DECLARATION

I hereby declare that the thesis is my original work and it has been written by me in its entirety. I have duly acknowledged all the sources of information which have been used in the thesis.

This thesis has also not been submitted for any degree in any university previously.

SUN MING

28 January 2013
ACKNOWLEDGEMENTS

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SUMMARY

Hydrogen is a clean energy carrier, because a great deal of energy will be released when it reacts with oxygen to form water, besides this it is an essential reducing reagent in many chemical reactions. As the primary industrial process to produce hydrogen, the steam reforming (SR) of natural gas (mainly methane) has attracted increasing attention with aim of improving energy-efficiency of this process. In contrast to the SR of methane, partial oxidation of methane (POM) is mildly exothermic and hence more energy-efficient. However, there are still several critical challenges for the industrial application of POM, such as high cost of cryogenic air separation to produce oxygen, coking and sulphur susceptibility of the Ni-based POM catalyst, and the sintering of the supported Ni catalytic sites at high temperatures. This PhD research thesis investigated two challenging topics as they will significantly improve energy efficiency subject to development of mesoporous carbon adsorbent to strip sulphur-containing compounds from natural gas and integration of air separation through mixed electronic-ionic conductor (MEIC) membrane with POM that consumes oxygen at the permeate side of membrane and thus drives permeation of oxygen to traverse the membrane.

Regarding the first topic of study, the interest lied in understanding how cellulose polymer backbone affects generation of micro/mesoporous activated carbon (AC) adsorbents were developed. Hence 2-hydroxyethyl cellulose (HEC), methyl cellulose, α-cellulose and cellulose acetate were selected as precursor of
preparation. The study explicitly confirmed that the pendant groups of cellulose main chain, in terms of their molecular structures, affect the surface properties of AC generated from carbonizing the precursors. Indeed, a special type of AC containing predominant mesoporous structure was attained from HEC. The chemical mechanism of carbonization comprehended from the experimental scrutiny revealed the significance of the size and functionality of polyaromatic hydrocarbon (PAH) flakes derived from pyrolysing a cellulose precursor, which impact the key structural features of AC developed from the subsequent thermal treatment and annealing. The resulting AC samples were characterized by H₂S removing capability and capacity as well. The HEC-derived AC manifested the performance. Furthermore, to enhance the meso-porosity in AC, a template-free method was explored to synthesize mesoporous AC matrix through creating interchain bonding in HEC precursor. The HEC chains were covalently cross-linked with different carboxylic acids by esterification reaction. As found previously, the type of cross-linker and the cross-linking degree cause different degrees of substitution and sizes of PAH rings as well as formation of aliphatic carbons in the pyrolysis products. These transitional structural features then determine the mesoporous structure of AC.

Regarding the second topic of study, the problem to solve was whether an oxygen permeation membrane in tubular design could be fabricated by using the MEIC with perovskite structure, La₀.₄Ba₀.₆Fe₀.₈Zn₀.₂O₃₋δ (LBFZ), and furthermore, if POM could be incorporated into the membrane. LBFZ showed promising oxygen conductivity and chemical stability in reducing atmosphere in the previous study of
our lab. The initial trials identified structural cracks in tubular membrane in the oxygen permeation temperature range (800-950 °C) if the tubular membrane was made of LBFZ alone. The cause of this mechanical failure originates from the greater structural stress under a high oxygen partial pressure gradient throughout the tubular LBFZ membrane. Therefore, the use of a second phase to reinforce the LBFZ phase would be an appropriate solution to the problem. This second phase must be chemically strong and oxygen ionic conductive. Gadolinium doped ceria (CGO) besides being an oxygen ionic conductor was recognized in this study to be chemically inert and compatible with LBFZ at high temperatures. Hence a composite consisting of LBFZ and CGO phases was prepared by powder mixing, compression moulding and co-sintering. The CGO phase forms a continuous network interpenetrating with the LBFZ phase in the resulting tubular membrane, and hence upholds the structure as well as provides another oxygen transport avenue.

The optimal content of CGO and LBFZ phases after balancing mechanical stability and oxygen conductivity was found to be 40 wt. % CGO - 60 wt. % LBFZ. This membrane displayed a high oxygen permeation flux of 0.84 cm³·cm⁻²·min⁻¹ at 950 °C under an oxygen partial gradient of 21 kPa/1.1 kPa.

It was recognized that there was a diffusion of Ba²⁺ into CGO phase at high temperatures. To rectify this defect a mixed alkaline earth metal ion doping in the A-site instead of individual Ba²⁺ doping in LBFZ was found effective. Several mixed A-site doping compositions, La₀.₂BaₓSr₀.₈₋ₓFe₀.₅Zn₀.₅O₃₋δ (LBSFZ, 0.2≤x≤0.6), were screened. The revamped LBSFZ samples displayed higher oxygen
permeability than LBFZ. Consecutively, dual phase composite membrane, CGO-LBSFZ-2 manifested a desired trade-off between oxygen permeation and chemical endurance against syngas caused structural deterioration. The membrane reactor assembled by CGO-LBSFZ-2 tubular membrane and commercial Ni catalyst achieved an oxygen permeation flux of 6.14 cm$^3$.cm$^{-2}$.min$^{-1}$ at 950 °C when 50 % CH$_4$/He was used as the feed gas in the permeate side of membrane.
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\( t \) tolerance factor in Eq. 2.4; breakthrough time in Eq. 3.1
\( t_i \) ionic transfer numbers -
\( t_e \) electronic transfer numbers -
\( V_o^- \) lattice oxygen vacancy with two positive charges -
\( V \) volume \( \text{cm}^3/g \)

**Greek letters**

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1.1 Background

Natural gas is a fossil fuel containing 70-90% methane, which is a clean and abundant energy source. Thus, how to effectively utilize natural gas and derive valuable chemicals from it [1] represent a contemporary research area. Nowadays, two technologies are prevalent in this area: one is to synthesize longer-chain hydrocarbons from methane, such as ethylene and ethane; and the other is to convert methane to syngas, a mixed gas of hydrogen and carbon monoxide. There are still many challenges for the advancing these two technologies, such as low yields of the catalytic growth of longer-hydrocarbon chains directly from methane, which is unfeasible for industrial use. Additionally, although a high conversion rate has been achieved in the catalytic reforming of methane, the energy consumption and operation life of catalyst of this technology is still an industrial concern and has a large room to improve.

With the increasing demand for hydrogen, more attention is being paid to obtaining hydrogen from syngas [2, 3] through methane reforming. Currently, several methods have been developed to carry out methane reforming, including steam reforming, drying reforming, and partial oxidation of methane (POM). In steam reforming, syngas is produced from the reaction of methane with overheated steam (CH$_4$ + H$_2$O $\rightarrow$ CO + 2 H$_2$). This reaction is highly endothermic ($\Delta H^0_{298K}$ = +206.2 KJ/mol), a high temperature is needed to attain a high production yield
therefore. Drying reforming is realized through the reaction of methane with carbon
dioxide \((\text{CH}_4 + \text{CO}_2 \rightarrow 2 \text{CO} + 2 \text{H}_2)\), which is more intensive endothermic
\((\Delta H^{\circ}_{298K} = +274.7 \text{ KJ/mol})\) than the steam reforming. On the contrary, POM is the
partial oxidation of methane with oxygen \((\text{CH}_4 + 0.5 \text{O}_2 \rightarrow \text{CO} + 2 \text{H}_2)\), which is
mildly exothermic \((\Delta H^{\circ}_{298K} = -36 \text{ KJ/mol})\). Hence, compared with steam and drying
reforming process, POM process is more energy effective and can be self-sustained
upon ignited.

Despite tremendous endeavours made to advance POM catalytic technology
towards industrial application, there are still several obstacles in front of it. One
obstacle is catalyst poisoning due to the presence of sulfides in natural gas. The
catalyst used for POM reaction is usually composed of Groups 8-10 metals (Ni, Co,
Fe, Ru, Rh, Pd, Ir, and Pt) on a ceramic support. Chemical adsorption of sulphur on
the metal catalytic sites causes deactivation. The sulfide concentration in raw natural
gas varies from several parts per million (ppm) to 5 %, but it is reduced to less than
10 ppm industrially before distribution in the pipeline. Nevertheless, sulfur odorants
such as dimethyl sulfide and tetrahydrothiophene are purposely added in pipeline
natural gas for safe handling during transportation and utilization [4]. In contrast to
this, the content of sulfides in the purified natural gas has to be less than 1 ppm
before it could be fed into the catalytic reformer for carrying out in particular POM
reaction. [2]. The other main obstacle is the high production cost of oxygen [5, 6].
Oxygen is produced primarily in industrial scale by cryogenic air separation, which
is an energy intensive process. Even though adsorption and polymer membrane
separation technology have been used in gas industry, they cannot meet the requirements for extremely pure oxygen and nitrogen. Oxygen-permeable ceramic membrane (OPCM) is an emerging technique as it offers absolutely pure oxygen because of its unique electrochemical separation mechanism and hence it is likely to cut the production cost of oxygen. What’s more, integrating OPCM with POM is to greatly enhance the oxygen permeation flux through the membrane because POM in the permeate side imposes a strong chemical potential gradient of oxygen across the OPCM with respect to air in the purging side. This membrane reactor design requests adequate chemical stability of membrane in the reducing atmosphere of POM at high temperatures. Most of membrane materials, such as perovskite oxides La$_{1-x}$Sr$_x$Co$_{1-y}$Fe$_y$O$_{3-δ}$, with high oxygen permeation flux usually have poor chemical stability and shatter rapidly upon decomposition caused by the reduction of cobalt and iron ions. This is the most challenging issue to realization of the commercial sense OPCM-POM membrane reactor. In addition, an optimal trade-off between catalytic activity and performance stability of POM catalyst is also crucial to this membrane reactor. Some factors such as coke deposition, sintering of metal crystallites and oxidation of metal atoms can cause the deactivation of catalyst and then spoil the membrane reactor [2]. In short, de-sulfurization from natural gas stream and POM-driven oxygen permeation through OPCM represent the two unresolved issues for establishing natural gas-based energy source.
1.2 Objectives and scope

This research work explores the following topics:

(1) Removal of sulfides from natural gas by novel carbon adsorbents with specific porous structure, which will focus on the development of mesoporous carbon and getting insight into the effects of carbonization process on pore structures.

(2) Fabrication of tubular dual-phase composite ceramic membranes used for oxygen separation from air. Assemble composite membrane reactor for POM reaction and evaluate its performance.

The details of the research scope are highlighted as follows:

(1) Preparation of micro/mesoporous AC from cellulose precursors bearing different functional groups, to study the effects of functional groups on final porous structure and surface properties during carbonization process, by which getting insight into the carbonization chemistry and mechanism of mesopore formation.

(2) Based on the selection of cellulose precursors, develop a template-free method to enhance the mesoporous structure of AC and evaluate the adsorption capacity of prepared ACs by removal of H₂S from a H₂S/N₂ gas stream.

(3) Fabrication of tubular dual-phase composite ceramic membrane by cold isostatic press, in which gadolinium doped ceria (CGO) and yttrium stabilized zirconia (YSZ) as the candidates of oxygen ionic phase and $\text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (LBFZ) as the mixed conductive phase. Characterization of the prepared membranes to examine their phase compatibility, chemical stability and oxygen permeability.
(4) Chemical modification of the perovskite oxide LBFZ by part substitution of A-site cations with \( \text{Sr}^{2+} \) to study its effects on oxygen permeability and chemical stability. Fabrication of tubular dual-phase membranes composed of modified LBFZ oxides with CGO phase and evaluation of their oxygen permeation fluxes. Assembly of a membrane reactor for POM reaction.
Chapter 1

1.3 Thesis organization

Chapter 2 presents a detailed literature review about mesoporous AC, which includes adsorption properties of porous AC and preparation methods of mesoporous AC, and mixed conductive ceramic membrane including the background of mixed conduction, mechanism of oxygen separation, POM into syngas and recent progresses on ceramic membrane reactor.

Chapter 3 introduces the impacts of pendant functional groups on the generation of pore structure of AC, in which cellulose precursors with different types of side chain group are selected to prepare AC. Effects of the side chain groups on the structure of carbonaceous intermediates are scrutinized by infrared spectroscopy and X-ray photoelectron spectroscopy. The carbonaceous intermediates consist of polyaromatic hydrocarbon (PAH) flakes of different sizes and with various oxy-groups. These structural differences in PAH flakes affect the final pore structures of ACs formed in the subsequent activation. The results show that the hydroxyethyl group is most effective in facilitating formation of large surface area and high micro- and mesopore volumes.

In Chapter 4, a template-free method was developed to prepare mesoporous AC, based on the hydroxyethyl cellulose selected in Chapter 3. Its polymer chains were covalently crosslinked with different types of carboxylic acids by the esterification reaction. The effect of esterification crosslinking on formation of mesoporous structure was examined. The BET surface analysis of the resulting ACs reveals an explicit correlation between the number of carboxylic acid groups on benzene ring.
and the mesoporous structures of a synthesized AC. Moreover, it is also found that an optimal crosslinking degree for attaining the maximum volume fraction of mesopores exists with respect to each type of the crosslinker used. The mesoporous ACs synthesized were assessed by their capability of stripping H$_2$S.

In Chapter 5, tubular dual-phase composite membranes made of ionic conductor (CGO and YSZ) and mixed conductor (LBFZ) were successfully fabricated. XRD results display that CGO as the ionic conductor has much better compatibility with LBFZ than YSZ in the composite membranes, due to less interfacial reactions caused by the phase interdiffusion. CGO-LBFZ composite membrane can survive under high oxygen partial pressure gradients, although its oxygen permeation flux will decrease to some extent. According to the calculated and experimental results of oxygen permeation flux, 40 wt. % CGO-60 wt. % LBFZ membrane has the lowest extent of phase interdiffusion.

In Chapter 6, Sr$^{2+}$ was used to substitute part of Ba$^{2+}$ in A-site cations of LBFZ to reduce the formation of Ba$^{2+}$-containing impurity phases when LBFZ was used for a dual-phase composite membrane. The new membranes La$_{0.2}$Ba$_x$Sr$_{0.8-x}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-δ}$ (LBSFZ) exhibited higher oxygen permeability than LBFZ membrane, due to the increase of A-site doping level. Through the characterizations of XRD and TPR, it showed that Ba-doping was more favourable than Sr-doping for the improvement of chemical stability under 5% H$_2$/N$_2$ reducing atmosphere. However, LBSFZ single phase tubular membranes still didn’t have the enough mechanical strength for a long-time run.
In Chapter 7, the material LBSFZ modified in Chapter 6 was used to fabricate dual-phase composite membrane with fluorite phase CGO, to improve the chemical stability under reducing atmosphere. The XRD patterns can clearly show that the impurity phase gradually reduces with the decrease of Ba$^{2+}$ content in LBSFZ. As expected, CGO-LBSFZ-2 membrane has the highest oxygen permeation flux due to the lowest phase interdiffusion, which was also supported by the O$_2$-TPD results. CGO-LBSFZ-2 membrane was assembled with a commercial Ni-based catalyst to obtain the membrane reactor for POM reaction.

In Chapter 8, conclusions of this thesis and recommendation for the future work are presented. In this work, mesoporous carbon adsorbents and MEIC dual-phase composite membranes were fabricated and studied. The development of asymmetric membrane reactor and modification of membrane surface are important for the improvement of oxygen permeation flux, which may be the future directions.
Chapter 2 Literature review

2.1 Desulfurization by micro/mesoporous activated carbon

2.1.1 Background of desulfurization from natural gas

Up to date, catalytic reforming of methane is considered as the most economical way to produce hydrogen. Natural gas as the source of methane is abundant fossil fuel with well-developed supply infrastructure and safety in handling [7]. It is typically composed of methane, ethane, propane, butane, carbon dioxide, oxygen, nitrogen, hydrogen sulfide and rare gases. The sulfide concentration in raw natural gas varies from parts per million to 5%, and it will be reduced to less than 10 ppm by amine solution before distribution in the pipeline. In addition, sulfur odorants such as dimethyl sulfide, methyl mercaptan and tetrahydrothiophene (THT) will be added into pipeline natural gas for safe handling during transportation and utilization [4]. However, these sulfides will cause catalyst poisoning in the reforming reaction. The content of sulfides should be less than 1 ppm before pipeline natural gas is fed into the catalytic reformer. Adsorption is thought to be one of the most effective methods for further desulfurization. A good adsorbent [7] used for desulfurization should have high adsorption capacity and selectivity to reduce the total sulfide concentration to a desired level, have no side reactions or chemisorptions with methane, have tolerance to possible contaminants in natural gas and have low production cost of adsorbent easy to regenerate or dispose. A lot of
adsorbents such as activated carbon, zinc oxide, zeolite and alumina can be used for the desulfurization of natural gas [4, 8-10]. Activated carbon and zinc oxide has been used in the desulfurization of pipeline gas in commercial fuel cell systems [4]. Activated carbon has the advantages of large specific surface area, well-developed porosity, low adsorption capacity to alkanes, and ambient using temperature.

**2.1.2 Adsorption of activated carbon**

Activated carbons are excellent adsorbents applied for many aspects, such as removal of color and odor, purification of waste water, and stripping of gaseous pollutants. They can be prepared from any carbonaceous material by carbonization under inert atmospheres and the subsequent activation process. During carbonization process, most of the non-carbon elements will be removed from the precursor, the residual carbon atoms are assembled in the form of aromatic sheets, and the random packing of aromatic sheets will give rise to pores of different sizes, which endow activated carbon with a large specific surface area and highly-developed pores. Besides carbon, the elemental composition of activated carbon can also contain a small percentage of heteroatoms such as hydrogen, oxygen, nitrogen and sulphur. These hetero-atoms appear in the form of surface groups which influence the surface basicity, polarity and some other physico-chemical properties of the carbon [11]. When activate carbons are exposed to a gas, the gas molecules will be adsorbed on the sites where possess unsaturated and unbalanced forces. Physical adsorption and chemisorption will happen, dependent on the nature of forces involved. For physical
adsorption, it is caused by Van der Waals forces, which include Keesom forces, Debye forces, and London dispersive forces; for chemisorption, it arises from valency forces due to the redistribution of electron clouds between carbon surface and gas molecules.

Based on the nitrogen adsorption-desorption mechanism, International Union of Pure and Applied Chemistry (IUPAC) classified pores into three groups according to their size: micropores with widths less than 20Å in width, mesopores with widths ranging from 20 Å to 500 Å and macropores with widths above 500 Å [12]. In an activated carbon sample, usually there is more than one type of pores existing and the predominant pores will dominate the properties of the carbon sample.

The porous structure of activated carbon is made up of interconnected pore networks, in which the mesopores play the role of linking micropores with macropores. In a typical activated carbon, the total surface area and pore volume are determined by micropores and mesopores. For adsorbates having dimensions smaller than micropores, the adsorption capacity is greatly dependent on micropores. Due to the extremely strong Van der Waals forces, micropores are the main adsorptive sites; mesopores have weaker Van der Waals forces in comparison, and mainly function as channels with lowered mass transfer or diffusion resistance for the transportation of adsorbates to the microporous sites. Similar to mesopores, the main function of macropores is in the transport of adsorbate molecules by providing a less resistant mass transfer path within the activated carbon. Hence, for a
mesoporous carbon, the reduction in tortuosity would enhance the purification of a
gas stream due to a more efficient transport to the microporous active sites [11, 13].

Although the porous structure of activated carbons will determine its adsorption
capacity, the chemical structure also has an important influence on the final
adsorption capacity. Oxygen-containing functional groups, such as carboxyl groups,
carbonyl groups, lactones and quinones, have been correlated with the surface
properties of carbon, which include the surface acidity, hydrophobicity, immersional
heat of wetting and activity of catalytic reactions. In order to improve adsorption
capacity of activated carbon to sulfides, surface modifications have been studied by
oxidation, reduction and impregnation methods. Dependent on the nature of
adsorbate, the corresponding modification method can be selected. For example,
THT is a polar molecule of basicity. The surface acidity of carbon is postulated from
carboxyl groups, phenol groups and lactones. Through oxidation by HNO$_3$/H$_2$SO$_4$,
carbon surface can bear more carboxyl groups or other acid surface groups, which
can increase the adsorption capacity of THT due to acid/base interactions or weak
hydrogen bonds[14]. In contrast, H$_2$S is a polar molecule of acidity and its
adsorption will decrease if the activated carbon was oxidized to have more acid
surface groups. When the activated carbon is impregnated with Na$_2$CO$_3$, KIO$_3$ and
metal salts [11], the adsorption capacity of sulfides will be greatly improved due to
the increase of acidic/basic adsorption sites, which can enhance the chemical
interactions and surface complexing.
Although a lot of studies found that both surface chemistry and pore structure of activated carbons are important for the removal of sulfides by adsorption, the nature of sulfide adsorption onto the surface of activated carbon is still not clear. The relative contributions of the two factors seem to be correlated with the detailed experiment conditions.

2.1.3 Preparation methods for mesoporous carbon

An activated carbon adsorbent is usually dominated by micropores whereas its specific volume of mesopores is less than 0.2 cm$^3$/g [11]. Highly mesoporous AC powders have industrial relevance, such as for desulfurization [15-17], adsorption of large molecules [18, 19], catalyst supports [20] and high capacitance-carbon electrodes [21, 22], because mesopores can facilitate faster kinetics of mass transfer as well as accommodation for molecules or atomic clusters greater than micropores. The contemporary approaches to prepare mesoporous carbon include hard template method [23-26], soft template method [24, 27, 28] and template-free method [29-31]. Continuous pursuit of better strategies for evolving desired mesoporous carbon structures still remains active.

2.1.3.1 Hard template method

Hard template is usually a kind of porous inorganic material, such as silica and zeolite. The general procedures in the making of mesoporous AC using the hard template are as follows: firstly, impregnating the porous templates with carbon precursor to obtain a precursor-template composite; secondly, carbonizing the
composite to get AC; finally, removing the template by the use of strong reagents such as hydrofluoric acid, hydrochloric acid and sodium hydroxide to get mesoporous AC [32]. Mesoporous AC can be prepared by volume template method and surface template method. Highly porous channels were impregnated with the carbon precursor in volume template method and the carbon precursor was coated on the surface of the porous substrates in surface template method. Preparing mesoporous carbon by hard template was first reported by Ryoo [33] and Hyeon with their co-workers in 1999 [34]. Ryoo’s group used mesoporous silica MCM-48 as the template and sucrose as the carbon precursor, followed by polymerization, carbonization and removal of silica template to obtain mesoporous carbon. Hyeon’s group made phenol and formaldehyde polymerize in the pores of aluminium-implanted MCM-48 to get phenol resin, from which an activated carbon with regular 2 nm mesopores were synthesised.

Over the past decades, mesoporous silica templates other than MCM-48 have been developed, such as SBA-15, HMS, MgO and MSU-H [35]. The pore size of carbon prepared from MCM-48 is difficult to adjust because the wall thickness of MCM-48 is hard to adjust. However, SBA-15 template can be adjusted by changing synthesis conditions, so the pore size of carbon templated from SBA-15 can be changed. In addition, colloidal silica particles and silica gels have also been used as the hard template to synthesize mesoporous carbon with larger pore size by Hyeon’s group [36] and Jang’s group [37]. All the hard template methods mentioned above share the advantages of having a highly ordered mesoporous structure, and
variations to the pore dimensions of hard templates provide control over the pore width in the final activated carbon. However, these templates need to be removed by HF or NaOH solutions, which makes this process wasted and environmentally unfriendly, although Morishita et. al. [38] reported that the use of MgO as substrate which allowed the reuse and recycle of MgO. Besides the need for using strong acids and bases during template removal, the activated carbons produced via the template method are often too porous with a narrow pore size distribution, and thus large scale production was reported to be difficult.

