Properties of the PVDF hollow fiber substrates.

Properties	PVDF ^a	PVDF ^b [147]	PVDF ^c [78]
	In-house made	Commercial	Commercial
Dynamic contact angle, °	111.5 ± 3.9	110.0 ± 2.9	98.1 ± 0.2
Peak pore size, nm	530	44	100
Overall Porosity, %	—	85	89
Tensile's modulus (E _t), MPa	17.5 ± 1.0	26.2 ± 2.4	23.9 ± 1.8
Strain at break(ε _b), %	44.2 ± 5.7	97.4 ± 4.1	90.9 ± 5.3

^a for development of fTiO₂-SiO₂/PVDF composite hollow fiber membranes (Chapter 4);

^b for development of biocatalytic composite hollow fiber membranes (Chapter 5);

^c for development of mZIF-8 based mixed matrix composite hollow fiber membranes (Chapter 6).

Table 3-2. Chemical reagents used for experiments.

Chemical	Synonym	Formula	Molecular weight (g·mol ⁻¹)	Assay	Supplier
Sodium hydroxide		NaOH	40	≥99%	Merck
Titanium(IV) isopropoxide	TTIP	Ti[OCH(CH ₃) ₂] ₄	284.22	97%	Sigma-Aldrich
Tetraethyl orthosilicate	TEOS	Si(OC ₂ H ₅) ₄	208.33	≥99%	Sigma-Aldrich
Diethanolamine	DEA	HN(CH ₂ CH ₂ OH) ₂	105.14	≥99%	Sigma-Aldrich
1H, 1H, 2H, 2H-perfluorodecyltriethoxysilane	PFTS	C ₁₆ H ₁₉ F ₁₇ O ₃ Si	610.38	97%	Sigma-Aldrich
Dopamine hydrochloride		(HO) ₂ C ₆ H ₃ CH ₂ CH ₂ NH ₂ ·HCl	189.64		Sigma-Aldrich
Polyethylenimine, branched	PEI	H(NHCH ₂ CH ₂) _n NH ₂ (M _w =800)			Sigma-Aldrich
Tris(hydroxymethyl) aminomethane	Tris	NH ₂ C(CH ₂ OH) ₃	121.14	≥99.8%	Sigma-Aldrich
Hydrochloric acid		HCl	36.46	37%	Sigma-Aldrich
Carbonic anhydrase from bovine erythrocytes	CA		(≥3500 W-A units/mg protein)	≥95%	Sigma-Aldrich
Glutaraldehyde	GLU	OHC(CH ₂) ₃ CHO	100.12	50% in H ₂ O	Sigma-Aldrich
4-nitrophenyl acetate	p-NPA	CH ₃ CO ₂ C ₆ H ₄ NO ₂	181.15		Sigma-Aldrich
4-nitrophenol	p-NP	O ₂ NC ₆ H ₄ OH	139.11		Sigma-Aldrich
Zinc nitrate hexahydrate		Zn(NO ₃) ₂ ·6H ₂ O	297.49	98%	Sigma-Aldrich
2-methylimidazole	Hmim	C ₄ H ₆ N ₂	82.10	99%	Sigma-Aldrich
(3-aminopropyl) triethoxysilane	APTES	H ₂ N(CH ₂) ₃ Si(OC ₂ H ₅) ₃	221.37	99%	Sigma-Aldrich
Sylgard® 184 silicone elastomer kit		base/curing agent =10/1 wt. %			Dow Corning
Isopropyl alcohol	IPA	(CH ₃) ₂ CHOH	60.10	≥99.7%	Sigma-Aldrich
Methanol	MeOH	CH ₃ OH	32.04	≥99.9%	Merck
Ethanol	EtOH	C ₂ H ₅ OH	46.07	≥99.9%	Merck
<i>n</i> -hexane		CH ₃ (CH ₂) ₄ CH ₃	86.18	≥96.0%	Merck
Ethanolamine	MEA	NH ₂ CH ₂ CH ₂ OH	61.08	≥99%	Sigma-Aldrich
Taurine		H ₂ NCH ₂ CH ₂ SO ₃ H	125.15	≥99%	Merck
Carbon dioxide		CO ₂	44		Singapore Oxygen Air Liquide Pte Ltd
Biogas		CO ₂ /CH ₄ = 40/60 (v/v) %			Singapore Oxygen Air Liquide Pte Ltd

3.2. Characterizations of membranes

The outer surface and cross-section morphologies of the prepared membrane samples (hollow fibers were fractured in liquid nitrogen) were observed using a field emission scanning electron microscope (FE-SEM, JSM-7600F JOEL, Japan) at an operation voltage of 5 kV, which were sputtered with a thin layer of platinum by a sputter coater prior to analysis (JEC-3000FC, JEOL, Japan). The associated electron dispersive X-ray (EDX) spectroscopy was employed to detect the elemental composition on the outer surface and cross-section of the prepared composite hollow fiber membranes.

The chemical structures of the outer surface chemical functional groups of the prepared hollow fiber membranes were measured by a fourier-transform infrared spectroscopy—attenuated total reflectance (ATR-FTIR, IRPrestige-21, Shimadzu, Japan) over a scan range of 400—4000 cm^{-1} with a resolution of 4 cm^{-1} . The chemical composition of the outer/inner surfaces of hollow fibers was investigated by X-ray photoelectron spectrometers (XPS, Thermo ESCALAB 250, USA for Chapter 4 work; AXIS Supra, Kratos Analytical, UK for Chapter 5 work; Quantera II, Physical Electronics, Inc. (PHI), USA for Chapter 6 work) using monochromatic Al K α excitation source at 1486.7 eV and with the sampling depth of 6—10 nm. The C 1s peak with the corrected energy at 284.5 eV was used as reference for spectra calibration. All XPS spectra for elements were analyzed by CasaXPS software. The detailed description for the measurement can be found in literature [148].

To evaluate the surface properties of fibers, a tensiometer (DCAT11 Dataphysics, Germany) was used to perform dynamic water contact angle measurement. The dynamic contact angles of hollow fiber membranes were calculated by wetting force according to the Wilhelmy method. Three cycles of immersion into and emersion from DI water were

carried out for each sample, and each run was repeated at least three times. In addition, the static water contact angle was also measured by using a goniometer (Contact Angle System OCA 15EC, DataPhysics, Germany) via sessile drop method. To minimize experimental errors, water contact angles were obtained by averaging three measurements.

The membrane pore size and pore size distribution were measured by a capillary flow porometer (CFP 1500A, PMI, Porous Material. Inc., USA). The hollow fiber membranes were glued to the sample holder using epoxy and wetted thoroughly by a low surface tension GalwickTM solution ($16.0 \times 10^{-3} \text{ N}\cdot\text{m}^{-1}$). The detailed experimental principles and procedures had been described in previous literature [41].

The membrane surface microstructures were examined by an atomic force microscopy (AFM, XE-100, Park System, Korea) in $5 \mu\text{m} \times 5 \mu\text{m}$ scan size. Each sample was repeated at least three times. The parameters of membrane surface roughness are represented by the roughness average (R_a) and the root-mean-squared roughness (R_q).

A Zwick Roell Z0.5 universal testing machine was used for determining the mechanical properties of the hollow fiber membranes. Tensile modulus (E_t), tensile stress at break (σ_b) and strain at break (ε_b) were measured to indicate the mechanical stiffness and strength, and deformation of membrane under a given load. Each sample was repeated at least five times.

To evaluate the structural stability of the skinned layer of the composite membranes, the prepared composite hollow fiber membranes underwent ultrasonic treatment at 25 kHz for 5 min in an ultrasonication bath (FB 15068, Fisher Scientific, USA) to remove any surface substances attached by van der Waals's force before characterization measurements.

3.3. CO₂ absorption performance in GLMC tests

Lab-scale modules were prepared by sealing predetermined pieces of hollow fibers in both ends of glass or Teflon tubings with epoxy resin for preventing leakage. In case of leakage, gas bubbles in the shell phase can be directly and clearly observed through the glass tube. Pure CO₂ or biogas as feed gas flowed in the lumen side of the hollow fibers, which was controlled and measured by a mass flow controller (Cole-Parmer®, USA) and a digital bubble meter (Bios-Dender 510L), respectively; the liquid absorbent was controlled by a digital peristaltic pump (MasterFlex® L/S, USA) and flowed over the shell side of the hollow fibers in a counter-current direction. The micro gas chromatograph (6890 Hewlett Packard, TCD) was used to analyze the inlet and outlet mixed gas compositions. All data collected after the experiment were operated for 30 min at 25 °C to ensure that the system has reached steady state. The results of each run were averaged from five times of sampling. The schematic illustration for the GLMC experimental setup is shown in Fig. 3-1. And the characteristics of membrane modules and operation conditions in GLMC processes are summarized in Table 3-3. The contacting process could be spontaneously proceeded at room temperature. In order to prevent bubbling problem, no extra or quite low pressure was required for the feed gas. Surface modifications were carried out on shell side of the three employed PVDF hollow fiber substrates due to the same side for the selective layers of the substrates. Therefore, the absorbent liquids flowed over the shell sides, and the feed gases flowed through the lumen sides.

The CO₂ absorption flux was used to evaluate the membrane CO₂ removal efficiency rate, which can be calculated by Eq. 3-1:

$$J = \frac{P(Q_{in} - Q_{out})}{RTA_m} \times 10^3 \quad (3-1)$$

where J is the CO₂ absorption flux (mol·m⁻²·s⁻¹) of the hollow fiber membrane, Q_{in} and Q_{out} are the specific CO₂ flow rates (10⁻³ m³·s⁻¹) of feed-in and feed-out, respectively, R is

the ideal gas constant of $0.083 \text{ bar}\cdot\text{L}\cdot\text{mol}^{-1}\cdot\text{K}^{-1}$, T is the operating temperature of 298 K, A_m is the membrane surface area (m^2), and P is the operating pressure in gas phase (bar).

The CO_2/CH_4 selectivity was used to describe the separation efficiency, which can be calculated by Eq. 3-2:

$$\alpha_{\text{CO}_2/\text{CH}_4} = \frac{C_{\text{CO}_2,F}/C_{\text{CO}_2,R}}{C_{\text{CH}_4,F}/C_{\text{CH}_4,R}} \quad (3-2)$$

where $\alpha_{\text{CO}_2/\text{CH}_4}$ represents the CO_2/CH_4 selectivity. $C_{\text{CO}_2,F}$ and $C_{\text{CO}_2,R}$ are the CO_2 concentrations in feed and retentate stream, respectively. $C_{\text{CH}_4,F}$ and $C_{\text{CH}_4,R}$ are the concentrations of CH_4 in feed and retentate stream, respectively.

Fig. 3-1. Schematic diagram of CO_2 absorption in the GLMC process.

Table 3-3. Characteristics of membrane modules and operation conditions in GLMC processes.

	Chapter 4	Chapter 5	Chapter 6
Characteristics of modules			
Module type	Glass	Glass	Teflon
Module ID, mm	6.4	6.4	6.4
Module length, mm	83	83	220
Fiber OD, mm	1.22	1.53	1.47
Fiber ID, mm	0.71	0.84	0.76
Contact area (eff.), mm ²	1000	640	2530
Number of fibers, N	6	3	5
Operation conditions in GLMC			
Temperature, °C	25	25	25
Gas pressure, bar ^a	1	1	1.07
Feed gas	Pure CO ₂ and biogas	Pure CO ₂	Pure CO ₂ and biogas
Feed absorbent	1M MEA and 1M ST	Water and 1M MEA	Water and 1M MEA
Gas phase	in the lumen side of hollow fiber		
Liquid phase	in the shell side of hollow fiber		

^a refers to absolute pressure.

3.4. Long-term performance

Long-term performance tests of the proposed composite hollow fiber membranes (in Chapters 4 and 6) were carried out periodically. After each run of CO₂ absorption test, the membranes modules were filled with water, MEA or ST solution to ensure that the outer surface of membranes were continuously in contact with the absorbents. The membranes surface morphologies and water contact angles (in Chapter 4) were also examined periodically over the testing period.

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Chapter 4 Development of Low Mass-Transfer-Resistance Fluorinated TiO₂-SiO₂/PVDF Composite Hollow Fiber Membrane Used for Biogas Upgrading in Gas-liquid Membrane Contactor¹

4.1. Introduction

GLMC is a promising alternative to the conventional absorption processes which could achieve a high efficiency for CO₂ capture. However, membranes used in GLMC are prone to pore wetting due to insufficient hydrophobicity and low chemical resistance, consequently resulting in significant increase in mass transfer resistance [26, 27]. Inorganic materials such as ceramic membranes, have been proposed to be employed for CO₂ capture in harsh conditions due to their excellent chemical resistance, thermal stability, and mechanical properties [47-49]. However, high capital cost and brittleness of ceramic membranes are the main drawbacks that limit their wide applications. Inorganic/organic composite membrane, as a new class of hybrid type, is considered as the promising materials in overcoming these drawbacks. The organic membrane substrate serves as a low-cost, flexible, and highly porous support, while the thin inorganic layer provides protection by preventing the organic substrate from direct contacting with chemicals or other harsh operating conditions [149]. Our previous works [78, 150] have successfully prepared an inorganic/organic composite ultra-filtration hollow fiber membrane by using an amphiphilic copolymer to facilitate the bonding between hydrophobic organic substrate and hydrophilic inorganic layer, thus achieving an improved performance as well as enhanced mechanical and chemical stabilities. However, for the GLMC application, the

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copolymer bonding may limit the degree of adhesion stability, as it can easily be damaged by the chemical absorbent vapor in GLMC operation, thus affecting its long-term performance.

In this study, we aim to design and fabricate a low mass-transfer resistance $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ composite membrane via facile *in-situ* vapor-induced hydrolyzation method, followed by hydrophobic modification. The surface hydroxylation was employed for generating stable and permanent anchoring sites on macroporous PVDF substrates by alkali treatment. The microstructure of membrane was tuned by controlling the amount of doped Si precursor to form an integrated mesoporous $\text{TiO}_2\text{-SiO}_2$ layer. The physical and chemical properties of the prepared $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ membranes were characterized. The CO_2 absorption performance and the long-term stability were examined by using two types of absorbents (ST [32-33] and MEA) in the GLMC process. The schematic illustration (Fig. 4-1) showed the development of the inorganic/organic composite hollow fiber membranes and their anticipated effects in the GLMC application.

Fig. 4-1. Schematic illustration of the $\text{fTiO}_2\text{-SiO}_2/\text{PVDF}$ composite hollow fiber membrane and CO_2 removal in the GLMC application.

4.2. Experimental

Materials and chemicals used in this study have been summarized in Section 3.1 of Chapter 3.

4.2.1. PVDF surface hydroxylation

The chemical modification of surface hydroxylation involves PVDF surface treatment using an aqueous alkali solution. Firstly, the PVDF membranes were thoroughly rinsed with DI water to remove the glycerol preservatives. Secondly, the cleaned PVDF hollow fibers were immersed into 1 M NaOH solution under magnetic stirring for 3, 6 and 12 h, at a heating temperature of 60 °C. After alkali treatment, the hollow fibers were rinsed with DI water, and then dried at 50 °C in an oven for 12 h.

4.2.2. Preparation of a fTiO₂-SiO₂/PVDF composite hollow fiber membrane

The pretreated PVDF hollow fibers were used as substrates for TiO₂-SiO₂ film deposition. The modification solution was synthesized as follows: a desired amount of TTIP and/or TEOS were dissolved into IPA solvent with vigorous stirring for 120 min. After that, a desired amount of DEA used for tuning the reaction rate of hydrolyzation were sequentially dissolved into the as-prepared solution with vigorous stirring for 60 min, and then the precursor solution was obtained. The compositions of the precursor solutions are summarized in Table 4-1.

Table 4-1. Compositions of precursor solutions for preparation of TiO₂-SiO₂/PVDF composite hollow fiber membranes.

Membrane ^a	TEOS (g)	DEA (g)
TiO ₂ -SiO ₂ -0/PVDF	0	0.5
TiO ₂ -SiO ₂ -0.5/PVDF	0.5	0.8
TiO ₂ -SiO ₂ -1/PVDF	1	1.0

^a IPA content = 60 g; TTIP content = 2 g (same amount for all types of membranes).

