Development of Advanced Mixed Electronic and Carbonate Ion Conducting Membranes and Reactors for Combined CO2 Capture and Conversion

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Abstract

Global warming and climate change resulted from CO\textsubscript{2} emissions have been increasingly observed to impact our daily life and damage our economy in recent human history. To deal with this grand challenge, carbon capture and storage (CCS) has been established as a key technology to curb CO\textsubscript{2} emission from fossil-fueled power plants. The core of the CCS technology is to capture CO\textsubscript{2} at emission sources and geologically bury it for permanent storage or enhanced oil recovery (OER). As the first step of CCS, carbon capture technologies are currently being developed for three power-generation related combustion processes that are responsible for ~78\% of the global stationary carbon emissions: pre-combustion, post-combustion and oxy-combustion. A major challenge to the full implementation of the current carbon capture technologies such as imine-based “chemical washing” process is, however, the high-energy penalty, which significantly reduces plant efficiency and increases the cost of electricity. Developing cost-effective, energy-efficient and CO\textsubscript{2}-selective carbon-capture processes/methods is, therefore, highly desirable.

The state-of-art CO\textsubscript{2} capture technologies are either based on a reversible chemical/physical sorption processes by liquid solvents and solid sorbents as CO\textsubscript{2} scrubber or on a membrane based molecular filter. However, both technologies have intrinsic drawbacks. Solvent and sorbent based CO\textsubscript{2} scrubber is usually costive, application of
which into existing power plants adds a 30% parasitic energy. The membrane based technology is susceptible to poor selectivity at high permeability since it is size excluded. In particular, those polymeric membranes are incompatible with high temperature streams from which CO$_2$ is captured. So far, only a few of these technologies are commercially available for large-scale application.

The previous works carried out by our group have demonstrated a high-performance, dual-phase membrane for CO$_2$ capture from post-combustion flue gas. The dual phase consists of an electron conducting silver matrix withholding a carbonate-ion conducting molten carbonate phase, making the membrane a mixed electronic and carbonate ion conductor (MECC). The driving force for this new type of inorganic membrane is the gradient of electrochemical potentials of CO$_2$ and O$_2$ existing on the opposite surfaces of the membrane. Thus, no external electronic devices are needed to drive CO$_2$ and O$_2$ through the membrane, which makes it low cost and energy efficient. Furthermore, since only electrochemically active species such as CO$_3^{2-}$ can pass through the membrane, the membrane selectivity is not bound by permeability like conventional polymeric counterparts, thus can be very high. Another advantage of this new membrane is that it operates at high temperatures in a continuous manner, making it well suited to directly capture CO$_2$ from high-temperature flue gas steams. Despite all these advantages and promises, the long-term stability of MECC membranes is a major challenge to be met for ultimate commercial applications.

Therefore, the first objective of this dissertation work is to develop methods to fabricate stable MECC membranes while maintaining high CO$_2$ capture rate at the
operating temperature. Chemical dealloying and electrochemical dealloying methods have been selected for the first time to fabricate porous Ag matrix for MECC membranes. The result show that the porous Ag matrices derived from these two methods contain much smaller pores than traditional ones made by pore former method. Chemically dealloyed porous Ag matrix contains three types of pore structures with a larger pore around 10 µm and smaller pore less than 2 µm. Electrochemically dealloyed Ag matrix contains a very homogenous pore structure with an average pore size of less than 1 µm. Flux measurements indicate that the chemically dealloyed MECC membranes exhibit a superior CO$_2$/O$_2$ flux density and stability over 900 h testing period. It is concluded that the high CO$_2$/O$_2$ flux arises from H$_2$ in Ar as the presence of H$_2$ on the sweep side significantly increases the electrochemical gradient of O$_2$. The electrochemically dealloyed MECC shows a stability and high flux over 500 h with a very low N$_2$ leakage, which is attributed to its fine and homogenous microstructure. A bi-path gas transport mechanism is also proposed to explain the sudden change of CO$_2$ and O$_2$ ratio at 130-h marker in the test.

After CO$_2$ capture at the point sources, the next step is CO$_2$ storage. However, large-scale geological storage of CO$_2$ is still in the early development and has not been fully deployed in the US. An attractive alternative to geologic storage is to convert the captured CO$_2$ back into fuels. Several methods that have been developed so far for CO$_2$ conversion including thermolysis, thermochemical cycles and electrolysis. Among all those technologies, high-temperature co-electrolysis is of particular interest since it can utilize high-temperature steam/CO$_2$ directly from a point source, and convert it instantly
into syngas without change process condition for the downstream F-T liquid fuel synthesis, which makes it an efficient fuel synthesis technology.

Thus, the second objective of this thesis is to theoretically analyze the energy efficiency and economics of a combined “MECC-SOEC” reactor that integrates the newly developed high-temperature MECC membranes with conventional high-temperature solid oxide electrolysis cell (SOEC). Life cycle analysis (LCA) has been carried out on a plant consisting of CO$_2$ capture reactor, SOEC reactor, heat recovery system and fuel delivery system. The analysis shows that the parasitic energy of MECC plant for CO$_2$ capture can be as low as 321 kJ/kg CO$_2$, about half of traditional monoethanolamine (MEA) plant. The whole system efficiency can be as high as 82%. It also shows that the active area of SOEC can significantly affect MECC parasitic energy, but has little effect on system efficiency. The price of syngas and resultant FT-fuels have also been estimated and the latter is further compared with that of biomass to liquid (BTL). In order to compete with the price of BTL-fuels, the analysis indicates that the price of nuclear/renewable (carbon neutral) electricity utilized in the steam/CO$_2$ electrolysis has to be lower than $0.059$/kwh for Ag-MECC conversion/capture system and lower than $0.096$/kwh for NiO-MECC conversion/capture system. This modeling work provides useful guidance for future development of combined CO$_2$ conversion/ capture reactor system.
Table of Contents

Acknowledgements.......................................................................................................................... iii

Abstract........................................................................................................................................ iv

List of Tables .................................................................................................................................... x

List of Figures ................................................................................................................................... xi

Chapter 1 General Introduction: CO\textsubscript{2} Capture and Dissociation Technologies Overview.. 1

1.1 INTRODUCTION ......................................................................................................................... 1

1.2 POST COMBUSTION PROCESS FOR CO\textsubscript{2} CAPTURE....................................................... 2

1.3 H\textsubscript{2}O AND CO\textsubscript{2} DISSOCIATION TECHNOLOGIES ..................................................... 16

Chapter 2 Fundamentals of Mixed Electronic Carbonate Ion Conductor (MECC) Membranes and “MECC-SOEC” Reactor .............................................................. 27

2.1 WORKING MECHANISM OF MECC MEMBRANES.................................................................... 27

2.2 WORKING MECHANISM OF “MECC-SOEC” REACTOR............................................................ 34

Chapter 3 Synthesis and Characterization of MECC Membranes ........................................... 37

3.1 SYNTHESES OF POROUS METAL MATRIX AND MECC MEMBRANES.............................. 37

3.2 CHARACTERIZATION TECHNIQUES IN POROUS METAL MATRIX AND MECC MEMBRANES ................................................................................................................................. 43

3.3 PROPERTIES OF POROUS METAL MATRIX AND MECC MEMBRANES ............................... 44

Chapter 4 Transport Properties of Chemical and Electrochemical Dealloyed MECC Membranes and “MECC-SOEC” Reactor .......................................................... 54
4.1 CHARACTERIZATIONS OF MECC DUAL-PHASE MEMBRANES AND “MECC-SOEC” REACTOR ................................................................. 54

4.2 GAS TRANSPORT PROPERTIES OF CHEMICAL DEALLOYED MECC ................. 59

4.3 GAS TRANSPORT PROPERTIES OF ELECTROCHEMICAL DEALLOYED MECC ............ 66

4.4 PRELIMINARY RESULTS OF “MECC-SOEC” REACTOR ........................................ 73

Chapter 5 Synthetic Fuel Cycle from Combined CO₂ Capture and Conversion Membrane Reactor ............................................................................................................. 75

5.1 INTRODUCTION ........................................................................................................... 75

5.2 SYSTEM MODELING .................................................................................................. 76

5.3 ENERGETIC ANALYSIS RESULTS ........................................................................... 81

5.4 ECONOMICAL ANALYSIS OF “MECC-SOEC” REACTOR ...................................... 89

Chapter 6 Concluding Remarks .................................................................................. 98

References .................................................................................................................. 101

Appendix A Permission to Reprint ............................................................................. 109
List of Tables

Table 3.1 Comparison of microstructures of porous Ag derived from different methods. ................................................................. 49

Table 5.1 Parameters used in baseline study. LSGM is a short for La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$. ............................................................... 80

Table 5.2 Molar flow rates of each process stream in the baseline study. .......................... 81

Table 5.3 Power and heat sources and power sinks in the MECC module in the baseline study........................................................................................................... 83

Table 5.4 Power and heat sources and power sinks in “MECC-SOEC” for the baseline study ................................................................................................................. 86

Table 5.5 Parameters used in cost analysis of Ag-MECC and NiO-MECC Reactors .......... 93

Table 5.6. Parameters used in cost estimation in the baseline study for CO$_2$ conversion ......................................................................................................................... 93
List of Figures

Figure 1.1 Block diagram illustrating post-combustion, pre-combustion and oxy-combustion process. ........................................................................................................................................... 3

Figure 1.2 CO₂ capture technologies and corresponding methods. [10] ................. 4

Figure 1.3 Schematic illustration of a typical absorption-based CO₂ capture unit. [7] .... 5

Figure 1.4 Reaction occurs between CO₂ and (a) primary or secondary, (b) tertiary amine-based solvents in chemical absorption process. [10] ........................................................................................................... 6

Figure 1.5 Reaction between cation functionalized ionic liquid and CO₂. [20] .......... 8

Figure 1.6 Two types of carbonate species with bent CO₂ sites and bi-coordination.[27, 28] ............................................................................................................................................. 10

Figure 1.7 Unique structures of MOFs. From left to right: MOF-210; MOF-74; ZIF-8; Zn-TBC.[38] .............................................................................................................................................. 12

Figure 1.8 Schematic illustration of (a) non-dispersive contact via a microporous membrane; (b) gas permeation membrane. [45] ................................................................. 15

Figure 1.9 Robeson “upper bound” in CO₂/N₂ gas mixture and H₂/CO₂ gas mixture. [50] ............................................................................................................................................. 16

Figure 1.10 Molecular structure of PIM-1.[50] ................................................................... 16

Figure 1.11 Polarization curves for different types of state-of-art electrolyzers. E_{th,water} and E_{th,steam} are the thermoneutral voltages for water and steam electrolysis. E_{rev} is standard state reversible potential for water electrolysis.[65] ................................................................. 24

Figure 2.1 Schematic illustration of working mechanism of dual phase MECC membranes using Ar and H₂ containing Ar as sweep gas. ................................................................. 28

Figure 2.2 A cooperative “cogwheel” transport mechanism of CO₃²⁻ in MC. CO₃²⁻ serves as oxygen carrier in this model.[79] ........................................................................................... 33
Figure 2.3 The structures of reactant, transition state (TS) and product as well as relative energy (kJ/mol) for CO$_2$ transport in lithium carbonate (Li$_2$CO$_3$)$_4$. Distance is in Å and grey, red and purple balls represent C, O, Li respectively.[79] ................................. 33

Figure 2.4 Bi-pathway gas transport mechanism in this study. ................................. 34

Figure 2.5 Schematic illustration of “MECC-SOEC” reactor................................. 36

Figure 3.1 Schematic illustration of dealloying method to produce porous metal.[84] .. 40

Figure 3.2 (a) Schematic illustration of corrosion cell; (b) A typical electrochemical dealloying current profile employed, corresponding to a sample weight ($w_{Ag_{50}Zn_{50}}$) of 2.0065g and a ramping current rate ($\Delta i$) of 0.414 mA/h. ................................. 42

Figure 3.3 (a) Ag-Al phase diagram; (b) XRD patterns for original Ag$_{50}Al_{50}$ and dealuminized silver after 48h. ................................. 45

Figure 3.4 Microstructures of (a) Ag$_{50}Al_{50}$ (etched in 3M HCl at 90°C for 3min to reveal grains and grainboundaries); (b)48h-Ag$_{50}Al_{50}$ (overall); (c) $\alpha$-Al-derived porous Ag matrix; (d) $\gamma$-Ag$_2$Al-derived porous Ag matrix. ................................. 46

Figure 3.5 (a) Ag-Zn phase diagram; (b) XRD patterns for pre-dealloying Ag$_{50}Zn_{50}$ and resultant EC-10mA-400. ................................. 47

Figure 3.6 SEM image of (a) starting Ag$_{50}Zn_{50}$; (b) as-dealloyed porous Ag ................................. 48

Figure 3.7 Comparison of porous structure of (a) pore former derived porous Ag; (b) chemical dealloying derived porous Ag; (c) electrochemical dealloying derived porous Ag. ................................. 49

Figure 3.8 A detailed comparison of chemical dealloyed sample (a)-(d) with electrochemical dealloyed sample (e)-(h). ................................. 49

Figure 3.9 (a)SEM-BSE and (b) SEM images of cross-section of a chemical dealloyed Ag-MC MECC; a SEM images(c) MC; (d) Ag under high magnification; (e)-(h) corresponding EDS mapping of (d), confirming MC can be infiltrated into porous Ag with small pores. 52

Figure 3.10 SEM images of pristine electrochemical dealloyed Ag-MC MECC. Darker part corresponds to MC while grey/lighter part corresponds to Ag. ................................. 53
Figure 4.1 Schematic illustration of experiment set up for permeation test of dual MECC membrane. 1-4: gas cylinder; 5: Mass flow controllers; 6: Furnace; 7: Inner feed tube; 8: second alumina tube; 9: MECC; 10: Ag paste; 11: thermocouple; 12: supporting alumina tube; 13: inner sweep tube; and 14: gas chromatography(GC). [73, 75, 95].............56

Figure 4.2 Arrhenius plots of CO\textsubscript{2} and O\textsubscript{2} flux density of sample 48h-Ag50Al50. Feed gas: simulated flue gas containing 15%CO\textsubscript{2}, 10%O\textsubscript{2}, and 75%N\textsubscript{2}; sweep gas: 9.41%H\textsubscript{2}-Ar .....60

Figure 4.3 The effect of H\textsubscript{2} concentration in the sweep gas on CO\textsubscript{2} and O\textsubscript{2} flux densities. Feed gas: 15%CO\textsubscript{2}, 10%O\textsubscript{2}, and 75% N\textsubscript{2}. .................................................................63

Figure 4.4 CO\textsubscript{2} and O\textsubscript{2} flux densities as a function of time operated at 600\textdegree C under a simulated flue gas 10% O\textsubscript{2}, 15% CO\textsubscript{2} and 75% N\textsubscript{2} as the feed gas and 9.41%H\textsubscript{2}-Ar as the sweep gas........................................................................64

Figure 4.5 Comparison of long term stability between chemical dealloyed sample 72h-Ag50Al50 with Al\textsubscript{2}O\textsubscript{3} coated MECC donated as Al\textsubscript{2}O\textsubscript{3}-Ag[74-76]. Al\textsubscript{2}O\textsubscript{3}-Ag is tested under 650 \textdegree C with 50 ml/min.cm\textsuperscript{2} CO\textsubscript{2}, 50 ml/min.cm\textsuperscript{2} O\textsubscript{2} on the feed side and 50 ml/min.cm\textsuperscript{2} N\textsubscript{2} on sweep side..................................................................................65

Figure 4.6 Microstructures of chemical dealloyed MECC membrane. (a) Pre-test; (b) post-test ........................................................................................................66

Figure 4.7 Arrhenius plots of CO\textsubscript{2} and O\textsubscript{2} flux density of sample EC-10mA-400. And Arrhenius plots of chemical dealloyed sample 48h-Ag50Al50 were also plotted for comparison purpose. A simulated flue gas with composition of 10% O\textsubscript{2}, 15% CO\textsubscript{2} and 75% N\textsubscript{2} was used as the feed gas, while 9.44% H\textsubscript{2}-Ar was used as sweep gas. .................68

Figure 4.8 CO\textsubscript{2}, O\textsubscript{2} and N\textsubscript{2} flux densities as a function of time at 600 \textdegree C under a simulated flue gas containing 15% CO\textsubscript{2}, 10% O\textsubscript{2}, 75% N\textsubscript{2} as feed gas and 9.44% H\textsubscript{2}-Ar as sweep gas.................................................................69

Figure 4.9 Schematic illustration of the proposed bi-pathway transport mechanism (a) in the initial stage; (b) in the transitional stage. .................................................................72

Figure 4.10 Microstructures of EC-10mA-400; (a) before and (b) after 500-h permeation test. ......................................................................................................................72

Figure 4.11 SEM image of the state of sweep-side surface after test.................................73

Figure 5.1 (a) Block flow diagram; (b) flowsheet diagram of proposed combined “MECC-SOEC” plant for CO\textsubscript{2} capture-conversion. The inlet temperature of H\textsubscript{2} and flue gas are 100 \textdegree C and 150 \textdegree C, respectively. The product syngas in the outlet is at 25 \textdegree C and 22 atm. The
flue gas mixture in figure 5.1(b) consists of both stream #1 and stream #2 listed in Figure 5.1(a) for simplification. ................................................................. 79

Figure 5.2 Validation of SOEC model by VI curve under 650 °C. The operating current density is selected at I=2,922 A/m² in the model. [105] ............................................. 80

Figure 5.3 Energy and mass flow chart in the MECC module........................................... 83

Figure 5.4 Mass and energy flow chart of “MECC-SOEC” all in one reactor system. .... 85

Figure 5.5 The effect of SOEC area on (a) SOEC’s overpotential (η) and \( QO_{\text{ohmic}} \); (b) MECC parasitic energy (PE). The circled point in (b) corresponds to the baseline.............. 88

Figure 5.6. The effect of SOEC area on system efficiency ............................................... 88

Figure 5.7. Estimate of compressed syngas cost as a function of SOEC area using assumptions in Table 5.5 and Table 5.6 for (a) Ag-MECC capture/conversion system; (b) NiO-MECC capture/conversion system. SOE-N-ELE: nuclear electricity cost in SOEC; SOE-CAP: Capital cost in SOEC including material cost and system of balance cost; SOE-HEAT: high-temperature heat cost in SOEC; Extra-H₂: cost of extra amount of inlet H₂; Ag-MECC-CAP: material cost of Ag-MECC; NiO-MECC-CAP: material cost of NiO-MECC; MECC-OP: operational cost of CO₂ capture. ........................................................................................................... 94

Figure 5.8. Synthetic gasoline price from (a) Ag-MECC capture/conversion system; (b) NiO-MECC capture/conversion system under different SOEC area with a constant renewable electricity price of $0.096/kwh. The red triangle in (a) corresponds with synthetic gasoline price in baseline study and in (b) corresponds with NiO-MECC capture/conversion system with a SOEC area of 30 m². The area between two dotted lines corresponds with BTL derived synthetic gasoline. ........................................................................................................... 94

Figure 5.9. The effect of cost of renewable electricity on synthetic gasoline price under a SOEC area of 30 m......................................................................................... 97
Chapter 1 General Introduction: CO$_2$ Capture and Dissociation Technologies

Overview

1.1 INTRODUCTION

Energy and environment issues have been one of the major concerns in the 21st century. In the electricity generation sector, there is an increasing demand worldwide for carbon based fossil fuels. However, global warming and climate change resulted from combustion of fossil fuels and emission of CO$_2$ have been frequently observed to disrupt our daily life and economy in recent decades. Carbon capture and separation technologies (CCS) is deemed the sole feasible near-term solution to mitigate CO$_2$ emissions[1, 2]. In the transportation sector, petroleum derived hydrocarbon liquids have been the dominant energy sources for decades. However, petroleum derived liquids are not sustainable and depletion of it is a matter of time. Alternative hydrocarbon liquids such as biomass derived hydrocarbon liquids are currently being developed as a replacement to traditional petroleum based fuels [3]. Parallel to this effort, another attractive solution to produce hydrocarbon liquids is by reducing CO$_2$ and water using renewable and/or nuclear energy, in which CO$_2$ emitted from large industrial sources can be recycled back to the fuel form. There are several benefits from this strategy. First, recycling CO$_2$ emitted
from industrial sources results in a net reduction of CO₂ emission. Second, by combining renewable and/or nuclear energy in CO₂ and water dissociation process, intermittent renewable/nuclear energy can be stored in the form of liquid fuels, providing a time-flexible solution for renewable electricity. Production of CO₂-recycled synthetic liquid fuels requires both CO₂ capture process and CO₂/water dissociation process.