2.1.3.2 Soft template method

Compared with the hard template, soft template is easier to be removed in the pyrolysis process. Soft templates are self-assembling organic templates, otherwise known as block copolymers, which rely on the chemical bonds between the precursors and the templates in order to yield a stable porous structure at the end of the carbonization process [35]. One of the first soft template processes for the synthesis of mesoporous carbons was developed by Liang and his co-workers [39] in 2004. In their approach, the carbon precursor chosen was resorcinol formaldehyde resin (RFR), a highly cross linked, thermosetting polymer; the thermosetting property of RFR would allow the mesoporous structure to withstand the high temperature experienced during pyrolysis. Due to the need for strong interactions between the precursor and the block copolymer, polystyrene-block-poly (4-vinylpyridine) (PS-P4VP) was chosen since P4VP is able to form strong, extensive hydrogen bonds with resorcinol. After pyrolysis of the polymer precursor,
a hexagonal carbon-channel array was obtained. Zhao and his co-workers [40] have made great progress in the soft template synthesis by using PEO-containing polymer as the template. Due to the hydrogen bonding interaction between PEO block and carbon precursor, an ordered meso-structure of copolymer composite can be formed. This composite will be pyrolyzed to mesoporous carbon at temperatures above 600 °C.

Mesoporous carbons prepared by the soft templates avoid the disadvantages of hard templates, because the soft template can be removed during carbonization. However, the mesopore size of carbon cannot be easily tuned to a larger pore size using soft template method, by which the size is usually less than 10 nm. In addition, the soft template method relies on an existing thermosetting polymer in which aromatic frameworks are desirable.

2.1.3.3 Non-template method

Non-template methods rely on the selection or modification of a pertinent polymer. It has been known that thermal degradations of organic functional groups affect the formation of carbon porous structure through pyrolysis. The template-free synthesis although has broader precursor candidates than the soft template method, the complicated nature of pyrolysis makes it difficult to attain the porous structures needed from a readily available polymer precursor. Currently, there are only few reports about mesoporous carbon prepared by non-template methods. However, chemical modification on polymer chain through a simple chemical reaction provides a way to pursue the desired porous structure of AC.
Cyclic pore-widening method devised by X. Py and co-workers [41] comprises numerous cycles of an oxidative step using either sodium hypochlorite solution or atmospheric oxygen in air as the oxidative agent followed by pyrolysis. The use of sodium hypochlorite solution was coined the “wet” cyclic method while that involving atmospheric oxygen was termed the “dry” cyclic method. Most of oxygen containing functional groups on carbon surface would be eliminated together with some carbon from the oxidized precursor following thermal treatment at high temperatures under nitrogen atmosphere. This would reduce burn offs at pore mouths and create additional pore volume in the carbon. The dry method produced larger increase in average pore size of 0.1 to 0.2 nm per cycle compared to 0.04 nm per cycle for the wet method.

Vázquez-Santos et al., [30, 42] successfully utilized as spun and high-modulus polymers poly (p-phenylene benzobisoxazole) (PBO), which carry oxazole function groups in the repeating units, as the precursor to prepare activated carbon fibers (ACFs). It was found that the obtained ACFs are dominated by micropores with a small amount of narrow mesopores, which are determined by the burn-off extent during CO₂ activation. The pores are gradually widened with the increase of activation degree. The maxima of pore size distribution of ACFs are observed at 0.6, 1.3, 2.5 and 20 nm. In addition, the high-modulus PBO shows a higher proportion of mesopores than the as spun PBO.
2.2 Mixed conducting ceramic membrane reactor for POM

2.2.1 Background of mixed conduction

Mixed electronic-ionic conductor (MEIC) has both oxygen ionic conductivity and electronic conductivity, which makes it have tremendous potential applications in oxygen separation, solid oxide fuel cells (SOFCs) and ceramic oxygen-electrolyte membrane reactors (COMRs). Takahashi’s group [43] initially studied the sintered oxide system of Bi$_2$O$_3$-BaO, in which they found the mixed conduction existing in the mixed phases less than 20-mol% BaO or more than 28-mol% BaO. The concept of MEIC was further introduced by Cales and Baumard [44, 45]. They investigated the calcia-stabilized zirconia and ZrO$_2$-CeO$_2$-Y$_2$O$_3$ materials used for the preparation of oxygen semipermeable membranes at high temperatures. In recent several decades, the study of MEIC materials has been gained more and more attentions for their potential applications and numerous new MEIC materials have been developed.

2.2.1.1 Structure of mixed conducting ceramic materials

It is found that preferred MEIC materials usually have fluorite (A$_4$O$_8$) or perovskite (ABO$_3$) structures[46]. Although there are still some other compounds can be used as mixed conductors[47-50], such as pyrochlore (A$_2$B$_2$O$_7$), brownmillerite (A$_2$B$_2$O$_5$), Ruddlesden-Popper series (A$_{n+1}$B$_n$O$_{3n+1}$), orthorhombic K$_2$NiF$_4$-type structure materials and Sr$_4$Fe$_{6-x}$Co$_x$O$_{13}$ compounds, they exhibit inferior qualities in comparison with fluorite and perovskite compounds. Some typical MEIC materials are listed in Table 2.1.
Table 2.1 Examples of typical MEIC materials

<table>
<thead>
<tr>
<th>Name</th>
<th>Structure</th>
<th>Examples</th>
</tr>
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</table>
| Perovskite        | $\text{ABO}_3$    | $\text{La}_{0.6}\text{Sr}_{0.4}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta}$  
|                   |                    | $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ |
| Fluorite          | $\text{A}_4\text{O}_8$ | $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$  
|                   |                    | $\text{Ce}_{0.8}\text{Pr}_{0.2}\text{O}_{2-\delta}$ |
| Pyrochlore         | $\text{A}_2\text{B}_2\text{O}_7$ | $\text{Gd}_2(\text{Ti}_{1-x}\text{Mo}_x)_2\text{O}_7$ |
| Brownmillerite    | $\text{A}_2\text{B}_2\text{O}_5$ | $\text{Sr}_{0.8}\text{Ba}_{0.2}\text{CoO}_2.5$ |
| Ruddlesden-Popper | $\text{A}_{n+1}\text{B}_n\text{O}_{3n+1}$ | $\text{Pr}_2\text{Ni}_{0.9}\text{Fe}_{0.1}\text{O}_{4+\delta}$ |

The ideal fluorite-type compound has a face-centred cubic (fcc) structure, which consists of anions in simple cubic packing with half of the interstices occupied by cations. Pure $\text{ZrO}_2$ phase (Fig. 2.1) has the cubic fluorite-type structure at temperature higher than $2300 \, ^\circ \text{C}$, but it will transform into monoclinic and tetragonal structures at low temperatures. Through doping with larger aliovalent cations, such as $\text{Ca}^{2+}$ and $\text{Y}^{3+}$, $\text{ZrO}_2$ can keep the cubic structure all the way and bring in oxygen vacancies. $8$-$15$ mol% $\text{Y}_2\text{O}_3$ stabilized $\text{ZrO}_2$ (YSZ) is a very stable oxygen ionic conductor with high mechanical strength in both reducing and oxidizing atmosphere at high temperatures. YSZ cannot be individually used as oxygen permeable membrane due to its low electronic conductivity. Gadolinium-doped $\text{CeO}_2$ ($\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$, CGO) has the same cubic fluorite structure as YSZ, but it shows both high oxygen ionic conductivity and high electronic conductivity under reducing atmosphere, which results from the reduction of $\text{Ce}^{4+}$ to $\text{Ce}^{3+}$. Choi’s group [51] studied the electrical conductivity of CGO at high temperatures. The results show that CGO is a MEIC at $1400$-$1600 \, ^\circ \text{C}$, which makes it have the good oxygen permeability.
Figure 2.1 Schematic of the ideal $A_4O_8$ fluorite-type structure

Figure 2.2 Schematic of the ideal $ABO_3$ perovskite structure

The ideal cubic perovskite-type structure has a stoichiometry of $ABO_3$, in which A is a larger cation than B. A-site cations include Lanthanides and alkaline earth elements such as La$^{3+}$, Sr$^{2+}$, Ca$^{2+}$, and Ba$^{2+}$; B-site cations include the transition metal elements such as Mn$^{4+}$/Mn$^{3+}$, Fe$^{3+}$/Fe$^{2+}$ and Co$^{3+}$/Co$^{2+}$. BaTiO$_3$ is a typical compound with perovskite structure. The larger A-site Ba$^{2+}$ is surrounded by 12 nearest neighbour O$^{2-}$ and the B-site Ti$^{4+}$ is located in the centre of a TiO$_6$ octahedron, as seen in Fig. 2.2. The structural stability of perovskite compound can be described by Geometric Goldschmidt tolerance factor ($t$) [52] defined by Eq. 2.4, in which $r$ is the
ionic radii. When the value of $t$ is between 0.78 and 1.05, the perovskite structure can be preserved.

$$t = \frac{r_A + r_O}{\sqrt{2}(r_B + r_O)}$$ (2.4)

Partial substitution of the A-site or B-site cations in ABO$_3$ compound can result in numerous perovskite-type compounds with modified electrical conductivity and stability. For example, partial substitution of La$^{3+}$ cations in LaCoO$_3$ by alkaline earth metal ions (Ca$^{2+}$, Sr$^{2+}$ and Ba$^{2+}$) can bring oxygen vacancies, which are responsible for the improvement of oxygen ionic conduction.[53]

### 2.2.1.2 Defect theory

The electrical conductivity of MEIC material is dependent on the extent of defects, which can be classified into electronic defects and structural defects. Electronic defects are related to the generation of electrons and holes by the intrinsic ionization or excitation of electrons. Structural defects include point, line and plane defects, which may be caused by the formation of vacancies, interstitials, dislocation, grain boundary, surface diffusion and the presence of foreign atoms. Ionic conductivity is related to the structure defects while the electronic conductivity is determined by the electronic defects. The overall electrical conductivity ($\sigma_t$) can be calculated by the Eq. 2.5, in which $c$, $n$ and $q$ are the densities of ions, electrons, and holes, $q$ is the charge and $\mu$ is the mobility. The conductivity can be improved by increasing the mobility or the concentration of the carriers. The mobility is determined by the composition, processing conditions and temperature, while the
concentration of carriers depends on the doping level of aliovalent impurities and deviation from ideal stoichiometry by oxidation or reduction. [52]

\[ \sigma_t = \sum c_i q_i \mu_i + n q_e \mu_e + p q_h \mu_h \]  

The defects reactions can be described by electrons, holes, vacancies and interstitials, which obey the mass, charge and site balances. A lot of such works have been conducted to elucidate the defect chemistry. For example, the defect models of perovskite-type oxides have been developed by Van Roosmalen [54] and Poulsen [55]. The defect reactions can be written by the Kröger Vink notation, as shown in Eqs. 2.6-2.7. When LaMO$_{3-\delta}$ (M= Cr, Mn, Fe, Co, Ni) was reduced, an oxygen atom will be removed from the lattice and then an oxygen vacancy is left with two liberated electrons (Eq. 2.6), and M cations are reduced from M$^{3+}$ to M$^{2+}$ (Eq. 2.7). A simple cluster model was suggested for the perovskite system to describe the oxygen deficiency by extended defects.

\[ \begin{align*}
O_0^{\times} & \leftrightarrow V_0^- + 2e' + \frac{1}{2}O_2 \\
2M_M^{\times} + 2e' & \leftrightarrow 2M_M'^{\times}
\end{align*} \]  

Figure 2.3 Schematic drawing of oxygen permeation through MEIC membrane [56].
The oxygen permeation through the MEIC membrane can be represented by Fig. 2.3. Oxygen is chemisorbed and incorporated into the membrane on the high oxygen partial pressure side, the oxygen ions transfer to the low oxygen partial pressure side, and then the oxygen is released.

2.2.1.3 Preparation methods of mixed conductive oxides

Mixed oxides (MOs) can be prepared conventional methods or new technologies, which can be roughly classified into solid-state reactions, liquid-phase reactions (co-precipitation and hydrothermal methods), sol-gel techniques and vapor phase process (spray and freeze drying), as summarized in Table 2.2.

The solid-state reaction [57] is a conventional method, by which the mixture of metal oxides, carbonates, hydroxides or slats is fully ground and then calcined at high temperature (above two thirds of the melting point) for periods up to 10 h. The MEIC materials have been wildly prepared by this method. For example, Xu’s group [58] prepared the mixed oxide \( \text{La}_{0.2}\text{Sr}_{0.8}\text{Co}_{0.2}\text{Fe}_{0.8}\text{O}_{3-\delta} \) using three methods, i.e. EDTA pyrolysis, modified citrate pyrolysis and solid state reaction, and it was found that solid state reaction is the most effective method, which can be easily controlled and synthesized in a large amount.

Co-precipitation [52, 57] method is comprised of mixing desired components in an aqueous solution, precipitation, filtration, drying and thermal decomposition to get the final oxides. The control of precipitating agent, pH, mixing rate and precipitation temperature is important to obtain the ideal stoichiometric material; otherwise non-homogenous co-precipitation may be formed. For example,
perovskite powders strontium lanthanum manganite (LSM) and lanthanum ferrite (LSF) were prepared by oxalate, carbonate, and cyanide co-precipitations [59]. All co-precipitated powders were transformed into perovskite structure after calcination at 1100 °C, except the powder prepared by cyanide rout, in which the phase transformation occurred at 450 °C. Overall, the morphology, purity and homogeneity acquired by co-precipitation method are good.

In a sol-gel route [52, 57], the chemicals (alkoxides, organic salts, nitrates and hydroxides) are dispersed in a solution, and then the solution is dehydrated at low temperature to form an amorphous gel. Further heat treatment is needed to remove the organic species and form the crystal structure. Sol-gel techniques include alkoxide route, alkoxide-salt rout and EDTA/citrate complexation route. The major advantages of this method are the lower sintering temperature and production of small-sized particles. Pechini method is a typical sol-gel process, in which ethylenediaminetetraacetic acid (EDTA), citric acid, glycine and other organic ligands are used as cleating agents. The degree of complexation can be controlled by the pH value, and the addition of a water-soluble polymer is used to form a homogenous gel after drying. A lot of fluorite and perovskite compounds are synthesized by EDTA/citrate complexation method [60, 61].

The hydrothermal method [52] is usually conducted at temperatures between the boiling point and the critical temperature of water and a pressure high as 15 MPa. The advantages of this method are inexpensive precursors (hydroxides and salts), elimination of high calcination temperature, small-sized particles, high purity and
the control of morphology in some conditions. For example, crystalline nanotubes of 
BaTiO$_3$ and SrTiO$_3$, which has an outer diameter range from 8 to 15 nm and a length 
range of 50 to 500 nm, were synthesized at low temperature by hydrothermal 
method. Hydrothermal synthesizes of mixed oxides, such as BaTiO$_3$, BiFeO$_3$, LaFeO$_3$, 
and La$_{0.5}$Ba$_{0.5}$MnO$_3$, have been wildly reported [62]. Hence, hydrothermal method 
has potential feasibility for commercial scale in the future.

Spray drying makes the solvent in small droplets, which contain required 
solutions of cations, evaporate rapidly, whereas the removal of solvent by freeze 
drying method is a slow sublimation process [52]. Both spray drying method and 
freeze drying method can obtain a highly pure and homogenous fine mixed oxide. 
For example, spray pyrolysis has been used to synthesize many multicomponent 
powders. Pb(Zr$_{0.52}$Ti$_{0.48}$)O$_3$ powders were synthesized by a twin-fluid atomization 
spray pyrolysis, in which the aqueous solution of precursors was atomized to small 
droplets (8-13 micron) and then the droplets were introduced into a 3 stage furnace 
for thermally decomposition to form the products [63]. La$_{0.7}$Ca$_{0.3}$MnO$_3$ powders 
were synthesized by a freezing method, in which the solution of La and Mn acetates 
and Ca nitrate was sprayed into 100-200 micron of droplets followed by stirring in 
liquid nitrogen, tray-drying and thermally decomposition to get the product [64].
Table 2.2 Comparison of metal oxide processes [65]

<table>
<thead>
<tr>
<th>Item</th>
<th>Solid-state reaction</th>
<th>Co-precipitation method</th>
<th>Sol-gel techniques</th>
<th>Hydrothermal method</th>
<th>Spray and freeze drying</th>
</tr>
</thead>
<tbody>
<tr>
<td>State of development</td>
<td>Commercial</td>
<td>Commercial</td>
<td>Commercial; Research and development</td>
<td>Demonstration</td>
<td>Demonstration</td>
</tr>
<tr>
<td>Size of particle (nm)</td>
<td>&gt;1000</td>
<td>&gt;10</td>
<td>&gt;10</td>
<td>&gt;100</td>
<td>&gt;10</td>
</tr>
<tr>
<td>Homogeneity</td>
<td>Poor</td>
<td>Good</td>
<td>Very good</td>
<td>Very good</td>
<td>Very good</td>
</tr>
<tr>
<td>Purity</td>
<td>Poor</td>
<td>Very good</td>
<td>Excellent</td>
<td>Very good</td>
<td>Excellent</td>
</tr>
<tr>
<td>Temperature of calcination</td>
<td>&gt;1000</td>
<td>500-1000</td>
<td>500-1000</td>
<td>80-374</td>
<td>&gt;150</td>
</tr>
<tr>
<td>Agglomeration</td>
<td>Moderate</td>
<td>High</td>
<td>Moderate</td>
<td>Low</td>
<td>Low</td>
</tr>
<tr>
<td>Costs</td>
<td>Low to moderate</td>
<td>Moderate to high</td>
<td>Moderate to high</td>
<td>Moderate</td>
<td>Moderate to high</td>
</tr>
</tbody>
</table>
2.2.2 MEIC membrane for oxygen separation

2.2.2.1 Transport mechanism

A driving force must be provided for oxygen to permeate through a membrane. For a MEIC membrane (Fig. 2.4), the driving force is the oxygen partial pressure difference on the two sides of the membrane. Based on the different mechanism, MEIC membranes can be classified to single phase membrane and dual-phase membrane. The single phase membrane is consisted of only one phase for oxygen ionic and electronic conduction, while the dual-phase membrane is composed of two phases, i.e. electronic conductive phase and oxygen ionic conductive phase.

![MEIC membrane types based on mixed conduction mechanism.](image)

The oxygen transport process includes the following steps: first the oxygen molecules are chemisorbed and incorporated into membrane by the surface-exchange reaction on high oxygen partial pressure side; and then the oxygen charged species and electrons/holes transport by the bulk diffusion; finally, the oxygen molecules desorbed by the surface-exchange reaction on lower oxygen partial pressure side. The
slowest process is regarded as the limiting step for the whole rate of oxygen permeation. If the limiting step was the bulk diffusion, oxygen permeation flux can be described by Wagner theory [52, 66] as shown in Eqs. 2.8-2.9. For example, in fluorite-type MEIC membrane, the oxygen ionic conductivity is much higher than electronic conductivity, so the oxygen permeation flux is dominated by the electronic conductivity in the bulk phase and then it can be expressed by Eq. 2.11 derived from Eq. 2.8.

\[ J_{O_2} = \frac{1}{16F^2L} \int_{\mu^{0}_{O_2}}^{\mu^{''}_{O_2}} t_i t_e \sigma_t d\mu_{O_2} \] (2.8)

\[ t_i = \frac{\sigma_i}{\sigma_i + \sigma_e} = \frac{\sigma_i}{\sigma_t} \] (2.9)

\[ d\mu_{O_2} = RT d\ln(P_{O_2}) \] (2.10)

\[ J_{O_2} = \frac{RT}{16F^2L} \int_{\mu^{0}_{O_2}}^{\mu^{''}_{O_2}} \sigma_e d\ln(P_{O_2}) = \frac{RT\sigma_e^0}{16F^2L} \left( P_{O_2}^{-1/4} - P_{O_2}^{''-1/4} \right) \] (2.11)

However, the oxygen transport resistance in bulk phase will be decreased by reducing the thickness of membrane or improving ionic or electronic conductivity, in which the limiting step will be changed from the bulk-diffusion to surface-exchange reaction.

**2.2.2.2 Single-phase membrane**

For single-phase MEIC membranes, there is only one phase used for both electronic conduction and oxygen ionic conduction. The material of the single phase can be fluorite-type material or perovskite material, as shown in Table 2.3. For fluorite-type membrane, its oxygen permeation flux is in the range of $10^{-9}$ to $10^{-7}$ mol·s⁻¹·cm⁻² between 850 and 950 °C; while, for perovskite membrane, the oxygen
permeation flux has a magnitude of $10^{-8}$ to $10^{-6}$ mol·s$^{-1}$·cm$^{-2}$ between 850 and 950 °C. It is clearly that the perovskite membranes have superior oxygen permeability than fluorite membranes.