The surface modification was carried out by immersing dried pretreated PVDF hollow fibers into the as-prepared solutions via stirring for 30 min. The membranes were then placed in a humidity chamber for *in-situ* vapor-induced hydrolyzation reaction at 100 °C for 30 min. Hydrolyzation of Ti and Si precursors resulted in formation of TiO₂ and SiO₂ on the PVDF membrane surface during the reaction. After that, the prepared membranes were rinsed with excess DI water to remove loosely bound and stacked layer of TiO₂ and SiO₂ nanoparticles on the inorganic film layer, followed by drying at 50 °C for 12 h.

For hydrophobic modification, the prepared TiO₂-SiO₂/PVDF membranes were further treated by 2 wt.% of PFTS in EtOH at 60 °C for 24 h. The membranes were then dried in an oven at 70 °C for 12 h. After the drying process, the membranes were rinsed with excess ethanol and DI water to remove any unreacted PFTS residue. The membranes were subsequently dried at 50 °C for 12 h.

4.2.3. Membrane characterizations

The morphologies of the hollow fibers were observed by FE-SEM. EDX was employed to detect the elemental composition on cross-section of fTiO₂-SiO₂/PVDF membranes. The membrane pore size and pore size distribution were measured by CFP. The chemical composition of the outer surface of hollow fibers was investigated by XPS. Surface dynamic water contact angle and static water contact angle were measured by tensiometer and goniometer, respectively. The mechanical properties were also been conducted. Ultrasonic treatment was used for evaluating the structural stability of the skinned layer of the composite membranes. The procedures of the mentioned characterizations have been described in Section 3.2 of Chapter 3.

4.2.4. CO₂ absorption and long-term performances in GLMC

The CO₂ absorption and long-term operation for the developed composite hollow fiber membranes in the GLMC process were conducted, which have been introduced in Sections 3.3 and 3.4 of Chapter 3.

4.3. Results and discussion

4.3.1. Surface hydroxylation of PVDF substrates by alkali treatment

The dynamic water contact angle and mechanical strength were utilized to evaluate the surface hydroxylation of PVDF substrates after alkali treatment. As shown in Fig. 4-2(a) and (b), the surface hydrophilicity increased while the mechanical property decreased during the test, indicating that the PVDF surface might have changed due to the dehydrofluorination after alkali treatment [35-36]. Thus, high surface-energy functional groups of carbonyl (C=O, 531.5 eV) and hydroxyl (C-O, 533.2 eV) were generated, and the dehydrofluorinated CHF (288.6 eV), CF₂-CHF (290.8 eV) and CF₃ (293.8 eV) could also be detected, as shown in Fig. 4-2(c) and (d) [37-39]. It should be noting that a significant enhancement of hydrophilicity (dynamic water contact angle of 71°, which is ~36.0% drop from initial value) with only a slight mechanical property deterioration (tensile strength of 16.2 MPa, which is ~7% drop from initial value), and this could be obtained after 6 h of alkali treatment. Therefore, the PVDF substrate obtained by surface hydroxylation for 6 h was selected for further study.

Fig. 4-2. Comparisons of (a) surface hydrophilicity, (b) mechanical property, and XPS spectra on (c) C 1s and (d) O 1s of PVDF substrate after surface hydroxylation with different hours of treatment.

The PVDF substrate morphologies and microstructures were further characterized before and after surface hydroxylation for 6 h. The pristine PVDF substrate was highly porous with a peak pore size of ~530 nm (Fig. 4-4). From the surface FE-SEM images in Fig. 4-3(a), however, the largest surface pore size was ~1 μ m that may result in the penetration of the top modification layer and forming defects. Apparently, this type of surface structure was not suitable for GLMC. The mesoporous layer deposited onto such macroporous substrates should be an integrated layer, which will be discussed in section

4.2.2. After the surface hydroxylation process, shown in Fig. 4-3(b) and Fig. 4-4, there was no significant change in surface morphology and microstructure. This implies that the surface hydroxylation for 6 h has not caused severe damage of the microstructure of the substrate.

Fig. 4-3. FE-SEM images of shell surfaces of PVDF substrate (a) before and (b) after the surface hydroxylation process for 6 h.

Fig. 4-4. Pore size and pore size distributions of PVDF substrate before and after the surface hydroxylation process for 6 h.

4.3.2. Membrane Characterization

4.3.2.1. Morphologies and microstructures of fTiO₂-SiO₂/PVDF composite hollow fiber membranes

The surface morphologies of fTiO₂-SiO₂/PVDF composite hollow fiber membranes with different amounts of doped Si precursors are presented in Fig. 4-5. For the fTiO₂-SiO₂-0/PVDF membrane (without Si), shown in Fig. 4-5(a), it could be observed that the fTiO₂ nanoparticles deposited on the PVDF substrate, but could not cover the big pores and form the continuous layer. Moreover, an additional peak showing a slightly smaller pore size after modification with fTiO₂ layer emerged, and this is due to the blocking of some large macropores by the inorganic particles. After adding 0.5 g of Si precursor dopant, the fTiO₂-SiO₂-0.5/PVDF membrane was formed. From this, the clusters of nanoparticles could be observed more obviously, and the surface pore size significantly decreased to ~260 nm with a narrow pore size distribution, shown in Fig. 4-6. By continuing to increase the amount of Si doped, shown in Fig. 4-5(c), a relatively uniform and integrated fTiO₂-SiO₂ layer was formed with a peak pore size of ~25 nm (Fig. 4-6). This indicates that the Si precursor doping induced a microstructure tuning effect on the macroporous substrate. In addition, for the fTiO₂-SiO₂-1/PVDF membrane (1 g of Si precursor), a small amount of pores with an average size of ~180 nm could also be detected in Fig. 4-6. This is likely to be as a result of the PVDF substrate possessing large surface pores (> 1 μ m), which cannot be fully covered by the TiO₂-SiO₂ modification layer.

Fig. 4-5. FE-SEM images of shell surfaces of (a) $\text{fTiO}_2\text{-SiO}_2\text{-0/PVDF}$, (b) $\text{fTiO}_2\text{-SiO}_2\text{-0.5/PVDF}$, and (c) $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes.

Fig. 4-6. Pore size and pore size distributions of $\text{fTiO}_2\text{-SiO}_2\text{-0/PVDF}$, $\text{fTiO}_2\text{-SiO}_2\text{-0.5/PVDF}$, and $\text{fTiO}_2\text{-SiO}_2\text{-1/PVDF}$ composite hollow fiber membranes, respectively.

There is a trend for the pore size of the $\text{fTiO}_2\text{-SiO}_2$ layer to decrease with an increasing amount of doped Si precursor. This could be due to water attacking the strained Si-O-Si bonds at high temperature during the hydrothermal treatment, leading to bond cleavage via hydrolysis. Thus the bond cleavage promoted the reconstruction of the Si-O-Si network, and then the relatively stable bonds accompanied with densified silica network

were formed via condensation by water molecule removal [40-41]. Consequently, the fusion of SiO₂-TiO₂ nanoparticles sealed the grain boundaries and large pores during the hydrothermal process of vapor-induced *in-situ* hydrolyzation, thereby forming an integrated layer.

FE-SEM and EDX analysis were carried out on the cross-section of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane to examine its morphology and the distribution of TiO₂-SiO₂ particles. As shown in Fig. 4-7(a), the PVDF substrate exhibited a sponge-like structure. The fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane, on the other hand, had a denser top layer deposited on the macroporous PVDF substrate, as shown in Fig. 4-7(b). The top layer, with a thickness of 1.4 μm, was composed of inorganic nanoparticles that formed the packed pore structures. According to the EDX line scanning result in Fig. 4-7(c), the Ti (red line) and Si (blue line) elements were mostly deposited on the surface of the prepared hollow fiber membrane, with a small amount deposited on the inner structure of the PVDF substrate. The minor amount of internally distributed Ti and Si elements might be ascribed to the diffusion of precursors into substrate pores during modification. Moreover, to some extent, it proved that the skin layer has infiltrated into the substrate, which also leads to an enhancement in mechanical and bonding performance for fTiO₂-SiO₂/PVDF membranes.

Fig. 4-7. The cross-section images of (a) PVDF substrate, and (b) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane, and (c) EDX line scan of Ti (red) and Si (blue) elements across the cross-section of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane.

4.3.2.2. Chemical composition of fTiO₂-SiO₂/PVDF composite hollow fiber membranes

The chemical composition and the nature of the chemical bonding of the fTiO₂-SiO₂/PVDF composite hollow fiber membrane was analyzed using XPS, as shown in Fig. 4-8(a) and (b). The Ti 2p peaks at 458.8 and 464.6 eV were corresponding to the Ti-O-Ti bonds [42-43]. The Si 2p peak at 102.2 eV was corresponding to Si-O-Si bond located at from SiO₂, as shown in Fig. 4-8(c) and (d) [43-44]. For the C 1s shown in Fig. 4-8(e) and (f), the reduction of the presented CH₂-CF_x peak could be attributed to surface hydroxylation. The stronger peak of CF₃ could be ascribed to the PFTS modification.

Fig. 4-8. The XPS spectra of (a) Ti 2p, (c) Si 2p, and (e) C 1s on fTiO₂-SiO₂-1/PVDF membrane and PVDF substrate; and the corresponding curve fittings of (b) Ti 2p, (d) Si 2p, and (f) C 1s for fTiO₂-SiO₂-1/PVDF membrane.

According to the above results, it is believed that the formation of the inorganic layer and subsequently hydrophobic modification are based on the following mechanism: Ti and Si precursors were firstly exposed to water vapor at a high temperature of ~ 100 °C and thus hydrolysis occurred, resulting in nucleation and growth of inorganic nanoparticles via condensation, and formed the Ti-O-Ti, Si-O-Si and Ti-O-Si bonds. When uniform Ti and Si precursors were deposited on the PVDF substrates, the hydrolyzed nucleation would lead to interconnected clusters, which finally grew and formed the integrated layer [45-46].

For the subsequent hydrophobic modification, the silane groups of PFTS were first hydrolyzed to form silanol groups. This was followed by reaction with hydroxyl groups

from TiO_2 or SiO_2 on the membrane surface via condensation. The long fluorinated chains of PFTS grafted on the TiO_2 - SiO_2 surface had low surface energy, thus rendered the surface to be hydrophobic as discussed below.

4.3.2.3. Surface hydrophobicity and adhesion characterization of fTiO_2 - SiO_2 /PVDF composite hollow fiber membranes

The surface hydrophobicity of hollow fiber membranes with different Si precursor modifications were investigated, as shown in Fig. 4-9. It could be detected that the dynamic water contact angle decreased to 68° after surface hydroxylation treatment. After deposition of the fTiO_2 - SiO_2 layer, water contact angle increased to 117° , and this is believed to be due to the successful grafting of low surface-energy PFTS. By continuously increasing the amount of doped Si precursor to 1 g, a further enhancement in dynamic water contact angle up to $\sim 124^\circ$ was detected. This is because the more integrated surface of fTiO_2 - SiO_2 -1/PVDF membrane ratherly introduce more hydroxyl sites for PFTS grafting. Thus, the fTiO_2 - SiO_2 -1/PVDF membrane was selected for further adhesion characterization studies. The bonding stability between the fTiO_2 - SiO_2 layer and the PVDF substrate was investigated by assessing the change in hydrophobicity before and after ultrasonication for 5 min. It could be observed that the hydrophobicity of fTiO_2 - SiO_2 -1/PVDF composite hollow fiber membrane presented no significant change, with the dynamic water contact angle decreasing by less than $\sim 5\%$. This confirmed the good bonding stability between the top fTiO_2 - SiO_2 -1 layer with the PVDF substrate.

Fig. 4-9. Surface hydrophobicity with different modification treatments and adhesion characterization after ultrasonication.

The adhesion of the top inorganic layer with the PVDF substrate was examined through ultrasonication, shown in Fig. 4-10. It could be observed that the surface of fTiO₂-SiO₂-1/PVDF membrane without surface hydroxylation was not integrated well with a large amount of big defects (Fig. 4-10(a)) as compared to the more integrated membrane with surface hydroxylation (Fig. 4-10(c)). After ultrasonication, the fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane without surface hydroxylation was significantly stripped off (Fig. 4-10(b)), in which the pore size and pore size distribution of the large defects expanded. In contrast, for the fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane with surface hydroxylation treatment, a slight change in surface morphology could be observed. A minor peak at 55 nm emerged, by shifting from the smallest pores of 26 to 39 nm, shown in Fig. 4-10(c) and (d). The improved adhesion stability could be attributed to the coordination between the surface anchoring groups of carbonyl and hydroxy functionalities, and the Ti, Si precursors. This facilitated the bonding and growth of the inorganic particles, and verified that the surface hydroxylation was one of the key steps to fabricate a coherent membrane by improving the bonding strength of fTiO₂-SiO₂ layer with the PVDF substrate.

Fig. 4-10. FE-SEM images of (a) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane without surface hydroxylation before and (b) after ultrasonication, (c) fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane with surface hydroxylation before and (d) after ultrasonication.

4.3.3. Performance of fTiO₂-SiO₂/PVDF composite hollow fiber membranes in the GLMC application

4.3.3.1. Pure CO₂ absorption and synthetic biogas upgrading performance

In order to examine the performance of the fTiO₂-SiO₂/PVDF composite hollow fiber membranes were prepared with different amounts of doped Si precursor. The CO₂ absorption flux and the synthetic biogas upgrading performance of the pristine PVDF substrate, fTiO₂-SiO₂-0.5/PVDF and fTiO₂-SiO₂-1/PVDF composite hollow fiber membranes were tested using the absorbents of 1 M MEA and ST, shown in Fig. 4-11. For both pure CO₂ and synthetic biogas feeds, the composite hollow fiber membranes exhibited higher CO₂ flux compared to the pure PVDF membrane. In fact, there is a trend of increasing CO₂ flux with an increased amount of Si precursor doping. This becomes more

pronounced at higher absorbent flow rates and using pure CO₂ as the feed.

Fig. 4-11. (a) pure CO₂ absorption flux and (b) synthetic biogas upgrading performance of various membranes with different modification treatments.

The CO₂ absorption flux presented a rising trend when the absorbents of MEA and ST flow velocities increased from 0.1 to 0.3 m·s⁻¹, indicating that the liquid phase boundary layer governs most of the mass transfer resistance. Since the reaction between the chemical absorbents and CO₂ occurred near the gas-liquid boundary, the depletion of untreated MEA or ST might have limited the rate of CO₂ absorption. Therefore, an increase in absorbent flow velocity allowed a sufficient amount of unreacted absorbents to flow through the gas-liquid boundary, thus enhancing the CO₂ absorption flux [8]. Moreover, the CO₂ absorption flux was higher when using the MEA absorbent than ST. This could be attributed to the faster reaction rate for CO₂-MEA depletion compared to CO₂-ST according to the mechanism of reaction kinetics [32-33].

For the pristine PVDF substrate, the CO₂ flux remained relatively low and started decreasing when the absorbent flow rate exceeded 0.2 m·s⁻¹. This may be due to the partial wetting of the membrane pores which becomes more severe when higher shear forces are generated by the absorbent flow velocity. This leads to a significant increase in mass transfer resistance for CO₂ diffusion in the GLMC application. For the fTiO₂-SiO₂/PVDF

composite hollow fiber membranes, in contrast, the CO₂ absorption flux increased almost linearly with an increase in absorbent flow velocity. This indicates a non-wetted improvement compared with the pristine PVDF substrate, which could be ascribed to the tighter and more hydrophobic surface after fTiO₂-SiO₂ modification. Moreover, it is noted that the fTiO₂-SiO₂-0.5/PVDF membrane was also subjected to pore intrusion by absorbents at a higher liquid velocity of 0.3 m·s⁻¹. However, the CO₂ absorption flux of fTiO₂-SiO₂-1/PVDF membrane increased linearly and reached a relatively high value of 8.6 and 6.3 × 10⁻³ mol·m⁻²·s⁻¹ for absorbents of MEA and ST, respectively. One possibility that the fTiO₂-SiO₂-1/PVDF membrane had a more suitable pore size and better hydrophobicity, hence presenting a higher wetting resistance for the GLMC application.