1.2 POST COMBUSTION PROCESS FOR CO₂ CAPTURE

CO₂ capture is the first step in a “CO₂ recycled synthetic fuel cycle”. There are three industrial processes which are identified as point sources in CO₂ capture: post-combustion, pre-combustion and oxygen fuel combustion[4-6]. Among these, post-combustion CO₂ capture has the highest potential to be applied in traditional coal pulverized power plant [7-9]. Fig. 1.1 illustrates the working principle for each type of CO₂ capture technology. In Post-combustion process, CO₂ is captured after the combustion of fossil fuel, which can be retrofitted to most existing coal-fired power plant. However, with a low partial pressure of CO₂ in the combusted gas mixture, additional compression and thus additional cost is needed for sequestration. In pre-combustion process, new gasification technology along with a water gas shift unit are used to produce combustible gas and CO₂ is removed before combustion process. In this case, CO₂ partial pressure and thus the driving force for CO₂ capture is relatively high. Therefore, the compression unit may not a necessary in this process, leading to a reduction of cost. In oxy-fuel combustion, fossil fuels are burned in a pure oxygen atmosphere rather than in air, resulting in CO₂ and steam rich gas stream. And the following separation of CO₂ from steam is easier.
However, in order to obtain pure \( \text{O}_2 \), \( \text{O}_2 \) need to be separated from \( \text{N}_2 \) at first place, requiring additional cost.

![Block diagram illustrating post-combustion, pre-combustion and oxy-combustion process.](image)

**Figure 1.1** Block diagram illustrating post-combustion, pre-combustion and oxy-combustion process.

Fig. 1.2 highlights the potential methods and technologies corresponding with three industrial \( \text{CO}_2 \) capture processes mentioned above. Except cryogenic distillation, the rest of \( \text{CO}_2 \) capture technologies are all rely on certain materials. Since the technology in this study is designed to be utilized in post-combustion process, the major post-combustion \( \text{CO}_2 \) capture technologies are reviewed in 1.1.
1.2.1 Solvent based absorption technologies for CO$_2$ capture

The working mechanism of absorption based CO$_2$ capture can be described as Fig. 1.3. First, CO$_2$ rich flue gas passes through an absorber consisting of CO$_2$-lean solvents and a vessel, where chemical reaction or/and physical absorption occur between CO$_2$ and solvents. After the absorption process, CO$_2$-rich solvent passes through a second vessel, called stripper, where the solvent is heated by steam and regenerated. Then the released CO$_2$ is collected for compression and transportation while the CO$_2$-lean solvent is returned to the first vessel for further utilization.
Solvent based CO₂ capture can be divided into two categories based on different absorption mechanism: (1) physical scrubbing process represented by a Rectisol process [11]; (2) chemical scrubbing process represented by amine scrubbing technology [12].

In physical scrubbing process, absorption of CO₂ occurs at high pressure and low temperature. And the uptake capacity of a CO₂ scrubber is proportional to CO₂ partial pressure at constant temperature. Some typical types of physical solutions include propylene carbonate (Fluor Solvent process), cold methanol (Rectisol process), polyethylene glycol (Selexol process) and so on. CO₂ uptake in a typical Rectisol process (MeOH) can achieve as high as 36 wt% at 253 K [13].

In chemical scrubbing process, absorption of CO₂ is realized by reacting with a type of base solution. Absorbents used in this process typically consist of either amine based solution or alkaline based solution. During the following regeneration, chemical bonds between CO₂ and absorbent are broken by heat and CO₂ concentrated stream is released [12].

Figure 1.3 Schematic illustration of a typical absorption-based CO₂ capture unit. [7]
Amine based CO$_2$ scrubbing has become a well-established technology for CO$_2$ capture in both oil and chemical industries. So far three types of amines have been developed as chemical absorbent: primary amine (RNH$_2$) such as monoethanol amine (MEA); secondary amine (R$_2$NH) such as diethanolamine (DEA); and tertiary amine (R$_3$N) such as triethanolamine (TEA). Among them, MEA is the most widely used type of chemical scrubber for CO$_2$ capture [10]. Fig. 1.4 illustrates the major chemical reactions between CO$_2$ and amine during CO$_2$ scrubbing process. Despite different types of amines, carbamates are formed in all reactions.

![Chemical Reaction Diagram]

Figure 1.4 Reaction occurs between CO$_2$ and (a) primary or secondary, (b) tertiary amine-based solvents in chemical absorption process. [10]

Conventional MEA system operates between 40-60 °C, which put a stringent in inlet temperature of the gases in absorber system [14]. The flue gas exhausted from coal fired power plant usually has a temperature higher than 60 °C and therefore cooling is
necessary before it is introduced to absorber. Besides, desulfurization is also needed before scrubbing since impurities like NO$_x$ and SO$_x$ would lead to the degradation of the absorbent by reacting with MEA irreversibly. A tradeoff exists between spending money in flue gas desulfurization and spending money on adding additional solvent to compensate for solvent degradation[15].

Other types of amines such as N-methyl-diethanolamine (MDEA) and diethanolamine (DEA) have been studied as an alternative to traditional MEA. Those technologies have advantages including a lower energy input in solvent regeneration [15] and a lower degradation rate of the solvent [16]. Despite they have a wide application in CO$_2$ capture, some intrinsic limitations exist: low pressure of flue gas, corrosive reactants resulted from unfavorable reactions between SO$_x$ and amine and solvent degradation in oxidizing environment [17].

Therefore, ionic liquids (ILs) have received much attention as a new type of chemical scrubber for CO$_2$ capture. It has many unique properties like low regeneration energy penalty and chemical tenability [18, 19]. ILs containing either amine or carboxylate moiety can capture CO$_2$ at a low partial pressure more effectively than traditional MEA. Fig. 1.5 illustrates the reaction between cation functionalized ionic liquid and CO$_2$ [20]. Despite its potential advantages, the major limitation of this technology is the low physical solubility of CO$_2$ in the solvent at atmospheric pressure and room temperature [19]. Several strategies are proposed to improve CO$_2$ solubility in ILs. Davis’s group developed a amio-functionalized IL. By combining the traditional amine with ILs, they introduce additional chemical absorption into ILs and thus increased CO$_2$ solubility in
solvent to a large extent [21]. What is more, some dual amino-functionalized ILs are also developed in which both cation and anion ions were tethered with an amine group for a more efficient CO₂ absorption [22]. Despite all these improvements, it should be noticed that ILs are usually toxic and thus the industrial implication is needed to be addressed carefully [23].

![Chemical structure](image)

**Figure 1.5** Reaction between cation functionalized ionic liquid and CO₂. [20]

### 1.2.2 Sorbent based adsorption technologies for CO₂ capture

Both traditional porous materials like activated carbon, silica aerogels, zeolites and new porous materials like amine-based sorbents and MOFs can be applied as sorbents for CO₂ capture [24]. Those materials usually exhibit an open pore structure and a high surface area. During CO₂ adsorption process, pore structure, surface area along with gas pressure and temperature determine the material’s adsorption capacity and selectivity of CO₂. Among these factors, the pore structure has the most influential effect on CO₂ capture under a low CO₂ partial pressure while the pore volume and the surface area become dominant under high pressure [25].

Zeolites are the most widely used solid adsorbents in CO₂ capture. They are porous crystalline aluminosilicates, with a framework consisting of joined tetrahedrons of SiO₄ and AlO₄. They have open lattice structure with a pore size in molecular level, letting gas
molecules penetrate. Substitution of an AlO$_4$ tetrahedron by SiO$_4$ tetrahedron introduces negative charge into zeolites, which is further balanced by cations such as Na$^+$,Mg$^{2+}$ within the lattice. Thus, cation properties including size, density and distribution [26] greatly affect absorption capacity of zeolites. Study of adsorption mechanism of CO$_2$ in zeolites reflects a linear oriented ion-dipole interaction existing between CO$_2$ molecule and metal ion as shown in reaction 1.1 [27, 28].

$$metal\ ion^{x+} \ ... \ O^{\delta-} = C = O^{\delta+}$$  \hspace{1cm} (1.1)

Besides this, newly formed carbonate species with bent CO$_2$ sites and bi-coordination are also observed as shown in Fig. 1.6, indicating CO$_2$ can be bound more strongly with cations [27, 28]. Different zeolites groups including X[29, 30],A[31] and CHA [32] with high surface area, high crystalline and highly porous 3-D structures have been investigated. Siriwardane [33] studied zeolites 13X and 4A, obtaining a CO$_2$ adsorption capacity of 3.64 and 3.07 mmol/g respectively under 1 atm and 25 °C. Inui [34] concluded that CHA and 13X are the best candidates for zeolites in CO$_2$ capture process after evaluating their different behaviors in pressure swing adsorption (PSA) process. One of the limitations of zeolites is their poor performance under moisture [10]. The existence of H$_2$O in flue gas not only compete CO$_2$ for active adsorption sites but may detriment stability of zeolites framework. Also, the regeneration process is quite energy intensive for zeolites based CO$_2$ capture.
Another popular research area in CO$_2$ capture adsorbents is metal organic frameworks (MOFs). They are a new type of porous materials, constructed from transition metal ions and bridging organic ligands [35]. Studies have proved that MOFs have many unique advantages over other solid sorbents. They can be made either into rigid or flexible frameworks [36] and their structures and so does the properties can be designed and adjusted by adding second building blocks [37]. Over the past two decades, lots of unique framework structures of MOFs have been developed (Fig. 1.7) [38]. There are several breakthroughs in MOFs compared with other adsorbents. For example, MOF-210 has the highest CO$_2$ storage capacity: it achieves a CO$_2$ uptake of 2400 mg g$^{-1}$ at 25°C and 50 bar. And it also has the highest BET surface area (6240 m$^2$ g$^{-1}$) among all crystalline materials [39]. The following requirements also need to be satisfied for MOFs to be utilized commercially: 1. high CO$_2$ capture capacity; 2. high selectivity over other gas components in flue gas stream; 3. corrosion resistance; 4. high thermal stability. Although show extraordinary CO$_2$ storage capacity under pure CO$_2$ stream, most of MOFs perform poorly under flue gas [40]. What is worse, their performance further degrades under a gas mixture in dynamic conditions like in a power plant [41]. Therefore, lots of research in
MOFs focus on improving the CO$_2$ capture capacity under low CO$_2$ partial pressure and mixed gas stream by modifying the metal ions or/and organic linkers.

There are many other types of porous materials being applied as solid sorbent for CO$_2$ capture, including carbon based sorbents, mineral derived sorbents, alkali metals and so on. All of them have some unique advantages over other types of sorbents. For example, carbon based sorbents are quite inexpensive compared with others (e.g. zeolite 13X) [10]; alkali metals has a low degradation rate and can sustain a high sorption capacity even after a few cycles of CO$_2$ capture [42]; and mineral derived sorbents consume much less energy compared to a conventional liquid absorption process [43]. However, all those technologies encounter the major challenges too, which prevent them from being utilized in industrial power plant. For carbon based sorbents, a low capacity and selectivity make them unsuitable for separating CO$_2$ from flue gas mixture in power plant [10]. For alkali metals, the slow reaction rate with CO$_2$ make them impossible to be commercialized today [44].

Despite of the varieties in solid sorbents, the major challenge in this field is to develop an inexpensive material with both a high capture capacity and a slow degradation rate after being exposed to many cycles in real power plant gas conditions.
1.2.3 Membrane based CO$_2$ capture

Membrane technologies begin to gain their popularity in CO$_2$ separation recently due to their less energy requirement and high CO$_2$ capture capability. Although they are in the research and development stage, possible breakthroughs in new membrane materials may make this technology be utilized in large scale industrial process. Fig. 1.8 illustrate mass transportation mechanism for two major types of CO$_2$ separation membranes: (1) non-dispersive contact via a microporous membrane; (2) supported liquid membrane [45].

Non-dispersive contact via a microporous membrane has two layers (Fig 1.8 (a)): a top microporous membrane layer and a bottom liquid absorbent layer. It separates gas in a similar way as solvent scrubbers despite the additional top layer serves as a barrier layer between gas and liquid phases. The performance of the membrane is heavily dependent on the pore structure of top membrane layers. On one hand, the porosity determines mass transfer rate of gas species. On the other hand, the membrane materials as well as its pore size affects the wettability between membrane layer and bottom liquid.
layer, further influencing the long-term stability. As indicated by its name, the contact between top membrane layer and bottom liquid layer is non-dispersive, bringing many operational advantages including independent control over gas and liquid flow rates, controlled interfacial area and less energy demand [45]. Since the bottom solvents are typically highly polar such as ionic liquid or MEA solution, the top membranes need to be hydrophobic to keep a non-dispersive contact. Thus, polymeric membranes such as PP, PVDF and PTEF are widely used in top layer. The major limitation of this technology is its limited stability over a long period of time especially when the membranes are implemented in large-scale.

Polymeric based gas permeation membrane is the most developed type of membrane in CO₂ separation (Fig. 1.8 (b)). Two important criteria are used to evaluate its performance: gas permeability (Pᵢ) and permselectivity (αᵢ,j). The following expressions correlate intrinsic properties of membranes in binary gas mixture with these two criteria.

\[
Pᵢ = Sᵢ \times Dᵢ
\]

\[
αᵢ,j = \frac{Pᵢ}{Pⱼ} = \frac{Sᵢ \times Dᵢ}{Sⱼ \times Dⱼ}
\]

Where \(Sᵢ\) and \(Dᵢ\) are the solubility and diffusivity of gas species i through the membrane. \(Sⱼ\) and \(Dⱼ\) are the solubility and diffusivity of gas species j though the membrane. Robeson “upper bounds” concept has been proposed in 1991 [46] and illustrated in Fig. 1.9. It says that in polymeric membranes there is a tradeoff between gas permeability and selectivity. That is, the higher the permeability, the lower the selectivity. Developing a type of polymeric membrane that above the “upper bound” is the goal in this area.
The polymeric membranes exhibit many unique advantages compared with other types of commercial gas permeation membranes like high separation performance, high mechanical stability and low cost [47, 48]. Traditional polymeric membranes are represented by glassy polymers where diffusion dominates gas transport process and rubbery polymers where gas transport is dominated by gas solubility in polymers. Polymer with intrinsic microporosity (PIM) is a representative of new polymeric membranes, which gains a lot of attention these days [49]. PIM combines free volume elements engineered in nano-scale for high surface area with adaptable property of polymers. One example is PIM-1 and Fig. 1.10 illustrates its structure [49]. It has been reported to have a BET surface area of 800 m²/g. It is also identified as an “upper bound” material for CO₂/N₂ separation with both a high CO₂ permeability and selectivity at same time. Despite of the advances in PIM membranes, most gas permeation membranes are more suitable for pre-combustion process, e.g. separate CO₂ from CO₂/H₂ mixture at a higher CO₂ pressure. Nevertheless, they may be considered in a post-combustion process when the fraction of CO₂ in flue gas is larger than 10% and the membrane selectivity is larger than 120.