The oxygen permeation flux of fluorite-type membranes are commonly dominated by the electronic conductivity. On the contrary, the oxygen permeation flux of perovskite-based membranes, which electronic conductivity accounts for a larger portion in the overall electrical conductivity, is more dependent on their oxygen ionic conductivity. For ABO$_{3-\delta}$ perovskite materials, the A-site alkaline-earth or rare-earth ions are related with the concentration of oxygen vacancy, while the B-site transition metal ions contribute to the electronic conductivity. It was found that the addition of dopants to A-site and B-site cations can obtain a modified perovskite structure with a formula of $A_{1-x}A'^xB_{1-y}B'yO_{3-\delta}$, which has the enhanced electrical conductivity. For example, the A-site Ba of BaFeO$_{3-\delta}$ was partially substituted by 5 % of Na, Rb, Ca, Y and La cations [67], in which the partial substitution with Ca, Y and La succeeded in stabilizing a cubic perovskite structure due to their smaller ionic radius than Ba and improving oxygen permeation flux in the temperature range of 600 to 780 °C. The B-site doping in La$_{0.4}$Ba$_{0.6}$FeO$_{3-\delta}$ by partial substitution of Fe with Zn was studied by Gong et al. [68]. It was found that the modified membrane La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ presented a higher oxygen permeation flux with superior chemical stability under reducing atmosphere.
### Table 2.3 Oxygen permeation fluxes of single-phase membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (°C)</th>
<th>$J_{O_2}$ (mol·s$^{-1}$·cm$^{-2}$)</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>$P_{O_2}'$ (bar)</th>
<th>$P_{O_2}$ (bar)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fluorite-type</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(ZrO$<em>2$)$</em>{0.8}$(Y$_2$O$<em>3$)$</em>{0.2}$</td>
<td>900-1000</td>
<td>2.100<em>10$^{-9}$ to 5.500</em>10$^{-9}$</td>
<td>Film</td>
<td>0.003-0.016</td>
<td>0.01</td>
<td>1*10$^{-13}$</td>
<td>[69]</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Gd$</em>{0.2}$O$_{2-\delta}$</td>
<td>1400-1600</td>
<td>9.976<em>10$^{-8}$ to 6.295</em>10$^{-6}$</td>
<td>Disk</td>
<td>2.0</td>
<td>0.21</td>
<td>0.015 to 1*10$^{-8}$</td>
<td>[51]</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Pr$</em>{0.2}$O$_{2-\delta}$</td>
<td>850-950</td>
<td>1.334<em>10$^{-8}$ to 3.350</em>10$^{-8}$</td>
<td>Disk</td>
<td>1</td>
<td>0.21</td>
<td>0.021</td>
<td>[70]</td>
</tr>
<tr>
<td>Gd$<em>{0.15}$Ce$</em>{0.85}$Pr$<em>{0.2}$O$</em>{2-\delta}$</td>
<td>850-950</td>
<td>5.957<em>10$^{-9}$ to 1.995</em>10$^{-8}$</td>
<td>Disk</td>
<td>1</td>
<td>0.21</td>
<td>0.021</td>
<td>[70]</td>
</tr>
<tr>
<td>Gd$<em>{0.2}$Ce$</em>{0.8}$Pr$<em>{0.2}$O$</em>{2-\delta}$</td>
<td>850-950</td>
<td>7.499<em>10$^{-9}$ to 2.661</em>10$^{-8}$</td>
<td>Disk</td>
<td>1</td>
<td>0.21</td>
<td>0.021</td>
<td>[70]</td>
</tr>
<tr>
<td>Bi$<em>{1.5}$Y$</em>{0.3}$Sm$_{0.2}$O$_3$</td>
<td>825-875</td>
<td>4.400<em>10$^{-7}$ to 6.360</em>10$^{-7}$</td>
<td>Tube</td>
<td>1.2</td>
<td>0.21</td>
<td>0.05 to 0.15</td>
<td>[71]</td>
</tr>
<tr>
<td><strong>Perovskite-type</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Zn$<em>{0.2}$Fe$</em>{0.8}$O$_{3-\delta}$</td>
<td>800-975</td>
<td>1.116<em>10$^{-7}$ to 2.604</em>10$^{-7}$</td>
<td>Disk</td>
<td>1.45</td>
<td>0.21</td>
<td>0.01</td>
<td>[72]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-\delta}$</td>
<td>700-950</td>
<td>5.012<em>10$^{-7}$ to 1.000</em>10$^{-6}$</td>
<td>Disk</td>
<td>1.00</td>
<td>0.212</td>
<td>0.085</td>
<td>[73]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.8}$Fe$</em>{0.2}$O$_{3-\delta}$</td>
<td>800-900</td>
<td>7.068<em>10$^{-7}$ to 2.307</em>10$^{-6}$</td>
<td>Tube</td>
<td>1.5</td>
<td>0.09-1</td>
<td>0.0093 to 0.1147</td>
<td>[74]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.75}$Zr$</em>{0.05}$Fe$<em>{0.2}$O$</em>{3-\delta}$</td>
<td>700-950</td>
<td>3.5<em>10$^{-7}$ to 3.070</em>10$^{-6}$</td>
<td>Hollow fiber</td>
<td>0.28</td>
<td>0.21</td>
<td>-</td>
<td>[75]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.70}$Zr$</em>{0.10}$Fe$<em>{0.2}$O$</em>{3-\delta}$</td>
<td>700-950</td>
<td>3.0<em>10$^{-7}$ to 2.660</em>10$^{-6}$</td>
<td>Hollow fiber</td>
<td>0.28</td>
<td>0.21</td>
<td>-</td>
<td>[75]</td>
</tr>
<tr>
<td>Ba$<em>{0.5}$Sr$</em>{0.5}$Co$<em>{0.60}$Zr$</em>{0.20}$Fe$<em>{0.2}$O$</em>{3-\delta}$</td>
<td>700-950</td>
<td>2.0<em>10$^{-7}$ to 2.440</em>10$^{-6}$</td>
<td>Hollow fiber</td>
<td>0.28</td>
<td>0.21</td>
<td>-</td>
<td>[75]</td>
</tr>
<tr>
<td>La$<em>{0.4}$Ba$</em>{0.6}$Fe$<em>{0.9}$Zn$</em>{0.2}$O$_{3-\delta}$</td>
<td>800-950</td>
<td>2.083<em>10$^{-7}$ to 5.432</em>10$^{-7}$</td>
<td>Disk</td>
<td>1.1</td>
<td>0.21</td>
<td>-</td>
<td>[68]</td>
</tr>
<tr>
<td>La$<em>{0.4}$Ba$</em>{0.6}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_{3-\delta}$</td>
<td>900</td>
<td>5.357*10$^{-7}$</td>
<td>Disk</td>
<td>0.55</td>
<td>0.21</td>
<td>-</td>
<td>[76]</td>
</tr>
<tr>
<td>La$<em>{0.4}$Ba$</em>{0.6}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_{3-\delta}$</td>
<td>860</td>
<td>1.536*10$^{-6}$</td>
<td>Disk</td>
<td>1.5</td>
<td>0.21</td>
<td>-</td>
<td>[77]</td>
</tr>
<tr>
<td>La$<em>{0.4}$Ba$</em>{0.6}$Co$<em>{0.2}$Fe$</em>{0.8}$O$_{3-\delta}$</td>
<td>850-900</td>
<td>4.000<em>10$^{-8}$ to 1.050</em>10$^{-7}$</td>
<td>Tube</td>
<td>0.219</td>
<td>0.212</td>
<td>-</td>
<td>[78]</td>
</tr>
</tbody>
</table>
2.2.2.3 Dual-phase membrane

It is quite hard for a single phase membrane to exhibit both high electronic and oxygen ionic conductive at the same time. Besides electrical properties, the requirements for mechanical strength, chemical stability and operating temperature also must be met for the real applications. An ideal MEIC membrane was designed, in which one phase is for oxygen ionic conduction and the other phase is for the electronic conduction, and the two phases form a continuous or percolative network. The properties of the dual-phase membrane can be adjusted by the selection of two phases. According to the type of materials, the dual-phase membranes can be divided into ceramic-metallic membrane and ceramic-ceramic membranes.

In the ceramic-metallic membranes, the ceramic phase is functioned as the oxygen ionic conductor and the noble metal Ag, Pd, Pt and Au as the electronic conductors. For example, the membrane (BYC)_{0.6}(Ag)_{0.4} (in Table 2.4) show a very high oxygen permeation flux at low temperature, which is due to the well-connected BYC and Ag networks to ensure the simultaneous migration of oxygen ions and electrons. Hence, a continuous and percolative network is crucial for the success of dual-phase membrane, which need the volume fraction of each phase exceed 30 %. For the metallic phase, the cost is too high for real application. In addition, the mismatch of thermal expansion during the two phases is easy to spoil the membrane.

To overcome the disadvantages of ceramic-metallic membranes, the ceramic-ceramic membranes are proposed, in which the electronic conductive phase is a perovskite oxide. Kharton et al. [79] studied a series of CGO-based composite
membranes, in which CGO was applied as the oxygen ionic conductor; LSFC and LSM were used as electronic conductor. The oxygen permeation fluxes of these membranes are not high and only have a magnitude of $10^{-8}$ mol·s$^{-1}$·cm$^{-2}$ at 950 °C (Table 2.4), which is attributed to the formation of impurity phases with poor oxygen ionic conduction caused by the inter-phase diffusion. In addition, it was found that the pure electronic phase such as noble metal and some perovskite oxides can block the transport of oxygen ions between the oxygen ionic conductor grains, so a mixed conductive perovskite oxide was proposed to replace the pure electronic phase in ceramic-ceramic membrane. Just like the $(\text{CGO})_{0.55}(\text{GSF})_{0.45}$ membrane in Table 2.3, CGO phase is for the oxygen ionic transport and GSF phase is for both oxygen ionic and electronic transport. This dual-phase membrane presented a two times higher oxygen permeation flux than the GSF membrane in the same conditions. As shown in Fig. 2.5, the oxygen ions can transfer between the mixed conductor GSF and ionic conductor CGO, which can decrease the path tortuosity for oxygen ionic conduction and then improve the oxygen permeation flux.

![Figure 2.5 Schematic illustration of oxygen transport in ionic-electronic conductor composite membrane and ionic-mixed conductor composite membrane. [80]]
Table 2.4 Oxygen permeation fluxes of dual-phase membranes

<table>
<thead>
<tr>
<th>Membrane</th>
<th>Temperature (°C)</th>
<th>$J_{O_2}$ (mol·cm⁻²·s⁻¹)</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>$P'_{O_2}$ (bar)</th>
<th>$P''_{O_2}$ (bar)</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td><em>Ceramic-metallic type</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(BEO)$<em>{0.6}$(Ag)$</em>{0.4}$</td>
<td>600</td>
<td>2.000<em>10⁻⁸ - 2.700</em>10⁻⁸</td>
<td>Disk</td>
<td>0.2-2</td>
<td>0.21</td>
<td>0.003</td>
<td>[81]</td>
</tr>
<tr>
<td>(BYC)$<em>{0.6}$(Ag)$</em>{0.4}$</td>
<td>600-780</td>
<td>1.995<em>10⁻⁸ - 1.514</em>10⁻⁷</td>
<td>Disk</td>
<td>1.02</td>
<td>0.21</td>
<td>-</td>
<td>[82]</td>
</tr>
<tr>
<td>(SSC)$<em>{0.5}$(Pd)$</em>{0.5}$</td>
<td>750-900</td>
<td>2.069<em>10⁻⁸ - 6.695</em>10⁻⁸</td>
<td>Disk</td>
<td>0.90</td>
<td>0.21</td>
<td>-</td>
<td>[82]</td>
</tr>
<tr>
<td>(YSZ)$<em>{0.6}$(Pd)$</em>{0.4}$</td>
<td>900-1100</td>
<td>1.227<em>10⁻⁸ - 4.295</em>10⁻⁸</td>
<td>Disk</td>
<td>2</td>
<td>0.21</td>
<td>1.1*10⁻⁴</td>
<td>[83]</td>
</tr>
<tr>
<td>(YSZ)$<em>{0.5}$(Pd)$</em>{0.5}$</td>
<td>1100</td>
<td>1.488<em>10⁻⁶ - 1.563</em>10⁻⁶</td>
<td>Disk</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>[84]</td>
</tr>
<tr>
<td>(YSZ)$<em>{0.5}$(Pt)$</em>{0.5}$</td>
<td>1100</td>
<td>1.339*10⁻⁶</td>
<td>Disk</td>
<td>0.8</td>
<td>-</td>
<td>-</td>
<td>[84]</td>
</tr>
<tr>
<td><em>Ceramic-ceramic type</em></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>(CGO)$_{0.5}$-(LSM$<em>1$)$</em>{0.5}$</td>
<td>950</td>
<td>1.585<em>10⁻⁸ - 7.943</em>10⁻⁸</td>
<td>Disk</td>
<td>0.6</td>
<td>0.21</td>
<td>0.015 - 0.124</td>
<td>[79]</td>
</tr>
<tr>
<td>(CGO)$<em>{0.5}$-(LSFC)$</em>{0.5}$</td>
<td>950</td>
<td>1.202<em>10⁻⁸ - 3.802</em>10⁻⁸</td>
<td>Disk</td>
<td>1.35</td>
<td>0.21</td>
<td>0.012 - 0.100</td>
<td>[79]</td>
</tr>
<tr>
<td>(CGO)$<em>{0.55}$-(GSF)$</em>{0.45}$</td>
<td>950</td>
<td>8.912<em>10⁻⁸ - 5.012</em>10⁻⁷</td>
<td>Disk</td>
<td>1.0</td>
<td>0.21</td>
<td>0.030 - 0.175</td>
<td>[79]</td>
</tr>
<tr>
<td>(SDC)$<em>{0.6}$-(LSC)$</em>{0.4}$</td>
<td>950</td>
<td>2.976<em>10⁻⁶ - 5.580</em>10⁻⁷</td>
<td>Disk</td>
<td>0.5</td>
<td>0.21</td>
<td>0.047 - 0.007</td>
<td>[80]</td>
</tr>
<tr>
<td>(ZYO)$<em>{0.6}$-(LSC)$</em>{0.4}$</td>
<td>750-950</td>
<td>7.031<em>10⁻¹⁰ - 5.105</em>10⁻⁹</td>
<td>Tube</td>
<td>1.23</td>
<td>0.21</td>
<td>-</td>
<td>[86]</td>
</tr>
<tr>
<td>(BYS)$_{0.6}$-(LSM$<em>2$)$</em>{0.4}$</td>
<td>650-850</td>
<td>3.491<em>10⁻⁸ - 3.162</em>10⁻⁷</td>
<td>Disk</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>[87]</td>
</tr>
<tr>
<td>(LSGF)$<em>{0.928}$-(BSCF)$</em>{0.072}$</td>
<td>700-917</td>
<td>7.559<em>10⁻⁻⁸ - 3.519</em>10⁻⁷</td>
<td>Disk</td>
<td>0.21</td>
<td>-</td>
<td>-</td>
<td>[88]</td>
</tr>
</tbody>
</table>

Abbr.: YSZ= (ZrO$_2$)$_{0.94}$(Y$_2$O$_3$)$_{0.06}$, BYC= (Bi$_{1.75}$Y$_{0.25}$O$_3$)$_{0.95}$(CeO$_2$)$_{0.05}$, SSC= Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$, CGO= Ce$_{0.8}$Gd$_{0.2}$O$_{2-δ}$, BEO= Bi$_{1.5}$Er$_{0.5}$O$_3$, LSFC= La$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Co$_{0.2}$O$_{3-δ}$, LSC= La$_{0.8}$Sr$_{0.2}$CrO$_{3-δ}$, SDC= Ce$_{0.8}$Sm$_{0.2}$O$_{2-δ}$, ZYO= Zr$_{0.8}$Y$_{0.2}$O$_{1.9}$, BYS= Bi$_{1.5}$Y$_{0.3}$Sm$_{0.2}$O$_{3-δ}$, LSM$_1$= La$_{0.7}$Sr$_{0.3}$MnO$_{3-δ}$, LSM$_2$= La$_{0.8}$Sr$_{0.2}$MnO$_{3-δ}$, LSGF= La$_{0.15}$Sr$_{0.85}$Ga$_{0.3}$Fe$_{0.7}$O$_{3-δ}$, BSCF= Ba$_{0.5}$Sr$_{0.5}$Co$_{0.8}$Fe$_{0.2}$O$_{3-δ}$, GSF= Gd$_{0.2}$Sr$_{0.8}$FeO$_{3-δ}$
2.2.3 Partial oxidation of methane into syngas

Preparation of syngas from methane can be achieved by steam reforming, CO\textsubscript{2} reforming and partial oxidation of methane. POM is based on the reaction of methane with oxygen (\(\text{CH}_4 + 0.5\ \text{O}_2 \rightarrow \text{CO} + 2\ \text{H}_2\)), which is mildly exothermic (\(\Delta H_{298K}^0 = -36\ \text{KJ/mol}\)) and hence less energy is required, while steam reforming and CO\textsubscript{2} reforming are endothermic reactions, as seen in Fig. 2.6. According to the equilibrium calculations, it can be revealed that both conversion and selectivity of syngas will be improved by increasing temperature, and the increase of pressure will have an adverse effect on the conversion of methane.

![Diagram of partial oxidation of methane into syngas](image)

*Figure 2.6 Thermodynamic representation of the partial oxidation of methane [89].*

Two mechanisms (an indirect mechanism and a direct POM mechanism)[57] have been proposed to explain the POM reaction. The indirect mechanism was first reported by Prette et al. in 1946. First, the methane is totally combusted in the entrance section of the catalytic bed, producing CO\textsubscript{2} and H\textsubscript{2}O. After then, the
remaining methane is converted to syngas by steam reforming and CO$_2$ reforming reactions along the rest part of the catalytic bed. The direct POM mechanism was also validated by the fact that a high CO yield could be achieved when the residence time is very short. In this mechanism, syngas is produced directly from methane by recombination of surface carbon and oxygen species on the surface of the catalysts.

There are three main types of catalysts [89], which include supported nickel, cobalt or iron catalysts [90-92], supported noble metal (Ru, Rh, Pd, Pt) catalysts and transition metal carbide catalysts, having been widely investigated for POM into syngas. Ni metal is identified as the active component for POM into syngas. However, carbon decomposition easily occurs on the nickel and then deteriorates the activity of Ni-based catalyst. In order to improve the properties of catalyst, lots of work has been done on the modification of the support [93-95]. For example, the addition of Li$_2$O and La$_2$O$_3$ into the catalyst NiO/γ-Al$_2$O$_3$ can obviously improve the stability of catalyst and inhibit the coke formation [96], which is probably because the oxygen atoms on the support can help oxidizing the deposited carbon atoms. In addition, the introduction of La$_2$O$_3$ to γ-Al$_2$O$_3$ support can make the NiO be easily reduced to its active form (metallic Ni), and then ensure a very high catalytic activity for POM reaction [95]. Besides the modification of support, the addition of active components such as Co, Fe or noble metal into catalyst can also reduce the coke formation. Besides coke formation, sintering of metal crystallites and oxidation of metal atoms by oxygen or steam are also the reasons for the deactivation of POM catalyst. Hence, the development of highly effective and stable POM catalyst is still a challenged
problem need to solve.

2.2.4 Ceramic membrane reactor for air separation and POM

![Figure 2.7 Schematic diagram of a ceramic catalytic membrane reactor](image)

A catalytic membrane reactor (CMR), which couples membrane separation with chemical reaction, can obtain a synergy effect to enhance separation or reaction. This concept has been proposed in early 1960s and a lot of studies and efforts have been done in this field [6, 97-105]. The recent progress in this field has been reviewed by Jin’s group [97]. The membrane reactor integrating oxygen separation with POM reaction can easily realize the conversion of methane into syngas. As shown in Fig. 2.7, the membrane reactor is at least composed of a dense oxygen permeable membrane and a POM catalyst bed. The oxygen molecules are reduced into $O^{2-}$ ions by surface exchange reaction, and then the $O^{2-}$ ions diffuse through the dense membrane and reacts with methane into syngas in the catalyst bed. The MEIC membrane reactors for POM can be generally classified into disk-shaped membrane reactor, tubular membrane reactor and hollow fiber membrane reactor, according to their configurations.
Lu et al. [73] investigated the performances of disk-shaped membrane reactor fabricated by perovskite $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ (BSCFO), which is successfully operated under POM conditions for 500 h and showed a high oxygen permeation flux of 11.5 ml·cm$^{-2}$·min$^{-1}$ at 875 °C with methane conversion higher than 97 % and CO selectivity greater than 95 % by using LiLaNiO$_x$/\(\gamma\)-Al$_2$O$_3$ as catalyst. When this BSCFO membrane was operated at 850 °C and a high pressure of 5 atm., it had an oxygen permeation flux of 15.5 ml·cm$^{-2}$·min$^{-1}$ with 92 % of methane conversion and 90 % of CO selectivity. Although the perovskite structure doped by cobalt in B-sties can achieve a high oxygen permeation flux, these perovskite oxides are not stable in reducing atmosphere due to the easy evaporation and reduction of cobalt [106]. Hence, many cobalt-free perovskite MEIC membranes with high oxygen permeation fluxes have been investigated. For example, Gong et al. [68] developed a disk membrane made of $\text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ perovskite oxide. This membrane presents a high chemical stability under reducing atmosphere of POM and can reach a high oxygen permeation flux of 11.8 ml·cm$^{-2}$·min$^{-1}$ at 950 °C with 55 % of methane conversion and 99.6 % of CO selectivity.

Although the fabrication of disk membrane reactors is much easier than the tubular and hollow fiber membranes, the disk membranes has a limited membrane area and also difficulty in sealing at high temperatures to scale up. Many tubular MEIC membrane reactors have been studied and developed. For example, a dense $\text{BaCo}_{0.7}\text{Fe}_{0.2}\text{Nb}_{0.1}\text{O}_{3-\delta}$ (BCFNO) tubular membrane reactor with Ni-based catalysts was fabricated for partial oxidation of CH$_4$ in coke oven gas [107]. This membrane
shows an oxygen permeation of 10 ml·cm⁻²·min⁻¹ at 870 °C with 95 % of methane conversion and 99 % of CO selectivity. The BCFNO membrane also exhibits a good stability under reducing atmosphere. Asymmetric tubular membrane reactor, which has a dense selective layer and a porous support layer, can effectively reduce the thickness of the dense MEIC layer and then improve oxygen permeability [108]. For example, a stable asymmetric membrane reactor was fabricated by spray deposition of a dense thin film of La₀.₅Sr₀.₅Fe₀.₈Ga₀.₂O₃₋δ on a porous α-alumina tube with a rhodium catalyst in the shell side [106]. Air was fed into the tube and methane to the shell side. Its oxygen permeation flux can reach 2.5×10⁻⁷ mol·cm⁻²·s⁻¹ at 850 °C with 97 % of methane conversion and nearly 100 % of CO selectivity. However, the perovskite MEIC membranes, especially in tube geometry, with high oxygen ionic conductivity are not mechanically stable under a large oxygen partial gradient, which is due to the mismatch of lattice expansion between the oxygen lean side and rich side and then the formation of cracks in the tubular membrane. The development of new materials, such as dual-phase composites, is possible way to solve this problem.

Recently, the hollow fiber membrane reactors [109, 110] have been paid more attentions due to their obvious advantages, such as large membrane area/volume ratio and thin membrane layer. For example, a dual-phase composite hollow fiber membrane was prepared by cubic Ce₀.₈Sm₀.₂O₂₋δ (SDC) and perovskite La₀.₇Ca₀.₃CrO₃₋δ (LCC) phase using phase-inversion/extrusion method [109]. The obtained membrane has an oxygen permeation flux of 3.9×10⁻⁶ mol·cm⁻²·s⁻¹ at
950 °C under air/CO gradient and exhibits satisfactory stability. However, the low mechanical strength of hollow fiber membranes is a problem when they are assembled into membrane reactors.

In a word, a feasible membrane reactor for POM in industry should meet several basic requirements, which include a high oxygen permeation flux as high as 5-10 cm³·cm⁻²·min⁻¹, high chemical stability under POM reducing atmosphere, enough mechanical strength, low membrane fabrication or material costs and a highly active and stable POM catalyst.
Chapter 3 Impacts of the pendant functional groups of cellulose precursor on the generation of pore structures of activated carbons

Cellulose-based polymers with four types of side chain group are selected to prepare activated carbon (AC). Effects of the side chain groups on the structure of carbonaceous intermediates, obtained from pyrolysis of the cellulose polymers, are scrutinized by infrared spectroscopy and X-ray photoelectron spectroscopy. The carbonaceous intermediates consist of polyaromatic hydrocarbon (PAH) flakes of different sizes and with various oxy-groups. These structural differences in PAH flakes impact the final pore structures of ACs formed in the subsequent activation. Of the four types of functional groups in question, the hydroxyethyl group is most effective in facilitating formation of large surface area and high micro- and mesopore volumes. The AC powders are assessed for their ability to capture H₂S from a gas stream.