The CO₂ separation performance in synthetic biogas upgrading using MEA chemical absorbent provided insight into the performance of the composite hollow fiber membranes in a more realistic scenario. As shown in Fig. 4-11(b), the CO₂ absorption flux of the pristine PVDF substrate and fTiO₂-SiO₂/PVDF membranes with biogas was relatively lower than that with pure CO₂ as feed gas. It could be explained by the fact that biogas with 40% CO₂ concentration was employed in the GLMC process. The lower CO₂ concentration led to the lower driving force of CO₂ diffusion from the lumen side (gas phase, high CO₂ concentration) to shell side (liquid phase, low CO₂ concentration), thus resulted in lower CO₂ absorption flux. The CO₂ absorption performance of the PVDF support and the fTiO₂-SiO₂-0.5/PVDF membrane with biogas decreased gradually with the liquid velocity increasing, which is similar to the case of using pure CO₂. This could also be attributed to the partial wetting of large pores or defects caused by infiltration of chemical absorbents. However, the CO₂ absorption of fTiO₂-SiO₂-1/PVDF membrane increased linearly without declining, which further verifies its desirable CO₂ removal capacity in GLMC due to its better integrated membrane surface.

4.3.3.2. Long-term performance in GLMC

Long-term deterioration in membrane stability due to the reaction between the membrane and the chemical absorbents can strongly affect their performance and efficiency. In this study, the long-term CO₂ absorption performance of the PVDF substrate and fTiO₂-SiO₂-1/PVDF composite hollow fiber membranes were carried out for 31 days by using 1 M MEA and ST solution as absorbents, respectively.

As shown in Fig. 4-12(a), for the MEA absorbent, the CO₂ absorption flux of pristine PVDF continuously decreased, implying the occurrence of progressive wetting, resulting in an increase in membrane mass transfer resistance. The CO₂ flux was eventually stabilized at a value of $1.8 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, or a 61% drop from the initial value after the 18-day test. This indicated that the PVDF membrane may be completely wetted during the long-term running. In contrast, the CO₂ absorption flux of fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane decreased by merely 10% over the 31-day test and maintained a relative high value of $6.1 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, indicating a significant improvement in GLMC long-term operation. The slight flux decline could be attributed to the partial wetting caused by capillary condensation of MEA vapors in the hollow fiber substrates. Considering that the hollow fibers were soaked stagnantly in MEA solution during the long-term operation tests in each CO₂ absorption run, diffusion and condensation of MEA vapors into the membranes was inevitable, hence resulted in slight declines of the CO₂ absorption flux and hydrophobicity.

Fig. 4-12. Long-term performances of (a) CO₂ absorption flux (at absorbent velocity of 0.25 m s⁻¹) and (b) surface hydrophobicity of PVDF substrate and fTiO₂-SiO₂-1/PVDF composite hollow fiber membrane under the absorbents of MEA and ST over a period of 31 days.

The dynamic water contact angles were tested periodically during the long-term operation in MEA solution. As shown in Fig. 4-12(b), the dynamic water contact angle of the pristine PVDF membrane decreased from ~112° to 85°, implying that a chemical and/or physical change(s) occurred on the membrane surface due to the interaction with MEA. Nevertheless, the water contact angle of the fTiO₂-SiO₂-1/PVDF membrane showed only a slight decrease from ~124° to 119°. According to Sadoogh *et al.* [47], the PVDF substrate performance drop might be ascribed to the chemical degradation at the PVDF and MEA interface, and this resulted in dehydrofluorination of the PVDF surface. In addition, for the long-term performance tests using ST as the absorbent, the curves of CO₂ absorption flux and dynamic water contact angles were similar to the MEA absorbent, but they presented a lower degree of performance deterioration. It could be explained by the higher surface tension of ST as well as its lower non-volatile property. This leads to a reduced tendency for pore intrusion, and better long-term performance was achieved compared to the MEA absorbent [48]. The presence of a highly hydrophobic and chemically robust fTiO₂-SiO₂ top layer effectively prevents the PVDF substrate from corrosion in MEA and ST solution, and thus ensuring relatively stable CO₂ flux during long-term GLMC operation.

The morphologies and pore size distributions were also characterized after the 31-

day operation in MEA and ST solutions, as shown in Fig. 4-13. It could be observed that after the 31-day operation, most of the fTiO₂-SiO₂ surface layer still remained its original morphology as compared to the pristine PVDF membrane with larger surface pore structures, which further verified that the robust fTiO₂-SiO₂ layer prevented chemical absorbents attacking and pore wetting during the long-term test. However, some small defects could also be observed over the fTiO₂-SiO₂ layer, probably due to the vapour condensation of MEA or ST in the PVDF support from the large pores of fTiO₂-SiO₂ layer, causing a bit PVDF swelling and thus cracks formed on the fTiO₂-SiO₂ layer. This also explained the reduced tendency of long-term CO₂ absorption flux in Fig. 4-12.

Fig. 4-13. FE-SEM images and pore size distributions of PVDF support and fTiO₂-SiO₂-1/PVDF composite HF membranes (a1-b1) before and after 31-day operation in (a2-b2) MEA and (a3-b3) ST solution, respectively.

4.3.4. CO₂ flux comparison in various membranes for GLMC

Compared with the state-of-the-art CO₂ removal performance in GLMC applications from literature, the fTiO₂-SiO₂ composite hollow fiber membrane prepared in the current work exhibited competitive performance in terms of CO₂ absorption flux under a relatively low MEA concentration and liquid velocity, shown in Table 4-2. It could be explained by the lower mass-transfer-resistance nature of the macroporous PVDF substrate with relatively large pore sizes, and the mesoporous fTiO₂-SiO₂ modification layer deposited onto the substrate. This combines the advantages of highly porous organic membranes with chemically robust inorganic materials.

Table 4-2. Overall comparison of CO₂ absorption flux on various membranes in GLMC

Membrane substrate	Modification layer	Feed gas	Absorbent	Lumen side	Substrate pore size (nm)	Surface pore size (nm)	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
PVDF	— ^a	Pure CO ₂	Water	Gas	20	—	0.25	0.8	[9], 2006
PEI	Polydimethyl-siloxane	Pure CO ₂	Water	Gas	148 ^b	—	0.11	0.8	[11], 2015
PEI	Hydrophobic montmorillonite	Pure CO ₂	Water	Liquid	331	79	0.5	1.1	[25], 2015
PSf	Surface-modifying macromolecules	Pure CO ₂	Water	Gas	—	21	300 ml·min ⁻¹	4.8	[17], 2015
PAI	Fluorolink S10	Pure CO ₂	Water	Gas	—	—	0.25	0.7	[49], 2011
PEI	Fluorinated SiO ₂	Pure CO ₂	2M ST	Gas	30	—	0.25	6.8	[50], 2014
PP	— ^a	14% CO ₂	1M MEA	Gas	20	—	0.1	5.9 ^d	[51], 2007
PVDF	Low-density polyethylene	20% CO ₂	1M MEA	Gas	—	—	50 ml·min ⁻¹	3.1	[52], 2013
PVDF-Cloisite	— ^a	Pure CO ₂	1M MEA	Liquid	—	—	1.1	20.3	[53], 2017
PVDF	— ^a	Pure CO ₂	2M MEA	Liquid	—	—	12.4 ml·min ⁻¹	13.0	[10], 2013
PTFE	— ^a	Pure CO ₂	30 wt.% (≈ 4.9M) MEA	Liquid	30-80	—	28 ml·min ⁻¹	1.1 ^e	[7], 2014
Al ₂ O ₃	Fluorinated ZrO ₂	12.5% CO ₂	5 wt.% (≈ 0.8M) MEA	Liquid	—	200	10 ml·min ⁻¹	1.3	[12], 2015
PVDF	Fluorinated TiO ₂ -SiO ₂	Pure CO ₂	1M MEA	Gas	530	25	0.25	8.0	This work
PVDF	Fluorinated TiO ₂ -SiO ₂	Pure CO ₂	1M ST	Gas	530	25	0.25	5.6	This work

^a non-modified membrane;^b predicted pore size;^{d, e} after converting the units of (mol·m⁻²·h⁻¹), (mol·m⁻²·min⁻¹) to (10⁻³ mol·m⁻²·s⁻¹), respectively.

4.5. Conclusions

This study aims to propose a facile method of *in-situ* vapor-induced hydrolyzation process incorporated with PFTS grafting for preparing fTiO₂-SiO₂/PVDF composite hollow fiber membranes for biogas upgrading in GLMC. The surface hydroxylation was found to be effective in bridging the TiO₂-SiO₂ nanoparticles and the PVDF substrate due to its hydrophilic nature. The surface microstructure could be fine-tuned by controlling the amount of doped Si precursor, and an integrated mesoporous fTiO₂-SiO₂ layer onto a macroporous PVDF substrate. The fabricated membrane exhibited a high CO₂ absorption flux of $8.0 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$. Compared with the pristine PVDF membrane, the long-term performance of the fTiO₂-SiO₂/PVDF composite hollow fiber membrane was significantly improved due to its high chemical resistance and hydrophobicity that effectively prevented the PVDF substrate from corrosion by chemical absorbents of MEA and ST. Overall, the fTiO₂-SiO₂/PVDF composite hollow fiber membrane prepared in this work out-performed most of the state-of-the-art membranes for CO₂ removal in GLMC applications. This work may provide useful insights and routes into the preparation of a new generation of inorganic-organic composite hollow fiber membranes for the GLMC process.

In order to extent the application of developed fTiO₂-SiO₂/PVDF composite hollow fiber membranes for CO₂ absorption beyond laboratory-scale and off-grid installations, more researches are required to investigate the stability of CO₂ absorption and the durability of modified layers, membrane substrates and modules in a longer operating period under realistic and harsh conditions. The fabrication/modification procedures should be further optimized and simplified for achieving continue running and reproducibility. A detail economic analysis of this entire GLMC system for biogas upgrading is necessary to explore the feasibility for enlargement.

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Chapter 5 Biocatalytic PVDF Composite Hollow Fiber Membranes for CO₂ Removal in Gas-liquid Membrane Contactor²

5.1. Introduction

In Chapter 4, a high-efficiency robust fTiO₂-SiO₂/PVDF composite hollow fiber membranes was designed and fabricated for biogas upgrading in the GLMC process using MEA solution as absorbent which is one of the amine-based aqueous solutions commonly used in CO₂ absorption processes. Considering the potential disadvantages of amine-based absorbent for the GLMC process mentioned in Chapter 1 Section 1.2, the environmentally benign solvents are highly demanded to guarantee the stable and long-term operation of the GLMC application. Recently, a biocatalysis approach has been proposed by using CA enzyme as catalyst for CO₂ capture, to address the rate-limiting problem of CO₂ hydration [52, 53]. Owing to the efficient capture efficiency of CA enzyme, mild absorbent, such as water, can be used as the environmentally benign solvent to enhance the CO₂ loading capacity.

Based on the catalytic CO₂ hydration equations discussed in Chapter 2 Section 2.1.4.3, we can extrapolate to CO₂ absorption processes using a biocatalytic membrane in GLMC as described follows [112, 113, 151-153]: the active site of the CA enzyme refers to a Zn²⁺ coordinated by three histidine side-chains. A water molecule occupies the fourth coordination and contributes to the active site as well. Thus, the Zn²⁺ bound H₂O (Zn²⁺—H₂O) acts as the origin of the donor and acceptor of the proton, from which a proton is released and transferred to the fourth histidine then to solvent, resulting in negatively

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charged Zn^{2+} bound hydroxide ion ($\text{Zn}^{2+}\text{—OH}^-$). The CO_2 diffuses from gas bulk through membrane phase and then reaches the biocatalytic layer. The CO_2 molecule attaches to ($\text{Zn}^{2+}\text{—OH}^-$) then converting to HCO_3^- , by nucleophilic attack of ($\text{Zn}^{2+}\text{—OH}^-$) on carbon atom of CO_2 . Subsequently, the internal proton is transferred to form a Zn^{2+} bound HCO_3^- ($\text{Zn}^{2+}\text{—HCO}_3^-$), which is finally bound with H_2O to form ($\text{Zn}^{2+}\text{—H}_2\text{O}$), meanwhile the HCO_3^- is released to solvent. This speculation will be confirmed through a comprehensive characterization in this study.

In literature, enzymatic CO_2 capture has been widely studied for facilitating the CO_2 conversion in absorption, adsorption and sequestration [54]. However, the drawbacks of free enzyme such as short lifetime and low stability under harsh operating conditions restrict its practical applications in CO_2 capture. To address these concerns, the preparation of biocatalytic materials based on enzyme immobilization has been proposed as a solution to improve the stability of the enzyme and thus increase the possibility of enzyme recovery and reuse [55, 57-59].

Different from reported works on CA immobilization, herein, we aim to design and fabricate a biocatalytic CA-polydopamine (PDA)/PEI-PVDF (referred to as CA-m-PVDF) composite hollow fiber membranes via two-step co-desorption and cross-linking method for GLMC applications. The excellent adhesive feature of dopamine (DA)/PDA and rich amino functional groups of PEI were introduced to develop the PDA/PEI carrier for PVDF substrate functionalization, which is in favour of further enzyme immobilization [154]. The CA was subsequently *in-situ* immobilized on the amine-functionalized PVDF membrane via cross-linking with GLU. The optimum conditions of preparing the biocatalytic composite membranes were investigated based on enzyme activity and activity recovery. Subsequently, different characterization tests were performed on the prepared biocatalytic hollow fiber membranes. Their CO_2 absorption performance was examined by using water

and MEA as liquid absorbents in a bench-scale GLMC setup. Finally, the long-term stability of the biocatalytic membranes was examined. As shown in Fig. 5-1, the schematic illustration indicates the development of the biocatalytic composite hollow fiber membranes and their anticipated catalytic effects in the GLMC process.

Fig. 5-1. Schematic illustration of the biocatalytic composite hollow fiber membrane and CO₂ absorption in the GLMC process.

5.2. Experimental

Materials and chemicals used in this work have been summarized in Section 3.1 of Chapter 3.

5.2.1. Preparation of an amine-functionalized membrane support

The commercial hydrophobic PVDF hollow fibers were used as substrates for PDA/PEI co-deposition on their shell side surface. Firstly, dopamine hydrochloride (2 mg·mL⁻¹) and PEI (2 mg·mL⁻¹) were dissolved in the Tris buffer solution (50 mM, pH=8.5) [154, 155]. Thereafter, pristine PVDF hollow fibers with their two sealed ends were immersed into the prepared deposition solution, shaking at 45 rpm for 3, 5, and 8 h

(OM10E, OVAN, Spain). Finally, the treated hollow fibers were rinsed with DI water and then dried at 50 °C in an oven for 12 h. Hereon, the prepared amine-functionalized PVDF membranes are designated as the m-PVDF membranes.

5.2.2. Fabrication of a biocatalytic composite hollow fiber membrane

The m-PVDF membranes were used as supports for enzyme immobilization. The hollow fibers (with two ends sealed with epoxy) were soaked in CA solutions with varied concentrations ranging from 100 to 1000 $\mu\text{g}\cdot\text{mL}^{-1}$ in Tris buffer (50 mM) mixed with GLU with shaking at 40 rpm for certain times at different temperatures. After immobilization, the prepared biocatalytic hollow fibers were rinsed thoroughly with DI water and dried at room temperature for 24 h. Hereon, the developed biocatalytic PVDF composite hollow fiber membranes are referred to as CA(x)-m(y)-PVDF membranes, in which x and y refer to the concentration of CA solution and the coating time of PDA/PEI, respectively.

5.2.3. Enzyme activity assay and loading efficiency

The esterase activity of CA was determined by the rate of its catalyzing the hydrolysis of p-NPA to p-NP. Solutions of p-NP in water with concentrations ranging from 0.01 to 0.40 mM were prepared for drawing the p-NP standard curve, measured by a UV-vis spectrophotometry (UV-1800, SHIMADZU, Japan) at 384 nm. The p-NPA solution (3 mM) in water was prepared for the activity assays [116]. For the free CA enzyme, 0.1 mL of CA solution was mixed with 1.9 mL of Tris buffer (50 mM, pH 8) and 1 mL of p-NPA (3 mM). The mixture was stirred for 3 min and its absorbance was immediately measured. For the biocatalytic membranes, the hollow fiber sample was immersed in the assay solution (2 mL Tris buffer (50 mM, pH 8) and 1 mL p-NPA (3 mM)) and stirred for 3 min. After removing the hollow fiber sample, the absorbance of solution was quickly measured.