Besides exploring novel “upper bound” polymers, another research challenge in this area is investigating polymeric membranes with high thermal stability. Most most polymer membranes can’t sustain high-temperature flue gas exhausted. Usually, a cool-down process is needed before gas separation.
Figure 1.8 Schematic illustration of (a) non-dispersive contact via a microporous membrane; (b) gas permeation membrane. [45]
1.3 H$_2$O AND CO$_2$ DISSOCIATION TECHNOLOGIES

In a “CO$_2$ recycled fuel cycle”, dissociation of H$_2$O and CO$_2$ consumes most of energy since this is where energy is stored in fuel. Equation (1-4), (1-5) and (1-6) depicts what happens during the dissociation process and the enthalpy of reactions listed at the
end of equation (1-4) and (1-5) are the theoretical minimum energy requirement in H$_2$O and CO$_2$ splitting.

\[ \begin{align*}
H_2O & \rightarrow H_2 + \frac{1}{2}O_2 \quad \Delta H_r^\theta = 286 kJ/mol \quad (1 - 4) \\
CO_2 & \rightarrow CO + \frac{1}{2}O_2 \quad \Delta H_r^\theta = 283 kJ/mol \quad (1 - 5) \\
H_2 + CO_2 & \leftrightarrow H_2O + CO \quad (1 - 6)
\end{align*} \]

Generally speaking, both electricity and heat can be utilized to drive the H$_2$O and CO$_2$ dissociation process. Although heat is usually much more inexpensive than electricity, handling heat-derived dissociation is a more complicate process. It not only requires careful handling of materials and managing of heat but also put very stringent requirements on materials.

1.3.1 Thermolysis via solar energy

Thermolysis is a high temperature method splitting H$_2$O and CO$_2$ by direct utilization of heat under a temperature above 2000 °C. Solar heat produced from concentrated solar furnaces can be applied as energy source. Although the ideal temperature range for fully splitting reactant gases is 3000~4000 °C, recent studies [51-53] suggested an upper limit (2500 °C) considering the fact that high temperature ceramics like zirconia starts to decompose above this temperature. Under 2500 °C, the equilibrium constants of H$_2$O and CO$_2$ dissociation reactions are less than 0.1. Besides, recombination between product gases occurs very quickly at this temperature, further
reduces conversion efficiency. An effective separation process is needed to improve gas conversion efficiency.

Jensen has demonstrated H$_2$O and CO$_2$ splitting by using concentrating sunlight as a direct energy source [54]. In his study, a thermolysis chamber made of zirconia is utilized for splitting reactant gases. A 5% conversion efficiency from solar energy to chemical energy is demonstrated. Although the product gases yield is low, the additional heat is generated and can be further utilized to drive a steam turbine for electricity generation, which gives an additional 25% efficiency in total conversion efficiency (assuming generated electricity is used in H$_2$O and CO$_2$ dissociation via electrolysis). It is further analyzed that if a 20% conversion efficiency from solar energy to chemical energy can be achieved in a more mature system in the future, the total conversion efficiency can be as high as 50%. This may indicate a promising process, however, electricity constitutes the majority part of energy output and can be produced more cheaply by many other methods. Besides, the disadvantages such as need for expensive materials as well as complicated product gases handling can outweigh the advantages brought by high efficiency. Despite some promising results, this technology is not economically feasible in the near future [52].

1.3.2 Thermochemical cycles by metal oxides

In thermochemical cycles, H$_2$O and CO$_2$ are split through a series of chemical reactions by heat under a temperature below 2000 °C. O$_2$ and H$_2$(or CO) are yield in separate steps. Nuclear energy and solar energy are the most two common energy
sources used in thermochemical cycles [52]. Different systems involve different numbers of cycles.

During a 2-step cycles, O₂ is produced in the first step by reducing a metal oxide and H₂ (or/and CO) is produced in the second step by oxidizing a lower-valence metal oxide as illustrated by (1-7) and (1-8):

\[
M_x O_y + heat \rightarrow M_x O_{y-1} + \frac{1}{2} O_2(g) \quad (1-7)
\]

\[
M_x O_{y-1} + H_2 O(g) \rightarrow M_x O_y + H_2(g) \quad (1-8)
\]

The 2-step cycle is usually a high-temperature cycle since the first step needs a temperature up to 2000 °C. Because of this, concentrated solar heat is usually considered as heat source. ZnO/Zn is one example of 2-step cycle, the working mechanisms of which are illustrated below:

\[
ZnO + heat \rightarrow Zn + \frac{1}{2} O_2(g) \quad (1-9)
\]

\[
Zn(s) + H_2 O(l) \rightarrow ZnO(s) + H_2(g) \quad (1-10)
\]

The first step in ZnO/Zn cycles occurs at temperature ranging from 1600 to 2000 °C while the second step occurs at 300-400 °C. There are several issues in it. First, during first step, Zn is a gas phase due to a high operating temperature and this gaseous phase is easy to recombine with produced O₂. An immediate quenching is needed to avoid the recombination. Second, passivating layer of ZnO forms in the second step, resulting in a retard reaction rate [55, 56].
Other 2-step cycles are based on alternative metal oxides like CO, Ni or Mn substituted ferrites [55, 57] and ceria-based oxides [58]. They are developed to overcome these issues. Among these materials, a lower reduction temperature (<1500 °C) for metal oxide is needed and therefore both reduced and oxidized phases are in the solid form. One example of the promising materials developed for thermochemical cycles is ceria and doped ceria. They can maintain their crystal structure in the reduction of metal oxide [58]. Studies has also shown that ceria-based materials have a stable long-term performance and are ideal medium for thermochemical cycles [59].

3-step cycles are also studied by many researchers. A typical 3-step cycles can be illustrated by reactions (1-11), (1-12) and (1-13):

\[
M_xO_y + \text{heat} \rightarrow M_xO_{y-1} + \frac{1}{2}O_2(g) \quad (1 - 11)
\]

\[
M_xO_{y-1} + 2NaOH \rightarrow Na_2O \cdot M_xO_y + H_2(g) \quad (1 - 12)
\]

\[
Na_2O \cdot M_xO_y + H_2O \rightarrow M_xO_y + 2NaOH \quad (1 - 13)
\]

A 3-step cycle usually has a faster reaction rate since NaOH introduced in the second step has a higher reactivity than H$_2$O. However, the corrosive nature of NaOH, the difficult separation of M$_x$O$_y$ from liquid NaOH along with a reduction in efficiency all present challenges in 3-step cycles.

The common obstacles in thermochemical cycle process incudes: (1) High operating temperature requires expensive materials and leads to short material lifetimes; (2) The separations of chemical intermediates are difficult; (3) Energy is lost from the multiple steps from heat exchangers; (4) Undesired side reactions occur during each step.
1.3.3 Electrolysis

Electrolysis differs from either themolysis or thermochemical cycles in the way that it directly utilizes electricity to split $\text{H}_2\text{O}$ and $\text{CO}_2$. The whole process can be completed in a single step in an electrolysis cell. Furthermore, product gases are released separately from electrolysis cell with $\text{H}_2$ and $\text{CO}$ released at cathode and $\text{O}_2$ released at anode. Thus, recombination is no longer an issue in electrolysis. Renewable energy sources like solar, wind or nuclear energy are usually utilized as energy sources for electricity generation. From this point, electrolysis provides a way to store the renewables into fuel. Two types of electrolysis technologies are described in the following sections.

1.3.3.1 Low-temperature electrolysis cell for $\text{H}_2\text{O}$ dissociation

Low–temperature electrolysis technologies have been investigated for $\text{H}_2\text{O}$ splitting. There are two major types of cells: alkaline water electrolysis cells and proton exchange membrane (PEM) cells. The operating temperature for both types of cells ranges from 70 °C to 100 °C.

The state of art alkaline water electrolysis cells dominated today’s market of electrolysis cell [60]. The electrode reactions are:

Cathode: $2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^-(aq) \quad (1 - 14)$

Anode: $2\text{OH}^-(aq) \rightarrow 2e^- + \frac{1}{2}\text{O}_2(g) + \text{H}_2\text{O}(l) \quad (1 - 15)$

The electrodes are usually made of Raney nickel and the fabrication has two steps. The first step is electrodepositing a type of nickel alloy like Ni-Al or Ni-Zn onto a metal substrate. And the second step is deriving porous Ni by chemical leaching. The final
products are porous nickel electrodes. The electrolyte is alkaline solution (e.g. 30 wt% KOH).

Conventional alkaline cells have been shown to exhibit a very good stability with a typical lifetime from 10 to 20 years [60, 61]. Even operating under intermittent renewable electricity, alkaline cells developed most recently [60, 61] do not show too much degradation. However, alkaline electrolyzers usually have a high capital cost ($7.5-9/GJ of H₂ produced), which is further increased under an intermittent operation condition. Advanced alkaline electrolysis cells with nano-porous electrodes [62] are developed to operate at a higher temperature or/and pressure [63]. Enhanced H₂ production rate (current density) is observed under the same operating voltage. The long-term stability has also been demonstrated [62]. This technology is currently at pre-commercial stage.

The other representative of low-temperature electrolysis cells is PEM cells. Working at a similar temperature ranges as alkaline water electrolysis cells, their electrodes reactions can be described as:

\[
\text{Cathode: } 2H^+(aq) + 2e^- \rightarrow H_2(g) \tag{1 - 16}
\]

\[
\text{Anode: } H_2O(l) \rightarrow 2H^+(aq) + 2e^- + \frac{1}{2}O_2(g) \tag{1 - 17}
\]

The electrolyte is usually a H⁺ conducting polymer membrane while the electrodes contain both Pt-based catalyst and expensive membranes. With nobel metals used in electrodes, the capital cost of PEM cells is even higher than alkaline cells. Although a PEM cell with a current density of 1A/cm² at 1.54 V at 80 °C under atmospheric pressure has been demonstrated [64], the total savings from high current density cannot compensate
for the high capital cost. More economical materials are needed to make PEM cells commercialized.

1.3.3.2 High-temperature electrolysis cell

As indicated by its name, high-temperature electrolyzer dissociate H₂O or/and CO₂ at a relatively high temperature (compared with low-temperature electrolyzer) ranging from 600 °C to 1000 °C. Compared with low-temperature electrolyzers, they have two major advantages as illustrated in Fig. 1.11. The first advantage is their relatively low open circuit potential (OCV) resulted from a higher operating temperature. A low OCV results in a higher current density thus a higher H₂ production rate under the same operating voltage, which further leads to a low capital cost assuming the total amount H₂ produced is same. The second advantage is their faster reaction kinetics under a higher operating temperature, which leads to a lower overpotential. Besides, a faster reaction rate also reduces the need for expensive catalyst on electrodes, which further reduce the cost.

Solid oxide electrolysis cells (SOECs) is the major type of high-temperature electrolyzer and their electrode reactions are:

\[ \text{Cathode: } H_2O(g) + 2e^- \rightarrow H_2(g) + O^{2-} \quad (1 - 18) \]

\[ \text{or } \quad CO_2(g) + 2e^- \rightarrow CO(g) + O^{2-} \quad (1 - 19) \]

\[ \text{Anode: } O^{2-} \rightarrow 2e^- + \frac{1}{2} O_2(g) \quad (1 - 20) \]
Figure 1.11 Polarization curves for different types of state-of-art electrolyzers. $E_{\text{th, water}}$ and $E_{\text{th, steam}}$ are the thermoneutral voltages for water and steam electrolysis. $E_{\text{rev}}$ is standard state reversible potential for water electrolysis. [65]

The state-of-art SOEC usually constitutes three parts: a porous cathode based on Ni-YSZ, a porous anode composed of lanthanum strontium manganite (LSM) and YSZ, a dense YSZ electrolyte in between cathodes and anodes.

Operated at a much higher temperature than alkaline water electrolyzer, SOECs have the potential to obtain higher current density and a faster reaction kinetics. It has been reported that at 950 °C, a current density of -3.6 A/cm$^2$ can be achieved at an operating voltage 1.48 V [66] in steam electrolysis. Also, a low area specific resistance (ASR) is reported (0.19 Ω cm$^2$) for H$_2$O electrolysis under 850 °C when current density ranges from 0 A/cm$^2$ to -0.16 A/cm$^2$ [67].
Recent studies focused on optimizing SOEC’s electrode structures as well as electrode materials to improve its durability in steam electrolysis [66-68], CO₂ electrolysis [66, 68] as well as CO₂ and H₂O co-electrolysis [67, 69, 70]. It has been found that, the behavior of SOEC is much more stable at a lower current density [67]. For example, In Ebbesen’s study, the SOEC showed little or no degradation up to a current density of -0.75 A/cm² when the impurities were removed from inlet gases [71, 72]. Unfortunately, the cell degradation rate speed up at a higher current density. Despite of a fast degradation rate, a high current density also brings some benefits from the economical perspective. It usually means a low capital cost of SOEC stacks especially when cells are operated under an intermittent energy sources. Therefore, future studies on improving the stability of SOECs are still necessary and important for the commercialization.

Despite the advantages resulted from a higher operating temperature, it also has some undesirable effects on cell performance. One of the major consequences is the sintering and agglomeration of Ni particles in cathode, leading to a coarsened electrode microstructure and a depredated cell performance. An optimal operating temperature determined by the specific cell materials and structure is needed to be selected carefully to avoid the side effects.

Overall, SOEC is a more promising technology in H₂O and CO₂ dissociation than alkaline water electrolysis from both an economical perspective and a fuel synthesis perspective. First, it results in a lower capital cost as mentioned previously. Second, unlike alkaline water electrolyzer which can only produce H₂, it can produce syngas directly
through co-electrolysis of H$_2$O and CO$_2$, eliminating the requirement of another RWGS reactor during fuel production and thereby reducing the total system cost.
Chapter 2 Fundamentals of Mixed Electronic Carbonate Ion Conductor (MECC)

Membranes and “MECC-SOEC” Reactor

2.1 WORKING MECHANISM OF MECC MEMBRANES

In the first part of this dissertation work, a type of mixed electronic carbonate ion conductor (MECC) membrane has been systematically studied for CO$_2$ separation from flue gas. Figure 2.1 is a schematic illustration of MECC membrane. As illustrated in this figure, it consists of two phases: Ag and molten carbonate (MC). Ag works as an electronic conductor for electron transport while MC works as a carbonate ion conductor transporting CO$_3^{2-}$ and CO$_4^{2-}$.

2.1.1 Classic CO$_3^{2-}$ transport model in MECC membrane

The previously-developed widely-accepted working principle of MECC membrane [73-77] can be described as below. At the feed side, CO$_2$ and O$_2$ are reduced into CO$_3^{2-}$ by combining with electron e$^-$ from metal phase:

$$\text{CO}_2 + \frac{1}{2} \text{O}_2 + e^- = \text{CO}_3^{2-} \quad (2-1)$$

The formed CO$_3^{2-}$ migrates through membrane MC phase, accompanied by a charge-balancing flow of e$^-$ in an opposite direction. On the sweep side, transport CO$_3^{2-}$ releases into CO$_2$ and O$_2$ if pure Ar is used as sweep gas (2-2) or react with H$_2$ to produce CO$_2$ and
H₂O if H₂ containing Ar is used on sweep side (2-3).

\[ CO_3^{2-} = CO_2 + \frac{1}{2} O_2 + e^- \]  \hspace{1cm} (2 - 2)

\[ CO_3^{2-} + H_2 = CO_2 + H_2O + 2e^- + \Delta \]  \hspace{1cm} (2 - 3)

The overall reaction under pure Ar can be written by

\[ CO_2(feed) + \frac{1}{2} O_2(feed) = CO_2(sweep) + \frac{1}{2} O_2(sweep) \]  \hspace{1cm} (2 - 4)

The overall reaction under H₂ contained Ar can be expressed as:

\[ CO_2(feed) + H_2(sweep) + \frac{1}{2} O_2(feed) = H_2O(sweep) + CO_2(sweep) + \Delta \]  \hspace{1cm} (2 - 5)

The driven force of MECC membrane are the partial pressure gradients of CO₂ and O₂ species across the membrane, thus it is expected that application of H₂ contained sweep gas will consume permeated O₂ and increase partial pressure gradient between sweep side and feed side and thus results in an increased flux density of CO₂ and O₂.

Figure 2.1 Schematic illustration of working mechanism of dual phase MECC membranes using Ar and H₂ containing Ar as sweep gas.
2.1.2 Newly developed CO$_4^{2-}$ transport model in MECC membrane

2.1.2.1 Overall surface reactions

CO$_4^{2-}$ has been proved to be a possible active surface species in molten carbonate by recent experiments as well as DFT studies [78-81]. The detailed transport process is described as below. On the feed side surface,

\[ CO_3^{2-} + \frac{1}{2} O_2 = CO_4^{2-} \quad (2 - 6) \]

On the sweep side, when pure Ar is applied as sweep gas:

\[ CO_4^{2-} = CO_3^{2-} + \frac{1}{2} O_2 \quad (2 - 7) \]

When H$_2$ contained Ar is used as sweep gas:

\[ CO_4^{2-} + H_2 = CO_3^{2-} + H_2O \quad (2 - 8) \]

The overall reaction under pure Ar sweep gas can be written as:

\[ CO_3^{2-}(MC) + \frac{1}{2} O_2(feed) = CO_3^{2-}(MC) + \frac{1}{2} O_2(sweep) \quad (2 - 9) \]

The overall reaction under H$_2$ contained Ar sweep gas can be written as:

\[ CO_3^{2-}(MC) + \frac{1}{2} O_2(feed) + H_2(sweep) = CO_3^{2-}(MC) + H_2O \quad (2 - 10) \]

2.1.2.2 Two mechanisms of CO$_4^{2-}$ formation

Equation (2-6) is an overall reaction describing CO$_4^{2-}$ formation. There are two possible pathways as studied by reference [78-81]. The first mechanism is based on O$_2^{2-}$ intermediate species [80] and the detailed reaction steps are illustrated by (2-11) to (2-13).

\[ CO_3^{2-} \leftrightarrow O^{2-} + CO_2 \quad (2 - 11) \]
\[
\frac{1}{2} O_2 + O^{2-} \leftrightarrow O_2^{2-}
\]  
(2-12)

\[
CO_2 + O_2^{2-} \leftrightarrow CO_4^{2-}
\]  
(2-13)

Thus, the overall surface reaction is illustrated as (2-6). Figure 2.2 shows the Raman spectra of Li/K carbonate at 923K when atmosphere switches from 1 atm O\textsubscript{2} to 1 atm O\textsubscript{2} and CO\textsubscript{2}. The 832 cm\textsuperscript{-1} band and 982 cm\textsuperscript{-1} band are assigned to O\textsubscript{2}\textsuperscript{2-} and CO\textsubscript{4}\textsuperscript{2-} species respectively. It can be seen by Raman spectra that with the increase of CO\textsubscript{2} content, CO\textsubscript{4}\textsuperscript{2-} peak became more considerable while O\textsubscript{2}\textsuperscript{2-} band lessened rapidly, indicating the proceeding of reaction (2-13).