3.1 Introduction

In this work, we attempt to gain insight into how the structure of a polymer might affect the porous structure of the AC derived from the polymer. For this purpose, four cellulose-based polymers were selected as starting materials or precursors for the preparation of AC. Cellulose is the prevalent component in most biomass and therefore well suited as the model for a study on the pyrolysis of
A review article written by Sanders et al. [112] has elucidated the thermal elimination mechanisms and described the main organic fragments produced during the pyrolysis. In addition, the functional groups arising from the solid residue of pyrolysis, viz. carbonaceous substance, had also been characterized by spectroscopic methods [113, 114]. These functional groups will further influence the evolution of porous structures during thermal condensation of the carbonaceous substance [115]. The cellulose-based polymers, including hydroxyethyl cellulose (HEC), methyl cellulose (MEC), alpha-cellulose (ALC) and cellulose acetate (CAC), form a typical series for this study as they differ from each other only in the type of pendant (or side-chain) group. When they are subjected to pyrolysis (or carbonization) at 400 °C under argon, carbonaceous substances, comprising of polyaromatic hydrocarbon (PAH) flakes, are produced. The carbonaceous substances differ from each other primarily in the sizes of PAH flakes produced and in the distributions of various oxy-groups attached to PAH. Furthermore, these differences in PAH structure affect elimination of functional groups and the growth of PAH flakes in the subsequent activation step, where the surface structures of the AC are shaped. The different AC samples synthesized were further examined by evaluating their ability to capture H$_2$S from a stream of N$_2$-H$_2$S mixture. The outcome of this test justifies the critical roles played by the specific surface area, the volume fraction of mesopores and the surface pH value of adsorbent.
3.2 Experimental

3.2.1 Synthesis of activated carbons

In a typical procedure, ALC or one of its analogs (MEC, HEC or CAC) of 10 g was placed in the middle position of a quartz tube (diameter: 50 mm; length: 1200 mm). The tube was then purged with an Ar stream (500 cm³/min) and heated to a carbonization temperature \( T_c \) of 400 or 500 °C using a heating rate of 6 °C/min. The sample was held at the carbonization temperature for 1 h. Then the resultant carbonaceous substance was subsequently heated to an activation temperature by the same heating rate under Ar atmosphere. The activation was conducted for 2 h under CO₂ (500 cm³/min, 1 atm) at one of the following temperatures: 600, 700, or 800 °C. After that, the purging stream of Ar was resumed and maintained until the reactor was cooled down to room temperature.

After the activation step, the obtained product was ground to fine powder and washed several times using deionized water to extract soluble impurities. The filtration cake was dried in a vacuum oven at 80 °C for 24 h to complete the preparation. The AC samples obtained from ALC, MEC, HEC and CAC are denoted by AC_ALC, AC_MEC, AC_HEC and AC_CAC, respectively. A two-digit suffix is used, whereby the first digit stands for the carbonization temperature and the second one the activation temperature. For example, AC_HEC47 is made by carbonizing HEC at 400 °C and then conducting activation at 700 °C, while AC_HEC40 symbolizes the same carbonization temperature but no activation is carried out.
3.2.2 Instrumental characterizations

3.2.2.1 Thermal analysis

Thermogravimetric (TG) and derivative thermogravimetric (DTG) diagrams of cellulose precursors were obtained from a thermal analyzer (DTG-60AH, Shimadzu) using a sample of ca. 10 mg. The analytical conditions included a heating rate of 10 °C/min, a purging gas of N₂ (10 cm³/min) and a temperature range from 50 to 950 °C.

3.2.2.2 Structural characterizations

The crystalline structures of ACs were examined by high resolution transmission electron microscope (HR-TEM, Hitachi H-7600). The porous features of the prepared ACs were obtained from nitrogen isotherms at 77 K by Brunauer-Emmett-Teller (BET) surface area measurement (Autosorb-1, Quantachrome instruments). Before each measurement, the samples were degassed at 300 °C for 6 h. The surface area (A_BET) is calculated from the linear region of adsorption isotherm under the relative pressure (P/P₀) from 0.05 to 0.3. The total volume (Vₜ) is defined as the volume of liquid N₂ adsorbed at the relative pressure of 0.99, since the obtained isotherms exhibit the apparent plateaus of type IV isotherm. The microporous volume (V_micro) is determined by Dubinin-Radushkevich (DR) method. The mesoporous volume (V_meso) is thus the difference between Vₜ and V_micro. The pore size distributions are calculated by the non-linear density functional theory (NLDFT) method, in which the N₂-carbon equilibrium transition kernel based on a
cylindrical pore model is used. This method is applicable in pore widths in the range from 0.35 to 40 nm.

3.2.2.3 Determination of organic functional groups and the surface pH value

The pendant organic functional groups of the prepared AC_xxx40 samples were characterized by Fourier transform infrared spectroscopy (FT-IR) using the KBr pellet method. The surface functionalities of the AC samples were also determined by X-ray photoelectron spectroscopy (XPS, Kratos Axis His System). The binding energy of C1s of graphitic carbon at 284.8 eV is used as the internal reference to calibrate the binding energies of the carbon atoms that bear different organic functional groups [12, 116]. For the determination of surface pH value, 0.4 g of AC powder was stirred in 20 ml deionized water overnight. Thereafter, the pH value of the water phase was measured by pH meter (AB15, Fisher Accumet).

3.2.3 H2S adsorption test

The assessment of H2S adsorption capacity of AC samples was conducted at 25 °C in a fixed bed reactor (diameter: 10 mm; length: 200 mm) where 0.5 g of the adsorbent was packed for each measurement. A H2S (1100 ppm)-N2 mixed gas stream was fed with a flow rate of 2000 cm³/h. The H2S concentration in the outlet gas was detected by an electrochemical sensor (MOT500-H2S, Keernuo Electronics Technology). The change of H2S concentration in the outlet stream is used to evaluate the adsorption capacity of the AC samples. The breakthrough time is defined as the time elapsed before the bed exit-concentration of H2S reaches 1 % of
Chapter 3 Impacts of the pendant functional groups of cellulose precursor on the generation of pore structures of activated carbons

the inlet concentration. The breakthrough capacity of H$_2$S can be calculated from the following equation [9]:

\[
\text{Breakthrough Capacity} \left( \frac{mg \ H_2S}{g \ \text{Carbon}} \right) = \frac{Q \left( \frac{ml}{min} \right) \times t(\text{min}) \times C_{H_2S} (\text{ppm}) \times M_{H_2S} \left( \frac{g}{mol} \right)}{22.4 \left( \frac{lit}{mol} \right) \times m_{\text{carbon}} (g) \times 10^6} \quad (3.1)
\]

where Q is the flow rate of the feed gas; t is the breakthrough time; $C_{H_2S}$ is the inlet concentration of H$_2$S; $M_{H_2S}$ is the molecular weight of H$_2$S and $m_{\text{carbon}}$ is the mass of carbon sample used.

3.3 Results and Discussion

3.3.1 Exploration of the effects of the side-chain groups of cellulose on pyrolysis

The thermal degradation profiles of the cellulose derivatives (Fig. 3.1) are the basis for the determination of carbonization (pyrolysis) and activation temperatures. The TG profile can be divided into four stages, I: 50-200 °C (for HEC), 50-250 °C (for ALC, MEC and CAC); II: 200-350 °C (HEC), 250-400 °C (ALC, MEC and CAC); III: 350-700 °C (HEC), 400-700 °C (ALC, MEC and CAC); and IV: 700-950 °C (for all cellulose precursors). The four precursors show the main mass-reduction in stage II, in which the four derivative curves exhibit their respective reduction rates varying with temperature. In this stage, the dehydration and the restructuring of carbon-carbon bond take place [112, 117, 118]. Most
organic functional groups that contain O, N and S atoms undergo thermal
decomposition in this stage [119], leaving behind a carbonaceous substance after
this major mass-reduction stage. Therefore, 400 °C is a turning point for all the four
celluloses that marks to a large extent the completion of carbonization.

HEC begins to decompose at about 200 °C, whereas the decomposition of ALC,
MEC and CAC occur at about 250 °C. It is rational to attribute the different thermal
tracks to the different organic side-chain groups of cellulose. The hydroxyethyl
group of HEC is thermally more reactive than the other three side-chain groups
(-OH, -OCH₃ and -OCOCH₃). Despite this, HEC displays a higher mass-retention
rate after stage II as compared to the other three precursors. This indicates that the
hydroxyethyl group leads to a thermally stable carbonaceous structure via a rapid
transformation during the carbonization. As a result, HEC presents a broad and
slightly inclined plateau in stage III, ranging from the completion of the first mass elimination (350 °C) to the start of the next mass-removing slope (700 °C). It will be subsequently proven that stage III includes the growth of PAH flakes as well as the condensation and elimination of oxy-groups, e.g. ether and quinine groups. Finally, the weight loss of HEC in stage IV marks further removal of the rest oxy-groups and reactive carbon moieties in the carbonaceous substance [120]. In contrast to this, the weight losses of ALC, MEC and CAC in range IV are smaller, following the order of MEC > ALC ≅ CAC, and do not show a clear setting-on point. Mass reduction in this temperature range signifies further polyaromatization [121, 122]. For instance, the FT-IR spectra of AC_HEC47 and AC_HEC48 (Fig. 3.2) display a broad absorption band in the range of 1434 to 1637 cm$^{-1}$, which can be attributed to the infrared spectral characteristics of the condensed aromatic rings [122]. Condensation of PAHs advances the formation of graphene sheets and stacking of these sheets to form graphitic domains, which results in densification of carbon matrix. A magnified view of sample AC_HEC48 (section 3.2.1 for denotation) by HR-TEM confirms the formation of local graphite structure (Fig. 3.3) at 800 °C. In consideration of the carbonaceous substance of HEC, holding a higher portion of eliminatable moieties over temperature stage III is crucial to attaining superior surface properties at the end of preparation. This is because voids are produced through removal of those moieties in stage IV, where local graphitization takes place as well at the same time. Therefore the activation temperature chosen should be around the onset point of stage IV (700 °C) in order to minimize the influence of
local graphitization. In addition, a broader stage III is expected since it involves a gradual mass elimination before the significant local graphitization that takes place over stage IV.

**Figure 3.2** FT-IR spectra of AC_HEC samples.

**Figure 3.3** HR-TEM micrograph of sample AC_HEC48.
The preparation of AC from HEC has been scrutinized to understand how the carbonization and activation temperatures affect the surface properties of the resulting AC (Table 3.1). The effect of varying activation temperature against a fixed carbonization temperature is then examined. With respect to either carbonization temperature of 400 or 500 °C, the activation at 700 °C gives the largest values of specific surface area, total specific pore volume and specific mesopore volume. In contrast, the activation temperature below it (at 600 °C) results in a slow reaction rate, while the temperature above it (at 800 °C) boosts the polyaromatization degree and hence the local graphitization. This will make CO2 less effective to create pores due to densification of carbon matrix [12]. Hence conducting activation at 700 °C not only allows for generating voids but also
minimizes graphitization. As shown by TG profile, the thermal degradation degrees of the four celluloses over stage III (350-700 °C) followed the sequence: HEC < CAC < ALC < MEC, in which the lower degree of degradation is found to give rise to the higher yield of AC after activation. Similarly, their specific surface area and total specific pore volume also display the same order as the yield (Table 3.1). This correlation supports the previous proposal that a lower mass retention over stage III implies a higher polyaromatization extent and is unfavourable to the generation of porous matrix due to stronger graphitization tendency.

![Figure 3.4](image)

**Figure 3.4** $N_2$ adsorption-desorption isotherms of AC_CAC47, AC_ALC47, AC_HEC47 and AC_MEC47 samples.

The $N_2$ adsorption isotherms of AC_HEC47, AC_MEC47 and AC_CAC47 display obvious hysteresis loops, indicating the presence of mesopores (in Fig. 3.4).
In contrast, AC_ALC47 does not show any hysteresis loop because it contains little mesoporous structure. In regards to the pore-distribution profile of AC_HEC47 (in Fig. 3.5), it contains abundant micropores and mesopores ranging from 2.4 to 5.4 nm, which displays two maxima at 2.8 and 3.9 nm. Compared with AC_HEC47, AC_MEC47 and AC_CAC47 present narrower mesopore width ranging from 2.4 to 4.6 nm. Unlike the above pore distribution curves, the AC_ALC47 curve reveals very little mesopores. Whether the organic functional groups of the cellulose derivatives impact on the formation of mesopores is therefore a question to study.

*Figure 3.5* Pore size distribution of the AC_CAC47, AC_ALC47, AC_HEC47 and AC_MEC47 samples calculated by the NLDFT method.
3.3.2 An investigation into the effect of organic functional groups on PAHs

![FT-IR spectra of carbonaceous substances of AC_MEC40, AC_ALC40, AC_HEC40 and AC_CAC40.](image)

*Figure 3.6 FT-IR spectra of carbonaceous substances of AC_MEC40, AC_ALC40, AC_HEC40 and AC_CAC40.*

From the previous examination of the TG profiles of the four cellulose-based polymers, the structural characteristics of the pyrolysis product from a cellulose precursor are crucial to the generation of pore structures of an AC sample. These structural characteristics include organic functional groups and sizes of PAH flakes. To explore this aspect, four AC_xxx40 samples, as defined by the suffix of symbols, are prepared by pyrolyzing their respective precursors at 400 °C for 1 h under argon. The resulting carbonaceous substances contain eliminable moieties that should
primarily be pendant oxy-groups according to the analysis of section 3.3.1. The IR spectra of the above samples (Fig. 3.6) contain a series of absorption bands that can be assigned to six types of functional groups (Table 3.2). The remarkable structural conversions accompanying the pyrolysis of a cellulose precursor are the generation of carbon framework of PAH and of meta-stable oxy-groups attached to PAH. The emergence of aromatic ring stretching band at 1591 cm$^{-1}$ and the out-of-plane C-H bending band in 736-875 cm$^{-1}$ verify the aromatic ring structures. More importantly, the stronger ring stretching over the out-of-plane bending implies the formation of PAH flakes which have high C/H ratios. The bands around 1685 cm$^{-1}$ show the presence of quinonoid C=O group and carboxyl C=O group, and the bands ranging from 1223 to 1434 cm$^{-1}$ stand for the C-O stretching modes. It could then be inferred that pyrolysis of the cellulose backbone contributes to the derivation of PAHs while thermal degradation of the cellulose side-chain groups contributes to the derivation of the oxy-groups and the saturated hydrocarbon segment as listed in Table 3.2.
Table 3.2 Classification of infrared absorption bands of the AC_xxx40 samples [11, 122, 123]

<table>
<thead>
<tr>
<th>Bond type</th>
<th>Pendant functional group types</th>
<th>Absorption frequency (cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O-H</td>
<td>Hydroxyl (phenol) or carboxylic</td>
<td>~ 3400</td>
</tr>
<tr>
<td>C-H</td>
<td>Aliphatic hydrocarbons</td>
<td>2937 and 2863 (stretching)</td>
</tr>
<tr>
<td></td>
<td>Aromatic hydrocarbons</td>
<td>875, 809, 736 (out-of-plane bending)</td>
</tr>
<tr>
<td>C=O</td>
<td>Carboxylic, quinonoid</td>
<td>~ 1685</td>
</tr>
<tr>
<td>C=C-C=C</td>
<td>Aromatic rings</td>
<td>1591</td>
</tr>
<tr>
<td>C-O-H</td>
<td>Carboxylic, phenol and ether</td>
<td>~ 1223, 1434, 1365 (phenol C-O-H in-plane bending)</td>
</tr>
</tbody>
</table>

Figure 3.7 The C 1s XPS spectra of AC_CAC40, AC_ALC40, AC_HEC40 and AC_MEC40 samples.
Chapter 3 Impacts of the pendant functional groups of cellulose precursor on the generation of pore structures of activated carbons

Table 3.3 Relative content of oxygen-containing functional groups in C 1s XPS spectra [12, 116]

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak I: 284.8 eV (graphitic peak)</th>
<th>Peak II: 286.2 eV (C-O peak)</th>
<th>Peak III: 287.5 eV (C=O peak)</th>
<th>Peak IV: 289.0 eV (O-C=O peak)</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC_HEC40</td>
<td>79.8</td>
<td>11.1</td>
<td>4.8</td>
<td>4.4</td>
</tr>
<tr>
<td>AC_ALC40</td>
<td>75.8</td>
<td>14.2</td>
<td>5.2</td>
<td>4.8</td>
</tr>
<tr>
<td>AC_MEC40</td>
<td>77.1</td>
<td>11.7</td>
<td>3.6</td>
<td>7.6</td>
</tr>
<tr>
<td>AC_CAC40</td>
<td>59.7</td>
<td>22.9</td>
<td>11.5</td>
<td>5.9</td>
</tr>
</tbody>
</table>

The carbonaceous intermediates, AC_xxx40, are further examined by XPS spectroscopy because the carbon atoms of different functional groups have different binding energy [11]. The C1s XPS spectra of the four AC_xxx40 samples (Fig. 3.7) can be deconvoluted into five peaks with binding energy of about 284.8, 286.2, 287.5, 289.0 and 290.7 eV, which correspond to graphitic peak, C-O (ether and phenol), C=O (quinone and carbonyl), O-C=O (carboxyl and ester) species and plasmon peak, respectively [12, 116]. Hence their relative contents based on the respective peak area values are listed in Table 3.3. The AC_CAC40 sample contains the highest concentration of oxy-functional groups, which is followed by the sequence, AC_ALC40, AC_MEC40 and AC_HEC40. In addition, AC_ALC40 and AC_HEC40 possess similar relative concentration ratios of the oxy-group types: C-O / C=O / O-C=O (> 1), but AC_MEC40 contains the highest O-C=O / C=O ratio. Different types of oxy-groups possess different thermal stabilities, which
subsequently impact on the evolution of pore structures of AC in the following calcinations as elaborated in the following paragraphs.

The carbonaceous substance degraded from HEC presents a higher mass retention rate than those from the other three precursors in the temperature range above 400 °C (Fig. 3.1). According to the IR spectra (Fig. 3.6) and the XPS measurement results (Table 3.3) of the four AC_xxx40 samples, the following structural characteristics can be summarized: (1) Of the four samples, AC_HEC40 contains the lowest content of O-C=O groups, which are thermally most vulnerable [120]; (2) Regarding the C-O functional groups, AC_HEC40 contains a higher content of thermally stable phenol groups (1434 and 1365 cm\(^{-1}\)) than the other three samples. These two structural characteristics AC_HEC40 possesses help retard aggregation of PAH flakes in the subsequent activation step. Such alleviating effect facilitates access of CO\(_2\) to the PAHs in the activation step. Hence, sample AC_HEC47 can achieve the highest desired surface properties (Table 3.1). Furthermore, the concentration of oxy-groups is significantly affected by the carbonization temperature used since the sample is held at this temperature for 1h. For instance, setting the carbonization temperature of HEC at 500 °C instead of 400 °C, resulting in AC_HEC57, apparently undermines the surface properties because the higher carbonization temperature causes removal of a large part of the oxy-groups before the activation. Compared with the IR spectrum of AC_HEC40, the spectrum of AC_HEC50 (Fig. 3.2) indeed shows drastic reduction in the IR bands of the oxy-groups, in which the C-O species were better preserved than the
C=O species. In addition, the stretching of aromatic rings also becomes weaker due to an increase in the sizes of PAHs. This change in the structure can also be justified by ca. 4% difference in the weight-loss curve between 400 and 500 °C on the TG diagram of HEC.

In regards to the impact of the functional groups of the celluloses have on the surface properties of the AC xxx47 samples (Table 3.1), the higher content of O-C=O groups would be adverse since it is easier to be removed than the other oxy-groups before being heated to the desired activation temperature, leading to a crammed PAHs packing. It can be seen from Table 3.3 that the content of O-C=O groups follows the order, AC_MEC40 > AC_CAC40 > AC_ALC40 > AC_HEC40, whereas according to their IR spectra, AC_HEC40 contains the highest content of phenol species as aforementioned. Hence the specific surface area and the total pore volume of the resultant AC xxx47 follow the order, AC_HEC40 >> AC_CAC40 > AC_ALC40 > AC_MEC40. It is also important to note that AC_HEC40 contains a small portion of the saturated hydrocarbon (Ar-C\textsubscript{n}H\textsubscript{2n}-Ar) moiety inferred from the C-H stretching (2937 and 2863 cm\textsuperscript{-1}) in its FT-IR spectrum (Fig. 3.6), which is attributed to the derivation from a small portion of 2-hydroxyethyl groups initially. In principle, these saturated groups could facilitate formation of pores as they have benzyl structure and can assist CO\textsubscript{2} with reforming aromatic carbons [12].

In short, the carbonization step is expected to produce planar PAH nano-flakes and reserve free spaces between them at the same time through the steric effect of those thermal stable organic functional groups.
3.3.3 The H₂S-removal by adsorption

![Graph showing H₂S breakthrough curves for AC_CAC47, AC_ALC47, AC_HEC47, and AC_MEC47.]

Figure 3.8 H₂S breakthrough curves of the samples AC_CAC47, AC_ALC47, AC_HEC47, and AC_MEC47.

From the above discussion, it has been concluded that AC_HEC47 has distinctive porous structures from AC_ALC47, AC_MEC47 and AC_CAC47. The H₂S adsorption tests of this series (Fig. 3.8) show the change of concentration ratio \( \frac{C}{C_0} \) in the outlet stream over the testing time for each AC. With respect to the same loading in the adsorption bed, the breakthrough time (defined in section 3.2.3) of the above four curves are 112, 65.5, 27.6 and 19.4 min, respectively. It indicates the H₂S adsorption capabilities of the four ACs. Table 3.2 gives the corresponding adsorption capacities: 12.47, 7.29, 3.07, and 2.16 mg H₂S/g carbon. As expected, the AC_HEC47 sample exhibits the superior H₂S adsorption capacity since it possesses both far larger surface area and pore volume than the rest of AC_xxx47 samples.
Chapter 3 Impacts of the pendant functional groups of cellulose precursor on the generation of pore structures of activated carbons

The order of adsorption capacity of the other three AC_xxx47 samples (Table 3.4) is more complicated, because not only the surface area and pore volume but also the basicity decides the order. For example, AC_CAC47, despite having the largest surface area and the highest pore volume among the three samples, displayed the lowest H_2S adsorption capacity.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Breakthrough Capacities</th>
<th>pH</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>mg/g</td>
<td>mg/cm^3</td>
</tr>
<tr>
<td>AC_HEC47</td>
<td>12.47</td>
<td>5.29</td>
</tr>
<tr>
<td>AC_ALC47</td>
<td>7.29</td>
<td>1.55</td>
</tr>
<tr>
<td>AC_MEC47</td>
<td>3.07</td>
<td>1.96</td>
</tr>
<tr>
<td>AC_CAC47</td>
<td>2.16</td>
<td>1.38</td>
</tr>
</tbody>
</table>

From the C1s XPS, AC_CAC40 has the highest content of oxy-functional groups, which implies the smallest sizes of PAH flake because the oxy-groups only attach to the edges of PAH flakes. In the activation stage, these oxy-groups are scavenged and hence the scope of most PAH flakes could be retained. As a consequence of this, the packing of small PAH flakes in AC_CAC47 would be favourable to achieve a large surface area and a high pore volume. However, AC_CAC47 has the weakest basicity among the four samples (Table 3.4), thus it has the lowest H_2S adsorption capacity. In regards to AC_ALC47 and AC_MEC47, with both having the similar surface pH values, hence their H_2S adsorption capacities depend primarily on the specific surface area. AC_ALC47 has a far smaller fraction.
of mesopore volume than AC_MEC47 but it still shows a H$_2$S adsorption capability well above AC_MEC47. It is thus suggested that there was a quick H$_2$S transport from mesopores to micropores since AC_ALC47 contains an apparently higher micropore volume.