In this work, one unit (U) of CA activity was defined by the amount of CA required to hydrolyze 1 μmol of p-NPA per minute at room temperature (25 °C). The units of the specific activities in the stock solution (free enzyme), on the biocatalytic membrane (immobilized enzyme), and remaining in the solution (un-immobilized enzyme) are $\text{U}\cdot\text{mg}^{-1}$ (enzyme), $\text{U}\cdot\text{m}^{-2}$ (membrane), and $\text{U}\cdot\text{mg}^{-1}$ (enzyme), respectively.

The enzyme activity recovery and enzyme mass specific loading are generally used for quality and quantity evaluation of enzyme loading efficiency [52]. In this work, we used enzyme activity recovery to reflect the enzyme loading efficiency. The enzyme activity recovery is the proportion of the activity of the immobilized enzyme on the membrane surface in activity of the total free enzyme, which can be calculated by Eq. 5-1 [156]:

$$AR = \frac{A_{TE} - A_{UE}}{A_{TE}} \times 100\% \quad (5-1)$$

where AR is the enzyme activity recovery (%) based on activity loss in the enzyme solution, A_{TE} and A_{UE} are the activities ($\text{U}\cdot\text{mg}^{-1}$ (enzyme)) of total free enzyme and un-immobilized enzyme in solution, respectively.

5.2.4. Membrane characterizations

The outer surface and cross-section morphologies and elemental composition of the hollow fiber samples were observed and detected by FE-SEM and EDX spectroscopy, respectively. The membrane surface microstructures were examined by AFM. The chemical functional groups of the outer surface of the hollow fibers were measured by ATR-FTIR. The chemical composition of the outer and inner surfaces of the hollow fibers were investigated by XPS. The membrane pore size and pore size distribution were measured by CFP. The dynamic water contact angle and mechanical properties were also examined. Ultrasonic treatment was conducted before characterization measurements. The

information of the related characterizations have been introduced in Section 3.2 of Chapter 3.

5.2.5. CO₂ absorption performance in GLMC

The procedures of CO₂ absorption performance of the proposed biocatalytic composite hollow fiber membranes in the GLMC process have been described in Section 3.3 of Chapter 3.

5.2.6. Long-term stability of the biocatalytic composite membranes

Several pieces of the proposed biocatalytic hollow fibers and free CA enzyme were soaked and dissolved in the water (as absorbent for CO₂ capture), respectively, storing at the room temperature of 25 °C for 40 days to simulate the real-scenario of the contact process and evaluate their long-term stabilities. The activities of the biocatalytic membrane (immobilized CA) and free CA were examined by p-NPA method, periodically (see Section 5.2.3).

5.3. Results and discussion

5.3.1. Amine-functionalized PVDF hollow fiber membranes

In order to visually inspect on the morphologies and microstructures of the m-PVDF hollow fiber membranes with different PDA/PEI deposition durations, FE-SEM characterization and pore size analysis were carried out (Fig. 5-2). As shown in Fig. 5-2(a1) and (a2), the pristine PVDF was highly porous with a pore size of approx. 44 nm. After 3h of coating, as shown in Fig. 5-2(b1) and (b2), it could be observed that PDA/PEI agglomerates were deposited on the PVDF substrate without fully covering its surface and forming a continuous layer, leading to a slight decrease in pore size (~36 nm). By further

prolonging the coating time to 5h, the agglomerates of PDA/PEI were uniformly deposited on the PVDF substrate and thoroughly covered the membrane pores, with a narrow pore size distribution and a smaller pore size of ~28 nm (shown in Fig. 5-2(c1) and (c2)). It was apparent that the pore size of the m-PVDF hollow fiber membrane decreases with increasing PDA/PEI coating time. After coating for 8h, the PDA/PEI agglomerates further deposited on the surface of PVDF and generated a stratified structure due to the large agglomerates and the pore size of the m(8h)-PVDF membrane decreased to ~16nm (Fig. 5-2(d1) and (d2)). Similar observations can be found in studies conducted by Chew *et al.* [154, 157] that the aggregation of PDA leads to the formation of hierarchical structures when the reaction time is prolonged. The co-deposition of PDA/PEI could have effectively covered most of the pores on the outer surface of the m-PVDF membrane and caused pore size reduction, which in turn could induce high membrane mass transfer resistance in the GLMC process, resulting in low CO₂ mass transfer.

Fig. 5-2. FE-SEM images of the outer surface morphologies and pore size distributions of the PVDF (a1 and a2), ultrasonicated m(3h)-PVDF (b1 and b2), m(5h)-PVDF (c1 and c2), and m(8h)-PVDF (d1 and d2) membranes.

The ATR-FTIR spectra verified the amine functionalization of the PVDF surface by co-deposition of PDA/PEI as shown in Fig. 5-3(a). The representative absorption peaks at 1339, 1474-1490, 1507-1577, 1610-1700 and 3000-3650 cm^{-1} could be attributed to the C-N stretching, aromatic C-C stretching of DA/PDA, amide II band (N-H bending (primary amines) and C-N stretching), amide I band (C=O stretching and C-N groups stretching),

and N-H stretching (secondary amines) with O-H stretching, respectively [158]. Moreover, with increasing coating time, the density of amine functional groups was enhanced as reflected by the stronger representative absorption peaks. After coating with PDA/PEI for 8h, the peaks of secondary amine together with hydroxyl functional groups were slightly stronger. This may be due to the more extensive cross-linking reactions between PDA and PEI thus consuming more primary amines. The DA in tris buffer solution could autoxidize to form different structures including dopamine quinone, leukochrome, aminochrome, 5,6-dihydroxyindole, and indole-5,6-quinone, and self-polymerize by covalently linking and/or intermolecular/supramolecular assembling various monomeric units to form PDA [159, 160]. The primary amines of PEI could react with dopamine derivatives, dihydroxyindole, and/or indole-5,6-quinone to form Schiff bases and/or Michael-type adducts via Schiff base reaction and/or Michael addition, respectively [154, 155, 161]. Therefore, PEI cross-linked with PDA by covalent bonding and deposited on the PVDF substrate, thus reduced the physical self-assembling of PDA, resulting in a more stable amine-functionalized coating layer. The dynamic water contact angles of the pristine PVDF, m(3h)-PVDF, m(5h)-PVDF and m(8h)-PVDF membranes are shown in Fig. 5-3(b), with the values of 110°, 64°, 61°, and 52°, respectively. It means that the hydrophobic PVDF substrate was altered to become hydrophilic after surface amine functionalization due to the hydrophilic properties of the PDA/PEI crosslinking layer.

Therefore, the m(5h)-PVDF membranes with integrated PDA/PEI layer exhibited better surface microstructure with tighter pore size of 28 nm, narrower pore size distribution and less aggregations, and provided sufficient amine functional anchoring sites for the subsequent enzyme immobilization as discussed in Section 5.3.2.

Fig. 5-3. ATR-FTIR spectra (a) and dynamic water contact angles (b) of the pristine PVDF, m(3h)-PVDF, m(5h)-PVDF and m(8h)-PVDF membranes.

5.3.2. Biocatalytic CA-m-PVDF hollow fiber membranes

5.3.2.1. Effects of amine-functionalized support, pH, temperature, and cross-linking time parameters on enzyme immobilization

In Fig. 5-4(a), different amine-functionalized support membranes were immersed in the pH 8, 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA solution mixed with 0.67 (v/v)% GLU to further investigate the ideal amine-functionalized membrane support for enzyme immobilization. The biocatalytic membrane with m(5h)-PVDF support presented the best activity and enzyme activity recovery, since high density of the primary amine functional groups were provided for direct cross-linking with enzyme via covalent bonding [55]. On the other hand, the CA-m(8h)-PVDF showed the relatively lowest enzyme activity and activity recovery. This could be explained by the fact that the longer chain of PDA/PEI enwrapped the enzyme and added steric hindrance between the support and the enzyme, thus resulting in enzyme activity reduction [162, 163]. The deeper oxidative polymerization of DA/PDA and cross-linking with PEI resulted in less primary amine functional groups on the surface of the support, thus restricted the space of enzyme loading. Therefore, it has been further verified that the m(5h)-PVDF composite membrane was an ideal polymeric support for enzyme immobilization.

As shown in Fig. 5-4(b), the effect of immobilization pH varying from 6.0 to 9.0 on enzyme activity and activity recovery was investigated because CA generally prefers a weak alkaline environment to maintain its activity. The CA activity as well as enzyme activity recovery increased with increasing pH value from 6.0 to 8.0, and afterwards decreased by continuing increasing the pH value to 9.0. When at high pH value conditions, the electrification state of the free CA and magnetic microspheres would be transformed, thus affecting the enzyme activity and immobilization procedure [58]. Therefore, the optimum pH for enzyme immobilization was 8.0.

The effect of temperature on relative enzyme activity and activity recovery on membrane support is shown in Fig. 5-4(c). The enzyme activity at 20 °C condition was the lowest, due to low temperature resulting in slower reaction rate. When the temperature increased to 25 °C, the activity and activity recovery both achieved the highest values, then decreased along with temperature, since enzymes are highly sensitive to high temperature.

As shown in Fig. 5-4(d), the effect of immobilization time varying from 6 h to 36 h on enzyme activity and activity recovery was explored. With an increase of reaction time, both CA activity and its recovery of the immobilized enzyme on the polymeric support increased. The best relative activity and activity recovery for CA immobilization on membrane support were achieved with a reaction time of 24 h, while the relative enzyme activity decreased by prolonging the immobilization time to longer than 24 h. This is likely due to the active site of the membrane support reaching the equilibrium status at 24 h. By continuously prolonging the immobilization time to 36 h, the enzyme could be multipoint cross-linked by GLU and the conformation of the enzyme might be influenced [55], thus resulting in enzyme activity degradation.

Fig. 5-4. Relative activity and enzyme activity recovery for biocatalytic CA-m-PVDF membranes at different (a) m-PVDF supports (0.67% GLU; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 25 °C; 24 h for enzyme immobilization), (b) pH values (m(5h)-PVDF; 0.67% GLU; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; 25 °C; 24 h), (c) temperatures (m(5h)-PVDF; 0.67% GLU; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 24 h), (d) reaction times (m(5h)-PVDF; 0.67% GLU; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 25 °C) for enzyme immobilization.

5.3.2.2. Effects of GLU and CA concentrations on enzyme immobilization

As shown in Fig. 5-5(a), the m(5h)-PVDF support membranes were immersed in the pH 8, 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA solution mixed with 0.33—2.00 (v/v)% GLU to explore the optimal dosage of cross-linking agent for biocatalytic membrane development. The enzyme activity and activity recovery exhibited an upward trend with increasing GLU concentration. Since GLU was introduced to bridge the membrane support and CA enzyme [57, 114, 164], there would be more active sites for enzyme immobilization. The immobilized enzyme on the membrane support likely reached saturation with GLU concentration of 0.67% based on activity and activity recovery. However, a significant decline was observed when the concentration of GLU exceeded beyond 1.33%. Since any

excess aldehyde groups of GLU would react with the enzyme, this might lead to a structural change in the enzyme and a subsequent decrease of activity.

In Fig. 5-5(b), the m(5h)-PVDF support membranes were soaked in the pH 8 CA solution with different concentrations of 100—1000 $\mu\text{g}\cdot\text{mL}^{-1}$ mixed with 0.67 (v/v)% GLU, to explore the optimal concentration of CA for achieving the best enzyme activity of the biocatalytic membrane. The activity of biocatalytic membrane increased with increasing concentration of CA solution for immobilization [55], where the highest activity was achieved by 600 $\mu\text{g}\cdot\text{mL}^{-1}$ CA concentration. However, by continuously increasing the CA concentration, enzymes might overcrowd on the support and aggravate the steric hindrance, thus resulting in the deterioration of enzyme activity on the biocatalytic membrane. In contrast, the enzyme activity recovery on membrane surface decreased with increasing enzyme concentration, which was in accordance with other reported works [156, 165, 166]. This is because a higher offered CA concentration led to a lower efficiency of enzyme immobilization, even though the amount of immobilized enzyme would be increased [166, 167]. The enzyme loading would almost reach the saturation level for the membrane support with a certain density of amine functional groups, when offered around 400—600 $\mu\text{g}\cdot\text{mL}^{-1}$ CA for immobilization.

Therefore, according to the measurements of activity and activity recovery of the prepared biocatalytic membranes based on various immobilization conditions, the biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membranes cross-linked by 0.67% GLU under the immobilization environments of pH 8.0 at 25 °C for 24 h could achieve the best activity of 498 $\text{U}\cdot\text{m}^{-2}$ (membrane) and the corresponding activity recovery of 31.5%, for the following membrane characterizations as well as CO₂ capture performance that will be discussed in Sections 5.3.3 and 5.3.4. The activity of the

biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membranes was comparable to a previously reported biocatalytic membrane [52].

Fig. 5-5. Relative activity and enzyme activity recovery for biocatalytic CA-m-PVDF membranes under different (a) concentrations of GLU (m(5h)-PVDF; 200 $\mu\text{g}\cdot\text{mL}^{-1}$ CA; pH 8.0; 25 °C; 24 h for enzyme immobilization), (b) concentrations of CA (m(5h)-PVDF; 0.67% GLU; pH 8.0; 25 °C; 24 h for enzyme immobilization).

5.3.3. Membrane characterizations

5.3.3.1. Morphologies and physical properties of biocatalytic CA-m-PVDF composite hollow fiber membranes

Fig. 5-6 shows the shell surface and cross-section morphologies of the biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membrane after ultrasonication. It could be observed that the biocatalytic layer remained integrated, implying a robust modification layer under harsh conditions. By comparison with the m(5h)-PVDF membrane, as shown in Fig. 5-2(c1) and (c2), it could be observed that the microstructures in terms of the surface morphologies and pore size/pore size distributions of the biocatalytic CA(600)-m(5h)-PVDF composite membrane were not significantly changed after the CA immobilization. However, for the m(5h)-PVDF membrane, the deposited PDA/PEI agglomerates on the PVDF substrate constructed a hierarchical geometry structure with a higher roughness, as presented in Table 5-1. In contrast, after the CA immobilization, the surface roughness of CA(600)-m(5h)-PVDF membrane slightly decreased, since the CA were filled in the low-

lying “valleys” during the immobilization process, with reference to Fig. 5-8. As shown in Fig. 5-6(c) and (d), the biocatalytic CA-PDA/PEI layer, with a thickness of around 0.25 μm , was deposited on the PVDF substrate with sponge-like structure.

Fig. 5-6. FE-SEM images of the outer surface (a and b) and cross-section (c and d), and pore size distributions (a) of the ultrasonicated CA(600)-m(5h)-PVDF membranes.

Fig. 5-7 shows the EDX characterization results of the shell surface and cross-section of the biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membranes. The elemental distributions of N, O, and Zn were selected as the distribution indicator for amine and amide groups of PDA, PEI, and CA. In Fig. 5-7(a1)—(a5), we can observe that the N, O, and Zn elements were evenly and thoroughly distributed on the membrane surface, verifying the formation of a continuous biocatalytic layer on the PVDF substrate surface. Fig. 5-7(b1)—(b5) presents the EDX mappings of membrane cross-section where the N and O elements were mostly deposited on the outer surface of the prepared hollow fiber membrane while small traces could be detected in the bulk of the PVDF substrate. This might be ascribed to the image noise of the N and O elements, or PDA/PEI solution penetrated into the PVDF substrate pores via the amine functionalization process. However, the Zn mapping image exhibited weak signal intensity due to the lower content

of Zn^{2+} in the immobilized CA molecules, since there is only one Zn^{2+} coordinated in one CA molecule theoretically. Therefore, it is hard to obtain the clear Zn elemental distribution via EDX scanning, especially for the cross-section EDX mapping of Zn element. Consequently, we examined the CA modification layer by tracing the elements of N, O, and Zn together, rather than tracing only one element of Zn. Moreover, the successful CA immobilization could be also ascertained by the enzyme activity assay and the CO_2 conversion performance in the GLMC application.

Fig. 5-7. (a1 and b1) the outer surface and cross-section images of biocatalytic CA(600)-m(5h)-PVDF composite membrane, and EDX mappings for (a2 and b2) C, (a3 and b3) N, (a4 and b4) O, (a5 and b5) Zn elements.