Figure 2.2 Raman spectra of Li/K carbonate at 923 K when the atmosphere switches to 1 atm O\textsubscript{2}+CO\textsubscript{2} from 1 atm O\textsubscript{2}. [80]

The second mechanism is supported by DFT study in which CO\textsubscript{5}\textsuperscript{2-} is proposed as the intermediate species [78]. Equation (2-14) and (2-15) below show the detailed steps.

\[
CO_2^{2-} + O_2 \leftrightarrow CO_5^{2-}
\]  
(2-14)

\[
CO_5^{2-} + CO_3^{2-} \leftrightarrow 2CO_4^{2-}
\]  
(2-15)
which also leads to an overall surface reaction described by (2-6).

Figure 2.3 shows the optimized structures of CO$_4^{2-}$ and CO$_5^{2-}$ calculated at B3LYP/6-31G(d) level. One thing need to notice that chemisorption occurs between O$_2$ and CO$_3^{2-}$ during which a weak covalent bond is formed between O$_2$-O$_3$ as illustrated in Fig. 2.3(b). The bond between O$_4$-O$_5$ is also covalent as illustrated by Fig. 2.3(a).

![Figure 2.3 Molecular structures of free CO$_4^{2-}$ and CO$_5^{2-}$ optimized at B3LYP/6-31G(d) level.[78]](image)

The potential energy surface (PES) of oxygen dissociation in Li, Na and K molten carbonates are shown in Fig.2.4. It can be confirmed that the chemisorption of gas oxygen on MC surface is energetic favorable in all three types of molten carbonates. The effective activation energy for the overall reaction is estimated to be 96.2, 15.1 and 68.6 kJ/mol in lithium, sodium and potassium molten carbonate respectively. The pseudo one-step reaction is exothermic and favored by chemical thermodynamics for Na and K, but slightly endothermic for Li.
2.1.2.3 Cogwheel transport model of CO$_4^{2-}$

Figure 2.5 illustrate the “cogwheel” transport model for CO$_4^{2-}$ in molten carbonate. This model involves rotation, breaking and reforming the O-CO$_3^{2-}$ bond during the transport. In this model, CO$_3^{2-}$ is perceived as an oxygen carrier and O$_2$ migrate through MC by means of O-CO$_3^{2-}$ bond breaking and reforming.

A more detailed model of oxygen migration in lithium carbonate is shown in Fig. 2.6. The top of Fig. 2.6 shows the local structure of [Li$_2$O(CO$_3^{2-}$)$_2$]$^{2-}$ where oxygen transfer occurs while the bottom represents the overall cluster of O-(Li$_2$CO$_3$)$_4$. At the beginning, O4 is bonded with O1 with a bond distance of 1.465 Å. The oxygen transfer is initiated by the O1-O4 stretching. The bond distance of O1-O4 was elongated to 1.869 Å and in the meantime O4-O5 bond distance was shortened to 1.94 Å, which represents a bond breaking and forming process. The energy barrier from reactant to TS is calculated to be 102.1 kJ/mol.
Figure 2.5 A cooperative “cogwheel” transport mechanism of CO$_3^{2-}$ in MC. CO$_3^{2-}$ serves as oxygen carrier in this model.[79]

Figure 2.6 The structures of reactant, transition state(TS) and product as well as relative energy(kJ/mol) for CO$_4^{2-}$ transport in lithium carbonate (Li$_2$CO$_3$)$_4$. Distance is in Å and grey, red and purple balls represent C, O, Li respectively.[79]

2.1.3 Combined bi-pathway gas transport model

Based on above two possible transport pathways for active gas species, a bi-pathway gas transport model in MECC membrane is therefore proposed as Fig. 2.7. In 3PB CO$_2$ and O$_2$ transport together through MC phase in the form of CO$_3^{2-}$ while in 2PB O$_2$...
react with CO$_3^{2-}$ to form CO$_4^{2-}$ which transport in a cogwheel mode as illustrated above through MC phase.

Figure 2.7 Bi-pathway gas transport mechanism in this study.

2.2 WORKING MECHANISM OF “MECC-SOEC” REACTOR

The second part in this dissertation work is applying MECC membrane in “MECC-SOEC” reactor. MECC is combined with a conventional high temperature solid oxide electrolysis cell (SOEC) for capture of CO$_2$ and instant conversion of CO$_2$ into CO riched syngas. Since they both operate at high temperature, the process conditions can remain
the same, which is expected to be energy efficient since it avoids cooling/reheating and
derpressurizing/pressurizing of captured CO$_2$ during conversion.

Figure 2.8 illustrate the central idea of the combined reactor. The detailed process
can be described as below. At the sweep side of MECC surface, H$_2$ is used as capture gas
and it reacts with permeated CO$_2$ and O$_2$ as illustrated below:

\[
\frac{1}{2}O_2 + H_2 = H_2O + \Delta \quad (2 - 16)
\]

Reverse water gas shift reaction (RWGSR) happens in the meanwhile:

\[
CO_2 + H_2 = H_2O + CO \quad (2 - 17)
\]

Then the steam, CO$_2$ rich stream are the feedstock for SOEC co-electrolysis and the final
product is syngas derived from (2-18), (2-19) and (2-17):

\[
H_2O = H_2 + \frac{1}{2}O_2 \quad (2 - 18)
\]

\[
CO_2 = CO + \frac{1}{2}O_2 \quad (2 - 19)
\]

There are three major benefits behind the design: 1. It recycles the capture CO$_2$
directly back to the fuel form, which saves the energy needed for CO$_2$ transportation; 2.
The heat released from reaction (2-16) can be directly utilized by the endothermic
reactions (2-18) and (2-19). By utilizing renewable energy such as nuclear and solar
sources, it stores them in the fuel form, which solves the intermittency problem
encountered in renewable industry.
Figure 2.8 Schematic illustration of “MECC-SOEC” reactor

\[
\begin{align*}
\text{H}_2 + 0.5\text{O}_2 & = \text{H}_2\text{O} + \Delta \\
\text{H}_2 + \text{CO}_2 & = \text{H}_2\text{O} + \text{CO} \\
\text{H}_2\text{O} + 2e^- & = \text{H}_2 + \text{O}_2^- \\
\text{H}_2 + \text{CO}_2 & = \text{H}_2\text{O} + \text{CO} \\
\text{CO}_2 + 0.5\text{O}_2 + 2e^- & = \text{CO}_3^{2-}
\end{align*}
\]
Chapter 3 Synthesis and Characterization of MECC Membranes

3.1 SYNTHESES OF POROUS METAL MATRIX AND MECC MEMBRANES

Here is a brief overview of the synthesis process of MECC membranes. The first reported MECC membrane was developed by Jerry Lin’s group [82]. They used stainless steel (SS) as the metal support and infiltrated molten carbonate into the metal support directly at 500-600 °C. Despite of a high CO$_2$ permanence (2.5x10$^{-8}$ mol.s$^{-1}$.Pa$^{-1}$), the membrane failed quickly due to the chemical reaction between SS and MC. Nansheng Xu [73] used Ag instead of SS as the metal matrix to prevent the chemical interaction between metal matrix and MC. Besides, instead of using direct infiltration method, he mixed Ag powder with MC powder at room temperature and sintered the mixture at 650 °C in one step. His sample shows a 6x higher CO$_2$ permeation flux than SS-MECC counterpart. However, he was not able to slow down the degradation process: his sample degraded very quickly after a few hours testing and post-test examination revealed a severe Ag sintering along with the loss of MC from silver matrix. Lingling Zhang fabricated


MECC in a 2-step process: first, producing porous Ag matrix by traditional pore former method; second, infiltrating MC into Ag matrix under 650 °C [73-75, 77]. Microcrystalline methylcellulose and carbon black are used as the pore formers in her studies. The former one results in Ag matrix with a pore size from 15 μm to 20 μm while the latter one reduces the pore size of Ag matrix to less than 10 μm [77]. Although this 2-step method greatly reduces the pore size of Ag matrix compared with the one-step process developed from Nansheng, the pores are still too large to generate enough capillary force. And MC loss from Ag matrix was observed under high operating temperature (e.g. 650 °C). Besides, silver sintering occurred rapidly at a high operating temperature, resulting in a fast growth of pore size and the coarsening of Ag matrix and thus a more severe loss of MC. To improve the wettability between Ag and MC and slow down the Ag coarsening process, Lingling coated Ag matrix with a thin layer of Al₂O₃ colloidal in her later study. It has been proved that MECC with a thin layer of Al₂O₃ can both maintain an original pore size and a 90% of its original flux density after 130h [26]. Jingjing modified Lingling’s study by coating Al₂O₃ using chemical vapor deposition (CVD), which results in a more uniform layer of Al₂O₃ on Ag matrix [76]. Peng Zhang deposited ZrO₂ onto pore-former derived porous Ag matrix and his study shows that Ag sintering can be greatly inhibited even at an operating temperatures larger than 800 °C with ZrO₂ on Ag matrix [83].

Parallel to these efforts, in this dissertation work, a different approach is proposed to slow down the silver sintering and MC loss. A new fabrication method is applied to produce Ag matrix with a finer microstructure and therefore an enough capillary force is produced at the first place. And in the later operation process, lowering the operating
temperature of Ag-MC MECC membranes, which ensures a relatively slow Ag sintering process. Chemical dealloying and electrochemical dealloying methods are selected here to create a porous Ag matrix with sub-micron pore size.

Dealloying method is a corrosion method applied to selectively dissolve one or more less noble elements from precursor alloys. Figure 3.1 illustrate the working principle of this method\cite{84}. During dealloying, the less noble component is dissolved first, moving away from the precursor alloy. The remaining nobler elements diffuse and agglomerate into a well-defined three dimensional bi-continuous nanoporous structure. In chemical dealloying, a corrosion electrolyte like acid or alkaline is applied and the less noble element is removed by reacting with electrolyte. In electrochemical dealloying, a corrosion cell is used to apply a constant current/voltage onto precursor alloy to remove less noble element from precursor. Dealloying methods has demonstrated its feasibility in producing nanoporous metals in many binary alloy system like Ag-Au\cite{85-87}, Ag-Al\cite{88-90} and Ag-Zn \cite{91}.

3.1.1 Synthesis of porous metal matrix by chemical dealloying

The alloy of choice for chemical dealloying is Ag50Al50 consisting of 50at% Ag and 50at% Al (from ACI Alloys) with Al as the fugitive element. The dealloying procedure is described as follows. Ag-Al alloy pellets in a diameter of $\phi 17$mm are first soaked in a hot 3M HCl aqueous solution at 90°C for a predefined period (48h and 72h). Then the de-aluminized samples are thoroughly washed in an ultrasonic cleaner with DI water. The samples are finally dried in oven and annealed at 650°C for 2 hours. Weight loss of delloyed samples are monitored to calculate corresponding pore volume. The total
weight losses for the 48h- and 72-h dealloyed samples are ~12% and 15%, equivalent to a pore volume of 29.6% and 37%, respectively.

Figure 3.1 Schematic illustration of dealloying method to produce porous metal.[84]

3.1.2 Synthesis of porous metal matrix by electrochemical dealloying

Ag50Zn50 made of 50 at% Ag and 50 at% Zn (from ACI alloys, donated as Ag50Zn50 hereinafter) with Zn as the fugitive element was selected as parent alloy in electrochemical dealloying experiments. The dealloying procedure is described as follows. A corrosion cell was employed consisting of a 1 L flask containing a 1 M NaCl electrolyte solution, two identical graphite counter electrodes and an Ag50Zn50 pellet with a diameter of 17 mm as the working electrode. A schematic illustration of the setup is shown in Fig. 3.2(a). One side of the working electrode pellet was covered with epoxy so that the dealloying process can only proceed in one direction to avoid delamination at the center of the sample.
The dealloying of zinc was carried out under the galvanodynamic mode using a Solartron 1287 potentiostat. The dealloying process was completed in two steps as schematically shown in Fig. 3.2(b). In the first step, a constant current of 10 mA was applied to the cell for a period of 50 h. In the subsequent second step, a linear current ramping down profile at a rate of $\Delta i$ mA/h starting from 10 mA and ending at 0 mA was applied. The average current in the second step was, therefore, 5 mA. The current scan rate ($\Delta i$) employed in the second step is calculated by

$$
\Delta i = \frac{10mA - 0mA}{t_2}
$$

(3 – 1)

The time, $t_2$, needed for the second stage dealloying is determined by

$$
t_2 = \frac{n \times F \times w_{2,Zn}}{i_{2,average} \times M_{Zn}}
$$

(3 – 2)

The remaining Zn, $w_{2,Zn}$, in the alloy after the first stage dealloying process is determined by

$$
w_{2,Zn} = \frac{w_{Ag50Zn50} \times M_{Zn}}{M_{Ag} + M_{Zn}} - \frac{i_1 \times t_1 \times M_{Zn}}{nF}
$$

(3 – 3)

where $M_{Zn}=65.38$ g/mol; $M_{Ag}=107.86$ g/mol; $n=2$ is the charges transferred during the electro-dealloying process; $F$ is the Faraday constant; $w_{Ag50Zn50}$ is the sample weight; $i_1 = 10mA$ is the current applied in the first stage; $t_1 = 50h$ is the deplating time used for the first stage; $i_{2,average} = 5 mA$ is the average current applied in the second stage of dealloying. After dealloying, the sample was thoroughly washed in acetone for 5 minutes to remove the epoxy, followed by a 10-minute washing in a DI water. The sample was finally dried in oven and annealed at 400 °C for 2 h before use. By annealing the as-
dealloyed sample at 400 °C, the mechanical strength of the porous Ag can be enhanced. The MECC membrane developed by this procedure is donated as EC-10mA-400 hereinafter.

It is worth mentioning that thus created pores in Ag phase are expected to be fully connected because of the Zn-content in the original Ag-Zn alloy is above percolation threshold. As the Zn-grains are gradually replaced by pores during the deplating process, the resultant pores are expected to replicate the Zn-grains and be fully connected. The pore volume should be very close to the volumetric fraction of the Zn phase in the parent alloy after all the Zn is removed.

Figure 3.2 (a) Schematic illustration of corrosion cell; (b) A typical electrochemical dealloying current profile employed, corresponding to a sample weight (wAg50Zn50) of 2.0065g and a ramping current rate (Δi) of 0.414 mA/h.

3.1.3 Synthesis of MECC membranes

The dual phase MECC membranes were fabricated by filling porous Ag matrix with a carbonate melt at high temperature. The infiltration procedure is described as follows.
The porous Ag pellets were first attached to a silver wire and then embedded in the solid carbonates contained in a crucible. The solid carbonates contain a eutectic composition of an alkaline carbonate mixture: 52 mol% Li$_2$CO$_3$ and 48 mol% Na$_2$CO$_3$. The sample assembly was then placed in a furnace at 650 °C. Driven by the capillary forces, the molten carbonate (MC) would eventually fill into the porous Ag pellet. After a 2h soak, the pellet filled with MC was then pulled out of the MC and hung over the crucible, followed by a 3 °C/min cooling to room temperature. Thus made MECC membrane was finally polished with sandpaper in the presence of ethanol to remove the residual carbonates from surfaces.

3.2 CHARACTERIZATION TECHNIQUES IN POROUS METAL MATRIX AND MECC MEMBRANES

3.2.1 XRD

The phase composition of pre-dealloyed sample and post-dealloyed sample were examined by X-ray diffractometer (XRD) equipped with a graphite-monochromatized CuKα radiation (λ=1.5418 Å). The 2θ scans were performed at a rate of 10°/min from 20 to 80°. The obtained XRD patterns then were analyzed by Jade software to identify phases in samples.

3.2.2 SEM

The microstructures of parent alloy, porous metal matrix as well as dense MECC membranes were characterized by a field emission scanning electron microscopy (FESEM, Zeiss Ultra) equipped with an energy dispersive X-ray spectroscopy (EDS) analyzer. For
dense MECC membranes examination, a thin layer of Au was coated on top of surface by a gold sputtering coater.

3.2.3 Krypton adsorption

The BET surface areas of de-aluminized Ag matrix were measured by Krypton adsorption using Autosorb-iQ from Quantachrome Instruments.

3.3 PROPERTIES OF POROUS METAL MATRIX AND MECC MEMBRANES

3.3.1 Properties of chemical dealloying derived porous Ag matrix

According to the Ag-Al phase diagram in Fig. 3.3 (a), the starting Ag50Al50 contains two phases: a minor α-Al and primary γ-Ag2Al phase. X-ray diffraction (XRD) patterns shown in Fig. 3.3 (b) confirms that original alloy consists of primary γ-Ag2Al and minor α-Al phase. Besides, XRD pattern for de-aluminized sample shows a complete removal of Al from minor α-Al phase. Although there is still a very small amount of γ-Ag2Al phase left in silver, it is not a concern because Al element when oxidized into Al2O3 is an excellent wetting agent for molten carbonates as confirmed by our previous study [75, 76].
Figure 3.3 (a) Ag-Al phase diagram; (b) XRD patterns for original Ag50Al50 and de-aluminized silver after 48h.