3.4 Conclusions

This work investigates how different pendant side-chain groups of cellulose-based polymers affect the surface structures of the resulting ACs. Four types of cellulose structures in addition to ALC, which carries -OH, including three other derivatives that bear pendant groups of -OCH$_3$ (MEC), -OCOCH$_3$ (CAC) and -CH$_2$CH$_2$OH (HEC), are selected to prepare ACs. The preparation includes carbonization, and subsequently, activation. The carbonization products are essentially a mixture of PAHs as characterized by FT-IR and XPS. The pendant groups of the celluloses influence the structures of PAHs through: (1) the sizes; (2) distribution of thermally derived oxy-groups that include carboxyl, quinonoid, phenol, and ether; and (3) the presence of saturated hydrocarbon moieties. Each particular type of pendant group of cellulose gives rise to a specific set of the above structural features. The desired carbonization product should ultimately contain an optimal size range of PAH flakes, which are upheld by the thermally stable oxy-groups, and have an appropriate C/O ratio, as well as a certain amount of the saturated hydrocarbon moieties as the reactive sites of the activation, i.e. the CO$_2$ gasification. Among the four celluloses, the carbonization product of HEC at 400 °C
best satisfied these criteria. As far as the activation is concerned, its effectiveness depends on the use of a proper temperature to ensure the CO$_2$ gasification rate of PAHs without causing extensive stacking (graphitization). The presence of stable oxy-groups between PAH flakes assists CO$_2$ to access reactive sites. The H$_2$S adsorption evaluation shows that, for an AC adsorbent, not only does the specific surface area, the total pore volume and the portion of mesopore volume affect its adsorption capacity, but also the basicity of PAH does as well. It is also observed that there is a cooperative relationship between micropores and mesopores that exist in the adsorption process of H$_2$S, and that the former structural trait is more influential.
Chapter 4 Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

Mesoporous matrixes of activated carbon (AC) are normally synthesized using the hard or soft template method. This work explores a template-free method to synthesize a mesoporous AC matrix through creating inter-chain bonding in its precursor. Hydroxyethyl cellulose (HEC) was adopted as precursor and its polymer chains were covalently crosslinked by the esterification reaction. Four types of organic carboxylic acids were used to examine the effect of esterification crosslinking on formation of mesoporous structure primarily through the course of pyrolysis. The BET surface analysis of the resulting ACs reveals an explicit correlation between the number of carboxylic acid groups on benzene ring and the mesoporous structures of a synthesized AC. Moreover, it is also found that an optimal crosslinking degree for attaining the maximum volume fraction of mesopores exists with respect to each type of the crosslinker used. An attempt was made to understand how a crosslinked HEC is converted to a porous structure of an AC. The mesoporous structures of the ACs synthesized were also assessed by their capability of stripping H₂S from a gas stream.
Chapter 4  Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

4.1 Introduction

How to obtain the AC with desired mesoporous structure by a simple and low-cost method is the bottleneck for its wide application. Currently, the methods used for preparing mesoporous carbon mainly include hard template [25, 26, 124, 125], soft template [28, 125, 126] and template-free method [29, 30, 42, 127]. Compared with the above two methods, template-free method, which mostly relies on the selection or modification of a pertinent polymer, is more convenient in preparation. Some certain functional groups of the polymer will endow the AC with a mesoporous structure during pyrolysis process.

In this work, we selected hydroxyethyl cellulose (HEC) as precursor and modified it through the esterification reaction between the pedant hydroxyl groups and the carboxylic groups of an organic compound. Four types of organic carboxylic acid compounds: succinic acid, terephthalic acid, benzoic acid and pyromellitic acid, were employed to examine the effects of (i) aromatic/aliphatic molecular structures and (ii) crosslinking density on the porous features of the resultant ACs. The finding is appealing because the ester bonds formed between chains of the precursor impose a strong effect on the generation of mesoporous structure of AC. Such effect is considered to originate from the restriction of the degree of chain motion freedoms of HEC, which in-turn affects the pyrolytic reactions and then the formation of polyaromatic hydrocarbon (PAH) rings in terms of size and substitution. Packing of
different PAHs in the subsequent activation process is responsible to the generation of different pore size distributions and pore volumes.

4.2 Experimental

4.2.1 Esterification between 2-hydroxyethyl groups of HEC and carboxylic groups

Four types of carboxylic acid compounds, succinic acid (SCA), terephthalic acid (TPA), benzoic acid (BZA) and pyromellitic acid (PMA) were used to react with HEC (Aldrich Mw=250,000), respectively. For each preparation, a pre-determined amount of a carboxylic acid compound in the range of 1 to 5 wt % of HEC was dissolved in 10 mL of N-pyrrolidone (NMP) and 40 mL of acetone in a 100ml round-bottom flask. Then 10 g HEC and 0.1 mL of H$_2$SO$_4$ (2-3 mol/L) were added into the resulting solution. Afterward, the flask equipped with a condensation column was immersed in an oil bath (65 °C) and the suspension was magnetically stirred under reflux for at least 10 hours. A viscous suspension mixture was obtained after the esterification. The mixture was transferred to an evaporating dish to remove the solvent. The entire drying process required ca. 10 h to complete in the temperature range from 80 to 100 °C. A control sample was also prepared by following the same steps except for not including a carboxylic compound into the system to calibrate the solvent effect on the porous structure of the final product. The modified HEC is denoted by HEC followed with the name of carboxylic acid
and the content of the acid used to carry out esterification. For example, HEC_TPA5p stands for the sample prepared through the esterification of 10 g HEC with 0.5 g TPA. The control sample is denoted by HEC_CTL.

As a typical preparation of AC, 10 g of the modified HEC was placed in the middle position of a quartz tube (diameter: 50 mm; length: 1200 mm). The sample was then purged with Ar gas (500 ml/min) and heated at 6 °C/min to the carbonization temperature of 400 °C for 1 h. After that, the carbonaceous substance obtained was subjected to activation process, which was carried out under a flow of CO₂ (500 ml/min) at 700 °C for 2 h. After the activation step, the obtained AC was cooled down under Ar atmosphere until reaching room temperature. Finally, the AC was ground to fine powder, washed several times by using deionized water to extract soluble impurities and dried in a vacuum oven at 80 °C for 24 h to complete the preparation.

An AC sample obtained is denoted by AC with two digit suffix followed by the afore-defined sample name, whereby the first digit stands for the carbonization temperature and the second one the activation temperature. For example, AC47_TPA5p was prepared by carbonizing HEC_TPA5p at 400 °C and then conducting activation at 700 °C, while AC40_TPA5p symbolizes the same carbonization temperature but no activation was carried out. The control sample was denoted as AC47_CTL.
Chapter 4  Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

4.2.2 Instrumental characterizations

4.2.2.1 Thermal analysis

The change in polymer matrix structure of HEC to HEC_CTL due to solvation was examined by a differential scanning calorimetry (DSC-822E, Mettler-Toledo) under nitrogen atmosphere. In this analysis, the samples were scanned from 25 to 200 °C at 20 °C/min. Derivative thermogravimetric (DTG) diagrams of the esterified HEC precursors were obtained from a thermal analyzer (DTG-60AH, Shimadzu). In this analysis, 10 mg sample was loaded in a sample holder and heated at a heating rate of 10 °C/min under a N₂ purge (100 ml/min).

4.2.2.2 Structural characterizations

The porous features of the prepared ACs were examined by the same method described in section 3.2.2.2 of chapter 3.

4.2.2.3 Determination of organic functional groups

The organic functional groups of the modified HEC and their AC samples were characterized by Fourier transform infrared spectroscopy (FTIR-8400, Shimadzu) in the wave number range from 400 to 4000 cm⁻¹ using the KBr pellet method. Solid state ¹³C-NMR (with CP/MAS) spectra of AC samples were recorded on a Bruker Avance 400 MHz spectrometer (DRX400). To determine surface pH value, 0.4 g of AC sample was stirred in 20 ml deionized water overnight and then the pH value of the water phase was measured by pH meter (AB15, Fisher Accumet).
4.2.2.4 H$_2$S adsorption test

The assessment of H$_2$S adsorption capacity of an AC sample was conducted in the same setup and conditions described in section 3.2.2.4 of chapter 3.

4.3 Results and Discussion

4.3.1 The effect of solvation of HEC on the surface properties of the resultant AC

![SEM micrographs of HEC before solvation (a); HEC after solvation (b).](image)

*Figure 4.1 SEM micrographs of HEC before solvation (a); HEC after solvation (b).*
In the previous work, a low apparent density HEC powder (from Aldrich) was used as a particular precursor to synthesize an AC with great specific surface area.
Chapter 4 Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

and mesopore volume [128]. The side-chain hydroxyethyl group was found to be responsible to the generation of favorable polyaromatic hydrocarbon (PAH) rings, characterized by the sizes of them, the distribution of the thermally derived oxy-groups, and the bridging role of -(CH₂)ₓ- between PAHs, in the pyrolysis step.

We observed in the present study that the solvation of HEC drastically undermines the specific surface area of AC produced. This finding came from the esterification of HEC that was carried out in the binary solvent (NMP-acetone, v/v= ¼). Before examining the impact of esterification crosslinking on the surface properties of AC, we first clarified how the solvation of HEC alone causes loss of specific surface area and mesopore volume of the AC. The solvated HEC after it was dried served as the control sample (denoted by CTL) for the esterification crosslinking. It showed a clearly higher apparent density than its original form due to heavy entanglements of HEC chains (Fig. 4.1). More insightful, HEC shows an intense endothermic absorption in contrast to the CTL sample that reveals a weak glass transition step (Fig. 4.2). This endothermic peak resembles the fusion heat of a crystal and is considered to be originated from a regular chain packing that permits a large extent of hydrogen bonding. Whereas the salvation by NMP causes chaotic chain entanglements of HEC, which leaves behind a random chain packing upon drying and a low extent of inter-chain hydrogen bonding through the pendant hydroxyethyl groups. The loss of inter-chain H-bonding also results in a slight increase in the temperature at which the maximum pyrolysis rate takes place (Fig. 4.3). Such a
variation in chain-packing structure indeed brings about a substantial impact on the surface properties of the resulting ACs. AC47_HEC has much larger specific surface area and pore volume (1297 m²/g, 1.057 cm³/g) than AC47_CTL (160 m²/g, 0.094 cm³/g). In conclusion, in light of the solvation of HEC, a detrimental factor to the surface properties of the AC generated, the CTL sample was therefore a relevant benchmark for the investigation of the effect of crosslinking by esterification on the surface properties of ACs prepared.

### 4.3.2 Use of aliphatic and aromatic carboxylic acid crosslinkers

![Figure 4.4 DTG curves of HEC_TPA5p, HEC_SCA5p and HEC_CTL samples.](image)

*Figure 4.4 DTG curves of HEC_TPA5p, HEC_SCA5p and HEC_CTL samples.*
Figure 4.5 FT-IR spectra of AC40_TPA5p, AC40_SCA5p and AC40_CTL samples.

Figure 4.6: $^{13}$C-NMR spectra of AC40_TPA5p, AC40_SCA5p, AC40_PMA5p and AC40_CTL samples.
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The first question to understand is how the rigidity of a di-ester (-OCO-R-OCO-) segment, which interlocks HEC chains, affects pyrolysis of the crosslinked HEC. Two types of diacids, SCA and TPA, were used to investigate this question since the aliphatic SCA is softer than the aromatic TPA. The DTG diagrams of them and the CTL sample display different peak temperatures corresponding to the maximum pyrolysis rates, respectively, in the range from 200 to 450 °C (Fig. 4.4). The sequence of peak temperature indicates that both crosslinking and rigidity of crosslinking segment enhance thermal stability, viz. leading to an order of HEC_CTL < HEC_SCA5p < HEC_TPA5p. In addition, their decomposition rates (in %/°C, Table 4.1) follow a trend: HEC_CTL < HEC_TPA5p < HEC_SCA5p, meaning that the crosslinking promotes degradation rate and that the network upheld by the softer segment undergoes faster pyrolysis than that held by the rigid segment.

Table 4.1 DTG characteristic of AC samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak position (°C)</th>
<th>Derivative Mass (%/°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>HEC_CTL</td>
<td>311.5</td>
<td>0.823</td>
</tr>
<tr>
<td>HEC_BZA5p</td>
<td>311.5</td>
<td>1.069</td>
</tr>
<tr>
<td>HEC_SCA5p</td>
<td>335.5</td>
<td>1.286</td>
</tr>
<tr>
<td>HEC_TPA1p</td>
<td>318.2</td>
<td>0.833</td>
</tr>
<tr>
<td>HEC_TPA3p</td>
<td>340.7</td>
<td>0.957</td>
</tr>
<tr>
<td>HEC_TPA5p</td>
<td>371.7</td>
<td>1.100</td>
</tr>
<tr>
<td>HEC_PMA1p</td>
<td>324.0</td>
<td>0.822</td>
</tr>
<tr>
<td>HEC_PMA3p</td>
<td>356.2</td>
<td>0.916</td>
</tr>
<tr>
<td>HEC_PMA5p</td>
<td>363.0</td>
<td>1.109</td>
</tr>
</tbody>
</table>
The IR spectra of the carbonaceous substances, generated from pyrolysis of the above three HEC precursors at 400 °C for 1 h (Fig. 4.5), suggest that PAHs be the main constituent since the absence of the strong aliphatic C-H stretching bands from their fingerprint range of 2850-2960 cm\(^{-1}\). Besides this notable structural characteristic, the AC40_SCA5p sample shows phenol and ether functionalities (the in-plane bending of C-O-H at 1392 cm\(^{-1}\), the C-O-C stretching at 1090 cm\(^{-1}\)), quinonoid functional group (1638 cm\(^{-1}\)), and PAHs with a relatively weaker carbon skeleton stretching -C=C- (1560 cm\(^{-1}\)) band and a broad out-of-plane C-H bending band (875-508 cm\(^{-1}\)). This broad aromatic C-H band can be related to random and multiple substitutions on aromatic rings by carboxyl, phenol, quinonoid and C-C interconnection between rings because the aromatic C-H bending absorptions are sensitive to the substitution degree on aromatic ring and the number of adjacent C-H bonds [129]. Hence, an extensive overlapping of the frequencies of C-H bending is the result of complexly substituted aromatic rings. On the contrary, the IR spectrum of AC40_TPA5p shows weaker quinonoid functional group (1638 cm\(^{-1}\)) but stronger carboxylic (1690 cm\(^{-1}\)) than that of AC40_SCA5p. More significantly, the spectrum of AC40_TPA5p presents a sharp peak (1560 cm\(^{-1}\)) for PAH skeleton stretching and a group of the distinct out-of-plane C-H bending peaks (508, 740, and 822 cm\(^{-1}\)). Both C-H bending pattern and intensity serve as an indication of the presence of discrete and regularly substituted PAH rings with smaller sizes because PAH rings contain more adjacent C-H bonds. In contrast to these two spectra, the IR spectrum
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of AC40_CTL shows a far weaker but broader aromatic skeleton stretching band at near 1560 cm\(^{-1}\) and also a weak aromatic C-H bending at 875 cm\(^{-1}\), representing the isolated C-H bond substitution environment. This spectral characteristic suggests multiple substitutions on PAH rings. The above structure assignment based on IR spectra was further verified by \(^{13}\)C-NMR spectra (Fig. 4.6). The peak at near 130 ppm is the chemical shift of aromatic carbons and those in the range of 0-50 ppm are of aliphatic carbons. In addition, the chemical shifts of carboxylic and ketone are 175 and > 200 ppm, respectively. AC40_TPA5p shows two sharp \(^{13}\)C NMR aromatic peaks. In contrast to this, both AC40_CTL and AC40_SCA5p display a much broader single peak with the same chemical shift. The increase in peak width implies the presence of multiple substitutions on aromatic rings since the multiple substitutions implement more variety of chemical environments to aromatic rings. This relation has been found by the C-H IR bending frequency and intensity as afore elaborated. In addition, both AC40_SCA5p and AC40_TPA5p display a clear carboxylic carbon peak at 175 ppm but AC40_CTL does not. This suggests that the carboxylic acids of the crosslinker participate in the formation of PAHs. It is also worth to note that despite strong aromatic carbon peak appearing on the NMR spectra of AC40_CTL, only very weak aromatic C-H bending peaks could be perceived on its IR spectrum. It is an indication of the occurrence of large and heavily substituted PAH rings in AC40_CTL. Furthermore, although the saturated C-H stretching bands could be barely found on the IR spectra of the above three
Chapter 4 Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

pyrolyzed products, the presence of aliphatic carbons is clear on the $^{13}$C-NMR spectra of them. These aliphatic carbons could thus be mainly quaternary carbon type ( $\equiv$C-). Moreover, AC40_CTL and AC40_SCA5p contain greater amounts of aliphatic carbons than AC40_TPA5p. On the basis of these two spectral analyses, it can be concluded that crosslinking HEC by the rigid aromatic diacid enhances generation of relatively smaller and regularly substituted PAH rings in pyrolysis. But the soft aliphatic diacid leads to complex PAH rings in terms of substitutions on aromatic rings as well as a higher content of aliphatic quaternary carbons.

![Figure 4.7 Pore size distributions of AC47_TPA5p, AC47_SCA5p and AC47_CTL samples.](image)

When these three carbonaceous substances were further subjected to the CO$_2$-aid activation reaction (section 4.2.1) for creating pores, a correlation between
Chapter 4 Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

A porous AC structure achieved and the structure of its carbonaceous substance can be found (Fig. 4.7). The AC47_TPA5p displayed not only greater specific volume in the small mesopore sizes range (2.65 - 3.79 nm) than the control, AC47_CTL, but also large mesopores ranging from 5 to 30 nm. The smaller and regularly substituted PAH ring structure in AC40_TPA5p as previously justified favours the development of mesoporous carbon matrix. In contrast to this, the aliphatic quaternary carbons and the PAH rings with complicated substitutions, which constitute AC40_CTL, give rise to nil mesopores with pore size larger than 3 nm. As clarified above, AC40_SCA5p although possesses similar PAH ring structure to AC40_CTL, it shows obviously poorer surface properties than AC47_CTL (Table 4.2). Hence it is considered that AC40_SCA5p be less reactive than AC40_CTL during the activation treatment. It is likely that the aliphatic carbons, which are more complicated and have higher content in AC40_SCA5p than in AC40_CTL according to their $^{13}$C-NMR spectra, are responsible to lower pore-forming reactivity. This presumes that the quaternary aliphatic carbons fasten PAH rings and prevent them from undergoing structural repacking under the activation treatment conditions.
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<table>
<thead>
<tr>
<th>Sample</th>
<th>$A_{\text{BET}}$ (m$^2$/g)</th>
<th>$V_t$ (cm$^3$/g)</th>
<th>$V_{\text{micro}}$ (cm$^3$/g)</th>
<th>$V_{\text{meso}}$ (cm$^3$/g)</th>
<th>$V_{\text{meso}}/V_t$</th>
</tr>
</thead>
<tbody>
<tr>
<td>AC47_CTL</td>
<td>160</td>
<td>0.094</td>
<td>0.074</td>
<td>0.020</td>
<td>0.215</td>
</tr>
<tr>
<td>AC47_BZA5p</td>
<td>132</td>
<td>0.079</td>
<td>0.062</td>
<td>0.0163</td>
<td>0.208</td>
</tr>
<tr>
<td>AC47_SCA5p</td>
<td>47.9</td>
<td>0.038</td>
<td>0.022</td>
<td>0.016</td>
<td>0.417</td>
</tr>
<tr>
<td>AC47_TPA1p</td>
<td>289</td>
<td>0.217</td>
<td>0.132</td>
<td>0.085</td>
<td>0.319</td>
</tr>
<tr>
<td>AC47_TPA3p</td>
<td>390</td>
<td>0.332</td>
<td>0.178</td>
<td>0.154</td>
<td>0.464</td>
</tr>
<tr>
<td>AC47_TPA5p</td>
<td>185</td>
<td>0.236</td>
<td>0.085</td>
<td>0.151</td>
<td>0.640</td>
</tr>
<tr>
<td>AC47_PMA1p</td>
<td>200</td>
<td>0.125</td>
<td>0.093</td>
<td>0.033</td>
<td>0.260</td>
</tr>
<tr>
<td>AC47_PMA3p</td>
<td>361</td>
<td>0.298</td>
<td>0.166</td>
<td>0.132</td>
<td>0.444</td>
</tr>
<tr>
<td>AC47_PMA5p</td>
<td>243</td>
<td>0.219</td>
<td>0.112</td>
<td>0.107</td>
<td>0.489</td>
</tr>
</tbody>
</table>

4.3.3 Effects of crosslinking degree based on using TPA

*Figure 4.8 DTG curves of HEC_TPA1p, HEC_TPA3p, HEC_TPA5p and HEC_BZA5p samples.*
As TPA has been identified to be more effective than SCA as a crosslinker of HEC for the formation of mesoporous carbon matrix, the crosslinking degree of the HEC_TPA network was scrutinized to understand its effect on the final pore structure of carbon. The DTG curve of HEC_TPA shows that both the maximum pyrolyzing rate and the temperature of it rise with the increase of the crosslinking extent of TPA from 1 % to 5 % (Fig. 4.8), which reflects the network strengthening effect as it is normally known. The second control sample HEC_BZA5p, as defined by the symbol, was prepared by affixing benzoic acid (5 % of HEC) to HEC in order to benchmark the effect merely caused by the steric occupancy of benzene ring. As expected, the maximum decomposition temperature of HEC_BZA5p sample is below that of HEC_TPA1p (Table 4.1). This outcome shows that 1 % crosslinking
of terephthalate is more effective than 5 % grafting of benzoate to enhance thermal stability of HEC. Furthermore, the IR spectroscopy study (Fig. 4.9) on the pyrolytic products of these four precursors reveals that the crosslinking degree affected the generation of PAHs. The increase of crosslinking degree results in the stronger aromatic ring stretching and aromatic out-of-plane C-H bending bands. This trend is caused by the formation of higher concentrations of regularly-substituted PAH rings as justified in the above section. It is also comprehensible: the higher thermal decomposition rate at the higher temperature brought about more energetic cracking and hence produced in majority discrete and similar PAH rings. Regarding the pyrolysis products of the control sample, AC40_BZA5p, the IR spectrum of it contains very weak aromatic ring stretching band, which is similar to that of AC40_CTL as given in Fig. 4.5. Grafting benzoate groups to HEC promotes slightly thermal cracking rate in comparison with the HEC_CTL (Table 4.1). Hence, it is rational to consider that AC40_BZA5p also comprise of complexly-substituted PAHs and aliphatic carbons because of its similar IR spectrum to that of AC40_CTL.

The crosslinking degree of HEC_TPA series shows a strong effect on the generation of mesoporous structure of AC. In contrast to AC47_BZA5p that was derived from the second control sample, AC47_TPA1p obtained from the least crosslinked precursor displays even greater surface properties (Table 4.2), in particular, the mesopore sizes in the range from 2.65 to 15 nm (Fig. 4.10). In
correlation with their IR spectral identities as discussed above, we could find that smaller and regularly substituted PAH rings favours the generation of mesoporous carbon structure. Following this correlation, AC47_TPA3p shows approximately double mesopore volume greater than AC47_TPA1p over the same range of pore size. But increasing the crosslinking extent from 3 % to 5 % produces a reversed result. AC47_TPA5p shows a lower specific surface area and pore volume.

![Pore size distributions of AC47_TPA1p, AC47_TPA3p, AC47_TPA5p and AC47_BZA5p samples.](image)

**Figure 4.10** Pore size distributions of AC47_TPA1p, AC47_TPA3p, AC47_TPA5p and AC47_BZA5p samples.

Of the specific surface properties of these three ACs (1p to 5p), sample AC47_TPA3p manifests the highest magnitudes. Compared to AC47_TPA3p, AC47_TPA5p displays a quick shrinkage of micropore volume and expansion of the sizes of mesopores (Fig. 4.10). This phenomenon can be attributed to the stacking of
randomly oriented PAH rings because the smaller sizes of PAHs and the lower content of aliphatic carbon would encourage local graphitization at the activation temperature, which represses micropores but promotes formation of nano-scale mesopores locating between graphite domains [128].