The mechanical properties and surface hydrophilicity were evaluated for the CA(600)-m(5h)-PVDF, m(5h)-PVDF, and PVDF membranes, as shown in Table 5-1. The m(5h)-PVDF and CA(600)-m(5h)-PVDF composite membranes presented slightly higher rigidity ascribing to the fragile nature of the PDA/PEI [168] and rigid structure of the immobilized enzyme [55]. The shell surface of the hydrophobic PVDF membrane was tuned to be hydrophilic after two steps of surface modification, since the amine-, amide-, and hydroxyl-functional groups of PDA/PEI and immobilized CA imparted hydrophilic properties to the m(5h)-PVDF and CA(600)-m(5h)-PVDF membrane surfaces.

Fig. 5-8. AFM images of the outer surface of (a) PVDF substrate, (b) m-PVDF membrane support, and (c) CA-m-PVDF composite hollow fiber membrane.

Table 5-1. Surface roughness parameters, mechanical properties and contact angles of the PVDF, m-PVDF and CA-m-PVDF hollow fiber membranes.

Membrane	Roughness		Mechanical properties			Dynamic contact angle (°)
	R_a (nm)	R_q (nm)	E_t (MPa)	σ_b (MPa)	ϵ_b (%)	
PVDF	10.67 ± 1.40	8.26 ± 1.12	26.2 ± 2.4	2.00 ± 0.09	97.4 ± 4.1	110.0 ± 2.9
m(5h)-PVDF	26.80 ± 0.94	33.35 ± 1.41	31.5 ± 2.8	2.27 ± 0.05	80.9 ± 4.8	60.9 ± 4.2
CA(600)-m(5h)-PVDF	23.67 ± 1.08	29.83 ± 1.32	28.4 ± 2.1	2.25 ± 0.11	85.2 ± 4.6	59.7 ± 2.2

5.3.3.2. Chemical composition of biocatalytic CA-m-PVDF composite hollow fiber membranes

The ATR-FTIR spectra of PVDF, m(5h)-PVDF and CA(600)-m(5h)-PVDF hollow fiber membranes to verify the two-step cross-linking procedure for immobilizing CA on the amine-functionalized PVDF membrane surface are shown in Fig. 5-9. It could be observed that after immobilizing CA on the m(5h)-PVDF membrane surface, the

absorption peaks of C-N, aromatic C-C, N-H (primary amines), and C=O were slightly weaker, while the peaks of N-H (secondary amines) with O-H were stronger. This is due to CA immobilized on the PDA/PEI layer by cross-linking with GLU through covalent bonding, which consumed the primary amine or amino groups of PDA/PEI and CA enzyme, resulting in denser secondary amine groups and less related functional groups of PDA/PEI on the membrane shell surface.

Fig. 5-9. ATR-FTIR spectra of the shell surfaces of the PVDF, m(5h)-PVDF and biocatalytic CA(600)-m(5h)-PVDF membranes.

XPS analysis was carried out to further investigate the elemental composition and chemical bonding of the PDA/PEI layer and the immobilized CA layer. As listed in Table 5-2, the inner surface elemental compositions of the PVDF substrate, m(5h)-PVDF, and CA(600)-m(5h)-PVDF membranes were similar, which indicates that the PDA/PEI and CA layers did not penetrate the bulk of the PVDF substrate, thus maintaining its hydrophobicity for resisting pore wetting. However, the elemental compositions of outer surface for obtained membrane are different. The peaks of the F 1s and Cl 2p were significantly weakened and eventually disappeared along with grafting PDA/PEI and then immobilizing CA on the shell surface of the PVDF substrate, while the peaks of N 1s and

O 1s strengthened accordingly, as shown in Fig. 5-10(a1—c1). It implies that the CA immobilized on PDA/PEI layer completely covered the pristine PVDF membrane surface. The deconvolution of C 1s spectra (Fig. 5-10(a2—c2)) were curve-fitted to five components with binding energies of 284.8 eV, 286.2 eV, 288.1 eV, 289.9 eV, 291.2 eV, respectively, which were assigned to the C-C/C-H, CH₂/C-N/C-O, O-C=O/CHF, CH₂CF₂, and CF₂ bonds, respectively [92, 154, 168]. And the deconvolution of N 1s spectra (Fig. 5-10(a3—c3)) were peak-fitted with two or three peak components with binding energies of 399.8 eV, 400.1 eV and 401.7 eV for the C-N band, the protonated amine-functional groups, and N-H bond, respectively. Compared with pristine PVDF substrate, the peak of C-C/C-H for the m(5h)-PVDF membrane was significantly enhanced, on the contrary, the peak of CH₂CF₂ was disappeared and the peak of CF₂ was weakened to slight level. Moreover, the new C-N peak as well as the protonated amine-functional group peak were generated, which could be ascribed to the co-deposition of PDA/PEI aggregates. For the CA(600)-m(5h)-PVDF composite membranes, the peaks of C-C/C-H and CH₂/C-O were further increased, which contributed to the CA cross-linked with GLU immobilized on the PDA/PEI layer, while the C-N peak became slightly weakened accordingly.

According to the above XPS spectra results, we attempted to propose the mechanisms of immobilization CA on the PDA/PEI support layer as follows: the PVDF was pre-activated by amine groups after co-depositing the PDA/PEI aggregates on the PVDF surface as carriers for enzyme immobilization [169]. The PDA/PEI layer provided abundant primary amine groups and multiple binding sites for immobilizing the enzyme via GLU as cross-linker [115, 162]. The GLU molecules multipointed covalently reacted with the three-dimensional structure of CA with α -amino groups of histidine residues, as well as reacted with the amino groups of the m(5h)-PVDF support, resulting in Schiff's base formation, then establishing intermolecular cross-linkages. The formation of the

immobilized CA became more rigid, which prevented conformational changes caused by temperature, pH, solvents, etc., intermolecular aggregation, and autolysis [55, 170].

Fig. 5-10. (a1, b1 and c1) XPS survey scan spectra, and high-resolution C 1s (a2, b2 and c2), N 1s (a3, b3 and c3) XPS spectra of the outer surfaces of the CA(600)-m(5h)-PVDF, m(5h)-PVDF and PVDF membranes.

Table 5-2. Elemental composition (%) of the outer/inner surfaces of the PVDF, m(5h)-PVDF and CA(600)-m(5h)-PVDF membranes.

	C 1s (%)	F 1s (%)	O 1s (%)	N 1s (%)	Cl 2p (%)
Outer surface					
PVDF	56.5	28.3	2.0	-	13.2
m(5h)-PVDF	71.6	3.1	15.5	9.8	-
CA(600)-m(5h)-PVDF	74.5	0.3	17.5	5.8	1.9
Inner surface					
PVDF	52.8	31.9	1.0	-	14.3
m(5h)-PVDF	54.5	30.3	0.6	-	14.6
CA(600)-m(5h)-PVDF	51.8	32.9	1.6	-	13.7

5.3.4. CO₂ absorption performance of the biocatalytic composite membrane in GLMC

In order to examine the performance of biocatalytic CA-m-PVDF composite membranes with different concentrations of CA enzyme, the CO₂ absorption flux performance of the CA(200)-, CA(400)-, CA(600)-, and CA(1000)-m(5h)-PVDF composite hollow fiber membranes and the m(5h)-PVDF membrane support as a comparison were measured. We can observe from Fig. 5-11(a) that the CO₂ fluxes of the developed biocatalytic composite membranes were significantly higher than that of the non-biocatalytic m(5h)-PVDF membrane. Since the biocatalytic membrane offered sufficient long chained PDA/PEI molecules that provided adequate space between the membrane and the enzyme, it leads to a good enzyme conformational flexibility and realizes a high activity for CO₂ conversion [115]. While CO₂ absorption in water is the physical process, the presence of the CA with active site of Zn²⁺ coordinated by three histidine side-chains can significantly enhance the kinetics of CO₂ conversion by catalysing CO₂ hydration to HCO₃⁻ and H⁺ [112, 113, 151-153]. Even though the biocatalytic and non-biocatalytic membranes could be partially wetted induced by their hydrophilicity, the significantly accelerated CO₂ conversion by the superb catalysis of the immobilized CA on membrane surface could circumvent the negative impact of membrane wetting [153]. However, the CO₂ fluxes of the biocatalytic membranes showed gently rising trends with liquid velocities from 0.1 to 0.3 m·s⁻¹. It may be ascribed to the fact that the CO₂ removal efficiency was mainly controlled by the immobilized CA catalyzing CO₂ hydration on the gas-liquid boundary rather than the refresh rate of the liquid absorbent.

It can be observed that the CO₂ fluxes of the biocatalytic composite membranes with different CA loadings presented positive correlation with the enzyme activities, thus further verified the enhancement of CO₂ mass transfer by the immobilized CA in the GLMC process. In particular, the CA(600)-m(5h)-PVDF composite membrane with the

highest activity presented the highest CO₂ absorption performance with flux value of $2.6 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at water velocity of $0.3 \text{ m} \cdot \text{s}^{-1}$. The other biocatalytic membranes offered with 200, 400, 1000 $\mu\text{g} \cdot \text{mL}^{-1}$ CA all exhibited similar CO₂ absorption performance due to their lower expressed enzyme activities at almost the same level (see Section 5.3.2.1).

In Fig. 5-11(b), the CO₂ absorption performances of the biocatalytic composite hollow fiber membranes were also examined using liquid absorbents of 1M MEA in order to verify the feasibility of biocatalysis for CO₂ conversion using traditional amine-based absorbents. The CO₂ flux of the biocatalytic membrane using MEA presented only a 7% increment over that of water, which is much lower than the reported result (~200% increment) [30]. This is due to the fact that the activity of immobilized enzyme could be compromised in extremely alkaline environment. Khameneh *et al.* [171] and Lv *et al.* [58] discovered that the activity of the immobilized CA could be reduced by up to 40~80% at pH 12. Moreover, due to the hydrophilic nature of the biocatalytic layer, the top layer of the composite membrane actually was partially wetted thus resulting in extra membrane resistance for CO₂ mass transfer, which was in good agreement with a study conducted by Iliuta *et al.* [153]. Therefore, low-efficiency of biocatalysis for CO₂ conversion in the extremely alkaline environment and induced high membrane resistance would severely restrict the performance of MEA for CO₂ absorption, resulting in an inadequacy in importing amine aqueous absorbent to the biocatalytic membrane in the GLMC process. Just using water as the absorbent for the prepared biocatalytic membrane could achieve a reasonable CO₂ removal performance. Coupled with the benefits of low-cost and environment-friendly, water can be an attractive option for CO₂ removal in GLMC processes.

Fig. 5-11. CO₂ absorption flux of biocatalytic CA-m-PVDF composite membranes with different (a) CA loading concentrations (200—1000 µg·mL⁻¹) and (b) liquid absorbents (water and 1M MEA).

5.3.5. Long-term stability of the biocatalytic composite membrane

The activities of two forms of enzyme—immobilized CA on membrane support and free CA in water (as catalyzers immobilized on the gas-liquid interface and dissolved in the liquid absorbent phase, respectively) were investigated at 25 °C for 40 days to evaluate their long-term stabilities, as shown in Fig. 5-12. The activity of biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membrane maintained a relative high value of 484 U·m⁻² of membrane with merely 3% reduction from the initial value of 498 U·m⁻² of membrane over a 20-day period. After 40 days, the activity of biocatalytic membrane retained 73% of its initial activity. In comparison, the activity of free CA enzyme continuously declined during the 40-day observation. The activity showed a 22% reduction, decreasing from 3.5 to 2.7 U·mg⁻¹ of enzyme after 20 days, and then sharply decreased to 0.9 U·mg⁻¹ of enzyme, losing 73% of its initial activity after 40 days. The immobilized CA on membrane surface presented a more robust long-term stability compared with free enzyme in solution, thus further validating the appealing features of the proposed biocatalytic composite membrane for CO₂ absorption in the GLMC application. This could be ascribed that the formation of multiple covalent bonds between the enzyme, cross-linker, and amine-functionalized membrane support reduced the

conformational flexibility and thermal vibration, resulting in the avoidance of enzyme unfolding and denaturation and enhancing the stability of CA [59, 115].

Therefore, we can conclude that the prepared biocatalytic CA(600)-m(5h)-PVDF composite membrane could achieve reasonable CO₂ removal performance as well as long-term stability, which provides useful insights into a potential biocatalytic composite hollow fiber membrane for CO₂ capture in the GLMC process.

Fig. 5-12. The long-term activities of biocatalytic membrane and free enzyme in absorbent of water over 40 days storage.

5.3.6. CO₂ absorption performance comparison with various membranes for GLMC

The CO₂ absorption performance of various microporous hollow fiber membranes in GLMC processes is summarized in Table 5-3. There have been very few research works introducing enzyme in GLMC processes [53, 56]. Compared with other works using traditional hydrophobic polymeric hollow fibers and water as liquid absorbent, the prepared biocatalytic CA(600)-m(5h)-PVDF composite hollow fiber membrane developed in this work exhibited competitive CO₂ removal performance, with a high flux value of $2.5 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at liquid velocity of $0.25 \text{ m} \cdot \text{s}^{-1}$. It is worth noting that the biocatalytic CA-m-PVDF composite membranes even outperformed some membranes applied with

MEA absorbents. This could be ascribed to the superior efficiency of CO₂ hydration on immobilized CA enzyme catalysis [53, 113].

Table 5-3. Comparison of CO₂ absorption flux of the various microporous hollow fiber membranes in GLMC.

Membrane substrate	Modification layer	Fiber OD/ID (mm)	Pore size (nm)	Lumen side	Feed gas	Absorbent	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
PVDF	CA-PDA/PEI	1.53/0.85	26	Gas	Pure CO ₂	Water	0.25	2.5	This work
PVDF	—	0.8/0.55	55	Gas	Pure CO ₂	Water	0.25	0.2	[172], 2013
PVDF-co-hexafluoropropylene	Fluorolink S10 & tetraethoxysilane	—	25	Gas	Pure CO ₂	Water	0.25	0.6	[42], 2011
PEIm	Fluorinated SiO ₂	1.1/0.8	40	Gas	Pure CO ₂	Water	0.25	1.3	[41], 2013
Poly(amideimide)	Octadecylamine	1.44/1.1	—	Gas	Pure CO ₂	Water	0.25	1.8	[125], 2012
PSf	—	1.0/0.5	11	Liquid	Pure CO ₂	Water	0.3	0.8	[103], 2010
PP	—	0.3/0.22	40	Liquid	20% CO ₂	Water	0.25	0.2	[28], 2006
PP	Fluorinated TiO ₂	2.7/1.8	200	Gas	20.4% CO ₂	0.1M buffer with 200 µg·mL ⁻¹ CA ^a	405 mL·min ⁻¹	0.2	[56], 2016
PVDF	—	1.0/0.65	200	Liquid	Pure CO ₂	2M MEA	2.1	2.6	[30], 2007
PTFE	—	2.44/1.83	30-80	Liquid	Pure CO ₂	30 wt.% MEA	28 mL·min ⁻¹	1.1	[173], 2014
Al ₂ O ₃	Fluorinated ZrO ₂	12.0/8.0	200	Liquid	12.5% CO ₂	5 wt.% MEA	10 mL·min ⁻¹	1.3	[110], 2015
PVDF	Fluorinated TiO ₂	1.46/0.76	25	Gas	Pure CO ₂	1M MEA	0.25	10.9	[78], 2018
PVDF	Fluorinated TiO ₂ -SiO ₂	1.2/0.7	25	Gas	40% CO ₂	1M MEA	0.25	3.2	[92], 2018

^a pH 10, 0.1 M sodium carbonate/sodium bicarbonate buffer with 200 µg·mL⁻¹ immobilized CA.

5.4. Conclusions

A two-step co-deposition and cross-linking method was proposed to prepare biocatalytic CA-m-PVDF composite hollow fiber membranes for CO₂ removal in the GLMC process. Different immobilization CA protocols were compared based on CA activity and activity recovery. For the GLMC application, the best biocatalytic CA-m-PVDF composite membranes exhibited high CO₂ removal flux with a value of $2.5 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$, by using water as absorbent with a liquid velocity of $0.25 \text{ m} \cdot \text{s}^{-1}$, increasing ~1.6 times higher than that of the pristine m-PVDF membrane without CA biocatalysis. A robust long-term activity of the biocatalytic CA-m-PVDF composite membranes was also realized in a 40-day observation. This work provides an insight into enzyme immobilization on polymeric supports for developing high-efficiency biocatalytic membranes for CO₂ capture in GLMC applications, which is cost effective and environmentally friendly.