The microstructure of the original Ag50Al50 alloy is shown in Fig. 3.4 (a), revealing both phases with the minor $\alpha$-Al phase preferentially locate at grain boundaries and $\gamma$-Ag$_2$Al phase locate inside large circular grains. The microstructures of porous Ag matrix after de-aluminizing in a hot 3M HCl aqueous solution at 90°C for 48h (denoted as 48h-Ag50Al50) are shown in Fig. 3.4 (b)-(d). During a typical de-aluminizing process, dissolution of Al is expected to start first in the intergranular region[92], forming open 3D channels as indicated in Fig. 3.4 (b). Those channels provide pathways for HCl to further penetrate in and thus dissolve Al in the minor $\alpha$-Al as well as primary $\gamma$-Ag$_2$Al phase. Since Al is much richer in $\alpha$-Al than in $\gamma$-Ag$_2$Al, it is expected that de-aluminizing rate in $\alpha$-Al phase is faster than that in $\gamma$-Ag$_2$Al, and thus pore creation from $\alpha$-Al phase are expected to happen at a faster and greater speed than that in the $\gamma$-Ag$_2$Al phase. Comparison of Fig. 3.4 (c) and (d) indeed indicates that the average pore size in the region belonging to $\alpha$-Al phase ranging from a few to tens $\mu$m, which is much larger than that in $\gamma$-Ag$_2$Al-belonging
regions where it is only less than 1μm. More interestingly, pores derived from those two phases have quite different shapes: pores with circular shapes are observed in the \( \gamma \)-Ag\(_2\)Al phase region while pores with laminar shapes are observed in the \( \alpha \)-Al phase region. Overall, the \( \gamma \)-Ag\(_2\)Al-derived porous Ag constitutes a much larger volume of finer pores than the \( \alpha \)-Al-derived counterpart, which turns out to be the fundamental reason for the high and stable CO\(_2\) and O\(_2\) flux densities to be shown in the future chapter.

Figure 3.4 Microstructures of (a) Ag\(_{50}\)Al\(_{50}\) (etched in 3M HCl at 90°C for 3min to reveal grains and grainboundaries); (b)48h-Ag\(_{50}\)Al\(_{50}\) (overall); (c) \( \alpha \)-Al-derived porous Ag matrix;(d) \( \gamma \)-Ag\(_2\)Al-derived porous Ag matrix.1: \( \alpha \)-Al; 2: \( \gamma \)-Ag\(_2\)Al; 3: porous Ag derived from \( \alpha \)-Al phase; 4: porous Ag derived from \( \gamma \)-Ag\(_2\)Al phase.

3.3.2 Properties of electrochemical dealloying derived porous Ag matrix

Figure 3.5 shows the phase diagram as well as phase compositions of the starting Ag\(_{50}\)Zn\(_{50}\) alloy and the resultant EC-10mA-400 sample. According to XRD results (Fig.
there are two phases present in the original Ag50Zn50 alloy: hexagonal $\zeta$-AgZn (PCPDF#29-1156) and $\beta$-AgZn (PCPDF#29-1155). However, according to the Zn-Ag phase diagram shown in Fig. 3.5 (a) [93], $\zeta$-AgZn is expected to be the only phase for this composition. The existence of metastable $\beta$-AgZn phase in starting Ag50Zn50 may result from the actual fabrication method which includes a fast quenching process. Despite that fact that two phases were observed in starting alloy, the XRD pattern of the dealloyed sample shows only fcc-Ag phase, indicating that Zn in either $\zeta$-AgZn or $\beta$-AgZn has been removed, resulting in a pure fcc-Ag phase. A complete removal of Zn from Ag50Zn50 results in a porosity of 47.2% in the resultant EC-10mA-400 sample. The attainment of a pure fcc-Ag phase demonstrates the suitability of using Zn as the sacrificial element in making porous Ag.

![Figure 3.5](image)

Figure 3.5 (a) Ag-Zn phase diagram; (b) XRD patterns for pre-dealloying Ag50Zn50 and resultant EC-10mA-400.

The microstructure of original Ag50Zn50 is shown in Fig. 3.6(a). It is obvious that the starting alloy exhibit a very uniform microstructure before dealloying since neither
grain boundaries nor phase boundaries could be observed under SEM images. After electrochemical dealloying, the microstructure is shown in Fig. 3.6 (b). It can be seen that as-dealloyed sample has a highly porous and fine microstructure with average pore size less than 1 μm.

![SEM image of (a) starting Ag50Zn50; (b) as-dealloyed porous Ag](image)

Figure 3.6 SEM image of (a) starting Ag50Zn50; (b) as-dealloyed porous Ag

3.3.3 Comparison between porous Ag derived from different methods

Improving the microstructure of previous pore former derived Ag matrix is the major task of applying novel methods to fabricate Ag matrix, thus it is important to compare microstructures of porous Ag developed from different methods. Figure 3.7 (a)-(c) compares porous silver derived from pore former method, chemical dealloying method and electrochemical dealloying method. It should notice that Fig. 3.7 (c) was taken under a much higher magnification than the other two figures. It is not too difficult to see the improvement in microstructure when comparing pore former derived porous Ag with chemical dealloyed porous Ag. Although chemical dealloyed sample has a non-uniform microstructure with two types of pores, even the size of bigger pores is smaller than the average pore size in pore former derived counterpart, let alone most pore
volume is constituted by smaller pores as indicated by Fig. 3.4 (d). Electrochemical dealloyed sample showed further improvement in microstructure by exhibiting an average pore size less than 1 µm and a more homogenous microstructure (Fig. 3.7 (c)) compared with both pore former and chemical dealloyed samples.

Figure 3.7 Comparison of porous structure of (a) pore former derived porous Ag; (b) chemical dealloying derived porous Ag; (c) electrochemical dealloying derived porous Ag. (c) is taken at a much higher magnification than (a) and (b).

A detailed comparison of microstructures of porous Ag derived from different methods is illustrated by table 3.1. The BET surface area measured by krypton adsorption further confirms the superiority of chemical dealloyed sample over pore former derived sample by showing a 5x increase in BET surface area for the former one.

Figure 3.8 (a)-(h) further compares Ag50Al50 alloy with Ag50Zn50 alloy as well as chemical dealloying derived microstructure with electrochemical dealloyed microstructure. One reason associating with a finer microstructure developed by electrochemical dealloyed sample is the homogenous microstructure observed in its parent alloy Ag50Zn50 as shown in Fig. 3.8(e). On the contrary, the precursor alloy Ag50Al50 exhibit large grains and grain boundaries. In addition, the two phases contained in the original Ag50Al50 exhibits very different dealloying activity: α-Al phase dissolves
faster than Ag$_2$Al phase, leading to the coarsening of $\alpha$-Al derived pores/ligaments during the chemo-dealloying. Although Ag50Zn50 also contains two phases, they have a similar electrochemical activity and thus is dealloyed at a similar rate [94]. The second reason is associated with electrochemical method. Since a controlled current rate is applied in system, zinc dealloying rate as well as Ag coarsening rate can be well controlled as well, which ultimately results in a more uniform microstructure with a tight pore size distribution.

3.3.4 Properties of dense MECC membranes

The microstructures of a chemical dealloyed Ag-MC MECC membrane are shown in Fig. 3.9 (a)-(h). It is evident from Fig. 3.9 (a) and (b) that a completely dense MECC membrane is achieved after infiltration process. Thus dense membrane prevent CO$_2$ and O$_2$ leakage and ensures a 100% permeation of CO$_2$ result from related ion species (e.g. CO$_3^{2-}$, CO$_4^{2-}$) rather from gas leak. Figure 3.9 (c) further confirms the existence of MC. One thing we concerned about the newly developed porous Ag is weather MC can be infiltrated into the area with small pores. Since our previous infiltration process in MECC all deal with relatively coarsened porous Ag with an average pore size larger than 10 μm, it is important to examine if MC is able to be infiltrated into those areas with much smaller pores. Figure 3.9 (d) shows the area developed from Ag$_2$Al where pore size is very small and it can be seen that MC can be infiltrated into those areas. EDS mapping in Fig. 3.9(e)-(h) further illustrates this point by showing the existence of C K, Na K and O K.
Table 3.1 Comparison of microstructures of porous Ag derived from different methods.

<table>
<thead>
<tr>
<th>Method</th>
<th>Pore Size (µm)</th>
<th>Microstructure</th>
<th>BET (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pore former</td>
<td>&gt;10</td>
<td>Non-uniform</td>
<td>0.049</td>
</tr>
<tr>
<td>Chemical dealloying</td>
<td>Large pores &gt;10</td>
<td>Uniform within each phase</td>
<td>0.301</td>
</tr>
<tr>
<td></td>
<td>Small pores &lt;2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Electrochemical dealloying</td>
<td>&lt;1</td>
<td>Uniform throughout whole structure</td>
<td></td>
</tr>
</tbody>
</table>

Figure 3.8 A detailed comparison of chemical dealloyed sample (a)-(d) with electrochemical dealloyed sample (e)-(h). (a) the original Ag50Al50 (b) porous Ag derived from Ag50Al50 with chemical dealloying (sample 48h-Ag50Al50); (c) porous Ag created from α-Al phase; (d) porous Ag created from Ag₂Al phase; (e) the original Ag50Zn50; (f) porous Ag derived from Ag50Zn50 with electrochemical dealloying (sample EC-10mA-400); (g) image (f) at higher magnification and (h) image (g) after 400 °C annealing.
The microstructure of electrochemical dealloyed Ag-MC MECC membranes is shown in Fig. 3.10. Despite the very fine microstructure, MC is successfully infiltrated into Ag matrix, resulting in a dense membrane. What is worth to mention that, unlike chemical dealloyed-MC MECC membrane, both Ag and MC phase distribute evenly throughout the microstructure in electrochemical dealloyed Ag-MC MECC membrane. This is because electrochemical dealloyed porous Ag has a more homogenous microstructure than chemical dealloyed counterpart. This dense and uniform microstructure make it possible for MECC membranes to operate with a low gas leak and stable performance.
Figure 3.10 SEM images of pristine electrochemical dealloyed Ag-MC MECC. Darker part corresponds to MC while grey/lighter part corresponds to Ag.
Chapter 4 Transport Properties of Chemical and Electrochemical Dealloyed MECC Membranes and “MECC-SOEC” Reactor

4.1 CHARACTERIZATIONS OF MECC DUAL-PHASE MEMBRANES AND “MECC-SOEC” REACTOR

4.1.1 Characterizations of MECC membranes

A homemade permeation cell was employed to measure CO\textsubscript{2} and O\textsubscript{2} flux densities. Detailed information about this setup can be found in Fig. 4.1 [73, 75, 95]. Below is a brief description. The MECC membrane was first sealed to a supporting alumina tube by silver paste (Synthetic Resins, Shanghai Research Institute), after which a second short alumina tube was placed on top of the membrane to confine the feed gas to MECC surface. After each round of silver paste sealant application, the membrane/alumina tube assembly was dried in furnace at 130 °C for half an hour. It usually took 4-5× silver paste applications to

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achieve a complete seal.

For all the measurements in this study, a simulated flue gas containing 15% CO\(_2\), 10% O\(_2\) and 75% N\(_2\) was used as the feed gas. Ar with different H\(_2\) concentrations (0, 4.35% and 9.41%) was used as the sweep gas in chemical dealloying derived MECC, while Ar-9.44% H\(_2\) was used as the sweep gas in electrochemical dealloying derived sample. A commercial gas flow controller (Smart-Trak, 50 series) was employed to control the mass flow rate of both feed and sweep gases, while an on-line Micro-GC (model 490, Agilent Technologies) was used to analyze the compositions of the sweep gas at room temperature and ambient pressure (T=25 °C, P=1 atm). Pre-calibrations with five standard gases of interest (CO\(_2\), O\(_2\), N\(_2\), H\(_2\), CO) were conducted before measurement. The N\(_2\) concentration in sweep gas was used as a tracer to correct for the leakage from sealing or membrane itself. The total flow rate of feed gas was set to 100 ml/min, while it was set to 50 ml/min for the sweep gas. The final CO\(_2\) and O\(_2\) flux densities were calculated from a leakage-corrected gas composition averaged from ten successive readings by Micro-GC multiplied by the sweep-gas flow rate. A 30-min stabilization time was given before each reading taken at each temperature.
Figure 4.1 Schematic illustration of experiment set up for permeation test of dual MECC membrane. 1-4: gas cylinder; 5: Mass flow controllers; 6: Furnace; 7: Inner feed tube; 8: second alumina tube; 9: MECC; 10: Ag paste; 11: thermocouple; 12: supporting alumina tube; 13: inner sweep tube; and 14: gas chromatography (GC). [73, 75, 95]

Following equations were applied to calculate flux densities from gas concentrations measured by micro-GC.

\[ J_{N_2,GC} = \frac{c_{N_2}}{(1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{CO})} \times \frac{Q_{Ar}}{S} \]  \hspace{1cm} (4 - 1)

\[ J_{CO_2,GC} = \frac{c_{CO_2}}{(1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{CO})} \times \frac{Q_{Ar}}{S} \]  \hspace{1cm} (4 - 2)

\[ J_{O_2,GC} = \frac{c_{O_2}}{(1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{CO})} \times \frac{Q_{Ar}}{S} \]  \hspace{1cm} (4 - 3)

\[ J_{H_2,GC} = \frac{c_{H_2}}{(1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{CO})} \times \frac{Q_{Ar}}{S} \]  \hspace{1cm} (4 - 4)
\[ J_{co,GC} = \frac{c_{co}}{(1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{co}) \times \frac{Q_{Ar}}{S}} \] (4 – 5)

\[ Q_{Ar} = (1 - c_{H_2, cylinder}) \times \frac{Q}{S} \] (4 – 6)

where \( c_{N_2}, c_{CO_2}, c_{O_2}, c_{H_2} \) and \( c_{co} \) are the measured concentrations of \( N_2, CO_2, O_2, H_2 \) and \( CO \) in micro-GC, respectively; \( c_{Ar} = 1 - c_{CO_2} - c_{N_2} - c_{O_2} - c_{H_2} - c_{co} \) is the concentration of the Ar in the sweep gas, which can be calculated from other gas’s concentration; \( Q_{Ar} = 50 \, ml/min \) is flow rate in the sweep gas; \( c_{H_2, cylinder} \) is the \( H_2 \) concentration in the tank, which is known; \( S=0.921 \, cm^2 \) is the effective area of the sample in this study. The flux density of \( H_2 \) before reacting with the permeated \( O_2 \) is calculated below to calibrate \( O_2 \) flux. The calibrated \( CO_2, O_2 \) flux densities are listed below.

\[ J_{H_2,total} = c_{H_2, cylinder} \times \frac{Q}{S} \] (4 – 7)

\[ J_{CO_2,calibrated} = J_{CO_2,GC} - n \times J_{N_2,GC} + J_{CO,GC} \] (4 – 8)

\[ J_{O_2,calibrated} = J_{O_2,GC} - m \times J_{N_2,GC} + \frac{J_{H_2,total} - J_{H_2,GC} - J_{CO,GC}}{2} \] (4 – 9)

Where \( n=0.2 \) is the ratio between \( CO_2 \) flow rate and \( N_2 \) flow rate on MECC feed side; \( m=0.13 \) is the ratio between \( O_2 \) flow rate and \( N_2 \) flow rate on the feed side.

4.1.2 Characterizations of “MECC-SOEC” reactors

The same experimental configuration is used in “MECC-SOEC” reactor except that the MECC pellet is sealed on top of a tubular SOE cell and SOE cell sits on top of the supporting \( Al_2O_3 \) tube as shown in Fig. 4.2. It worth to mention that a MECC pellet is used instead of proposed tubular MECC membranes. Despite of the traditional experimental set ups, an extra electrochemical workstation (To demonstrate the technique feasibility
of the combined reactor proposed in Chapter 2, a combined reactor using tubular SOEC and a planar MECC has been build up as shown in Fig. 4.12. It worth to mention that a MECC pellet is used instead of proposed tubular MECC membranes. Despite of the traditional experimental set ups, an extra electrochemical workstation (Solartron) was added to apply a certain current density on SOEC for H₂O electrolysis. Flux densities of each gas species are measured and calculated in the same way as in single MECC membrane as described in section 4.1.1.

There are several other parameters used to characterize “MECC-SOEC” performance: H₂ production rate in SOEC (donated as \( J_{H_2,SOE} \)), CO production rate (donated as \( J_{CO,RWGS} \)), H₂O conversion rate (\( CR_{H_2O} \)), CO₂ conversion rate (\( CR_{CO_2} \)) and current efficiency (CE). The detailed equation for those parameters are listed below:

\[
J_{H_2,SOE} = J_{H_2O,MECC} - J_{H_2O,GC} \quad (4 - 10)
\]

\[
J_{CO,RWGS} = J_{CO,GC} \quad (4 - 11)
\]

\[
CR_{H_2O} = \frac{J_{H_2,SOE}}{J_{H_2O,MECC}} \quad (4 - 12)
\]

\[
CR_{CO_2} = \frac{J_{CO,GC}}{J_{CO_2,GC} + J_{CO,GC}} \quad (4 - 13)
\]

\[
CE = \frac{J_{H_2,SOE}}{J_{H_2,th}} \quad (4 - 14)
\]

\( J_{H_2O,MECC} \) represents H₂O generated from reaction (2-17) and (2-18) and thus can be represented as

\[
J_{H_2O,MECC} = 2 \times J_{O_2,GC} + J_{CO,GC} \quad (4 - 15)
\]
\( J_{H_2,th} \) represents theoretical production rate of \( H_2 \) based on SOEC current density \( i \) and their relationship can be expressed as

\[
J_{H_2,th} \propto \frac{i}{nF}
\]  

(4 – 16)

Note that the unit of \( i/nF \) is mol/s.cm\(^2\), which is different from \( J_{H2,th} \). A unit conversion is needed to carry out to convert \( i/nF \) to \( J_{H2,th} \).

![Figure 4.2](image)

Figure 4.2 Configuration of “MECC-SOEC” reactor.

4.2 GAS TRANSPORT PROPERTIES OF CHEMICAL DEALLOYED MECC

4.2.1 Flux density vs temperature

The permeation flux densities of \( CO_2 \) and \( O_2 \) measured from the 48h-50Ag50Al sample are shown in Fig. 4.3 as a function of temperature under a simulated flue gas
containing 15% CO₂, 10% O₂ and 75% N₂ as the feed gas and a 9.41%H₂-Ar as the sweep gas. Both CO₂ and O₂ flux densities follow closely the Arrhenius relationship, indicating that the CO₂ and O₂ rates of transport are thermally activated. In addition, the close activation energies for CO₂ and O₂ flux densities, viz. 44.6 vs 45.2 kJ/mol, indicates that the CO₂ and O₂ fluxes are tightly coupled. The previously mentioned surface reaction of \( \text{CO}_2 + \frac{1}{2}\text{O}_2 + 2e^- = \text{CO}_3^{2-} \) is the primary reason that both CO₂ and O₂ are simultaneously needed in order for \( \text{CO}_3^{2-} \) to form and be transported across the membrane.