4.3.4 Effect of increasing crosslinking arms

*Figure 4.11 FT-IR spectra of AC40_PMA1p, AC40_PMA3p, AC40_PMA5p and AC40_BZA5p samples.*
Following the above investigation, crosslinking HEC through using the tetraprotic acid, PMA, instead of the diprotic acid crosslinker was undertaken. This change aims to examine how the increase in the crosslinking arms at a crosslinking point shapes surface properties of the AC derived eventually. It was indeed observed by IR (Fig. 4.11) that the carbonaceous AC40_PMA series presented more complex aromatic carbon skeletons than the AC40_TPA series. This is due to the effect of crosslinking points upheld by PMA. Despite this difference in the pyrolysis products, both series display the similar trend of thermal durability in connection with the dosage of crosslinker used (Table 4.1). In addition to this resemblance, the AC47_PMA series also displays a similar pattern of pore size distributions with the variation of PMA % (Fig. 4.12) to that the AC47_TPA series shows (Fig. 4.10).
Hence, AC47_PMA3p has the highest specific surface area, micropore volume and mesopore volume, while AC47_PMA5p has the highest mesopore volume fraction. However, compared with the AC47_TPA series, the AC47_PMA series endowed no improvement on porous structures in particular the specific total pore and mesopore volumes (Table 4.2). To understand this outcome, we examined the $^{13}$C-NMR spectra of both AC40_PMA5p and AC40_TPA5p, which are the pyrolysis products as defined before. The former spectrum shows two weak aliphatic peaks at near 0 ppm and 75 ppm while the later spectrum (AC40_TPA5p) shows only an even weaker peak at about 30 ppm (Fig. 4.6). AC40_PMA5p also has broader aromatic carbon peaks than AC40_TPA5p, indicating the presence of more complicated substitutions on PAHs. The above characterizations suggest that the increase in number of carboxylic acid group on benzene ring will not lead to a better precursor than HEC_TPA for attaining an AC with improved pore volumes. This outcome can be attributed to the generation of PAHs with complicated substitutions and undesired aliphatic carbon component in the resultant pyrolysis products. In conclusion, the similar thermal stability both HEC_TPA and HEC_PMA present implies similar apparent crosslinking degrees existing in both networks. It is likely caused by the steric hindrance that impedes effective esterification of the four carboxylic arms of PMA during the formation of network. In consequence, an uneven distribution of crosslinking density and a greater number of the pendant carboxyl groups in the HEC_PMA samples complicate the pyrolysis products.
4.3.5 A study on the H$_2$S-removal by adsorption

![H$_2$S breakthrough curves of the AC samples.](image)

**Figure 4.13** H$_2$S breakthrough curves of the AC samples.

**Table 4.3** H$_2$S breakthrough capacity of AC samples

<table>
<thead>
<tr>
<th>Sample</th>
<th>Surface pH</th>
<th>Breakthrough Time (min)</th>
<th>Breakthrough Capacities</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>mg/g</td>
</tr>
<tr>
<td>AC47_CTL</td>
<td>9.6</td>
<td>33.7</td>
<td>3.76</td>
</tr>
<tr>
<td>AC47_BZA5p</td>
<td>8.2</td>
<td>21.6</td>
<td>2.40</td>
</tr>
<tr>
<td>AC47_SCA5p</td>
<td>9.2</td>
<td>5.3</td>
<td>0.59</td>
</tr>
<tr>
<td>AC47_TPA1p</td>
<td>9.0</td>
<td>35.8</td>
<td>3.98</td>
</tr>
<tr>
<td>AC47_TPA3p</td>
<td>8.6</td>
<td>63.0</td>
<td>7.01</td>
</tr>
<tr>
<td>AC47_TPA5p</td>
<td>8.4</td>
<td>29.9</td>
<td>3.32</td>
</tr>
<tr>
<td>AC47_PMA1p</td>
<td>9.4</td>
<td>44.9</td>
<td>5.00</td>
</tr>
<tr>
<td>AC47_PMA3p</td>
<td>8.9</td>
<td>50.6</td>
<td>5.64</td>
</tr>
<tr>
<td>AC47_PMA5p</td>
<td>8.6</td>
<td>45.2</td>
<td>5.03</td>
</tr>
</tbody>
</table>
The AC adsorbents obtained from the crosslinked HEC networks as described above were used as adsorbent to test their adsorption capability of removing hydrosulfide. H$_2$S adsorption capacity of an AC adsorbent is in principal governed by the two factors: (i) the porous structure, such as specific surface area, pore volume and pore size distribution, and (ii) the Lewis basic sites on surface such as pyrone and chromene type groups [130]. Figure 4.13 displays the H$_2$S-adsorption breakthrough curves of various AC samples tested. On the basis of what have been elucidated in the above sections, the curves as listed in the first column of Table 4.2 can be divided into three groups.

(i) Regarding the first three AC samples, they represent the group possessing the lowest surface properties. It can be seen that the H$_2$S adsorption capacity of these three samples is clearly depended on the specific surface area and micropore volume while the specific mesopore volume is noncritical.

(ii) Regarding the second group denoted by AC47_TPA, the same structural features determine their adsorption capacity of H$_2$S, in which sample AC47_TPA3p shows an adsorption capability 1.76 times greater than sample AC47_TPA5p because it has about twice surface area and micropore volume larger than the latter. However, this porous structural effect gives way to the effect of surface acid-base property when the H$_2$S adsorption performances of AC47_CTL and AC47_TPA5p were compared. The latter sample has somewhat higher surface area as well as micropore volume than the former one (Table 4.2) but a lower H$_2$S adsorption
capacity (Fig. 4.13). We are inclined that this reversed order be caused by the surface basic sites that have been identified to have higher concentration in the former than in the latter sample (Table 4.3). It is also worth of note that the surface acidity of the AC47_TPA series increases with the loading of TPA in the precursor.

(iii) Regarding the third group denoted by AC47_PMA, all the three samples manifest better H$_2$S adsorption capacities than AC47_CTL, which is consistent with their obviously larger porous features, $A_{\text{BET}}$ and $V_{\text{micro}}$, than that of the control sample. We also noticed that AC47_PMA1p despite having evidently lower porous features displayed a superior adsorption capability over AC47_TPA1p. The influence of surface basicity provided the support to this reversed order. Moreover, the three samples in the AC47_PMA group presented higher surface basicity than their counterparts in the AC47_TPA group. Although as concluded above, the 4-arm crosslinker PMA does not promote total and mesopore volumes, it does improve $A_{\text{BET}}$ and $V_{\text{micro}}$ in contrast to TPA when 5 % crosslinker is used. Hence AC47_PMA5p exhibited a greater H$_2$S adsorption capacity than AC47_TPA5p. Finally, we found that all the adsorbents listed in Table 4.3 have almost the same mean adsorption rate. It suggests that the involved H$_2$S removal process is a thermodynamically rather than kinetically controlled process.
Chapter 4 Mesoporous activated carbon structure originated from crosslinking hydroxyethyl cellulose precursor by carboxylic acids

4.4 Conclusions

This study investigated how crosslinking HEC by esterification affects the formation of porous carbon structure through the course of carbonization and consecutively activation. Four carboxylic acids (SCA, TPA, BZA and PMA) were used to conduct the investigation. The insights gained from this study provide the evidence that the polymer precursor structure affects the substitution and sizes of PAH rings as well as the formation of aliphatic carbons constituting the pyrolysis products. When the benzene-borne polyprotic acids, i.e. TPA and PMA, were used, the increase in crosslinking degree from 1 wt% to 5 wt% caused an optimal outcome that happens at ca. 3 wt%. FT-IR and $^{13}$C-NMR spectral studies, in correlation with the BET surface analysis, show that this outcome originates from an optimal sizes and regular substitution of PAHs. The complicated substitution, big sizes of PAHs, and the presence of aliphatic carbons in the carbonization products do not favour graphitization of these PAHs, which in turn sacrifice both micro- and mesopores and surface area. On the other hand, smaller PAHs although allow ready local graphitization, they stifle the extension of micropore channels. With the aim of examining local crosslinking density, 4-arm PMA was used to crosslink HEC. In contrast to TPA, PMA brings about complex PAHs and higher aliphatic carbon contents, they virtually impedes the development of mesopores as a result of hindrance to graphitization. The synthesized AC samples were tested by the removal of H$_2$S from gas phase. The surface area and micropore volume were identified to be
the overriding factor to determine the adsorption extent of H\textsubscript{2}S. In addition, the presence of surface basic sites is also an influential factor.
Chapter 5 Reinforcing $\text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ by $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

Purification of methane to remove sulfide species is a necessary step for the survival of a membrane reactor, especially the reforming catalyst in it. Compared with desulfurization, selection of membrane material is more important to the success of a membrane reactor, because the properties of material will determine the performance of membrane reactor, such as oxygen permeability, chemical stability and chemical strength. In this chapter, a dual-phase composite ceramic membrane has been investigated.

A ceramic composite consisting of fluorite $\text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}$ (CGO) an O$^{2-}$ ionic conductor, and perovskite $\text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ (LBFZ), a MEIC, was designed to reinforce mechanically vulnerable LBFZ phase. The two phases was compatible each other and only displayed little interfacial phase according to XRD characterizations. In contrast to this, more interfacial phase was observed between LBFZ and another popular ionic conductor $\text{Y}_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}$. Compared with LBFZ membrane, CGO-LBFZ composite membrane possessed higher mechanical strength under high oxygen partial pressure gradient after a long-time operation and better chemical stability in TPR test, although its oxygen permeation flux will decrease to
some extent due to reduction of LBFZ volume fraction. The relative CGO to LBFZ phase content was optimized to satisfy requirement for oxygen permeability and mechanical strength.

5.1 Introduction

Mixed electronic-ionic conductors (MEICs), possessing both oxygen vacancies and free electrons, have been widely studied for the applications in oxygen separation, solid oxygen fuel cells (SOFCs) and gas sensor. The single-phase mixed conducting materials are difficult to meet all the requirements for the application. Usually, the improvement in one property will cause the degradation in other properties. Dual-phase composite material was composed of one oxygen ionic conductor and one electronic conductor. It was suggested as the candidate, since the properties of the dual-phase membrane can be adjusted through the selection two types of single-phase materials.

\( \text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta} \) (LBFZ) [68] has a high oxygen ionic and electronic conductivity but low mechanical strength under high oxygen partial pressure gradient. In this work, LBFZ phase was combined with CGO (Ce\(_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta}\)) / YSZ (Y\(_{0.08}\text{Zr}_{0.92}\text{O}_{2-\delta}\)) phase to improve its chemical stability and mechanical strength. The composite membranes CGO-LBFZ and YSZ-LBFZ were fabricated by cold isostatic pressing (CIP) in a tubular configuration, because the tubular membrane is much easier to scale up and avoid the edge leakage than disk membrane. The results show that only CGO-LBFZ composite membranes have better chemical stability and
mechanical strength than the pure LBFZ membrane. In addition, the effects of different proportions of CGO and LBFZ phases on the performance of oxygen permeation were also studied.

5.2 Experimental

5.2.1 Preparation of ceramic powders and tubular composite membrane

The LBFZ and CGO powders were prepared by Pechini method. A stoichiometric amount of \( \text{La(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}, \text{Ba(NO}_3\text{)}_2, \text{Fe(NO}_3\text{)}_2\cdot9\text{H}_2\text{O}, \text{Zn(NO}_3\text{)}_2\cdot6\text{H}_2\text{O} \) and ethylenediaminetetraacetic acid (EDTA) was dissolved in DI water by molar ratio of 2:3:4:1:10 to get a solution. The pH of above solution was adjusted to 8-9 by ammonia and then the color of this solution would become dark brown. After that, a little polyvinyl alcohol (PVA) was added to the dark brown solution as thickener to get solution S1. A stoichiometric amount of \( \text{Ce(NO}_3\text{)}_3\cdot6\text{H}_2\text{O}, \text{Gd(NO}_3\text{)}_3\cdot6\text{H}_2\text{O} \) citric acid and glycine was dissolved in DI water by molar ratio of 4:1:5:5 to get solution S2. The above solutions S1 and S2 were dried and thickened at 80-100 °C until gels G1 and G2 were formed, respectively. The resultant gels were precalcined at 400 °C for 2 h and then were subjected to calcinations at 1200 °C for 2 h under air atmosphere. After calcinations, ceramic powders LBFZ and CGO were obtained from G1 and G2, respectively.
LBFZ powder was mixed with CGO or YSZ (Stanford Materials) powder by predetermined weight proportion (2:3, 3:2 and 4:1), and then the mixture was dispersed in a mixed solvent (toluene and methylethyl ketone, v/v=1:1), which contained polyvinylbutyral (Butiva-79, 2 wt% of the mixture), to form a slurry. The obtained slurry was ball-milled with zirconia balls for 1 day to make sure intensive mixing. Then the organic solvent was removed from the slurry, and the resultant powder was ground and sieved to a particle size smaller than 45 μm. The powder was filled into a tubular mold and pressed to 35,000 psi in a cold isostatic press (Avure Technologies Inc.). The green tubes were sintered at 1400 °C for 4 h under air atmosphere to obtain the tubular composite membrane. After calcinations, the thickness of the membrane is in the range of 0.9-1.0 mm. The sample was denoted by its composition and relative content. For example, CGO60-LBFZ40 signifies this sample was fabricated by 60 wt. % of CGO powder and 40 wt. % of LBFZ powder. Pure LBFZ sample was also prepared as the control sample. The relative density of all the fabricated membranes was higher than 97 %, which was estimated by Archimedes method.

5.2.2 Instrumental characterizations

The XRD patterns of samples were obtained by a diffraction meter (SHIMASZU XRD-6000, Cu Kα radiation) in the range of 20 to 80° with a scanning rate of 3 °/min and a step width 0.02°. Surface morphologies of the tubular membranes were observed by a scanning electron microscopy (SEM) instrument. The oxygen
temperature-programmed desorption (O\(_2\)-TPD) and the temperature-programmed reduction (TPD) tests were conducted on Autosorb-1 (Quantachrome Instruments). The scan range of temperature was from 50 to 950 °C with a heating rate of 10 °C /min. For O\(_2\)-TPD, 500 mg of sample and 80 mL/min of Helium as carrier gas were used in each test; for TPR, 60 mg of sample and 80 mL/min of 5% H\(_2\)/N\(_2\) as reducing gas were used for each test. The samples after TPR run are also examined by XRD, which are denoted with a suffix “R”.

### 5.2.3 Oxygen permeation test

![Diagram of the setup for the measurement of oxygen permeation flux.](image)

**Figure 5.1** The sketch of the setup for the measurement of oxygen permeation flux.

The oxygen permeability of the tubular composite membrane was measured by a setup as shown in Fig. 5.1. The tubular membrane was first coated with silver colloid and then a ceramic sealant, except the central part (2 cm) was left for oxygen
permeation. After drying, the two ends of the membrane were connected with two small alumina tubes by using the ceramic sealant. After that, the membrane was sealed in a bigger alumina tube and vertically placed in a tube furnace, which length (15 cm) is shorter than the length of the fabricated tubular membrane. 200 cm$^3$/min of air was introduced from the shell side of the membrane to provide oxygen, and 40 cm$^3$/min of helium gas was introduced from the inner side as the sweep gas. The oxygen content in the exit gas stream of the permeation side was examined and quantified by GC (PerkinElmer ARNEL, Clarus 500). The oxygen permeation flux ($J_{O_2}$, cm$^3$·cm$^{-2}$·min$^{-1}$) can be calculated by the Eq. 5.1:

$$J_{O_2} = \left( \frac{C_{O_2}}{79} - \frac{28}{32} \times \frac{C_{N_2}}{C_{O_2}} \right) \times \frac{F}{S}$$  \hspace{1cm} (5.1)

$$Leakage = \frac{21}{79} \times \frac{28}{32} \times \frac{C_{N_2}}{C_{O_2}} \times 100\%$$  \hspace{1cm} (5.2)

in which $C_{O_2}$ and $C_{N_2}$ are the exit concentrations of oxygen and nitrogen in the sweep gas, respectively, $F^{\text{out}}$ (cm$^3$·min$^{-1}$) is the flow rate of the exit gas in the inner side of the membrane, and $S$ (cm$^2$) is the surface area of the tubular membrane used for oxygen permeation. The leakage due to imperfect sealing was calculated by Eq. 5.2, and the relative leakage was less than 5 % in all the oxygen permeation tests.

5.3 Results and discussion

5.3.1 Phase stability of YSZ/CGO-LBFZ composite membrane

60 wt. % of ionic conductor (CGO and YSZ) and 40 wt. % of mixed conductor
Chapter 5 Reinforcing \( \text{La}_{0.4}\text{Ba}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta} \) by \( \text{Ce}_{0.8}\text{Gd}_{0.2}\text{O}_{2-\delta} \) to form a dual phase composite membrane for oxygen separation from air

(LBFZ) were used to fabricate the dual-phase composite membrane, which ensures the two phases to form a continuous or percolative network. In order to investigate the compatibility of LBFZ with CGO/YSZ, XRD patterns of CGO60-LBFZ40 and YSZ60-LBFZ40 powders sintered at 1400 °C were examined, as shown in Fig. 5.2 and Fig. 5.3, respectively. The XRD patterns of LBFZ, CGO and YSZ powders sintered at 1400 °C were also examined as the controls.

![XRD patterns of LBFZ, CGO and CGO60-LBFZ40](image)

*Figure 5.2 XRD patterns of LBFZ, CGO and CGO60-LBFZ40, (*) \( \text{Ba(CeO}_3 \) or \( \text{Ba(Ce}_{0.9}\text{Gd}_{0.1})\text{O}_{2.95} \).
In Fig. 5.2, it was observed that CGO exhibited a fluorite structure and LBFZ shows a perovskite structure. The diffraction peaks of CGO60-LBFZ40 can be classified into two kinds of peaks, corresponding to the peaks of CGO and LBFZ, respectively. In addition, there are minor new phases detected (2θ=28.72°, 41.14° and 50.88°) in the spectrum of CGO60-LBFZ40, which is attributed to the formation of Ba(CeO₃) (JCPDS 82-2425) or Ba(Ce₀.₉Gd₀.₁)O₂.₉₅ (JCPDS 81-1385) caused by interfacial reactions between CGO and LBFZ phases at high temperatures. In Fig. 5.3, besides the peaks corresponding to the YSZ and LBFZ phases, there are several new peaks detected (2θ=30.36°, 43.44°, 53.94° 63.16° and 71.66°) in the spectrum of YSZ60-LBFZ40. These peaks are assigned to the formation of BaZrO₃ (JCPDS 74-1299) due to the interfacial reactions between YSZ and LBFZ phases. The above
results reveal that Ba\(^{2+}\) possesses a lower chemical potential in CGO and YSZ phases than in LBFZ phase. The interfacial reaction in YSZ60-LBFZ40 composite is obviously more severe than that in CGO60-LBFZ40 composite, which means that CGO phase has a better compatibility with LBFZ phase than YSZ phase.

To investigate the chemical stability of composite membrane under reducing atmosphere, TPR tests were conducted, which results were shown in Fig. 5.4. For the profile of LBFZ, there are three reduction peaks at ca. 448, 705 and 919 °C, which are caused by the reduction of iron ions from high oxidation state to lower oxidation state. The first peak is attributed to the reduction of Fe\(^{4+}\) to Fe\(^{3+}\), and the second and third peak correspond to the reduction of Fe\(^{3+}\) to Fe\(^{3+}/Fe^{2+}\) and Fe\(^{3+}/Fe^{2+}\) to Fe\(^{2+}\), respectively. Similar results have also been reported by Gong et al. [68]. Compared with LBFZ, CGO60-LBFZ40 composite has a similar TPR pattern. However, there are two obvious differences: one is the decrease of peak intensity due to lower LBFZ content in the composite; the other is the shift of the peak around 650 °C towards a higher temperature, which is related with the improvement of chemical stability by the interactions of CGO and LBFZ phases in the composite. For the profile of YSZ60-LBFZ40, it shows a very different pattern relative to that of LBFZ, and it has two overlapped strong reduction peaks at ca. 525 and 650 °C. The severe interfacial reactions between YSZ and LBFZ phases make lots of Ba\(^{2+}\) ions diffuse into YSZ phase and then spoil the perovskite structure of LBFZ, which causes the iron ions in the YSZ60-LBFZ40 composite are more easily reduced than those in LBFZ.
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

Figure 5.4 TPR profiles of LBFZ, CGO60-LBFZ40 and YSZ60-LBFZ40.

Figure 5.5 XRD patterns of LBFZ, CGO60-LBFZ40 and YSZ60-LBFZ40 samples before and after TPR.
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

The samples after TPR were examined by XRD, as shown in Fig. 5.5, to investigate the change of phase structure under reducing atmosphere. For LBFZ and CGO60-LBFZ40, the XRD patterns after TPR keep the similar pattern of the original spectra and shift entirely to the lower angle, which means the expansion of the lattice due to the reduction of iron ions. Compared with the XRD pattern of YSZ60-LBFZ40 before TPR, there is a new phase detected at 44.66° in the XRD pattern after reduction, which is thought to be the iron-containing oxide. From the above discussions, it can be seen that CGO60-LBFZ40 composite has a much better chemical stability under reducing atmosphere than YSZ60-LBFZ40 composite.

5.3.2 Oxygen permeation performance of YSZ/CGO-based composite membrane

![Graph showing oxygen permeation fluxes of LBFZ, YSZ60-LBFZ40, and CGO60-LBFZ40 membranes as a function of temperature.]

*Figure 5.6* Oxygen permeation fluxes of LBFZ, YSZ60-LBFZ40 and CGO60-LBFZ40 membranes as a function of temperature.
Chapter 5 Reinforcing La_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{3-δ} by Ce_{0.8}Gd_{0.2}O_{2-δ} to form a dual phase composite membrane for oxygen separation from air

Oxygen permeation fluxes of the tubular composite membranes were tested as a function of temperature, which are shown in Fig. 5.6. LBFZ membrane has the highest oxygen permeation flux among the three membranes at the same temperature, and can achieve a flux as high as $0.835 \text{ cm}^3 \cdot \text{cm}^{-2} \cdot \text{min}^{-1}$ at 950 °C. The oxygen permeation flux of a composite membrane is mostly determined by the oxygen ionic conductivity of the components, if the electronic conductivity is much larger than the oxygen ionic conductivity in the membrane. In CGO60-LBFZ40 membrane, LBFZ phase has higher oxygen conductivity than CGO phase. Therefore, the addition of the CGO in the membrane will decrease the oxygen permeation flux to some extent. The other reason why CGO60-LBFZ40 membrane has a lower oxygen permeation flux than LBFZ membrane is that the formation of Ba(CeO$_3$) or Ba(Ce$_{0.9}$Gd$_{0.1}$)O$_{2.95}$ interface layer, which is thought to have lower oxygen ionic conductivity. For YSZ60-LBFZ40 membrane, it has extremely low oxygen permeation flux, which is attributed to the formation of BaZrO$_3$ interface layer, which will block the transport of oxygen ions between YSZ and LBFZ phases. Furthermore, the membrane material is ground to powder to examine its oxygen desorption at different temperatures, as shown in the O$_2$-TPD profile (Fig. 5.7). The intensity of desorption peak decreases in the order of LBFZ, CGO60-LBFZ40 and YSZ60-LBFZ40, which is consistent with the order of their oxygen permeation fluxes. For LBFZ and CGO60-LBFZ40 samples, there are two obvious peaks around 450 and 650 °C, which correspond to desorption of surface oxygen species and lattice oxygen species [131, 132], respectively. For YSZ60-LBFZ40 sample, it
can be seen that the oxygen desorption peak is very weak, which may be caused by the formation of BaZrO$_3$ interface layer due to strong interdiffusion between YSZ and LBFZ phases.