There is still a long way to realize this technique for large-scale practical applications, since the application of biocatalytic membranes in GLMC process is still in the infant stage. Membrane wetting is crucial for its practical application. The long-term performance for biogas upgrading and durability of biocatalytic coating layers under realistic and harsh conditions should be further investigated in future works.

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Chapter 6 Synthesis of ZIF-8 Based Composite Hollow Fiber Membrane with a Dense Skin Layer for Facilitated Biogas Upgrading in Gas-Liquid Membrane Contactor³

6.1. Introduction

In the previous studies as discussed in Chapter 4 and Chapter 5, forming a robust fluorinated ceramic layer and a biocatalytic layer on pre-treated PVDF substrate presented outperformed anti-wetting property and high mass transfer [92]. These surface modification strategies, especially for the construction of inorganic/organic composite membrane in Chapter 4, have confirmed its effectiveness on overcoming the trade-off limitation between high CO₂ transfer efficiency and anti-wetting property. However, the developed porous composite membranes are non-selective for feed gas. Under this situation, CO₂ selectivity from mixed gases is determined by the loading capacity of liquid absorbents rather than the porous membranes.

Beside porous membranes, dense membranes have also been attempted to apply for CO₂ removal in GLMC processes [60-63], which indeed offered a remarkable wetting protection effect due to no pores present, along with enhanced biogas upgrading derived from its idiopathic selectivity for specific gas [64]. Even so, the dense membrane presented limited gas mass transfer under high transmembrane pressure because of its high transmission resistance [65, 66]. Therefore, designing a novel composite dense membrane with satisfactory CO₂ flux and selectivity is highly demanded in GLMC. Recently, the prosperous development of MOFs stimulates the promising strategy to prepare the desired composite membrane for CO₂ capture. Based on the intrinsic porous characteristics, unique

³ This chapter is reproduced with permission from Y. Xu, X. Li, Y. Lin, C. Malde, R. Wang, *Synthesis of ZIF-8 based composite hollow fiber membrane with a dense skin layer for facilitated biogas upgrading in gas-liquid membrane contactor* J. Membr. Sci., major revision.

chemical versatility and abundant functionalities of MOFs, it has been suggested that the MMMs via incorporating MOFs into dense polymeric membrane can significantly improve the CO₂ flux by providing extra channel in dense structure, while keeping its selectivity [68, 72, 73, 122, 174]. Meanwhile, the anti-wetting property can be further enhanced by the hydrophobic modification of MOFs surface. Major challenge is synthesizing a defect-free and hydrophobic MOF-based composite membrane with a dense skin layer due to the poor dispersion [74].

In this study, we firstly report on developing a MOF based composite hollow fiber membrane with a dense skin layer to enhance mass transfer for biogas upgrading in a GLMC process. Specifically, aminosilane-modified ZIF-8 (mZIF-8) nanocrystals dispersed into PDMS matrix formed a non-porous top layer on a macroporous PVDF substrate. The ZIF-8 nanocrystals were aminosilane-modified for improving the compatibility between ZIF-8 and PDMS matrix via covalent linkage by APTES. The optimum loading of mZIF-8 nanocrystals was investigated to obtain a defect-free and highly efficient composite hollow fiber membrane for CO₂ absorption. The hierarchical structure and surface chemistry of the prepared composite membranes were characterized comprehensively. The performance of CO₂ removal from biogas and the long-term stability were examined via a bench-scale GLMC process by using water and MEA as absorbents, respectively. Its performances and the selectivity of CO₂/CH₄ were studied and compared against those of other dense and porous membranes reported in literature to ascertain its applicability for biogas upgrading. As shown in Fig. 6-1, the schematic illustration indicates the hierarchical structure of a MOF based composite hollow fiber membrane and its anticipated CO₂ selecting effect for biogas upgrading in a GLMC process.

Fig. 6-1. Schematic illustration of a proposed MOF based composite hollow fiber membrane and CO₂ removal in a GLMC process.

6.2. Experimental

Materials and chemicals used in this study have been described in Section 3.1 of Chapter 3.

6.2.1. Synthesis of ZIF-8 and modified ZIF-8 nanocrystals

0.74 g of Zn(NO₃)₂·6H₂O and 2.05 g of Hmim were separately dissolved in 50 ml of MeOH with sufficient stirring. The zinc nitrate solution was then mixed with the Hmim solution under vigorous stirring for 30 min at room temperature (25 °C), with the final molar ratio of 1:10:1000 (Zn²⁺: Hmim: MeOH) [175]. The resultant homogeneous milky suspension was centrifuged at 10000 rpm for 10 min and washed with MeOH. Finally, ZIF-8 nanocrystals were obtained after repeating the centrifugation-washing process for three times.

For the aminosilane-modification of ZIF-8 nanocrystals, a batch of prepared ZIF-8 nanocrystals were added in 60 ml of 5 wt.% APTES methanol solution under vigorous stirring at 70 °C for predetermined times (6—24h) [176]. The product was also centrifuged at 10000 rpm for 10 min and washed with MeOH for three times. Hereon, the prepared aminosilane-modified ZIF-8 nanocrystals are designated as the m(x)ZIF-8, in which ‘x’ refers to the time of the aminosilane-modification.

For fabrication of ZIF-8 based composite membranes, the synthesized ZIF-8 and mZIF-8 nanocrystals were further washed with *n*-hexane and centrifuged to improve the compatibility with PDMS solution. The as-washed ZIF-8 and mZIF-8 nanocrystals were then re-dispersed in MeOH/*n*-hexane under ultrasonic treatment at 25 kHz (FB 15068, Fisher Scientific, USA), followed by vacuum-drying at 50 °C overnight for characterization.

6.2.2. Fabrication of a mZIF-8 based composite hollow fiber membrane

A 5 wt.% PDMS solution was firstly prepared by mixing vinyl-type PDMS base and curing agent of hydrosilyl-type cross-linker in *n*-hexane and stirred at room temperature for 1 h [177]. Certain amounts of ZIF-8 and mZIF-8 in *n*-hexane suspensions were transferred into the PDMS solution under vigorous stirring for 30 min. The resultant PDMS, ZIF-8/PDMS, and mZIF-8/PDMS mixed solutions were separately poured into three petri dishes for complete evaporation of the solvent at room temperature. This was followed by curing in an oven at 80 °C for 48 h to afford the PDMS matrix, ZIF-8@PDMS, and mZIF-8@PDMS mixed matrixes for subsequent characterizations.

The PVDF hollow fibers (with two ends sealed with epoxy) were soaked in each of the as-prepared mixtures of PDMS, ZIF-8/PDMS, and mZIF-8/PDMS with a range of mZIF-8 loadings (2.5—20%) under stirring for 4 h, and then rinsed thoroughly with MeOH

and cured in an oven at 80 °C for 48 h. The PDMS coated PVDF membrane, ZIF-8/PDMS coated PVDF membrane, and mZIF-8/PDMS coated PVDF membrane are referred to as Pp, Z-Pp and m(x)Z(y)-Pp composite hollow fiber membranes, respectively, in which ‘x’ and ‘y’ refer to the aminosilane-modification time for ZIF-8 crystals and mZIF-8 loading in mixed matrix layer, respectively. The schematic illustration of the development protocol for the mZIF-8 based composite hollow fiber membranes is shown in Fig. 6-2.

Fig. 6-2. Schematic illustration of construction of a mZIF-8 based composite hollow fiber membrane.

6.2.3. Characterizations of ZIF-8/mZIF-8 nanocrystals and composite membranes

The morphologies of powder ZIF-8 and mZIF-8 nanocrystals and the outer surface and cross-section morphologies of the prepared hollow fibers were observed by FE-SEM. EDX spectroscopy was employed to detect the elemental distribution on the cross-section of the hollow fiber samples. The details of FE-SEM and EDX measurements have been introduced in Section 3.2 of Chapter 3. A field emission transmission electron microscopy (FE-TEM, JEM 2100 F, JEOL) under 200 kV acceleration voltage was further used for visualization of ZIF-8 and mZIF-8 nanocrystals. The particle size distributions and zeta

surface potentials of powder ZIF-8 and mZIF-8 nanocrystals were measured by a dynamic light scattering (DLS) device (Malvern Zetasizer Nano, DKSH Technology Pte Ltd). X-ray diffraction (XRD) patterns of powder ZIF-8 and mZIF-8 nanocrystals and prepared nanocrystals mixed matrixes were obtained on a Bruker D8 Advance diffractometer (Cu-K α X-ray radiation, $\lambda = 1.54 \text{ \AA}$) over 5-50° with a 0.02° step size. The crystallite size can be calculated by the Scherrer's equation (Eq. 6-1) using XRD data.

$$D_p = \frac{0.94\lambda}{\beta_{1/2} \cos \theta_b} \quad (6-1)$$

where D_p is average crystallite size, β is line broadening in radians, θ_b is Bragg angle, λ is the X-ray wavelength.

The chemical structures of ZIF-8 and mZIF-8 nanocrystals and the outer surface of the prepared membranes were measured by ATR-FTIR. The chemical composition of the outer/inner surfaces of hollow fibers were investigated by XPS. The procedures of ATR-FTIR and XPS analyses have been described in Chapter 3 Section 3.2.

The surface charge of membrane was measured by an electrokinetic analyzer (SurPASS™ 3, Anton Paar, Austria). A 0.5 mM NaCl electrolyte solution was applied as the background electrolyte solution, adjusting the pH in a region of 3—9.5 by dosing with 0.05 M NaOH/HCl. Thermal stabilities of the prepared nanocrystals and nanocrystals based mixed matrixes were measured by thermal gravimetric analyzer (TGA, SDT Q600—V20.9 Build 20, USA) under a nitrogen flow of 100 ml/min at a heating rate of 10 °C/min from 50 to 800 °C. The membrane surface microstructures were examined by AFM, as introduced in Chapter 3 Section 3.2. The dynamic water contact angle was measured by tensiometer, of which the details has been described in Chapter 3 Section 3.2.

6.2.4. CO₂ absorption and long-term performances in GLMC

The procedures of the CO₂ absorption and long-term performances of proposed mZIF-8 based dense composite hollow fiber membranes in the GLMC process have been introduced in Chapter 3 Sections 3.3 and 3.4.

6.3. Results and discussion

6.3.1. Aminosilane-modification of ZIF-8 nanocrystals

The crystal structure of synthesized powder ZIF-8 and mZIF-8 nanocrystals were identified with XRD patterns and the results are shown in Fig. 6-3(a). The characteristic crystal planes of synthesized powder ZIF-8 and mZIF-8 matched well with that of simulated ZIF-8 (CCDC number: 823083) collected from the database in the Cambridge Crystallographic Data Center (CCDC) [24, 25], which indicated their highly crystalline structures, thereby confirming the successful synthesis of powder ZIF-8 nanocrystals. Meanwhile, it could be indicated that the crystalline structure of ZIF-8 after aminosilane-modification did not cause any collapse or decomposition.

The functional groups of powder ZIF-8 and mZIF-8 were confirmed by the ATR-FTIR spectra as shown in Fig. 6-3(b). The sharp absorption peak at 420 cm⁻¹ was related to Zn-N stretching vibration, which was the characteristic band of ZIF-8 nanocrystals [178]. The absorption peaks below 800 cm⁻¹ was associated with the out-of-plane imidazole ring bending, whereas the region of 950—1350 cm⁻¹ was attributed to the bending of the in-plane ring [179]. In particular, the intense bands at 995 and 1146 cm⁻¹ were associated with C-N stretching of ZIF-8 [131, 178]. The convoluted band in the region of 1350–1550 cm⁻¹ was assigned as the entire imidazole ring stretching. The peak at 1584 cm⁻¹ was specifically attributed to the C=N stretching. The characteristic absorption peaks at 3135 and 2930 cm⁻¹ were attributed to the aromatic ring and the aliphatic chain C-H stretching of the imidazole, respectively [174, 179]. After aminosilane-modification, the distinctive peak at 868 cm⁻¹ due to the Si-C stretching was observed. And with increasing modification time, the

characteristic peaks of the ring involved as well as C-N were enhanced, further demonstrating the successful modification of ZIF nanocrystals with APTES. Besides, the elemental compositions of the ZIF-8 and m(12h)ZIF-8 analyzed from XPS spectra are summarized in Table 6-1, which could also verify the APTES modification procedure.

Fig. 6-3. XRD patterns (a) and ATR-FTIR spectra (b) of powder ZIF-8, m(6h)ZIF-8, m(12h)ZIF-8 and m(24h)ZIF-8 nanocrystals.

Table 6-1. Elemental composition (%) of the powder ZIF-8 and m(12h)ZIF-8 nanocrystals.

	C 1s (%)	N 1s (%)	O 1s (%)	Zn 2p (%)	Si 2p (%)
ZIF-8	62.2	23.2	5.8	8.8	—
m(12h)ZIF-8	60.8	24.7	7.1	7.0	0.4

The morphological features of the synthesized ZIF-8 and mZIF-8 nanocrystals were observed with FE-SEM and FE-TEM, as shown in Fig. 6-4 and Fig. 6-5, respectively. The FE-SEM image revealed the homogeneous rhombic dodecahedral shape of ZIF-8 nanocrystals with the size of around 45 nm (Fig. 6-4(a)). The corresponding FE-TEM images (Fig. 6-5(a)) presented their sharp hexagonal faceted shape, which was in good agreement with literature [175]. However, the original sharp edge of ZIF-8 nanocrystals became round mildly after the aminosilane-modification (Fig. 6-4(c) and Fig. 6-5(c), sampled with m(12h)ZIF-8), although their crystal structures were still obvious. This could be attributed to the increased surface energy of mZIF-8 nanocrystals that promoted the

amorphization of the dodecahedral/hexagonal-like crystals to a spherical-like morphology under prolonged exposure time of SEM/TEM electron beam [122]. Comparing the FE-SEM/FE-TEM images of ZIF-8 and mZIF-8 (Fig. 6-4(b–d) and Fig. 6-5(b–d)), the estimated particle size (~ 40 nm) of mZIF-8 was smaller than that of ZIF-8. This result was similar with the tendency of the crystal size (listed in Table 6-2) calculated from XRD patterns by Scherrer's equation (Eq. 6-1), which was attributed to the slight dissolving of nanocrystals induced by the reaction between APTES and imidazole struts of ZIF-8 [176].

Fig. 6-4. FE-SEM images of (a) ZIF-8, (b) m(6h)ZIF-8, (c) m(12h)ZIF-8 and (d) m(24h)ZIF-8 nanocrystals.

Fig. 6-5. FE-TEM images of (a) ZIF-8, (b) m(6h)ZIF-8, (c) m(12h)ZIF-8 and (d) m(24h)ZIF-8 nanocrystals.

Table 6-2. Calculated average crystallite sizes and zeta potentials of ZIF-8 and m(6—24h)ZIF-8 nanocrystals.

Nanocrystal	Crystallite size (nm)	Zeta potential (mV)
ZIF-8	22.3 ± 7.0	15.7 ± 0.9
m(6h)ZIF-8	19.3 ± 5.9	16.5 ± 1.3
m(12h)ZIF-8	19.9 ± 6.9	22.1 ± 1.8
m(24h)ZIF-8	18.4 ± 5.4	17.5 ± 1.1

The mZIF-8 based composite hollow fibers with different APTES modification times (ZIF-8/mZIF-8 loading of 5 wt.% as example) were prepared for hydrophobicity characterization, and their dynamic water contact angles are shown in Fig. 6-6(a). The m(12h)Z-Pp composite hollow fiber membrane presented the highest hydrophobicity performance, as compared to the ZIF-8 based membrane and other mZIF-8 based membranes. Zeta potentials for ZIF-8/mZIF-8 nanocrystals and Z-Pp/m(12h)Z-Pp composite membranes were measured to provide information on the modification mechanism and its effect on hydrophobicity enhancement. As shown in Table 6-2, powder ZIF-8 and mZIF-8 were both positively charged. The m(6—24h)ZIF-8 nanocrystals presented higher zeta potentials due to the protonated $-\text{NH}_2$ and $-\text{NH}_2^+$, indicating the

modification was based on the reaction between alkoxy of APTES and imidazole of ZIF-8 [17, 18], which improved the hydrophilicity of mZIF-8 nanocrystals. By extending the modification time, the amount of unreacted alkoxy of APTES increased, thereby resulting in reduction of zeta potential when the modification process exceeded a certain time. Therefore, the zeta potential of m(24h)ZIF-8 was lower than that of m(12h)ZIF-8. However, the water contact angle measurement of Z-Pp and mZ-Pp composite membranes mentioned above showed the opposite results. In comparison to the Z-Pp composite membrane, the m(12h)Z-Pp membrane was more negatively charged when pH exceeded 5, (Fig. 6-6(b)). This could be explained by the reaction of amino groups on the outer surfaces of mZIF-8 nanocrystals with the chains of PDMS to form tertiary amine groups. Therefore, accompanying the consumption of amino groups, the hydrophobicity of mZIF-8 modified composite membrane together with the compatibility between nanocrystals and polymer matrix was enhanced. Considering the subsequent application in CO₂ absorption, m(12h)ZIF-8 nanocrystals were selected for the subsequent mZIF-8 based composite hollow fiber membrane construction. The discussion of mZIF-8 loading and other membrane characterizations will be discussed in Section 6.3.2.