![Figure 4.3 Arrhenius plots of CO₂ and O₂ flux density of sample 48h-Ag50Al50. Feed gas: simulated flue gas containing 15%CO₂, 10%O₂, and 75%N₂; sweep gas: 9.41%H₂-Ar](image)

The level of CO₂ flux density achieved by this membrane is also remarkable: 1.30, 1.02 and 0.73 ml·min⁻¹·cm⁻² for 700, 650 and 600°C, respectively. Compared to previous
studies using carbon black as a pore former[74-76], the CO₂ flux density achieved in this study is 3× higher. What is also intriguing from Fig. 4.3 is that the flux ratio between CO₂ and O₂ deviates from the ideal 2:1 to (1.71-1.79):1 in the temperature range of 550 to 700°C. This new flux ratio falls in between 2:1 to 1:1.5 with the former ratio signaling CO₃²⁻ as the active surface species and the latter ratio inferring CO₄²⁻ as the active surface species [80]. Therefore, the presence of both CO₃²⁻ and CO₄²⁻ species on the surface of a chemically dealloyed silver-carbonate membrane is possible. Based on this understanding, surface reactions of the primary reaction of CO₂+1/2O₂+2e⁻=CO₃²⁻ (CO₂:O₂=2:1) accompanied by the secondary reaction of 1/2O₂+CO₃²⁻=CO₄²⁻ (CO₃²⁻ acts as an O₂ carrier) are likely to occur simultaneously. The observed higher activation energies here compared to 32 kJ/mol for CO₃²⁻ conduction in pure molten carbonates [14] as well as the experimental observation of CO₄²⁻ on the surface of MC[80] seem to support the theory that a bulkier CO₄²⁻ may be involved in the CO₂ and O₂ transport.

It is worth mentioning that both CO₂ and O₂ can be transported through a MECC membrane as suggested by the enabling surface reaction shown above, which makes the membrane not strictly CO₂ selective. However, use of a fuel as the sweep gas such as H₂ and/or CO to react with O₂ can form a stream containing only CO₂ and H₂O following the reactions of H₂ + CO₃²⁻ = CO₂ + H₂O + 2e⁻ + Δ(heat) and CO + CO₃²⁻ = 2CO₂ + 2e⁻+ Δ. The yielded (CO₂ + H₂O + Δ) product can be an ideal feedstock of the downstream a high-temperature solid-oxide electrolyzer to convert CO₂ and H₂O into syngas. The reuse of captured CO₂ to make syngas has an important implication to the realization of a carbon-neutral energy future.
4.2.2 The effect of H$_2$ in sweep gas on flux density

From a performance point of view, use of fuel as sweep gas also increases the gradient of chemical potential of O$_2$ across the membrane, thus enhancing $J_{O2}$ as well as $J_{CO2}$ because of the coupled CO$_2$/O$_2$ transport. Therefore, the effect of adding H$_2$ into Ar as sweep gas on flux densities of CO$_2$ and O$_2$ was particularly explored in this study. Figure 4.4 shows $J_{CO2}$ and $J_{O2}$ measured at 600°C with different H$_2$ concentrations in Ar as the sweep gas. The results indicate that $J_{CO2}$ and $J_{O2}$ with 9.41%H$_2$-Ar are the highest, approximately 1.5× higher than 4.35%H$_2$-Ar and 2× higher than pure Ar, confirming that lowering partial pressure of O$_2$ can indeed significantly enhance both CO$_2$ and O$_2$ flux densities. It is to be noted that the higher CO$_2$ flux shown in Fig. 4.4 than in Fig. 4.3 is resulted from the fact that the flux density improves with time; data shown in Fig. 4.3 were measured at the beginning of the test whereas those in Fig 4.4 were measured after 160 h on-test. Overall, the enhanced flux density by H$_2$ in conjunction with the aforementioned product of (CO$_2$ + H$_2$O + Δ) enabled by the use of a fuel as the sweep gas and flue gas as the feed gas promises that MECC membranes will be an important carbon-neutral technology in the future.
Figure 4.4 The effect of H₂ concentration in the sweep gas on CO₂ and O₂ flux densities. Feed gas: 15%CO₂, 10%O₂, and 75% N₂.

4.2.3 Long-term flux stability test

The long-term stability of MECC membranes has been a major issue in the past. The much-improved long-term stability of the chemical-dealloying derived silver-carbonate MECC membrane is shown clearly in Fig. 4.5. Over the entire 900-h testing period, J_{CO₂} and J_{O₂} did not show significant degradation despite some fluctuations at the beginning. The fluxes became virtually stable after the first 100-h initialization period for the following nearly 800 hours. While it is not exactly clear why there was a sharp decrease in flux during the first 100-h followed by a recovery, the retention of a high flux has never
been observed for so long a period of time for our baseline pore-former derived membranes as well as those modified by Al$_2$O$_3$\cite{75, 76}.

![Graph showing CO$_2$ and O$_2$ flux densities as a function of time operated at 600$^\circ$C under a simulated flue gas 10% O$_2$, 15% CO$_2$ and 75% N$_2$ as the feed gas and 9.41%H$_2$-Ar as the sweep gas.]

Figure 4.5 CO$_2$ and O$_2$ flux densities as a function of time operated at 600$^\circ$C under a simulated flue gas 10% O$_2$, 15% CO$_2$ and 75% N$_2$ as the feed gas and 9.41%H$_2$-Ar as the sweep gas.

A detailed comparison between traditional Al$_2$O$_3$ coated MECC membrane with chemical dealloyed sample is shown in Fig. 4.6. A great improvement in long term behavior can be observed. It should mention that Al$_2$O$_3$ coated sample is tested under 650 $^\circ$C and with a different feed gas and sweep gas composition, thus it may not fair to compare the flux density directly. But it is reasonable to believe a 50 $^\circ$C increase in operating temperature will not detriment our sample too much. And thus it is fair to compare long term behavior between these two types of samples. We believe that the stable performance achieved demonstrates the importance of creating sufficiently small pores in a porous silver matrix, by which loss of molten carbonate, a leading cause for flux
degradation, can be effectively alleviated. The test was eventually terminated due to an increased N\textsubscript{2} leakage from 0\% at the beginning to 1.5\% at 900-h marker, indicating a significant loss of carbonate occurred. It is also need to mention that N\textsubscript{2} leakage gradually increases with time during the course of experiment, indicating a molten carbonate was lost in a gradual manner.

Figure 4.6 Comparison of long term stability between chemical dealloyed sample 72h-Ag50Al50 with Al\textsubscript{2}O\textsubscript{3} coated MECC donated as Al\textsubscript{2}O\textsubscript{3}-Ag\textsubscript{74-76}. Al\textsubscript{2}O\textsubscript{3}-Ag is tested under 650 °C with 50 ml/min.cm\textsuperscript{2} CO\textsubscript{2}, 50 ml/min.cm\textsuperscript{2} O\textsubscript{2} on the feed side and 50 ml/min.cm\textsuperscript{2} N\textsubscript{2} on sweep side.

Microstructural comparison of the post-test sample with the pre-test one is shown in Fig. 4.7; it suggests that a significant growth of silver grains has occurred during the 900-h testing. The grain growth gradually squeezed out molten carbonate and eventually resulted in a gas breakthrough. The observed flux fluctuations in Fig. 4.5 could also be
related to the silver sintering, during which MC’s mobility and thickness varied with time. Preventing silver from sintering appears to be necessary for future development. With the high-flux exhibited by using a fuel as the sweep gas, the operating temperature can be further decreased to a temperature such as 500°C as a means of alleviating the silver sintering.

Figure 4.7 Microstructures of chemical dealloyed MECC membrane. (a) Pre-test; (b) post-test

4.3 GAS TRANSPORT PROPERTIES OF ELECTROCHEMICAL DEALLOYED MECC

4.3.1 Flux density vs temperature

The permeation flux densities of CO$_2$ and O$_2$ measured from EC-10mA-400 sample are shown in Fig. 4.8 as a function of reciprocal temperature. A simulated flue gas containing 15% CO$_2$, 10% O$_2$, 75% N$_2$ was used as the feed gas, while 9.44%H$_2$-Ar was used as the sweep gas. Both CO$_2$ and O$_2$ follows closely the Arrhenius relationship, indicating the transport of CO$_2$ and O$_2$ are thermally activated. The close activation energies for CO$_2$ ($E_a=48.57$ kJ/mol) and O$_2$ ($E_a=53.35$ kJ/mol) indicates a likely coupled transport process
for those two gas species through MECC membrane. It is interesting to note that, unlike
membrane made from pore-former method that has a tight 2:1 CO₂/O₂ flux ratio [73-76],
the CO₂/O₂ flux ratio of this sample varied between 1.65 and 1.38 as temperature was
increased from 550 to 675 °C. This new flux ratio infers the involvement of CO₄²⁻ which is
the extra O₂ carrier as the active surface species [81]. Thus, two surface reactions
including the primary reaction of CO₂+1/2O₂+2e⁻=CO₃²⁻ and a parallel secondary reaction
of 1/2O₂+CO₃²⁻=CO₄²⁻ are proposed to occur simultaneously during the CO₂ separation
process. Compared with the activation energy of CO₃²⁻ conduction in pure molten
carbonates, i.e. 32 kJ/mol, the observed higher activation energy in this study may also
support the secondary pathway mechanism involving bulkier CO₄²⁻ species.

The CO₂/O₂ flux densities for the chemical-dealloyed sample are also plotted in Fig.
4.8 for comparison. For the electrochemical-dealloyed sample, the CO₂/O₂ flux densities
reached 0.6/xx, 0.74/xx, 0.89/xx and 1.02/xx ml/min-cm² at 600, 625, 650 and 675 °C
respectively. Compared with the previous pore-former derived MECC membrane
measured with pure He as the sweep gas [74-76], these flux densities represent 2~3×
improvement, which could be attributed to a combined microstructural and H₂-containing
sweeping gas effect as illustrated by previous study on chemical dealloying sample.

Compared to the chemical dealloyed sample in Fig. 4.8 obtained at the very
beginning of test when the T-dependence study was conducted, the electro-dealloyed
sample shows a slightly lower CO₂ flux density. At this point, the tortuosity (τ) of electro-
dealloyed sample was higher because of the smaller pore size, leading to a lowered flux
density according to the relationship that \( J \) is proportional to \( \varepsilon/\tau \) (\( \varepsilon \) is the porosity). As the time-on-test increases, the silver matrix begins to coarsen, resulting in a simultaneous reduction in tortuosity and porosity. The degree of reduction in tortuosity by the coarsening mechanism is expected to be greater than porosity for a fine-grain and fine-pore microstructure as suggested in ref [96], leading to a net increase of \( \varepsilon/\tau \), thus flux density. The latter is indeed observed in the time-dependence plot of Fig. 4.8 for the first 100 hours.

![Figure 4.8 Arrhenius plots of CO\(_2\) and O\(_2\) flux density of sample EC-10mA-400. And Arrhenius plots of chemical dealloyed sample 48h-Ag50Al50 were also plotted for comparison purpose. A simulated flue gas with composition of 10\% O\(_2\), 15\% CO\(_2\) and 75\% N\(_2\) was used as the feed gas, while 9.44\% H\(_2\)-Ar was used as sweep gas.](image)

Membrane thickness: 0.91 mm
4.3.2 Long-term stability test

The time-dependent flux density was investigated at 600 °C; the results are shown in Fig. 4.9. The feed gas and sweep gas remained the same as in Fig. 4.8. The overall behavior of the time-dependent CO$_2$ and O$_2$ flux density can be generally characterized by a gradual initial increase for the first 100 h, a fast decrease between 118~147 h, and a slight increase for the next 400 h. Furthermore, the CO$_2$/O$_2$ flux ratio also varied drastically from the initial 1.6 to the eventual 1.15, inferring a change in CO$_2$/O$_2$ transport.

![Graph showing CO$_2$, O$_2$, and N$_2$ flux densities as a function of time at 600 °C](image)

Figure 4.9 CO$_2$, O$_2$ and N$_2$ flux densities as a function of time at 600 °C under a simulated flue gas containing 15% CO$_2$, 10% O$_2$, 75% N$_2$ as feed gas and 9.44% H$_2$-Ar as sweep gas.

On the other hand, the leakage N$_2$ flux is very low during the 500 h-testing in comparison to CO$_2$ and O$_2$ fluxes. For example, N$_2$ leakage rate of the electrochemical-
dealloyed sample was very low ($J_{N_2} < 0.02 \text{ ml/min.cm}^2$) for 300 h. Even at the end of test, the detected $N_2$ leakage rate was still $< 0.05 \text{ ml/min.cm}^2$. The $CO_2/N_2$ ratio is $\sim 107$ for the first 136h and then drops to $\sim 58$ between 138h and 300h and further to 27 at the 300h marker. For the $O_2/N_2$ ratio, it is $\sim 65$ for the first 136h, then decreases to 50 between 138h and 300h and finally to 23 after 138h. This is in striking contrast to the chemical dealloyed counterpart, which showed a more rapid $N_2$ leakage after the first 100-h with $CO_2/N_2$ drop to 20 and $O_2/N_2$ to $< 10$, respectively, after the first 100h. Such a low leakage rate indicates a much better retention of molten carbonate by the electrochemical-dealloyed MECC membrane, which can be attributed to its much finer microstructure.

4.3.3 Bi-path transport mechanism

The dynamic change of $CO_2/O_2$ flux ratio shown in Fig. 4.9 is scientifically intriguing. If the initial increase in flux and higher $CO_2/O_2$ flux ratio ($\sim 1.6$) are attributed to the microstructural change (e.g. increased $\varepsilon/\tau$) aforementioned and parallel $CO_2/O_2$ transport mechanisms, respectively, the sudden change in flux at 118-147-h marker implies a change in mechanism of $CO_2/O_2$ transport.

We herein propose a mechanism involving the state of the sweep-side surface to explain the behavior. The schematic illustration of the mechanism is shown in Fig. 4.10. At the beginning of the test when Ag coarsening is still low, Fig. 4.10 (a), the sweeping-side surface is full of 3PBs (MC/Ag/gas) to allow the reaction $CO_3^{2-}=CO_2+1/2O_2+2e^-$ to dominate, while the secondary reaction $CO_4^{2-}=CO_3^{2-}+1/2O_2$ takes place at less populated MC/gas two-phase boundaries (2PBs). As the time-on-test increases and coarsening worsens,
more and more MC is “squeezed out” from the bulk of the porous Ag and accumulated on the bottom (sweep-side) surface. As the accumulation of MC on the sweep-side surface reaches a critical value, the primary 3PB-pathway is partially shut-down, while the secondary 2PB-pathway becomes a dominant reaction route as 2PB-sites are increased. Such a change in the dominance of the two parallel pathways has, therefore lead to a fast decrease in CO$_2$ flux and relatively flat O$_2$ (both pathways contribute to O$_2$ flux) flux observed in Fig. 4.9. We have provided strong evidence for the likelihood of a concurrent parallel CO$_4^{2-}$ transport mechanism in our previous study [81]. The mechanism for the flux changes during the transition period is schematically illustrated in Fig. 4.10(b).

The microstructures of the EC-10mA-400 sample before and after test are compared in Fig. 4.11. It is evident that the porous Ag has severely coarsened after 500-h operation. Although most of molten carbonate was still kept inside the porous Ag matrix, the loss of molten carbonate was obvious in some locations as indicated in Fig. 4.11 (b), explaining the gradual increase of N$_2$ leakage after the first 300-h.

To support the mechanism illustrated in Fig. 4.10, the sweep-side surface of the sample after test was examined by SEM; the image is shown in Fig. 4.12. It is evident that the sweep-side surface has been largely flooded/covered by MC as indicated by the yellow dash-lines. The 3PBs are also visible in Fig. 4.12. The observed MC partially flooded/covered sweep-side surfaces provides experimental evidence to support the proposed mechanism in Fig.4.10.
Figure 4.10 Schematic illustration of the proposed bi-pathway transport mechanism (a) in the initial stage; (b) in the transitional stage.

Figure 4.11 Microstructures of EC-10mA-400; (a) before and (b) after 500-h permeation test.
The SEM images of post-test samples derived from chemical-dealloying and electrochemical-dealloying both show a significant grain growth of silver after long-term exposure to high temperatures. The continual growth of silver grains and therefore the reduction of porosity can cause the porous Ag to lose its ability to retain molten carbonate as it not only repels MC from its volume, but also loses the capillary force to withhold MC as the pore size becomes larger, ultimately leading to gas breakthrough. Therefore, it is necessary to find a way to prevent silver sintering over time in our future study.

Figure 4.12 SEM image of the state of sweep-side surface after test.

4.4 PRELIMINARY RESULTS OF “MECC-SOEC” REACTOR

The effect of current density has been studied as shown in Fig. 4.13. Several conclusions can be drawn from it.

- Permeation flux of CO₂ and O₂ from MECC membrane are not affected by current density applied in SOEC as indicated by Fig. 4.13(a) and (b).
With an increasing in current density, both H₂ and CO production/conversion rate increase. The H₂ conversion rate (corresponding to the dotted line in Fig. 4.13(a)) can reach as high as 70% while that for CO (dotted line in Fig. 4.13(b)) can be as high as 82% when the current density is 55 mA/cm². Therefore, the overall syngas production rate also increases with an increasing current density (Fig. 4.13(c)).

Despite a different current density, the current efficiency is relatively low, around 30%-40%, which may result from the leakage of electrolyte as well as the sealing problem.