**Figure 5.7** $O_2$-TPD profiles of LBFZ, YSZ60-LBFZ40 and CGO60-LBFZ40 samples.

The tubular membranes showed different mechanical strengths after long time operation of oxygen permeation test. LBFZ membrane was very easy to have annular cracks and then broke. However, CGO60-LBFZ40 and YSZ60-LBFZ40 membranes had enough mechanical strength and no cracks were observed after long time operation. This was because LBFZ membrane has very high oxygen defects ($\delta=0.27$), which will result in a big structural mismatch in the membrane under different oxygen partial pressures. Thereafter, the structural mismatch will cause the accumulation of martial stress and then bring the formation of cracks. CGO and
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

YSZ phases have much lower oxygen defects than LBFZ phase, which will improve the mechanical strength of the composite membranes at the loss of some oxygen permeation fluxes. The morphologies of membranes before oxygen permeation are shown in SEM micrographs (Fig. 5.8). LBFZ membrane shows a bigger grain size than CGO60-LBFZ40 and YSZ60-LBFZ40 membranes. The LBFZ phase is embedded in the framework of CGO and YSZ phases of their respective composite membrane. The CGO and YSZ phases may improve the mechanical strength of composite membrane as the steel bar reinforces the concrete.
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

Figure 5.8 SEM micrographs of CGO60-LBFZ40 (a), LBFZ (b) and YSZ60-LBFZ40 (c) membranes sintered at 1400 °C for 4h.
5.3.3 Effects of relative content on chemical and phase stability of CGO-LBFZ membrane

According to the above discussions, the tubular composite membrane composed of CGO and LBFZ phases displayed good compatibility. In order to optimize the performances of the CGO-LBFZ composite membrane, the other two membranes with different relative content (CGO40-LBFZ60 and CGO20-LBFZ80) were fabricated. From the XRD patterns (Fig. 5.9) of CGO-LBFZ composites, it was found that they had a similar pattern with each other except peak intensity caused by different relative content. In addition, the intensity of diffraction peaks attributed to Ba(CeO$_3$) or Ba(Ce$_{0.9}$Gd$_{0.1}$)O$_{2.95}$ phases increased in order of CGO60-LBFZ40, CGO40-LBFZ60 and CGO20-LBFZ80. This means the interdiffusion between CGO and LBFZ phases becoming more severe with the increase of LBFZ content in the composite. The severe phase interdiffusion could cause the destruction of LBFZ and CGO phases and the formation of impurity phases. Therefore, the final performance of the CGO-LBFZ composite membranes will be greatly affected by the content of impurity phases.
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

Figure 5.9 XRD patterns of CGO-LBFZ samples before and after TPR.

Chemical stability of CGO-LBFZ composite powder under reducing atmosphere was investigated, as shown in Fig. 5.10. Since the iron ions in LBFZ phase are easily reduced by H$_2$ as discussed in section 5.3.1, the TPR profile mainly varies with content of LBFZ in the composite. The intensity of the first reduction peak, which is in the range of 300-550 °C, declines with the decrease of LBFZ content. What’s more, the second reduction peak, which is in the range of 700-850 °C, shifts to higher temperature with increase of CGO content. It can be concluded that CGO phase can reinforce LBFZ phase at higher temperature. From Fig. 5.9., it was found that XRD patterns of CGO-LBFZ composite powders after TPR test shift entirely to lower angel relative to the spectra before TPR, which means the
expansion of lattice structure. In order to further investigate the effects of CGO phase on LBFZ phase, the detailed constants of lattice structure are calculated and listed in Table 5.1. LBFZ phase in the CGO-LBFZ composite has a smaller lattice constant than that of pure LBFZ phase before or after TPR. Although the lattice constant of CGO phase in the composite also becomes larger after TPR due to reduction of Ce$^{4+}$ to Ce$^{3+}$, only a small amount of Ce$^{4+}$ is reduced because there is no obvious reduction peak attributed to it in the TPR profile (Fig. 5.9). In a word, CGO phase is more stable than LBFZ phase in reducing atmosphere and can limit the expansion of LBFZ lattice to improve its chemical stability in reducing atmosphere.

**Table 5.1 Lattice constant of CGO-LBFZ composite powders**

<table>
<thead>
<tr>
<th>Material</th>
<th>Before TPR (nm)</th>
<th>After TPR (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBFZ</td>
<td>$a_p = 0.39407$</td>
<td>$a_p = 0.39653$</td>
</tr>
<tr>
<td>CGO20-LBFZ80</td>
<td>$a_F = 0.54414$; $a_p = 0.39321$</td>
<td>$a_F = 0.54634$; $a_p = 0.39416$</td>
</tr>
<tr>
<td>CGO40-LBFZ60</td>
<td>$a_F = 0.54432$; $a_p = 0.39323$</td>
<td>$a_F = 0.54850$; $a_p = 0.39565$</td>
</tr>
<tr>
<td>CGO60-LBFZ40</td>
<td>$a_F = 0.54374$; $a_p = 0.39332$</td>
<td>$a_F = 0.54697$; $a_p = 0.39454$</td>
</tr>
</tbody>
</table>

$F$ stands for cubic fluorite phase of CGO; $P$ represents cubic perovskite phase of LBFZ.
5.3.4 Oxygen permeation performance of CGO-LBFZ membranes

The oxygen permeation results of CGO-LBFZ composite membranes are shown in Fig. 5.11. These three CGO-LBFZ composite membranes have very near oxygen permeation flux at different temperatures. CGO80-LBFZ20 has the highest oxygen permeation flux (0.606 cm$^3$·cm$^{-2}$·min$^{-1}$) at 950 ºC. In order to evaluate the block effect of the low conductive interdiffusion layer in CGO-LBFZ composite membranes, a theoretical oxygen permeation flux was calculated using the method reported by Zhu et. al [80]. Results of calculated oxygen permeation ($J_{O_2,cal}$) and experimental oxygen permeation ($J_{O_2,exp}$) are listed in the Table 5.2. The deviation

![Figure 5.10 TPR profiles of CGO-LBFZ samples.](image)
Chapter 5 Reinforcing La_{0.4}Ba_{0.6}Fe_{0.8}Zn_{0.2}O_{3-δ} by Ce_{0.8}Gd_{0.2}O_{2-δ} to form a dual phase composite membrane for oxygen separation from air

of $J_{O_2,exp}/J_{O_2,cal}$ from unity may imply the block degree of interdiffusion layer on the oxygen ionic transport in the CGO-LBFZ membranes. It can be seen that the value of CGO20-LBFZ80 has the largest deviation from unity in the three composite membranes. This means increasing LBFZ phase content in the CGO-LBFZ membrane cannot effectively improve the oxygen permeation flux to some extent. However, the $J_{O_2,exp}/J_{O_2,cal}$ value of CGO40-LBFZ60 has the smallest deviation from unity and then this composition, which is 40wt. % CGO-60 wt. % LBFZ, may be the optimal content for CGO-LBFZ composite membrane.

![Figure 5.11 Oxygen permeation fluxes of CGO-LBFZ composite membranes.](image)

**Figure 5.11** Oxygen permeation fluxes of CGO-LBFZ composite membranes.
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

Table 5.2 Oxygen permeation flux of CGO-LBFZ composite membrane at 950 °C

<table>
<thead>
<tr>
<th>Material</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>( \ln \left( \frac{p'<em>{O_2}}{p</em>{O_2}} \right) )</th>
<th>( J_{O_2,exp} )</th>
<th>( J_{O_2,cal} )</th>
<th>( \frac{J_{O_2,exp}}{J_{O_2,cal}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO20-LBFZ80</td>
<td>Tube</td>
<td>0.9</td>
<td>1.820</td>
<td>0.606</td>
<td>1.052</td>
<td>0.576</td>
</tr>
<tr>
<td>CGO40-LBFZ60</td>
<td>Tube</td>
<td>1.0</td>
<td>1.790</td>
<td>0.546</td>
<td>0.778</td>
<td>0.702</td>
</tr>
<tr>
<td>CGO60-LBFZ40</td>
<td>Tube</td>
<td>0.9</td>
<td>1.986</td>
<td>0.478</td>
<td>0.754</td>
<td>0.634</td>
</tr>
</tbody>
</table>

\( p'_{O_2} \) and \( p_{O_2} \) are the oxygen partial pressures at air side and sweeping side, respectively.

In addition, the CGO-LBFZ composite powders were also investigated by O$_2$-TPD (Fig. 5.12). From the profiles of O$_2$-TPD, it was observed that the three composite powders had similar oxygen desorption amount, compared with that of...
pure LBFZ in Fig. 5.7. It is reasonable to attribute this to the formation of interdiffusion layer between the CGO and LBFZ phases, which has low concentration of oxygen vacancies and then prevents the transport of oxygen species. Compared with CGO60-LBFZ40 sample, the other two samples have stronger desorption signal at higher temperate, which implies more desorption of lattice oxygen species. The results of O₂-TPD are consistent with the results of oxygen permeation test.

![Oxygen permeation fluxes of CGO-LBFZ membranes at 950 °C under different oxygen partial pressures.](image)

**Figure 5.13** Oxygen permeation fluxes of CGO-LBFZ membranes at 950 °C under different oxygen partial pressures.

The oxygen permeation fluxes of the membranes under different partial gradient were examined to study the limiting process of oxygen transport. The oxygen partial gradient was changed by adjusting the helium flow rate in the sweep
Fig. 5.13 shows the oxygen permeation fluxes at 950 °C with different oxygen partial gradients. The Wager theory shows that there is a linear relationship between the oxygen permeation flux and oxygen partial gradient, if the oxygen transport process is limited by the bulk diffusion. For pure LBFZ membrane, the oxygen flux increases almost linearly with the oxygen partial gradient, which indicates that the oxygen transport process is mainly limited by the bulk diffusion. For the CGO-LBFZ composite membranes, the oxygen transport process is mainly controlled by the surface exchange reaction. The obvious surface exchange limitation may be caused the low membrane surface area, since the membrane was sintered at a temperature as high as 1400 °C and no additional porous layer was coated. CGO20-LBFZ80 and CGO40-LBFZ60 membranes displayed similar oxygen flux under different oxygen partial gradient and had higher oxygen permeation flux than CGO60-LBFZ40 membrane. An oxygen permeation flux of 0.84 cm\(^3\)·cm\(^{-2}\)·min\(^{-1}\) can be achieved by CGO40-LBFZ60 membrane under a high oxygen partial gradient at 950 °C.

### 5.4 Conclusions

LBFZ-based composite tubular membranes were studied in this work. CGO as a chemically inert phase show much better compatibility with LBFZ than YSZ phase. The TPR and XRD tests reveal that CGO-LBFZ composite has a better chemical stability than pure LBFZ under reducing atmosphere and the LBFZ phase in the
Chapter 5 Reinforcing La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ by Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ to form a dual phase composite membrane for oxygen separation from air

composite can keep its perovskite structure after TPR. Although LBFZ membrane displayed higher oxygen permeation flux than the composite membranes, its high oxygen vacancy will also cause material stress and fractures in membrane under high oxygen partial gradient. However, CGO-LBFZ composite membranes show enough mechanical strength. Finally, the composition of CGO-LBFZ composite membrane was optimized; it was found that the oxygen permeation flux didn’t increase proportionally with the content of LBFZ because of the inter-phase diffusion. CGO40-LBFZ60 membrane can have an oxygen flux of 0.84 cm$^3$·cm$^{-2}$·min$^{-1}$ at an oxygen partial gradient of 21 kPa/1.1 kPa at 950 ºC.
Chapter 6 The effects of Ba\(^{2+}/Sr^{2+}\) in La\(_{0.2}\)Ba\(_x\)Sr\(_{1-x}\)Fe\(_{0.8}\)Zn\(_{0.2}\)O\(_{3-\delta}\) perovskite oxides on chemical stability and oxygen permeability

Compositing fluorite Ce\(_{0.8}\)Gd\(_{0.2}\)O\(_{2-\sigma}\) (CGO) with perovskite La\(_{0.4}\)Ba\(_{0.6}\)Fe\(_{0.8}\)Zn\(_{0.2}\)O\(_{3-\delta}\) (LBFZ) satisfactorily overcomes fragile mechanical strength of the single LBFZ membrane under oxygen permeation condition. These two ceramic phases are compatible and hence such trait allows for attaining a gas-tight matrix upon sintering although a trivial interfacial diffusion occurs between them. Contrary to this combination when Y\(_{0.08}\)Zr\(_{0.92}\)O\(_{2-\sigma}\) (YSZ) is used in place of CGO, a far deeper interfacial diffusion takes place, deteriorating lattice oxygen conductivity. Incorporation of CGO into LBFZ brings about a reduction in reducibility and oxygen desorbility of the LBFZ phase. In order to tackle the drawback of diffusion of Ba\(^{2+}\) ion to CGO phase, the LBSFZ perovskite oxides were proposed. Doping the A-site of LBFZ by using a mixture of alkaline earth metal ions (Sr\(^{2+}/Ba^{2+}\)) can lead the adjustment of the structural and chemical stability and also oxygen permeability. The LBSFZ oxides were characterized by XRD, TPR, O\(_2\)-TPD, FESEM, and oxygen permeation test. The results demonstrated that Ba\(^{2+}\) is better than Sr\(^{2+}\) in doping the A-site of LBSFZ perovskite membrane; however the presence of Sr\(^{2+}\) ion together with Ba\(^{2+}\) in the A-site may retard migration of Ba\(^{2+}\) ions towards CGO.
Chapter 6 The effects of $\text{Ba}^{2+}/\text{Sr}^{2+}$ in $\text{La}_{0.2}\text{Ba}_{x}\text{Sr}_{0.8-x}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ perovskite oxides on chemical stability and oxygen permeability

phase. The desired substitution stoichiometry of $\text{Sr}^{2+}$ for $\text{Ba}^{2+}$ was investigated; LBSFZ-6 demonstrated the highest oxygen permeation flux and the best chemical stability under reducing atmosphere.

6.1 Introduction

Perovskite oxides ($\text{ABO}_3$) have been widely applied to prepare MEIC membranes for oxygen separation from air, as these oxides have both high oxygen ionic and electronic conductivities. The larger A-site cations can be rare-earth or alkaline-earth ions and smaller B-site cations are the transition metal ions. The properties of perovskite-type materials, such as electrical conductivity and chemical or structural stability can be tuned by the substitution of A-site and B-site cations by aliovalent cations. When A-site cations are partially substituted by lower valence state cations, the oxygen vacancies and the valence state of B-site cations will be changed accordingly to maintain the electrical neutrality of the perovskite [133]. For example, Teraoka et al. [134] studied the $\text{La}_{1-x}\text{Sr}_x\text{Co}_{0.4}\text{Fe}_{0.6}\text{O}_{3-\delta}$ (LSCF; $x=0, 0.4, 0.8$ and 1) perovskite system. It was found that the oxygen permeation flux of LSCF membrane was improved with the increase of Sr content, due to the formation of oxygen vacancies caused by the substitution of $\text{La}^{3+}$ by $\text{Sr}^{2+}$. When A-site is doped by different divalent cations, their effects on the perovskite membranes are also different. Tsai et al. [76] investigated the $\text{La}_{0.4}\text{A'}_{0.6}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_{3-\delta}$ (LA'FC; $\text{A'}=$Ca, Sr and Ba) perovskite membranes, which exhibited an oxygen permeation flux in the order of $\text{A'}=\text{Ba} > \text{Ca} > \text{Sr}$. This result was attributed to the higher concentration of
oxygen vacancies and smaller metal-oxygen bond energy in Ba-doped membrane than those in Sr-doped or Ca-doped membranes. However, a contrary result was obtained by Stevenson et al. [135], in which the oxygen permeation flux of thick LA’FC membrane decreases as A’=Sr > Ba > Ca. The better performance of Sr-doped membrane than Ba-doped membrane was attributed to the smaller size of Sr$^{2+}$ than Ba$^{2+}$ and then the higher mobility of oxygen vacancies in Sr-doped membrane. In addition, Shao et al. [133] reported that the phase stability of SrCo$_{0.8}$Fe$_{0.2}$O$_{3-\delta}$ membrane was improved through the doping of Ba in A-site, which is due to the larger size of Ba$^{2+}$ than Sr$^{2+}$.

In the previous work, it was found that the Ba$^{2+}$ ions are easy diffusing into fluorite phases to form low ion-conductive impurity phases, when La$_{0.4}$Ba$_{0.6}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ (LBFZ) perovskite oxide was combined with YSZ or CGO fluorite oxides to fabricate dual-phase MEIC membranes. In addition, it has been reported that barium is reactive to CO$_2$ while strontium has the highest tolerance [136]. In this work, La$_{0.2}$Ba$_{x}$Sr$_{1-x}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ (LBSFZ, 0.2≤x≤0.6) perovskite oxides were investigated by replacing part of Ba$^{2+}$ with Sr$^{2+}$, for the further development of dual-phase MEIC membrane reactor. The effects of Ba$^{2+}$ and Sr$^{2+}$ cations on the oxygen permeation flux and chemical stability of LBSFZ membranes were studied. The results exhibited that the oxygen permeation flux of LBSFZ membranes decreased slightly with the increase of Sr content, while their chemical stability under reducing atmosphere were similar.
Chapter 6 The effects of Ba\(^{2+}/\text{Sr}^{2+}\) in La\(_{0.2}\text{Ba}_{x}\text{Sr}_{0.8-x}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}\) perovskite oxides on chemical stability and oxygen permeability

6.2 Experimental

6.2.1 Preparation of ceramic powders and tubular membrane

The LBSFZ perovskite oxides were prepared by Pechini method. A stoichiometric amount of La(NO\(_3\))\(_3\)·6H\(_2\)O, Ba(NO\(_3\))\(_2\), Sr(NO\(_3\))\(_2\), Fe(NO\(_3\))\(_2\)·9H\(_2\)O, Zn(NO\(_3\))\(_2\)·6H\(_2\)O was dissolved in EDTA-NH\(_3\)·H\(_2\)O (ethylenediaminetetraacetic acid and ammonia) solution by a predetermined molar ratio to obtain a dark brown solution. After that, a little polyvinyl alcohol (PVA) was added to the dark brown solution as thickener and then the solution was dried at 80-100 °C until a gel was formed. The resultant gel was calcined under air atmosphere at 400 °C for 1 h and then 1200 °C for 2 h with a heating rate of 3 °C/min. After calcinations, ceramic powders of LBSFZ were obtained. For a particular powder, it was denoted by LBSFZ with one-digit suffix, which means the content of Ba\(^{2+}\). For example, LBSFZ-2 stands for La\(_{0.2}\text{Ba}_{0.2}\text{Sr}_{0.6}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}\) (x=0.2).

LBSFZ powder was dispersed in a mixed solvent (toluene and methylethyl ketone, v/v=1:1), which contained an amount of Butiva-79, to form a slurry. The obtained slurry was ball-milled with zirconia balls for 1 day to make sure intensive mixing. Then the organic solvent was removed from the slurry, and the resultant powder was ground and sieved to a particle size smaller than 45 μm. The powder was filled into a tubular mold and pressed to 35,000 psi in a cold isostatic press (Avure Technologies Inc.). The green tubes were sintered at 1300 °C for 4 h under air atmosphere to obtain the dense tubular membranes with thickness of 0.9-1.0 mm.
The relative density of these membranes was higher than 97%, which was estimated by Archimedes method.

### 6.2.2 Instrumental characterizations

The XRD patterns of samples were obtained by a diffraction meter (Bruker D8 Advance, Cu Kα radiation) in the range of 20 to 80° with a scanning rate of 3°/min and a step width 0.02°. Surface morphologies of the tubular membranes were observed by a field emission scanning electron microscopy (FESEM, JEOL JSM-5600) instrument. O₂-TPD and TPD tests were conducted by the methods introduced in Section 5.2.2 of Chapter 5. The samples after TPR run are also examined by XRD, which are denoted with a suffix “R”.

### 6.2.3 Oxygen permeation test

The oxygen permeation fluxes of LBSFZ membranes were tested by the setup and method described in section 5.2.3 of chapter 5.

### 6.3 Results and Discussion

#### 6.3.1 An investigation into the crystal structure of LBSFZ oxides

Geometric Goldschmidt tolerance factor (t), as defined in Eq. 2.4, is wildly used to evaluate the structural stability of perovskite oxides ABO₃. When the value of t is between 0.78 and 1.05, the cubic perovskite structure can be preserved. As
LBSFZ oxide has more than one cations in A and B sites, the ionic radii \( r_A \) and \( r_B \) in the equation can be replaced by the weighted arithmetic mean radii of A and B cations. In addition, the radius of iron cation varies with its valence state. Hence, the tolerance factors of LBSFZ oxides were calculated according to the different valence state of Fe (as shown in Table 6.1). The values of ionic radius are as follows: La\(^{3+}\) (1.36 Å), Ba\(^{2+}\) (1.61 Å), Sr\(^{2+}\) (1.44 Å), Fe\(^{4+}\) (0.585 Å), Fe\(^{3+}\) (0.645 Å), Fe\(^{2+}\) (0.78 Å), Zn\(^{2+}\) (0.74 Å) and O\(^{2-}\) (1.4 Å) [137]. In oxidative atmosphere, iron will exist in the form of Fe\(^{4+}/\)Fe\(^{3+}\); while in reducing atmosphere, it will exist in the form of Fe\(^{3+}/\)Fe\(^{2+}\). For example, the tolerance factor of LBSFZ-2 will vary between 1.002 and 0.979 in oxidative atmosphere and in the range of 0.979 to 0.930 under reducing atmosphere. From Table 6.1, it was found that all these tolerance factors were in the range required for a stable perovskite structure and they became greater with the increase of Ba\(^{2+}\) mole fraction. When the tolerance factor is much closer to the unity, the perovskite structure is expected to be more stable.

<table>
<thead>
<tr>
<th>Material</th>
<th>Mole fraction</th>
<th>Tolerance factor (t)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>La(^{3+})</td>
<td>Ba(^{2+})</td>
</tr>
<tr>
<td>LBSFZ-2</td>
<td>0.2</td>
<td>0.2</td>
</tr>
<tr>
<td>LBSFZ-3</td>
<td>0.2</td>
<td>0.3</td>
</tr>
<tr>
<td>LBSFZ-4</td>
<td>0.2</td>
<td>0.4</td>
</tr>
<tr>
<td>LBSFZ-5</td>
<td>0.2</td>
<td>0.5</td>
</tr>
<tr>
<td>LBSFZ-6</td>
<td>0.2</td>
<td>0.6</td>
</tr>
</tbody>
</table>

Table 6.1 Variation of the tolerance factor of LBSFZ with Sr\(^{2+}\) doping extent
The structural stability of LBSFZ powders can also be exhibited from their XRD patterns, as seen in Fig. 6.1. LBSFZ-4 shows the pure cubic perovskite phase, while the other samples show the perovskite phases with trace impurity phases, which are assigned to strontium iron oxides for LBSFZ-2 and LBSFZ-3 and barium iron oxides for LBSFZ-5 and LBSFZ-6. It has been reported by Gong et al. [68] that the tolerance factor is important to the formation temperature of perovskite solid solution and a larger tolerance factor means a higher energy barrier for the formation of cubic perovskite structure. Therefore, it was speculated that the tolerance factor of LBSFZ-4 was the nearest to the unity and then can form the pure perovskite structure at 1200 °C. For the other samples, their tolerance factors deviate larger from the unity than that of LBSFZ-4, so a temperature higher than 1200 °C may be needed to obtain the pure perovskite structure.