Fig. 6-6. (a) Hydrophobicity and (b) zeta potential of different composite hollow fiber membranes.

6.3.2. mZIF-8 based composite hollow fiber membranes

The prepared ZIF-8 and mZIF-8 nanocrystals, and the pure PDMS, ZIF-8@PDMS and mZIF-8@PDMS mixed matrix membranes (the loading of ZIF-8/mZIF-8 is 5 wt.% as example) were selected for TGA and differential thermal gravimetric (DTG) analysis, as shown in Fig. 6-7(a). The as-synthesized powder ZIF-8 and mZIF-8 showed similar decomposition process in which imidazolate species firstly decomposed from 490 °C followed by the decomposition of carbon species from 600 °C [131, 175, 180, 181]. However, the mZIF-8 nanocrystals presented a reduced thermal stability in the region of 500—750 °C in TGA curve, which was attributed to organic decomposition of attached APTES functionalities accompanied by imidazolate disintegration [131, 182]. It also could be confirmed by exothermic peak of mZIF-8 nanocrystals shift to the left around 590 °C in DTG curve. The pure PDMS membrane showed strong thermal stability with only 35.7% weight loss from 300 to 800 °C, which could be associated to the tight Si–O frameworks [183]. However, with the introduction of ZIF-8/mZIF-8, the resultant ZIF-8@PDMS and mZIF-8@PDMS exhibited significant thermal stability reduction. This was possibly caused by the disruption of inherent cross-linking of PDMS chains and generation of fractional free volume in the PDMS matrix [73, 184], which may enhance the gas mass transfer through membrane for CO₂ absorption. Evidently, in the region of 450 to 650 °C, the dramatic decline of weight loss for ZIF-8@PDMS/mZIF-8@PDMS as compared to pure PDMS membrane indicated the disintegration of ZIF-8/mZIF-8 nanocrystals, which further confirmed the interaction between MOFs-based fillers and PDMS.

To verify the crystalline structure, XRD patterns of pure PDMS, ZIF-8@PDMS and mZIF-8@PDMS mixed matrixes are shown in Fig. 6-7(b). The pure PDMS showed a typical broad peak without crystalline reflections, indicating its amorphous structure [181]. The XRD pattern of ZIF-8@PDMS and mZIF-8@PDMS combined the pattern features of

ZIF-8 and PDMS, which further revealed the presence of the nanocrystals phase in polymer matrix [72]. The crystalline structures of ZIF-8 and mZIF-8 were maintained during the preparation procedure of mixed matrix membrane.

Fig. 6-7. TGA and DTG curves (a) and XRD patterns (b) of ZIF-8 nanocrystals, mZIF-8 nanocrystals, PDMS, ZIF-8@PDMS and mZIF-8@PDMS mixed matrixes.

In order to investigate the effect of mZIF-8 loading on the morphology of composite membrane, FE-SEM was applied to observe the shell surface of mZIF-8 based composite hollow fiber membranes. As shown in Fig. 6-8(a), the pure PDMS coated PVDF membrane (mZ(0%)-Pp or Pp) presented a smooth and non-porous surface, which indicated the uniform deposition of PDMS layer on porous pristine PVDF substrate (Fig. 6-8(g)). With an increase of mZIF-8 loading from 2.5 to 20 wt.%, more bumps evenly appeared on the surface of the PDMS layer, deriving from the embedment of mZIF-8 in PDMS matrix. Apparent defects such as interfacial voids and crystals aggregation could be observed in the mZIF-8 based composite membranes with mZIF-8 loading above 10 wt.%, which would result in the membrane wetting in the GLMC process. In addition, the surface morphology of Z-Pp composite membrane with well dispersed ZIF-8 nanocrystals is shown in Fig. 6-8(h). The surface roughness of the prepared membranes was also investigated, as shown in Table 6-3. In comparison to the PVDF substrate, the surface roughness of the Pp membrane was reduced due to its dense structure. With an increase of mZIF-8 loadings,

the surface roughness of the mZ-Pp composite membranes increased accordingly, which was in agreement with the results of FE-SEM images.

Fig. 6-8. FE-SEM images of the outer surface of (a)—(f) mZ-Pp composite membranes with mZIF-8 loading of 0, 2.5, 5, 10, 15 and 20 wt.%, respectively, (g) PVDF substrate and (h) Z-Pp composite membrane (5 wt.% ZIF-8 loading).

Table 6-3. Surface roughness parameters of the PVDF, Pp, Z-Pp and mZ-Pp hollow fiber membranes.

Membrane	Roughness	
	R_a (nm)	R_q (nm)
PVDF	19.18 ± 3.70	24.66 ± 4.39
Pp	12.65 ± 1.01	16.32 ± 1.65
Z-Pp	33.19 ± 2.33	42.93 ± 3.21
mZ(2.5%)-Pp	34.23 ± 3.76	45.99 ± 3.09
mZ(5%)-Pp	40.07 ± 5.59	52.29 ± 6.68
mZ(10%)-Pp	59.44 ± 4.10	64.18 ± 4.72
mZ(15%)-Pp	66.32 ± 6.14	79.50 ± 7.11
mZ(20%)-Pp	68.83 ± 5.72	83.92 ± 6.2

Moreover, the cross-section of PVDF substrate, Pp, Z-Pp and mZ-Pp membranes (5 wt.% ZIF-8/mZIF-8 loading as example) were also observed using FE-SEM, as shown in Fig. 6-9. The top layers of Pp, Z-Pp and mZ-Pp membranes presented dense structures with similar thicknesses around 3.5 μm , indicating the negligible effect of ZIF-8/mZIF-8 nanofillers addition on the thickness of the PDMS matrix. The EDX scanning images of mZ-Pp membranes (Fig. 6-9(d-Si) and (d-Zn)) showed that Si and Zn elements were evenly distributed on the top layer of the prepared hollow fiber membrane, verifying the formation of a continuous mZIF-8 based PDMS layer on the PVDF substrate surface. A minor amount of Si could be detected in the bulk of PVDF substrate (indicated with F element). This could be ascribed to the diffusion of PDMS dope solution into the substrate pores during the coating process, which could have resulted in an enhancement in the mechanical performance of the formed composite membranes.

Fig. 6-9. FE-SEM images for cross-section of (a) PVDF substrate, (b) Pp, (c) Z-Pp and (d) mZ-Pp hollow fiber membranes (the loading of mZIF-8 is 5 wt.% as example), of which the EDX mappings for F, Si and Zn elements.

To verify that the modified ZIF-8 mixed with PDMS was coated on the PVDF substrate, ATR-FTIR spectra of the shell surface of PVDF substrate, Pp, Z-Pp and mZ-Pp hollow membranes were detected and shown in Fig. 6-10(a). Compared with the PVDF spectrum, the characteristic absorption peaks of PDMS attributed to the Si-C stretching, Si-O-Si stretching, and Si-C stretching [185] could be detected at 1258, 1085—995 and 865—755 cm^{-1} , respectively. After embedding ZIF-8 nanocrystals in PDMS matrix, emerging absorption peaks at 1240, 1095, and 884/740 cm^{-1} were associated with the in-plane imidazole ring bending, C-N stretching, and out-of-plane ring bending of ZIF-8, respectively [179]. As for coating with mZIF-8@PDMS dense layer, the absorption peaks of Si-O (1085 and 1050 cm^{-1}) and Si-C (865 and 843 cm^{-1}) stretching were stronger. This

was due to APTES grafted on ZIF-8 nanocrystals introducing more Si-O and Si-C functional groups in the top layer.

Fig. 6-10. (a) ATR-FTIR spectra and (b) XPS survey scan spectra of the outer surfaces of PVDF substrate, Pp, Z-Pp and mZ-Pp membranes.

XPS analyses were carried out to further investigate the elemental compositions and chemical bondings of the prepared hollow fiber membranes, of which the elemental compositions of inner and outer surfaces of membranes are summarized in Table 6-4. The inner surface elemental compositions of the Pp, Z-Pp, mZ-Pp membranes were almost equal and all detected Si element in a certain amount, which indicated that PDMS could partially penetrate through the macropores of the PVDF substrate but could still maintain its hydrophobicity for resisting pore wetting. From the XPS survey spectra shown in Fig. 6-10(b), the peaks of the F 1s and Cl 2p were significantly weakened along with coating nanocrystals-based PDMS matrix top layer on the shell surface of PVDF substrate, resulting in strengthening the peaks of O 1s, Si 2p, and Zn 2p. The deconvolution of C 1s spectrum in Fig. 6-11(a) was curve-fitted to three components with binding energies of 284.5 eV, 285.5 eV and 289.5 eV, which were assigned to the C-Si/C-C/C-H, CH₂/C-O/C-N and CF₂ bonds, respectively [92, 154, 168]. The O 1s spectrum (Fig. 6-11(b)) was curve-fitted with three components with binding energies of 531.6 eV, 532.1 eV and 532.2 eV for the chemical states of Si-O-Si, CO_x bounds, and O-Si-O, respectively. The Si 2p spectrum

(Fig. 6-11(c)) was curve-fitted with two components with binding energies of 101.3 eV and 102.4 eV for the chemical states of Si-O-Si and O-Si-O, respectively. The Zn 2p_{3/2} core-level spectrum (Fig. 6-11(d)) presented one peak component at binding energy of 1022.0 eV, which was assigned to the Zn²⁺ of ZIF-8. The XPS analyses results were consistent with previous studies [186, 187].

Fig. 6-11. High-resolution XPS spectra of (a) C 1s, (b) O 1s, (c) Si 2p, and (d) Zn 2p on the outer surface of the mZ-Pp membrane.

Table 6-4. Elemental composition (%) of the outer/inner surfaces of the PVDF substrate, Pp, Z-Pp and mZ-Pp membranes.

	C 1s (%)	F 1s (%)	O 1s (%)	Cl 2p (%)	Si 2p (%)	Zn 2p (%)	N 1s (%)
Outer surface							
PVDF	65.4	17.0	9.8	5.8	2.1	—	—
Pp	47.2	4.7	26.2	1.7	20.2	—	—
Z-Pp	49.8	3.2	26.0	1.5	19.3	0.2	0.1
mZ-Pp	53.6	5.1	22.9	1.9	14.6	0.3	1.6
Inner surface							
PVDF	53.1	28.9	4.2	13.8	—	—	—
Pp	47.1	11.0	21.5	4.0	16.4	—	—
Z-Pp	51.2	10.1	15.5	5.8	17.4	—	—
mZ-Pp	48.6	16.9	17.2	5.2	12.0	—	—

The dynamic water contact angles of PVDF substrate, Pp, Z-Pp, mZ(2.5—20%)-Pp hollow fiber membranes were measured to investigate their hydrophobicities, as shown in Fig. 6-12. The hydrophobicity of Pp hollow fiber was significantly improved due to the coating of dense hydrophobic PDMS on the surface of porous PVDF substrate, and the contact angle increased from 98 ° to 115 °. The contact angle of Z(5%)-Pp hollow fiber increased slightly, which was caused by the rougher shell surface of membrane after introducing the ZIF-8 nanocrystals into the PDMS matrix. With the addition of mZIF-8 into PDMS, the overall hydrophobicity of mZ-Pp membrane was enhanced, which was consistent with the discussion in Section 6.3.1. The highest dynamic water contact angle was achieved by mZ(5%)-Pp composite membrane. However, the hydrophobicity of composite membrane would decrease when continuously improving the loading of mZIF-8. This could be ascribed to more hydrophilic amino groups of mZIF-8 exposing in the PDMS matrix and the interfacial voids formed by nanocrystals agglomeration, which are in agreement with other studies [188, 189]. Therefore, in view of its superb hydrophobic property, the mZ(5%)-Pp composite hollow fiber membrane was selected for the following investigation of CO₂ absorption performance in the GLMC process.

Fig. 6-12. Dynamic water contact angles of PVDF substrate, Pp, Z(5%)-Pp and mZ(2.5—20%)-Pp membranes.

6.3.3. Biogas upgrading performance in GLMC

To verify their CO₂ absorption performance, a series of mZ-Pp composite hollow fiber membranes were measured using water as liquid absorbent and fed with biogas (40% CO₂) in GLMC process. As shown in Fig. 6-13(a), the CO₂ absorption flux was improved by embedding the ZIF-8 nanocrystals into PDMS matrix deposited on PVDF substrate due to ZIF-8 nanocrystals creating multiple pore channels for molecule transportation pathway [72]. Meanwhile, the mZ-Pp composite membranes with modified ZIF-8 exhibited significantly higher CO₂ flux compared to Z-Pp membrane (ZIF-8/mZIF-8 loading is 5 wt.%), which could be explained by more pore channels provided by the cross-linking chains between APTES and PDMS for facilitating CO₂ mass transfer. The CO₂ removal flux of Z-Pp membrane showed a gently rising trend with increasing liquid velocities, and even reduced when velocity exceeded 0.25 m·s⁻¹. It may be ascribed to the partial wetting of membrane caused by its weaker hydrophobicity and generated defects such as interfacial voids derived from weaker compatibility between ZIF-8 nanocrystals and PDMS matrix. The CO₂ removal performances of mZIF-8 based composite hollow fiber membrane with different mZIF-8 loadings were evaluated and shown in Fig. 6-13(b). With increasing mZIF-8 loading from 2.5 to 5 wt.%, the CO₂ flux of composite membrane was significantly improved due to more pore channels supplied by mZIF-8 nanocrystals. When the loading is 5 wt.%, the CO₂ absorption flux of composite membrane reached $2.3 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ at a water velocity of 0.3 m·s⁻¹. However, the CO₂ absorption fluxes of mZ-Pp membranes decreased by further increasing mZIF-8 loadings from 5 wt.%. The severe agglomeration of mZIF-8 nanocrystals in PDMS matrix at high loading, as indicated in FE-SEM images (Fig. 6-8), would generate more non-selective interfacial defects, leading to accelerated membrane wetting. Therefore, the composite membrane with 5 wt.% of mZIF-8 nanocrystals loading was selected for following CO₂ absorption investigation. The CO₂ absorption performances of mZIF-8 based composite hollow fiber membranes using water

and 1M MEA as absorbents were presented in Fig. 6-13(c). Due to much higher CO₂ loading capacity of MEA [92], the CO₂ flux of the developed composite membrane using MEA presented around 188% higher than that of water. In the biogas-water system, the average CO₂/CH₄ selectivity of mZ-Pp membrane was ~1.5, while the selectivity was remarkably improved to ~17.0 using 1M MEA solvent, which was comparable with other studies [72, 131, 184].

Fig. 6-13. CO₂ absorption fluxes of Pp, Z-Pp and mZ-Pp membranes (a), of mZIF-8 based composite hollow fiber membranes (b) with different mZIF-8 loadings and (c) using different liquid absorbents.

6.3.4. Long-term performance

Long-term CO₂ removal from biogas with mZ-Pp composite hollow fiber membranes were carried out for 15 days by using water and 1 M MEA as absorbents to investigate the stability of membranes. As shown in Fig. 6-14, the mZ-Pp composite membrane presented a reasonable stability throughout 15 days of operation, with ~11% and 13% reductions of the initial CO₂ fluxes in biogas–water and biogas–1M MEA systems, respectively. In our previous study [78], the CO₂ absorption flux of pristine PVDF (the same material as this work) in the same biogas–1M MEA system showed a ~ 80% drop from the initial flux after 10 days of operation, in which the membrane had been completely wetted. It indicates that a significant improvement in long-term stability after construction of a mZIF-8 base PDMS dense layer on porous PVDF substrate was achieved. The slightly flux decline of mZ-Pp composite membrane seems to be inevitable. Since the hollow fibers

were soaked in water or MEA solution during long-term testing after each run, it led to capillary condensation of water/MEA vapor in the membrane substrate [92].