![Graphs showing the effect of current density on H₂ and CO production/conversion rate, syngas production rate, and current efficiency.](image)

**Figure 4.13** The effect of current density on (a) H₂ production/conversion rate; (b) CO production/conversion rate; (c) syngas production rate; (d) current efficiency. The data is collected at T = 650 °C under a flue gas condition 15% CO₂, 10% O₂ and 75% N₂ and a sweep condition of 9.43% H₂-Ar.
5.1 INTRODUCTION

The idea of CO$_2$ recycled synthetic fuel is not new. Steinberg and Dang first proposed the concept. In their studies [97-99], they captured CO$_2$ from atmosphere by various options using hydroxide and carbonate absorbents and produced H$_2$ by water electrolysis. Then they reacted captured CO$_2$ with H$_2$ to get methanol, during which process they proposed to use nuclear sources to produce electricity. In Phillip’s study [100], he described a different process by using CO$_2$ released from mineral carbonates and electrolyzing CO$_2$ by high temperature solid oxide electrolyzer. Yielded CO was further proposed to react with steam via a multi-step process to produce synthetic fuels. Hashimoto [101] proposed a CH$_4$ synthesis process by using CO$_2$ captured from industrial sources and H$_2$ derived from seawater electrolysis. The electrolysis for H$_2$ production is further to proposed to combine with solar panels in desert. Jensen [54] demonstrated a process in which CO$_2$ is split into CO by a high-temperature thermolysis process and the yielded CO is used for further fuel production. Mignard [102, 103] did both energy and

---

cost analysis for synthetic gasoline and methanol produced from wasted CO$_2$ at industrial sources and H$_2$ derived from marine energy driving low temperature electrolysis. Olah [104] developed a “methanol economy” in which methanol is produced from air captured CO$_2$ and low-temperature electrolysis derived H$_2$.

Despite all these efforts, no one has analyzed synthetic fuel cycle based on newly developed MECC membranes. Here we first time analyze the combined “MECC-SOEC” reactor based synthetic fuel cycle from both an energetic and economic perspective[105]. The working mechanism of the reactor has been illustrated in Chapter 2.2.

5.2 SYSTEM MODELING

5.2.1 Process description

The system model built by AspenPlus 8.4 contains basic components in the combined “MECC-SOEC” chemical plant. Figure 5.1 shows a detailed block flow diagram as well as the corresponding process flow sheet. In addition to the main function of CO$_2$ capture and conversion, the combined plant is also considered to generate electricity from the excess waste heat via two stage High Pressure (HP) steam #1, HP steam #2 and one stage Low Pressure (LP) steam as shown in Fig. 5.1(a). The balance of plant including pumps, heaters, heat exchangers as well as compressors are included in Fig. 5.1(b).

5.2.2 Assumptions made in system analysis

• Chemical species involved are: O$_2$, CO, CO$_2$, H$_2$, H$_2$O, and N$_2$.

• A 10kW MECC-SOEC combined CO$_2$ capture-conversion reactor plant is proposed.

The performances of MECC membrane and SOEC cell are scaled up from single cell
experimental data. The single MECC membrane (EC-10mA-400 described in Chapter 4), with an active surface area of 0.92 cm$^2$, has an average CO$_2$ flux density of 1.09 ml/min/cm$^2$ and an average O$_2$ flux of 0.81 ml/min/cm$^2$ at 600 °C for the first 300 h when CO$_2$/N$_2$ is high as shown in Fig.4.8. The I-V curve of SOEC is taken from reference [106] and validated by the model shown in Fig. 5.2. All parameters used in the baseline study are listed in Table 5.1.

- CO$_2$ and O$_2$ are captured from a nature gas power plant with a CO$_2$ emission rate of 0.453 kg/kwh, while the capture gas H$_2$ is assumed to be produced from a biomass gasification process, which makes the overall plant carbon-neutral if the electricity is renewable or nuclear.

- The CO$_2$ capture process is targeted to remove 90% of CO$_2$ in the combined flue gas stream (power plant gas + make-up-air).

- The following reactions are assumed take place on the permeate side of MECC membrane:

\[
H_2 + \frac{1}{2}O_2 \rightarrow H_2O \quad (5 - 1)
\]

\[
H_2 + CO_2 \rightarrow H_2O + CO \quad (5 - 2)
\]

- The generated H$_2$O from combustion reaction is electrolyzed into H$_2$ and O$_2$ through the reverse process of reaction (5-1), while the generated CO$_2$ is converted back to CO through reversed water gas shift (RWGS) reaction as shown in reaction (5-2).
• The operating temperature of combined MECC-SOEC reactor is fixed at 650 °C. Although the flux density of both CO₂ and O₂ are measured at 600 °C, it is assumed that a 50 °C increase in temperature will not result in great change in MECC flux.
• The SOEC is operated below thermoneutral voltage with additional heat requirement for H₂O electrolysis and RWGS.
• Joule heating produced from SOEC overpotential is utilized by SOEC for H₂O electrolysis.
• The produced syngas is pressurized to 22 atm at 25 °C as a feedstock for the Fischer-Tropsch (F-T) reaction.
• The electricity used in SOEC for CO₂ and H₂O conversion is considered to come from nuclear power sources in the baseline study.

5.2.3 Mass balance consideration

Table 5.2 lists the mass balance in the baseline study. The corresponding stream is numbered in Fig. 5.1(a). The inlet flue gas (stream 1) consists of the following gas species: 12.65 mol/min CO₂, 2.92 mol/min O₂, 66.2 mol/min N₂ and 15.58 mol/min H₂O, which is mixed with a make-up air (stream 2) before being fed to MECC feed side. A roughly 90% CO₂ in flue gas mixture along with the stoichiometric O₂ permeates through MECC. To obtain syngas with H₂/CO=2:1, the inlet H₂ (stream 3) is set to 23 mol/min. Roughly 79% of the inlet H₂ is utilized for CO₂ capture and the remaining 21% H₂ is used to protect Ni anode in SOEC from being oxidized. The combustion gas mixture (stream 5) contains 82% steam and CO₂. The product syngas (stream 6 and 7) contains 97% syngas with H₂/CO=2:1.
Figure 5.1 (a) Block flow diagram; (b) flowsheet diagram of proposed combined “MECC-SOEC” plant for CO₂ capture-conversion. The inlet temperature of H₂ and flue gas are 100 °C and 150 °C, respectively. The product syngas in the outlet is at 25 °C and 22 atm. The flue gas mixture in figure 5.1(b) consists of both stream #1 and stream #2 listed in Figure 5.1(a) for simplification.
Figure 5.2 Validation of SOEC model by VI curve under 650 °C. The operating current density is selected at I=2,922 A/m² in the model. [106]

Table 5.1 Parameters used in baseline study. LSGM is a short for La₀.₉Sr₀.₁Ga₀.₈Mg₀.₂O₃₋ₓ

<table>
<thead>
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<th>SOEC</th>
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<td>Electrolyte Material</td>
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<tr>
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<td>Area</td>
</tr>
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<td>0.9 mm</td>
<td>30 m²</td>
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</tr>
<tr>
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<td>650 °C</td>
</tr>
<tr>
<td>$J_{CO2}$</td>
<td>ASR</td>
</tr>
<tr>
<td>1.09 ml/min/cm²</td>
<td>0.18 Ω/cm²</td>
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</table>
Table 5.2 Molar flow rates of each process stream in the baseline study. Input stream includes stream #1, #2 and #3. Output streams: #7 and #8.

<table>
<thead>
<tr>
<th>Stream #</th>
<th>MECC</th>
<th>SOEC</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas species</td>
<td>Inlet flue gas (mol/min)</td>
<td>Air (mol/min)</td>
</tr>
<tr>
<td>CO₂</td>
<td>12.65</td>
<td>1.26</td>
</tr>
<tr>
<td>O₂</td>
<td>2.92</td>
<td>6.45</td>
</tr>
<tr>
<td>N₂</td>
<td>66.2</td>
<td>24.29</td>
</tr>
<tr>
<td>H₂O</td>
<td>15.58</td>
<td>15.58</td>
</tr>
<tr>
<td>CO</td>
<td></td>
<td>1.29</td>
</tr>
<tr>
<td>H₂</td>
<td></td>
<td>23</td>
</tr>
</tbody>
</table>

5.3 ENERGETIC ANALYSIS RESULTS

5.3.1 MECC parasitic energy (PE)

The MECC module is designed to capture CO₂ from post-combustion flue gas stream. Besides the functionality of CO₂ capture, additional electricity and heat are also generated. To calculate the net power consumption (NPC) of MECC, power sinks and power/heat sources need to be identified. Permeated O₂ will react with the inlet H₂ on the sweep side, producing steam while releasing heat \( \dot{Q}_{\text{com}} \). As shown in Fig. 5.3, the heat released from combustion (\( \dot{Q}_{\text{com}} \)) can be utilized in four ways described by:

\[
\dot{Q}_{\text{com}} = \dot{Q}_{\text{heater}} + \dot{Q}_{\text{SOE}} + \dot{Q}_{\text{RWGS}} + \dot{Q}_{\text{HP-1}} \quad (5 - 3)
\]
where \( \dot{Q}_{\text{heater}} \) is the heat used to preheat inlet flue gas; \( \dot{Q}_{SOE} \) is the heat for \( \text{H}_2\text{O} \) electrolysis; \( \dot{Q}_{RWGS} \) is the heat for RWGS and the rest of combustion heat \( \dot{Q}_{HP-1} \) is utilized to make high pressure steam (HP steam\#1) for electricity generation. All of those could be regarded as power or heat sources in the MECC module. The electricity loss due to the input of inlet \( \text{H}_2 \) is identified as the sole power sink in this module. The rationale behind using electricity loss as power sink rather than lower heating value of inlet \( \text{H}_2 \) is based on the definition of parasitic energy for carbon capture. Parasitic energy of a \( \text{CO}_2 \) capture plant has been defined as the loss of electricity production caused by carbon capture [107, 108]. Thus, in order to have a fair comparison, it is reasonable to convert the lower heating value of \( \text{H}_2 \) used in \( \text{CO}_2 \) capture (\( \dot{Q}_{H2-MECC} \)) back to electricity (\( \dot{W}_{H2-ele} \)) when calculating power sink. It is further assumed that the \( \text{H}_2 \)-to-power efficiency (\( \eta_{\text{therm}} \)) is 55%. Thus, the corresponding electricity loss due to \( \text{CO}_2 \) capture can be expressed as

\[
\dot{W}_{H2-ele} = \dot{Q}_{H2-MECC} \times \eta_{\text{thermal}}
\]  

(5-4)

Table 5.3 lists the corresponding expressions and values for power/heat sources and power sinks in the MECC reactor. It is worth to note that a heater is applied in high pressure steam generation with a thermal efficiency (\( \eta_{\text{heater}} \)) of 0.95. HP steam is further utilized in a Rankine cycle for electricity generation with a thermal-to-electricity efficiency of 40%. Thus, the final usable power output from high pressure steam (\( \dot{W}_{HP-1} \)) is 

\[
\dot{W}_{HP-1} = \dot{Q}_{HP-1} \times \eta_{\text{heater}} \times 0.4.
\]

Since in our design, MECC membrane is directly connected with an SOEC, it is reasonable to assume 80% heat can be transferred from the MECC module to the SOEC module. Thus, the effective heat transfer (\( \dot{Q}_{eff} \)) is 

\[
\dot{Q}_{SOE} \times 0.8 + \dot{Q}_{RWGS} \times 0.8.
\]
Figure 5.3 Energy and mass flow chart in the MECC module

Table 5.3 Power and heat sources and power sinks in the MECC module in the baseline study

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description</th>
<th>Expressions</th>
<th>Sources (w)</th>
<th>Sinks (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\dot{W}_{HP-1}$</td>
<td>Electricity from H.P steam-1</td>
<td>$\dot{Q}<em>{HP-1} \times \eta</em>{heater} \times 0.4$</td>
<td>13348</td>
<td></td>
</tr>
<tr>
<td>$\dot{Q}_{eff}$</td>
<td>Heat to H$2$O electrolysis and RWGS</td>
<td>$\dot{Q}<em>{SOE} \times 0.8 + \dot{Q}</em>{RWGS} \times 0.8$</td>
<td>23230</td>
<td></td>
</tr>
<tr>
<td>$\dot{W}_{H2-ele}$</td>
<td>Electricity loss due to carbon capture</td>
<td>$\dot{Q}<em>{H2-MECC} \times \eta</em>{thermal}$</td>
<td>39262</td>
<td></td>
</tr>
</tbody>
</table>

The net power consumption (NPC) of MECC membrane reactor can then be expressed by:

$$NPC \ (\text{watt}) = \dot{W}_{H2-ele} - \dot{W}_{HP-1} - \dot{Q}_{eff}$$  \hspace{1cm} (5 - 5)

The parasitic energy (PE) is calculated by dividing NPC by flow rate of CO$_2$ captured:
\[ PE \ (kJ/kg \ CO_2 \ captured) = \frac{NPC \ (watt)}{a(mol/min) \times \frac{60 \ (s/min)}{0.044 \ kg/mol \times 1000 \ g/kg}} \]  

(5 - 6)

where \( a \) is the molar flow rate of captured \( CO_2 \). Substituting the values listed in Table 5.3 into equation (5-5) and (5-6) yields a net power consumption (NPC) of 2682 W and the corresponding parasitic energy of 321 kJ/kg \( CO_2 \). It is less than half of the parasitic energy for a typical MEA plant, where parasitic energy is 702 kJ/kg \( CO_2 \), not including compression and transportation [107, 108].

5.3.2 System efficiency of “MECC-SOEC” plant

For the combined “MECC-SOEC” plant shown in Fig. 5.4, there are three power sources: electricity generated from extra combustion heat in MECC (\( \dot{W}_{HP-1} \)), heat recovery in compressed high-T syngas (\( \dot{W}_{HP-2} \)) and heat recovery in outlet syngas (\( \dot{W}_{LP} \)). The system also outputs syngas as a product with lower heating value of (\( \dot{Q}_{syngas-out} \)). The power sinks include electricity input to SOEC module (\( \dot{W}_{SOE} \)) and the chemical input to MECC (\( \dot{Q}_{H_2-in} \)). Figure 5.4 depicts energy and mass flow chart of the “MECC-SOEC” system. The system efficiency is defined as the total energy output dived by total energy input:

\[ \eta_{all \ in \ one} = \frac{\dot{Q}_{syngas-out} + \dot{W}_{HP-1} + \dot{W}_{HP-2} + \dot{W}_{LP}}{\dot{Q}_{H_2-in} + \dot{W}_{SOE}} \]  

(5 - 7)

The expressions of each term in eq. (5-7) are listed in Table 5.4, where \( \eta_{Heater} \) is the efficiency of heater; \( \eta_{HeatX} \) is the effectiveness of heat exchanger; the value 0.4 corresponds to thermal efficiency in HP steam electricity generation and 0.25
corresponds to thermal efficiency in LP steam electricity generation; $\dot{Q}_{HP-1}$, $\dot{Q}_{HP-2}$ and $\dot{Q}_{LP}$ correspond to heat recovered to produce HP steam #1, #2 and LP steam, respectively, as illustrated in Fig. 5.1(a); $LHV_{H_2}$ and $LHV_{CO}$ correspond to the lower heating value (LHV) of H$_2$ and CO, respectively; g and h correspond to the mole flow rates of outlet H$_2$ and CO while x represents mole flow rate of inlet H$_2$.

![Figure 5.4 Mass and energy flow chart of “MECC-SOEC” all in one reactor system.](image)

Substituting the corresponding values in Table 5.4 into eq. (5-7) yields 82% total thermal efficiency of the combined system.

5.3.3 The effect of SOEC area

To explore the effect of SOEC area (or the capital cost for SOEC stacks) on MECC CO$_2$ capture PE and system efficiency, other parameters including CO$_2$ flow rate, conversion rate, syngas production rate were all kept constant. It is worth to mention that a constant syngas production rate means a constant current, thus changing SOEC area can result in change of the current density as well.
Table 5.4 Power and heat sources and power sinks in “MECC-SOEC” for the baseline study

<table>
<thead>
<tr>
<th>Symbols</th>
<th>Description</th>
<th>Expressions</th>
<th>Sources (w)</th>
<th>Sinks (w)</th>
</tr>
</thead>
<tbody>
<tr>
<td>(\dot{W}_{HP-1})</td>
<td>Electricity from H.P steam-1</td>
<td>(\dot{Q}<em>{HP-1} \times \eta</em>{Heater} \times 0.4)</td>
<td>13348</td>
<td></td>
</tr>
<tr>
<td>(\dot{W}_{HP-2})</td>
<td>Electricity from H.P steam-2</td>
<td>(\dot{Q}<em>{HP-2} \times \eta</em>{Heater} \times 0.4)</td>
<td>4662</td>
<td></td>
</tr>
<tr>
<td>(\dot{W}_{LP})</td>
<td>Electricity from L.P steam</td>
<td>(\dot{Q}<em>{LP} \times \eta</em>{HeatX} \times 0.25)</td>
<td>1068</td>
<td></td>
</tr>
<tr>
<td>(\dot{Q}_{syngas-out})</td>
<td>Heating value of outlet syngas</td>
<td>(LHV_{H_2} \times g + LHV_{CO} \times h)</td>
<td>141741</td>
<td></td>
</tr>
<tr>
<td>(\dot{W}_{SOE})</td>
<td>Electricity input in SOEC</td>
<td>(\dot{W}_{SOE})</td>
<td>103430</td>
<td></td>
</tr>
<tr>
<td>(\dot{Q}_{H2-in})</td>
<td>Heating value of inlet H(_2)</td>
<td>(LHV_{H_2} \times x)</td>
<td>92383</td>
<td></td>
</tr>
</tbody>
</table>

The effect of SOEC area on SOEC’s overpotential (\(\eta\)) as well as Joule heat (\(\dot{Q}_{Ohmic}\)) are described in Fig. 5.5(a). The corresponding change in current density is also illustrated on the top x-axis in Fig. 5.5. The relationship between cell current density (\(i\)) and overpotential as well as with Joule heat can be approximately expressed by:

\[
\eta = i \times ASR \quad (5 - 8)
\]

\[
\dot{Q}_{Ohmic} = i^2 \times ASR \quad (5 - 9)
\]

where ASR is the area specific resistance of SOEC, which depends on temperature as well as material’s properties and can be regarded as a constant in this study. Based on the
relationship above, under a constant syngas production rate, a larger SOEC area resulting in a smaller current density leads to a lower cell overpotential and a lower $\dot{Q}_{\text{Ohmic}}$. A lower $\dot{Q}_{\text{Ohmic}}$ means more heat need to be provided for electrolysis from MECC membrane (a larger $\dot{Q}_{\text{SOE}}$). Remember that $\dot{Q}_{\text{SOE}}$ is a heat source when defining PE for MECC CO$_2$ capture. Thus, with the increase in $\dot{Q}_{\text{SOE}}$, the PE for MECC CO$_2$ capture decreases. The actual relationship between SOEC area with PE is illustrated in Fig. 5.5(b): increasing SOEC area leads to a decrease in PE. It is also worth to mention that an increase in $\dot{Q}_{\text{SOE}}$ leads to a decrease in $\dot{Q}_{\text{HP-1}}$ since the total combustion ($\dot{Q}_{\text{com}}$) heat remain the same. Although the decrease in $\dot{Q}_{\text{HP-1}}$ causes a decrease in the corresponding electricity output, the latter is less than the increase in heat output, resulting in a net increase in total energy output and therefore a net decrease in PE.