Fig. 6-14. Long-term performance of mZIF-8 based composite hollow fiber membrane over 15-day operation.

6.3.5. Comparison of CO₂ absorption fluxes of various membranes

The CO₂ absorption performances of various dense and porous hollow fiber membranes in GLMC processes are summarized in Table 6-5. It is worth noting that our developed mZIF-8 based dense composite membrane (5 wt.% m(12h)ZIF-8 loading) could achieve a high CO₂ absorption performance with the flux values of 2.3 and 3.8 × 10⁻³ mol·m⁻²·s⁻¹ at a liquid velocity of 0.25 m·s⁻¹ using water and 1M MEA as absorbents, respectively. It demonstrated a significantly enhanced CO₂ mass transfer efficiency as compared to other dense membranes, and even outperformed some other porous membranes applied with higher concentrations of feed CO₂ and chemical absorbents. Therefore, we can say that the aminosilane-modified ZIF-8 based composite hollow fiber membrane is well-designed to facilitate CO₂ mass transfer for biogas upgrading in GLMC processes.

Table 6-5. Comparison of CO₂ absorption flux of the various hollow fiber membranes in GLMC.

Membrane substrate	Modification layer	Pore size (nm)	Lumen side	Feed gas—Absorbent	Operating pressure (bar)	Liquid velocity (m·s ⁻¹)	CO ₂ flux (10 ⁻³ mol·m ⁻² ·s ⁻¹)	Reference
PVDF	mZIF-8@PDMS	Non-porous	Gas	40% CO ₂ —Water	1.07	0.25	2.3	This work
PVDF	mZIF-8@PDMS	Non-porous	Gas	40% CO ₂ —1M MEA	1.07	0.25	3.8	This work
Poly(acrylonitrile)	PolyActive™-PDMS	Non-porous	— ^a	Pure CO ₂ —Water	2.0	0.36	2.9 ^b	[65], 2016
Commercial P-240	PolyPhenylene Oxide	Non-porous	Gas	30% CO ₂ —Water	2.5	0.0004	0.03	[66], 2016
Commercial P-240	PolyPhenylene Oxide	Non-porous	Gas	35% CO ₂ —Water	8.0	0.09	0.3 ^c	[146], 2018
PAI	Octadecylamine	—	Gas	Pure CO ₂ —Water	1.0	0.25	1.8	[125], 2012
PVDF	—	55	Gas	Pure CO ₂ —Water	1.0	0.25	0.2	[172], 2013
PEI	Fluorinated SiO ₂	40	Gas	Pure CO ₂ —Water	1.0	0.25	1.3	[41], 2013
PVDF	CA-PDA/PEI	26	Gas	Pure CO ₂ —Water	1.0	0.25	2.5	[190], 2019
PTFE	—	30-80	Liquid	Pure CO ₂ —30 wt.% MEA	1.0	28 mL·min ⁻¹	1.1	[173], 2014
Al ₂ O ₃	Fluorinated ZrO ₂	200	Liquid	12.5% CO ₂ —5 wt.% MEA	1.0	10 mL·min ⁻¹	1.3	[110], 2015
PVDF	Fluorinated TiO ₂	25	Gas	Pure CO ₂ —1M MEA	1.0	0.25	10.9	[78], 2018
PVDF	Fluorinated TiO ₂ -SiO ₂	25	Gas	40% CO ₂ —1M MEA	1.0	0.25	3.2	[92], 2018
PTFE	Silica nanoparticles	—	Gas	40% CO ₂ —20 wt.% K ₂ CO ₃	10.0	75 mL·min ⁻¹	1.5	[191], 2018

^a flat sheet membrane;^b after conversion of mol·m⁻³·s⁻¹ to mol·m⁻²·s⁻¹.

6.4. Conclusions

A MOF based composite hollow fiber membranes were successfully constructed for biogas upgrading in the GLMC process by dispersing aminosilane-modified ZIF-8 nanocrystals into PDMS matrix deposited on porous PVDF substrate. The modification mechanism was revealed with zeta potential analysis, which was based on the dual link of APTES with ZIF-8 structure and PDMS matrix. As the modifier, APTES significantly ameliorated the compatibility of ZIF-8 with dense PDMS layer and improved the overall hydrophobicity of composite membranes, thereby enhancing the anti-wetting ability in the GLMC process. Benefitting from the extra pore channels provided by mZIF-8 nanocrystals, the optimized composite membrane achieved a competitive CO₂ mass transfer efficiency as well as good selectivity of CO₂/CH₄ using water and aqueous amine absorbents. Furthermore, robust long-term stability of mZIF-8 based composite membranes was confirmed in a 15-day operation. This work provides a new strategy to improve the biogas upgrading performance of dense composite membrane with modified MOFs in GLMC applications.

Composite membranes with dense layers have been an emerging area in recent years [65, 66]. Incorporating of ZIF-8 nanocrystals with multiple channels and inherent affinity towards CO₂ into PDMS dense matrix was almost firstly proposed in membrane contacting process. Some important aspects such as the mechanisms of entire membrane contacting process (*i.e.*, gas mass transfer through over the dense layer and permeability/selectivity of the dense layer), durability of mixed ZIF-8 nanocrystals and dense layer in a prolonged running time are still unclear and required further investigation by modeling and characterization. Synthesizing a defect-free and uniform ZIF-8-based composite membrane with good dispersibility and compatibility between MOF

nanocrystals and polymer matrix is still a challenge. Besides, cost analysis is required to explore the feasibility for enlargement.

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Chapter 7 Conclusions and Recommendations

7.1. Overall conclusions

This thesis presents the design and fabrication of novel composite hollow fiber membranes for highly efficient CO₂ removal from biogas using GLMC technology. As the major technical barrier, membrane wetting during GLMC processes restricts its application for CO₂ removal under long-term operation. To date, there is almost no commercial GLMC processes for the practical application of CO₂ capture. The wetting problem is mostly induced by low hydrophobicity, inappropriate pore size of applied membranes, swelling and degradation of membrane structures by corrosive chemical absorbents, and the low surface tension of absorption solvents.

In this study, in order to overcome the membrane wetting problem and achieve high absorption efficiency, three types of high-performance composite hollow fiber membranes were developed by the means of different surface modification strategies. A robust low-mass-transfer-resistance hydrophobic inorganic/organic composite membrane was designed and fabricated via a facile *in-situ* vapor-induced hydrolyzation method incorporated with hydrophobic modification, as presented in Chapter 4. A high-efficiency biocatalytic composite membrane was proposed by immobilization of CA enzyme on an amine-functionalized PVDF substrate, as presented in Chapter 5. A novel MOFs based dense composite membrane was designed and fabricated for biogas upgrading in GLMC by incorporating MOF nanocrystals into dense PDMS matrix on PVDF substrate, as presented Chapter 6. The major findings are summarized as follows:

From Chapter 4:

- fTiO₂-SiO₂/PVDF composite hollow fiber membranes were fabricated by *in-situ* synthesis of integrated TiO₂-SiO₂ layer on the macroporous hydroxylated PVDF substrate followed by PETS grafting.
- Surface hydroxylation for PVDF substrate could improve the adhesion stability between inorganic and organic layers. The microstructure of membrane surface could be tuned by controlling Si precursors, thus forming an integrated mesoporous fTiO₂-SiO₂ layer. As a result, the newly developed fTiO₂-SiO₂/PVDF composite hollow fiber membrane exhibited a tighter pore size of ~25 nm as compared to the microporous PVDF substrate with pore size of ~530 nm. Moreover, a high hydrophobicity of water contact angle of ~124° was achieved for the developed membrane, which demonstrated wetting-resistant property.
- Compared with the pristine PVDF membrane, the fabricated composite membrane exhibited a significantly improved CO₂ absorption flux as well as a stable long-term performance using pure CO₂ and biogas as feed gases and 1 M MEA and 1 M ST as chemical absorbents in GLMC over a 31-day operation.

From Chapter 5:

- A two-step co-deposition and cross-linking method was proposed to prepare biocatalytic composite hollow fiber membranes for CO₂ removal in the GLMC process. The co-deposition of PDA/PEI was employed to amine-functionalize a PVDF substrate as support for subsequent *in-situ* CA immobilization by cross-linking with GLU.
- Different immobilization CA protocols were compared for achieving a high CA activity and activity recovery on the biocatalytic composite membrane.

- A high CO₂ removal flux was realized for the biocatalytic composite membranes, exhibiting a value of $2.5 \times 10^{-3} \text{ mol} \cdot \text{m}^{-2} \cdot \text{s}^{-1}$ using water as absorbent, which was ~160% higher than that of the membrane without CA biocatalysis. A stable long-term activity performance was attained for the biocatalytic composite membranes in a 40-day observation.

From Chapter 6:

- A high-selectivity mZIF-8 based composite hollow fiber membrane with a dense skin layer was successfully constructed for biogas upgrading in the GLMC process by dispersing the mZIF-8 nanocrystals into PDMS matrix deposited on porous PVDF substrate.
- The aminosilane modification mechanism was revealed, which was based on the dual link of APTES with ZIF-8 structure and PDMS matrix. As the modifier, APTES significantly ameliorated the compatibility of ZIF-8 with dense PDMS layer and enhanced the overall hydrophobicity of composite membranes in terms of the dynamic water contact angle (improved from 98° to 131°), thereby enhancing the anti-wetting ability in the GLMC process.
- Benefitting from the extra pore channels provided by mZIF-8 nanocrystals, the optimized composite dense membrane achieved competitive CO₂ mass transfer efficiency as well as high selectivity of CO₂/CH₄ using water and 1M MEA absorbents in the GLMC process. The robust long-term stability of mZIF-8 based composite membranes were also confirmed in a 15-day operation.

It should be noted that biocatalytic composite membrane developed in Chapter 5 may present promising prospect for scale-up, considering the stability of PDA/PEI

layer and environmentally friendly of enzyme. The formed biocatalytic coating layer was stable for long-term contacting process. However, the duration of MOFs based coating layer (as designed in Chapter 6) may be compromised by the hydrolysis of ZIF-8 when encountering water for long-term operation, whereas presented outstanding hydrolytic stability in alkaline solvents [192]. Conversely, the stability for fTiO₂-SiO₂ coating layer (developed in Chapter 4) can also be trust due to the strong Si-O-Si bonding which will enhance the duration in long-term operation and practical modules.

Generally, the economic efficiency for designed membrane in this thesis was acceptable (as shown in Table 7-1). Less/no heating and pressure demand in these membrane fabrication processes, as compared with reported procedure. For the fTiO₂-SiO₂-PVDF membrane, enhanced chemical resistance and anti-wetting ability were confirmed, although longer fabrication time was needed (multiple modification process). Meanwhile, its membrane cost was satisfied. Comparably, less fabrication times for the CA-PDA/PEI-PVDF and the mZIF-8@PDMS-PVDF membranes were required. Both membranes indicated the competitive CO₂ flux. The mZIF-8@PDMS-PVDF membrane also exhibited high CH₄ enrichment performance and strong anti-wetting ability. More investigations will be focused on further reducing the fabrication time and cost for these developed membranes in the future studies.

Table 7-1. Summary of advantages/disadvantages and economic analysis for various membranes in GLMC applications.

Membrane	Advantages	Disadvantages	Economic analysis						Ref.
			Fabrication time	Membrane cost	Absorbent cost	Heating demand	Pressure demand	Power demand	
fTiO ₂ -SiO ₂ -PVDF	High CO ₂ flux; High CH ₄ enrichment; Low CH ₄ lose; Long-term stable; Chemical resistant; Less wettability	Multiple modification process; Heating demand; PVDF pre-treatment demand	++++	++++	+ / +++	++	—	+++	This study
CA-PDA/PEI-PVDF	High CO ₂ flux; Water as absorbent; Modifying/operating in room temperature	Membrane wetting; Long-term stability	+++	+++++	+	—	—	++	This study
mZIF-8@PDMS-PVDF	High CO ₂ flux; High CH ₄ enrichment; Long-term stable; Chemical stable; Less wettability	Multiple modification process; Heating demand	+++	+++++	+ / +++	++	+	+++	This study
PTFE	Chemical stable; High hydrophobicity	Low CO ₂ flux; Low porosity	++	+++++	+++	++++	+	+++	[193]
fZrO ₂ -Al ₂ O ₃	High hydrophobicity; Long-term stable; Chemical resistant	Less contacting area; Low packing density	+++	+++++	+++	+++++	—	++++	[110]
PDMS	Long-term stable; Less wettability	Low CO ₂ flux; High pressure demand	++	++++	+ / +++	—	++++	+++	[64]

Note: ‘+’ represents for the impact intensity; ‘+++++’ means the maximum impact intensity; ‘—’ means no demand.

7.2. Recommendations for future research

Although GLMCs for CO₂ absorption have attracted high attention in the last few decades, there is still a long way to realize this technique for large-scale practical applications. Currently, most of the studies are still at the laboratorial stage. In fact, there appears to be no consensus on the superiority of membrane contactors against other traditional CO₂ capture processes such as the amine-based absorption-desorption process, since the main challenge of membrane wetting affecting the entire system long-term stability is crucial from economic considerations. Therefore, a detailed plant-level economic analysis of the membrane contactor system for CO₂ capture is quite necessary to explore tradeoffs in absorption performance and cost control and identify the optimum system designs and R&D targets of advanced membrane material properties [194]. Park *et al.* [195] developed a novel pilot plant pressure-cascaded stripping configuration for biogas upgrading in a membrane contactor process. The proposed configuration could simultaneously achieve the recovery of CH₄ (90%) and purity of CH₄ (97%), which can meet the criteria of natural gas pipeline. A preliminary analysis illustrates that the proposed configuration offers cost benefits for some commercial large-scale plants.

Currently, most of the previous works using either pure CO₂ or mixtures with CO₂ and CH₄ or CO₂ and N₂ as feed gases were operated at room temperature and low pressure for CO₂ absorption in GLMC. However, in the industrial application, real gas streams such as biogas gas and flue gas normally with high pressure and temperature can significantly affect the absorption process in GLMC. These realistic and harsh conditions should be addressed by development of high pressure and thermal resistance membranes to fill the gap between the laboratorial scale and practical industrial scale [23].

Moreover, the module configuration also plays an important role in improving mass transfer in gas and liquid phases. Since mass transfer resistance in liquid phase is always

dominant among the overall mass transfer in GLMC, optimizing fluid flow conditions, improving the regularity of fibers, and identifying packing density to increase the overall module productivity can be subjects of future research [91].

Currently, GLMC processes are mainly focused on CO₂ absorption but limitation in solvent regeneration processes [83]. The solvents could be recovered by both stripping/desorption process and heat recovery. Further research on GLMC in both absorption and desorption process (lab-scale and large-scale) is required from energy consumption and costs view to convert it to practical applications.

Membranes for GLMC processes are particularly susceptible to fouling due to the hydrophobic nature of the membrane. However, as compared to pore wetting, membrane fouling in GLMC processes has received far less attention to date. A possible reason could be the lack of commercialization of absorption processes using MC. As a result, current studies, which focus on either bench or pilot-scale GLMC processes, are likely to utilize synthetic feed gases or liquids that are generally uncontaminated [83]. In reality, real feed gases (*e.g.*, raw biogas, flue gas) and liquids (*e.g.*, process water, inorganic absorbents for CO₂ absorption) have strong fouling (*e.g.*, scaling, biofouling, and organic fouling) propensity as they normally contain impurities such as moisture, dust particles, microorganisms, organic carbons, and inorganic salts [196, 197]. Fouling would significantly affect the CO₂ mass transfer in membrane phase as well as change the structure properties of membrane surfaces. However, exploration of membrane fouling in GLMCs is still in its infancy stage. The fouling mechanism in the MC process is different from osmotically-driven processes and this necessitates unique solution strategies. Hence, elucidating the fouling mechanism of membranes used in GLMC is necessary.

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