Unlike PE, the total system efficiency is not affected too much by the change of SOEC area, see Fig. 5.6. This trending can be easily understood by Table 5.4, where even though the change of SOEC area affects $\dot{Q}_{\text{HP-1}}$, the total amount of energy change in sources remains small as electricity generated from $\dot{Q}_{\text{HP-1}}$ only constitutes less than 10% in energy sources when considering the whole plant.
Figure 5.5 The effect of SOEC area on (a) SOEC’s overpotential (η) and $\dot{Q}_{\text{ohmic}}$; (b) MECC parasitic energy (PE). The circled point in (b) corresponds to the baseline.

Figure 5.6. The effect of SOEC area on system efficiency
5.4 ECONOMICAL ANALYSIS OF “MECC-SOEC” REACTOR

5.4.1 CO₂ capture cost

The following assumptions are made for the cost analysis:

- Ag is selected as metal matrix for MECC in the baseline study based on our previous experiments [73-76, 109, 110]. Parameters including porosity of Ag matrix (ε), membrane thickness (θ) are listed in Table 5.5.
- The total cost of CO₂ capture consists of two parts: operational cost (denoted as MECC-OP) and material cost (denoted as Ag-MECC-CAP).
- The operational cost of MECC membrane mainly consists of the cost of inlet H₂. It is further assumed that H₂ is produced from biomass gasification with a production cost of $0.0528/kwh [111].
- The value of products generated in MECC including HP-steam #1 generated electricity and high-temperature heat are regarded as credits and subtracted from H₂ cost when calculating the total operational cost of carbon capture.
- The cost of electricity (COE) of original natural gas power plant without carbon capture is assumed to be $0.06/kWh.
- The unit price of HP-steam generated electricity ($P_{HP-ele}$) is assumed to be $0.096/kwh which is higher than that of natural gas power plant.
- The unit price of high-temperature heat ($P_{heat}$) is equivalent to the unit price of electricity produced from natural gas power plant.
- According to the DOE goal of not increasing the cost of electricity (COE) by 35% or more above the baseline [112, 113], the COE with carbon capture considered in this study
should not exceed $0.081/kWh, which corresponds to a CO₂ capture cost less than $46.4/kWh.

- COE with carbon capture is calculated based on IECM framework that includes both capital expenses of the capture plant and electricity cost [114].

All the parameters used in cost analysis for CO₂ capture for the baseline study are listed in Table 5.5. The operational cost of carbon capture based on PE can be expressed by:

\[
MECC - OP = \frac{(\dot{Q}_{H₂-MECC} \times P_{H₂-MECC} - \dot{W}_{HP-1} \times P_{HP-ele} - \dot{Q}_{eff} \times P_{heat}) \times t \times C}{J_{CO₂}} \tag{5 - 10}
\]

Substituting the values of parameters in Table 5.5 into eq. (5-10) yields an operational cost of $5.36/ton CO₂ captured by MECC. The material cost of CO₂ capture using Ag matrix can be expressed by

\[
Ag - MECC - CA = A \times \theta \times \varepsilon \times \rho_{Ag} \times P_{Ag} + A \times \theta \times (1 - \varepsilon) \times \rho_{Li₂CO₃} \times v_{Li₂CO₃} \times P_{Li₂CO₃} \tag{5 - 11}
\]

which leads to $119.68/ton CO₂ captured. It is worth to mention here that the price of Na₂CO₃ is negligible compared to Li₂CO₃ and metal matrix, thus not considered here. Clearly, this cost is higher than the DOE requirement. In our study, it is easy to see that the material cost dominates the cost of CO₂ capture, thus if a cheaper material is available to replace Ag in MECC membrane, the total cost in CO₂ capture can be greatly reduced.
One option is to replace Ag with NiO. Our recent study has shown the feasibility of low-cost NiO as an electron conducting matrix in MECC membrane [115]. Additional studies on its performance under H\textsubscript{2} sweeping condition at 650 °C remain to be demonstrated. Since this paper aims at system performance, it is meaningful to analyze the technoeconomic performance of the potential NiO-MECC membrane reactor. For NiO-MECC membrane, the unit price of NiO is assumed to be $15/kg and the density is 6.67 g/cm\textsuperscript{2}. Keeping all other assumptions unchanged in Table 5.5, the material cost of NiO-MECC is estimated to be 2.58 $/ton CO\textsubscript{2} captured and the resultant total cost is only $7.94/ton CO\textsubscript{2} captured, much cheaper than Ag-MECC and below the DOE target. Overall, the low cost of combined MECC-SOEC carbon capture and conversion reactor is not only resulted from the elimination of carbon compression, transportation and storage process, but also from the added value of by-product generated by the plant.

5.4.2 Syngas production cost

To estimate the cost syngas produced, the following assumptions are made:

- The syngas production cost consists of two major parts: CO\textsubscript{2} capture and CO\textsubscript{2} conversion.
- CO\textsubscript{2} capture has been discussed in detail in section 5.2, including capital cost of MECC membrane and operational cost of carbon capture. For the cost of CO\textsubscript{2} conversion, it includes four parts: electricity cost in steam and CO\textsubscript{2} conversion (denoted as SOE-N-ELE), heat cost in steam and CO\textsubscript{2} conversion (denoted as SOE-
HEAT), material cost in steam/CO\textsubscript{2} conversion (denoted as SOE-CAP) and production cost of extra H\textsubscript{2} input in MECC inlet (denoted EXTRA-H\textsubscript{2}).

- Parameters used to estimate CO\textsubscript{2} conversion cost in each part are listed in Table 5.6. Figure 5.7 plots the syngas cost versus SOEC area based on both Ag-MECC capture/conversion system and NiO-MECC capture/conversion system. There are several important conclusions can be drawn from it:

  - Assuming that the NiO-MECC membrane demonstrates similar performance to Ag-MECC, replacing Ag with NiO in CO\textsubscript{2} capture results in a 15%-22% reduction in syngas price depending on SOEC areas. A smaller area (10 m\textsuperscript{2}) corresponds to a larger reduction (22%) and a larger area (90 m\textsuperscript{2}) corresponds to a smaller reduction (15%).
  
  - In both scenarios, electricity cost in SOEC makes up the majority of the total cost and this phenomenon becomes even more obvious under a low SOEC area.
  
  - The SOEC capital cost increases with increasing SOEC area and its effect on total cost becomes dominating when SOEC area becomes larger.
  
  - Although the electricity cost in SOEC decreases with increasing SOEC area, the amount of its reduction is far less than the amount of cost increase brought by a higher capital cost, leading to a net increase in syngas price.
  
  - Other factors like operational cost in MECC and heat cost in SOEC do not play an important role in the syngas price.
### Table 5.5 Parameters used in cost analysis of Ag-MECC and NiO-MECC Reactors

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\rho_{Ag}$</td>
<td>Ag-density</td>
<td>10.49 g/cm³</td>
</tr>
<tr>
<td>$\rho_{Li_2CO_3}$</td>
<td>Li$_2$CO$_3$-density</td>
<td>2.11 g/cm³</td>
</tr>
<tr>
<td>$v_{Li_2CO_3}$</td>
<td>Volume percentage of Li$_2$CO$_3$ in eutectic mixture</td>
<td>0.52</td>
</tr>
<tr>
<td>$\varepsilon$</td>
<td>Porosity of Ag matrix</td>
<td>0.4</td>
</tr>
<tr>
<td>$A$</td>
<td>MECC area</td>
<td>78.2 m²</td>
</tr>
<tr>
<td>$\theta$</td>
<td>MECC thickness</td>
<td>0.9 mm</td>
</tr>
<tr>
<td>$P_{H_2-MECC}$</td>
<td>H$_2$ production cost</td>
<td>$0.0528$/kwh</td>
</tr>
<tr>
<td>$P_{heat}$</td>
<td>Unit price of high-temperature heat</td>
<td>$0.06$/kwh</td>
</tr>
<tr>
<td>$P_{HP-ele}$</td>
<td>Unit price of HP steam produced electricity</td>
<td>$0.096$/kwh</td>
</tr>
<tr>
<td>$P_{Ag}$</td>
<td>Unit price of Ag</td>
<td>$584.18$ /kg</td>
</tr>
<tr>
<td>$P_{Li_2CO_3}$</td>
<td>Unit price of Li$_2$CO$_3$</td>
<td>$20$ / kg</td>
</tr>
<tr>
<td>$t$</td>
<td>MECC lifetime</td>
<td>43800 h</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacity factor</td>
<td>0.75</td>
</tr>
<tr>
<td>$I_{CO_2}$</td>
<td>CO$_2$ capture rate</td>
<td>987790 kg/lifetime</td>
</tr>
</tbody>
</table>

### Table 5.6. Parameters used in cost estimation in the baseline study for CO$_2$ conversion

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>T</td>
<td>Operating temperature</td>
<td>650 ºC</td>
</tr>
<tr>
<td>$i$</td>
<td>Current density</td>
<td>0.292 A/cm$^2$</td>
</tr>
<tr>
<td>ASR</td>
<td>Area specific resistance of SOEC</td>
<td>0.18 Ω /cm$^2$</td>
</tr>
<tr>
<td>$P_{cell}$</td>
<td>Unit price of electrolysis cell stack</td>
<td>$2000$/m$^2$ investment</td>
</tr>
<tr>
<td>$t$</td>
<td>Stack life</td>
<td>5 years</td>
</tr>
<tr>
<td>$P_{BS}$</td>
<td>Unit price of balance of System</td>
<td>$5000$/m$^2$ investment</td>
</tr>
<tr>
<td>$t_{BS}$</td>
<td>Life of balance of system</td>
<td>20 years</td>
</tr>
<tr>
<td>$C$</td>
<td>Capacity factor</td>
<td>0.75</td>
</tr>
<tr>
<td>$P_{r-ele}$</td>
<td>Unit price of renewable/nuclear electricity</td>
<td>$0.096$/kwh</td>
</tr>
<tr>
<td>$P_{heat}$</td>
<td>Unit price of high-temperature heat</td>
<td>$0.06$/kwh</td>
</tr>
</tbody>
</table>
5.4.3 FT fuel cost estimation

5.4.3.1 Producing FT fuels from syngas

To estimate liquid fuel cost from product syngas, further assumptions are made based on references [116-118].

- 95% of syngas in FT reactor is converted with 5% syngas being wasted;
- 80% energy in syngas are retained in FT product and the remainder is released as heat;
- There is 95% selectivity from FT process for heavier C5+ products while 5% selectivity from FT process for C1-C4 products;
• Only the heavier FT products can be converted into hydrocarbon liquid with an efficiency of 98%.

Therefore, the total energy conversion efficiency from product syngas to final hydrocarbon liquid is 71% by multiplying different efficiencies in each step above. It is further assumed that hydrocarbon liquid fuels are upgraded to diesel with a production cost of 1.5 €/GJ\textsubscript{FT-diesel} [117]. The LHV of FT diesel is 36.3 MJ/l [116]. The equation below gives the unit price of FT-diesel.

\[
P_{FT\text{-diesel}} \left[ \frac{€}{I} \right] = 0.0142 \times P_{\text{syngas}} \left[ \frac{€}{MW h_{LHV}} \right] + 0.0544
\] (5 - 12)

To keep the consistency of the unit between product syngas and FT-fuel, it is reasonable to convert €/L to $/L in above equation by multiple $1.3/€ (2010) on the right side of the equation (5-12).

5.4.3.2 FT-fuel cost estimation

Based on above assumptions, the price of FT-fuel produced from both Ag-MECC and NiO-MECC capture/conversion systems is illustrated in Fig. 5.8(a)-(b) as a function of SOEC area. Figure 5.8 is very similar to Fig. 5.7 even though Fig. 5.8 includes an additional cost: production cost from syngas to synthetic fuel which is depicted by the dark purple area. It is obvious that the production cost from syngas to FT fuel makes up less 10% of the total cost. Therefore, the renewable electricity cost still makes up the majority of total product cost. It would be interesting to know if synthetic fuels produced from the combined reactor is economically competitive to other carbon neutral synthetic fuels.
Thus, the unit price of synthetic gasoline is further compared with biomass to liquid (BTL) derived synthetic fuels as illustrated by area between two dotted lines in Fig. 5.8. It is obvious that for Ag-MECC capture/conversion system, the price of synthetic gasoline is not competitive with that of BTL fuel even if under a low SOEC area (low capital cost) and the renewable electricity price is at $0.096/kwh. However, for NiO-MECC capture/conversion system, the price of synthetic gasoline starts to be competitive with that of BTL fuels under a SOEC area lower than 30 m$^2$ and at the same renewable electricity price.

Figure 5.8. Synthetic gasoline price from (a) Ag-MECC capture/conversion system; (b) NiO-MECC capture/conversion system under different SOEC area with a constant renewable electricity price of $0.096/kwh. The red triangle in (a) corresponds with synthetic gasoline price in baseline study and in (b) corresponds with NiO-MECC capture/conversion system with a SOEC area of 30 m$^2$. The area between two dotted lines corresponds with BTL derived synthetic gasoline.
The sensitivity analysis of renewable electricity price on fuel price is also analyzed with an electricity price varying from $0.03/kwh~$0.13/kwh [120]; the results are shown in Fig.5.9. The synthetic FT-fuel price by Ag-MECC capture/conversion system can compete with BTL fuel price only when electricity price drops below 0.059$/kWh, while for the NiO-MECC capture/conversion system it can compete with BTL fuel at an electricity price lower than 0.096$/kwh. The analysis gives us an idea if we can build a MECC-SOEC plant in a place with renewable sources cheap enough to produce economically competitive synthetic fuels.

![Graph of synthetic gasoline price vs. cost of electricity](image)

**Figure 5.9.** The effect of cost of renewable electricity on synthetic gasoline price under a SOEC area of 30 m²
Chapter 6 Concluding Remarks

There are two central objectives in this thesis work: developing a high performance, stable, dual-phase, mixed electronic and carbonate ion membrane for post-combustion CO$_2$ capture and analyzing the energy efficiency and economics of a “MECC-SOEC” reactor in producing synthetic fuels. The main strategy adopted to achieve the first objective is to fabricate micro-porous Ag matrix by dealloying, while system modeling is selected for the second objective.

Chemical dealloying method has been applied first to fabricate micro-porous Ag. SEM results reveal that chemical dealloyed Ag contains three types of pore structures: long 3D channels created from intergranular area, micron-pores derived from $\alpha$-Al phase and submicron-pores developed from $\gamma$-$\text{Ag}_2\text{Al}$ phase. The utilization of H$_2$ in sweep gas greatly enhances the CO$_2$ and O$_2$ flux by increasing the chemical gradient of O$_2$ between permeate side and feed side. It also shows that chemically dealloyed MECC can stably operate for 900-h. The main reason behind the superior long-term stability is the smaller pores generated from $\gamma$-$\text{Ag}_2\text{Al}$, which enhances capillary force to withhold MC in the pores.

Parallel to chemical dealloying, electrochemical dealloying is also experimented to fabricate porous Ag. The results show that thus derived porous Ag matrix contains a much
smaller pore size (0.2-1 µm) than porous Ag derived from pore former and chemical dealloying. A 500-h long-term stability with a very low N₂ leakage rate has been demonstrated by the electrochemically dealloyed MECC, which further suggests porous Ag matrix derived from electrochemical-dealloying has a better retention ability of MC than porous Ag developed from other methods. A permeation mechanism involving the transition of dominant reaction site from 3PBs to 2PBs for gas transport is proposed based on our previous observation of active surface species of CO₄²⁻. The observed sudden change of CO₂ flux as well as the ratio of CO₂/O₂ can be reasonably explained by the transition model.

A combined “MECC-SOEC” reactor is proposed for the first time to effectively convert the captured CO₂ back to the fuel form. To realistically estimate the efficiency and cost, a life cycle analysis (LCA) has been conducted. The analysis shows that a parasitic energy of 321 kJ/kg CO₂ is required for MECC CO₂ capture, which is half the consumption by a typical MEA plant. The effect of SOEC area from both energetic and economical aspects have particularly been explored. It shows that an increase in SOEC area results in a decreased parasitic energy, while not significantly affecting the system efficiency. The electricity price dominates the syngas price under a low SOEC area, while the SOEC capital cost begins to dominate at a high SOEC area. The LCA further shows that the price of synthetic FT-fuels produced from Ag-MECC capture/conversion system is not competitive with the price of BTL fuel at an electricity price of $ 0.096/kwh. Replacing Ag with NiO can greatly reduce the capital cost of MECC membranes, resulting in a competitive price of FT-fuels. Sensitivity analysis of electricity price reveals an upper bound price of
$0.059/kwh for Ag-MECC capture/conversion system and $0.096/kwh for NiO-MECC capture/conversion system, below which the resultant FT-fuels price can compete with that of BTL-fuels.
References


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