**Figure 6.1** XRD patterns of LBSFZ powders sintered at 1200 °C for 2 h. (●) Strontium iron oxide and (♦) Barium iron oxide.
Chapter 6 The effects of Ba$^{2+}$/Sr$^{2+}$ in La$_{0.2}$Ba$_x$Sr$_{0.8-x}$Fe$_{0.8}$Zn$_{0.2}$O$_{3-\delta}$ perovskite oxides on chemical stability and oxygen permeability

6.3.2 Chemical and phase stability

The chemical stability of LBSFZ oxide under reducing atmosphere was examined by TPR test. From the TPR profiles in Fig. 6.2, it was found that all these oxides had a similar pattern, in which these peaks were attributed to the reduction of iron ions from high oxidation state to lower oxidation state. The peaks between 250 and 550 °C are attributed to the reduction of Fe$^{4+}$ to Fe$^{3+}$, the peaks in the range of 550 to 850 °C result from the reduction of Fe$^{3+}$ to Fe$^{3+}$/Fe$^{2+}$ and the peaks higher than 850 °C may be caused by the reduction of Fe$^{3+}$/Fe$^{2+}$ to Fe$^{2+}$. Compared with the TPR result of LBFZ in chapter 5, the reduction peaks of LBSFZ oxides are stronger, which implies LBSFZ oxides are more vulnerable than LBFZ oxide under reducing atmosphere. This vulnerability of LBSFZ oxides is caused by the larger doping extent of divalent cations (Ba$^{2+}$ and Sr$^{2+}$) in A site (LBSFZ=80% and LBFZ=60%) and then more oxygen vacancies. The major difference among the TPR profiles of LBSFZ oxides is their peak positions around 450 °C, which are in the order of LBSFZ-6 ≈ LBSFZ-5 > LBSFZ-4 ≈ LBSFZ-2 > LBSFZ-3. The temperatures of reduction peaks can reflect their relative chemical stabilities under reducing atmosphere. Generally, LBSFZ oxides with larger Ba-doping extent present a higher reduction temperature. This is reasonable because Ba$^{2+}$ has a larger ionic radius than Sr$^{2+}$ and then the LBSFZ oxides substituted by more Ba$^{2+}$ can improve chemical and structural stability under reducing atmosphere, as reported by other researchers [76, 133]. In addition, from the observation of tolerance factors under reducing
atmosphere in Table 6.1, LBSFZ-6 and LBSFZ-5 have the tolerances factors much nearer to the unity, which make them have better structural stability than other samples.

![Graph showing TPR profiles of LBSFZ and LBFZ perovskite oxides sintered at 1200 °C.](image)

**Figure 6.2** TPR profiles of LBSFZ and LBFZ perovskite oxides sintered at 1200 °C.

In order to investigate the effects of reducing atmosphere on phase stability, LBSFZ oxides after TPR were examined by XRD, as shown in Fig. 6.3. All LBSFZ oxides could preserve the perovskite structure but with phase decompositions to some extent. For LBSFZ-4, LBSFZ-5 and LBSFZ-6, the new phase formed is primarily the Ba₅SrLa₂Fe₄O₁₅; for LBSFZ-2 and LBSFZ-3, the new phases are assigned to La₀.₈Sr₀.₂FeO₃ and Ba₅SrLa₂Fe₄O₁₅. From the XRD patterns, it was inferred that LBSFZ-5 and LBSFZ-6 perovskite oxides had a better chemical stability under reducing atmosphere, because their impurity phases were much less than those of other samples. What’s more, the lattice constants of cubic perovskite...
phase in LBSFZ oxides before and after TPR were listed in Table 6.2. The lattice constants after TPR were greater than those before TPR due to the reduction of iron ions. The expansion of LBSFZ-6’s lattice after TPR was the largest among all samples, which may imply its lattice can keep the perovskite structure with the largest extent of lattice deformation.

Figure 6.3: XRD patterns of LBSFZ powders after TPR. JCPDS files: (*) 35-1480 La$_{0.8}$Sr$_{0.2}$FeO$_3$ and (°) 79-2142 Ba$_5$Sr$_2$La$_2$Fe$_4$O$_{15}$. 
### Table 6.2 Lattice constant of cubic perovskite phase in LBSFZ oxides

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice constant (before TPR, Å)</th>
<th>Lattice constant (after TPR, Å)</th>
<th>Lattice expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>LBSFZ-2</td>
<td>3.9095</td>
<td>3.9290</td>
<td>0.499</td>
</tr>
<tr>
<td>LBSFZ-3</td>
<td>3.9170</td>
<td>3.9418</td>
<td>0.633</td>
</tr>
<tr>
<td>LBSFZ-4</td>
<td>3.9370</td>
<td>3.9693</td>
<td>0.820</td>
</tr>
<tr>
<td>LBSFZ-5</td>
<td>3.9503</td>
<td>3.9822</td>
<td>0.808</td>
</tr>
<tr>
<td>LBSFZ-6</td>
<td>3.9591</td>
<td>3.9997</td>
<td>1.025</td>
</tr>
</tbody>
</table>

#### 6.3.3 Oxygen permeation performance of LSBFZ membranes

The oxidation properties of LBSFZ perovskite oxides at different temperatures were examined by O$_2$-TPD, as shown in Fig. 6.4, through which can reflect desorption of oxygen and the generation of oxygen vacancies. For LBSFZ samples, there are one obvious peak around 450 °C and a rising in the range of 500-900 °C, which correspond to desorption of surface oxygen species at low temperatures and lattice oxygen species at high temperatures. LBSFZ oxides have similar peak areas in the whole temperature range, which means they bear a similar concentration of oxygen vacancies under helium atmosphere. LBSFZ-4, LBSFZ-5 and LBSFZ-6 have relative stronger peaks at 450 °C and weaker risings from 500 to 900 °C than LBSFZ-2 and LBSFZ-3. The stronger desorption peaks at low temperatures may indicate the lower activation energy for the oxygen transportation, which is dependent on the bonding energy of metal-oxygen in the perovskite lattice. Compared with LBFZ perovskite oxide, LBSFZ have a higher A-site doping level and then higher concentration of oxygen vacancies. However, LBFZ has lower
activation energy for oxygen transportation than LBSFZ oxides due to LBFZ’s stronger desorption peak around 325 °C.

Figure 6.4 O$_2$-TPD profiles of LBSFZ and LBFZ perovskite oxides sintered at 1200 °C.
Chapter 6 The effects of $\text{Ba}^{2+}/\text{Sr}^{2+}$ in $\text{La}_{0.2}\text{Ba}_{x}\text{Sr}_{0.8-x}\text{Fe}_{0.8}\text{Zn}_{0.2}\text{O}_{3-\delta}$ perovskite oxides on chemical stability and oxygen permeability
Figure 6.5 Outer surface FESEM micrographs of fresh LBSFZ membranes: (a) LBSFZ-2; (b) LBSFZ-4; (c) and (d) LBSFZ-6.
The outer surface morphologies of fresh LBSFZ membranes are shown in Fig. 6.5. All these three LBSFZ membranes show the clear grain-boundary structures with grain size from several to tens micron. A dense membrane with coarse grain-boundary structures is thought to be favorable for the oxygen permeation, because the grain boundaries normally have a negative effect on the permeation. In addition, there are many terrace structures existing on the surface of LBSFZ membranes, which may be caused by the thermodynamically driven contraction to lower surface energy at high temperatures.

![Figure 6.6 Oxygen permeation fluxes of LBSFZ membranes as a function of temperature.](image)

**Figure 6.6** Oxygen permeation fluxes of LBSFZ membranes as a function of temperature.

Oxygen permeation fluxes of the tubular LBSFZ membranes were tested as a function of temperature as shown in Fig. 6.6. LBSFZ-6 and LBSFZ-4 membranes
show similar oxygen permeation fluxes in the temperature range from 800 to 950 °C, which are higher than that of LBSFZ-2 membranes. The results of oxygen permeation are consistent with the results of O$_2$-TPD tests. LBSFZ-6 has the highest oxygen permeation fluxes among the three membranes and can achieve a flux as high as 1.07 cm$^3$ cm$^{-2}$ min$^{-1}$ at 950 °C. It was concluded that the Ba-doping in A-site of perovskite structure was more favorable for oxygen transport than the Sr dopant, due to lower bonding energy of Ba-O than Sr-O. However, when the Ba-doping level was higher than a certain value, its contribution to oxygen transport would be limited, which can be demonstrated by the similar oxygen permeation fluxes of LBSFZ-4 and LBSFZ-6. This phenomenon is caused by the larger ionic radius of Ba$^{2+}$ than Sr$^{2+}$, because larger Ba$^{2+}$ will decrease the free volume of perovskite lattice and then inhibit the transport of oxygen vacancies. However, the mechanical strength of pure perovskite LBSFZ membrane, especially for tubular configuration, is still not enough. When there was an oxygen partial pressure gradient exerted across LBSFZ membrane, the tubular membrane has a higher oxygen vacancy concentration at the lower oxygen partial pressure side, which will cause a greater lattice expansion than the other side of the membrane. This will lead a stress in the membrane. After a long-time oxygen-permeation run, the leakage was found to be deteriorated, caused by the formation of cracks in the membrane (Fig. 6.7).
6.4 Conclusions

The effects of A-site dopants Ba$^{2+}$ and Sr$^{2+}$ on the properties of MEIC material LBSFZ were studied. The different doping composition will affect the structural stability and chemical stability of perovskite LBSFZ. Through the characterizations of TPR and XRD, it was found that Ba$^{2+}$ can stabilize the perovskite structure better than Sr$^{2+}$ under the reducing atmosphere due to its larger ionic radius. The oxygen permeation tests showed that LBSFZ membranes with higher Ba-doping level exhibited higher oxygen permeation flux from 800 to 950 °C under an air/He gradient. The O$_2$-TPD test manifested that LBSFZ perovskite oxide with higher Ba-doping level had lower activation energy for oxygen transport. LBSFZ-6
membrane could achieve an oxygen permeation flux of 1.07 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 °C, but its mechanical strength was not sustainable for a long-time run.
Chapter 7 Development of tubular CGO-LBSFZ MEIC membrane reactor to combine oxygen separation with POM

LBSFZ perovskite oxides developed in chapter 6 were combined with CGO phase to fabricate CGO-LBSFZ composite membranes. The CGO-LBSFZ composites were characterized by XRD, TPR, O$_2$-TPD, FESEM and oxygen permeation test, which showed that CGO-LBSFZ-2 had the desired phase compatibility, chemical stability and oxygen permeability. Hence, a membrane reactor made of CGO-LBSFZ-2 composite and Ni-based catalyst was assembled for POM into syngas. The performance of this membrane reactor was studied under different temperatures and feed gases, and a high oxygen permeation flux of 6.14 cm$^3$·cm$^{-2}$·min$^{-1}$ can be obtained.

7.1 Introduction

MEIC membrane reactors have been studied by many researchers due to their great potential application for oxygen separation and conversion of methane into syngas. The MEIC materials can be perovskite oxide, metallic-ceramic composite and ceramic-ceramic composite. The ideal MEIC material should meet several basic requirements, such as high oxygen permeability, high chemical stability under reducing atmosphere, enough mechanical strength, low membrane fabrication or material costs. Based on these considerations, ceramic-ceramic composite stands out
as the most promising candidate for the MEIC material.

Mixed conductive ceramic-ceramic composites were first investigated by Kharton et al. [79, 138-140], in which Ce$_{0.8}$Gd$_{0.2}$O$_{2-\delta}$ was used as oxygen ionic conductive phase and La$_{0.7}$Sr$_{0.3}$MnO$_{3-\delta}$ was functioned as electronic conductive phase. It was found that the inter-phase diffusion in the composites would decrease the oxygen ionic transport but have less effect on electronic conduction. A mixed conductive phase was suggested to substitute the pure electronic conductive phase in the composite membrane to enhance the oxygen ionic conduction by Zhu’s group [80]. They fabricated the $(Ce_{0.8}Gd_{0.2}O_{2-\delta})_{0.55}-(Gd_{0.2}Sr_{0.8}FeO_{3-\delta})_{0.45}$ membrane, which exhibited a high oxygen permeation flux of 0.80 cm$^3$·min$^{-1}$·cm$^{-2}$ under air/He and 5.0 cm$^3$·min$^{-1}$·cm$^{-2}$ under POM reducing atmosphere at 950 °C, respectively. The dual-phase membranes composed of Fe-based perovskite oxides and Ce-based fluorite oxides were selected as the best candidates in their recent work, after careful consideration of ionic conductivity, stability under reducing atmosphere and phase compatibility. $(Ce_{0.85}Sm_{0.15}O_{1.925})_{0.75}-(Sm_{0.6}Sr_{0.4}FeO_3)_{0.25}$ dual-phase membrane displayed the good chemical stability and oxygen permeability [141].

In this work, LBFSZ perovskite oxides developed in Chapter 6 were combined with CGO fluorite oxide to fabricate tubular dual-phase membranes. It was expected that the inter-phase diffusion in CGO-LBSFZ membrane could be greatly reduced and then its oxygen permeability would be enhanced, compared with that of CGO-LBFZ membrane in chapter 5. The XRD results exhibited that CGO-LBSFZ-2 oxide had the lowest inter-phase diffusion due to the lowest Ba-doping level among
CGO-LBSFZ samples. In addition, CGO-LBSFZ-2 membrane showed a better oxygen permeation flux than CGO-LBSFZ-4 and CGO-LBSFZ-6 membranes, which can also be demonstrated by the results of O$_2$-TPD tests. Finally, the CGO-LBSFZ-2 membrane was assembled with a commercial Ni-based catalyst to obtain a membrane reactor and then its oxygen permeation flux under POM atmosphere was investigated.

7.2 Experimental

7.2.1 Preparation of tubular composite membrane

LBSFZ perovskite oxide prepared in Chapter 6 was mixed with CGO by 1:1 weight ratio, and then the tubular CGO-LBSFZ membranes were fabricated following the method described in section 5.2.1 of chapter 5.

7.2.2 Instrumental characterizations

The XRD patterns of CGO-LBSFZ composites were obtained by a diffraction meter (Bruker D8 advance, Cu K$_\alpha$ radiation) in the range of 20 to 80° with a scanning rate of 3 °/min and a step width 0.02°. Surface morphologies of the tubular membranes were observed by a scanning electron microscopy (FESEM, JEOL JSM-5600) instrument. O$_2$-TPD and TPD tests were conducted by the methods introduced in section 5.2.2 of chapter 5. The samples after TPR run are denoted with a suffix “R”.
7.2.3 Oxygen permeation and POM test

The oxygen permeation fluxes of CGO-LBSFZ membranes were tested by the setup and method described in section 5.2.3 of chapter 5. When fabricating the membrane reactor for POM into syngas, 0.2 g of commercial Ni-based catalyst (Alfa Aesar, HiFUEL™ R-110, Ni loading: 15–40 wt.%) was loaded into the central part of the CGO-LBSFZ-2 membrane and 1.8 cm² of exterior surface area was left for oxygen permeation. 200 cm³/min of air was introduced from the shell side of the membrane to provide oxygen, and 20 cm³/min of CH₄-He mixed stream was fed into the tube for reaction. The oxygen permeation flux, conversion of methane and selectivity were calculated by the following equations:

\[ J_{O_2} = \frac{F_{CO}^{out} + 2F_{CO2}^{out} + F_{H2O}^{out} + F_{O2}^{out}}{2S} \]  \hspace{1cm} (7.1)

\[ X_{CH4} = \left(1 - \frac{F_{CH4}^{out}}{F_{CH4}^{out} + F_{CO}^{out} + F_{CO2}^{out}}\right) \times 100\% \]  \hspace{1cm} (7.2)

\[ S_{CO} = \frac{F_{CO}^{out}}{F_{CO}^{out} + F_{CO2}^{out}} \times 100\% \]  \hspace{1cm} (7.3)

in which \( J_{O_2} \), \( X_{CH4} \) and \( S_{CO} \) are oxygen permeation flux, conversion of methane and selectivity, respectively, \( F^{out} \) (cm³·min⁻¹) is the flow rate of the exit gas in the inner side of the membrane, and \( S \) (cm²) is the surface area of the tubular membrane used for oxygen permeation.
7.3 Results and Discussion

7.3.1 Chemical and phase stability of CGO-LBSFZ composites

![XRD patterns of CGO-LBSFZ powders sintered at 1400 °C for 4 h](image)

Figure 7.1 XRD patterns of CGO-LBSFZ powders sintered at 1400 °C for 4 h. (▽) LBSFZ perovskite oxides, (○) CGO oxide and (♦) Barium cerium oxide.

The CGO-LBSFZ composites were sintered at 1400 °C and then were examined by XRD to investigate their phase stability and phase computability between CGO and LBSFZ, as shown in Fig. 7.1. It was found that the XRD patterns of CGO-LBSFZ composites exhibited the fluorite phase CGO, perovskite phase LBSFZ and impurity phase Ba(CeO₃). The phase interdiffusion between CGO and LBSFZ became more severe with the increase of Ba-doping level in LBSFZ perovskite oxide, as the diffraction peak intensity of Ba(CeO₃) phase displayed a
positive linear relationship with the Ba content in CGO-LBSFZ composite. Besides the formation of impurity phases, the diffusion of Ba$^{2+}$ cations into CGO phase will also cause the decomposition of LBSFZ phases. The more Ba$^{2+}$ cations lost, the less LBSFZ phase was preserved. The main diffraction peaks of LBSFZ oxides around 32.1° are stronger than those of CGO around 28.4° for CGO-LBSFZ-2 and CGO-LBSFZ-3, but weaker for CGO-LBSFZ-4, CGO-LBSFZ-5 and CGO-LBSFZ-6.

Figure 7.2 TPR profiles of CGO-LBSFZ composites sintered at 1400 °C.
Chemical stability of CGO-LBSFZ composites under reducing atmosphere was investigated by TPR tests (Fig. 7.2), in which the Ce\textsuperscript{4+} in CGO phase and Fe\textsuperscript{4+/3+} in LBSFZ phase were reduced by 5\% H\textsubscript{2}/He gas stream, as discussed in section 5.3.1 of chapter 5 and section 6.3.2 of chapter 6. Fluorite phase CGO are much more stable than perovskite phase LBSFZ, so the TPR profiles of CGO-LBSFZ composites mainly exhibited the reduction peaks of LBSFZ oxides. Moreover, the reduction peak intensity of CGO-LBSFZ composites was greatly reduced compared with that of LBSFZ oxides, which was because not only the less content of LBSFZ in the composites but also the protective effects of CGO phase. After a careful scrutiny, it was found that the first reduction peak of CGO-LBSFZ-2 appeared at a
relative higher temperature around 474 °C than those of the rest CGO-LBSFZ composites. In addition, an interesting phenomenon was that the first reduction peak of CGO-LBSFZ-2 and CGO-LBSFZ-3 moved to a higher temperature compared with that of LBSFZ-2 and LBSFZ-3, while the first reduction peak of CGO-LBSFZ-4 and CGO-LBSFZ-5 moved to a lower temperature compared with that of LBSFZ-4 and LBSFZ-5. It was concluded that CGO phase had the best compatibility with LBSFZ-2 phase and could improve the chemical stability of LBSFZ-2 phase under reducing atmosphere. The XRD patterns of CGO-LBSFZ composites after TPR were shown in Fig. 7.3. Compared with their XRD patterns before TPR (Fig. 7.1), the diffraction peaks of LBSFZ phase shifted to lower angle, while the peaks of CGO phase kept the same angle. An obvious diffraction peak near 77° in the spectra of CGO-LBSFZ-2 and CGO-LBSFZ-3 disappeared after TPR tests. Hence, there was a little decomposition for the LBSFZ phase in the composites due to the reduction of iron cations as discussed in section 6.3.2. The lattice constants of CGO and LBSFZ phases in the composites were calculated and listed in Table 7.1. It can be found that the lattice constant of CGO phase had nearly no change after TPR test, while that of LBSFZ phase increased. This result was consistent with the TPR result, in which the reductive phase was mainly the LBSFZ phase. In a word, the CGO phase was more stable than LBSFZ phase under reducing atmosphere. The addition of CGO phase can help decreasing the reduction of LBSFZ phase and then improve chemical stability and mechanical strength of CGO-LBSFZ composites under reducing atmosphere.
Table 7.1 Lattice constants of CGO and LBSFZ oxides

<table>
<thead>
<tr>
<th>Material</th>
<th>Lattice constant (before TPR, Å)</th>
<th>Lattice constant (after TPR, Å)</th>
<th>Lattice expansion (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO-LBSFZ-2</td>
<td>$a_F=5.4353$</td>
<td>$a_F=5.4354$</td>
<td>0.002</td>
</tr>
<tr>
<td></td>
<td>$a_P=3.9059$</td>
<td>$a_P=3.9388$</td>
<td>0.842</td>
</tr>
<tr>
<td>CGO-LBSFZ-3</td>
<td>$a_F=5.4319$</td>
<td>$a_F=5.4324$</td>
<td>0.009</td>
</tr>
<tr>
<td></td>
<td>$a_P=3.9118$</td>
<td>$a_P=3.9475$</td>
<td>0.913</td>
</tr>
<tr>
<td>CGO-LBSFZ-4</td>
<td>$a_F=5.4268$</td>
<td>$a_F=5.4268$</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>$a_P=3.9163$</td>
<td>$a_P=3.9465$</td>
<td>0.771</td>
</tr>
<tr>
<td>CGO-LBSFZ-5</td>
<td>$a_F=5.4236$</td>
<td>$a_F=5.4235$</td>
<td>-0.002</td>
</tr>
<tr>
<td></td>
<td>$a_P=3.9236$</td>
<td>$a_P=3.9505$</td>
<td>0.686</td>
</tr>
<tr>
<td>CGO-LBSFZ-6</td>
<td>$a_F=5.4152$</td>
<td>$a_F=5.4152$</td>
<td>0.000</td>
</tr>
<tr>
<td></td>
<td>$a_P=3.9404$</td>
<td>$a_P=3.9602$</td>
<td>0.502</td>
</tr>
</tbody>
</table>

7.3.2 Oxygen permeation performance of CGO-LBSFZ composite membranes

The oxidation properties of CGO-LBSFZ composites at different temperatures were examined by O$_2$-TPD tests, as shown in Fig. 7.4. CGO-LBSFZ composites presented similar O$_2$-TPD profiles as LBSFZ oxides, but their peak intensity decreased due to the addition of CGO phase and the formation of impurity phase. The broad desorption peaks of CGO-LBSFZ composites can be divided into two regions: one at the lower temperature around 450 °C was attributed to desorption of surface oxygen; the other at the higher temperature greater than 525 °C was assigned to desorption of lattice oxygen species. Logically, the CGO-LBSFZ composites should have a similar desorption peak area if there was no phase interdiffusion in the
composites. However, CGO-LBSFZ-2 presented the largest desorption peak area and CGO-LBSFZ-6 exhibited the smallest area. It was reasonable to say that the intensity of desorption peak had a relationship with the extent of phase interdiffusion. The impurity phase formed by interdiffusion commonly had a lower concentration of oxygen vacancies and then lower oxygen ionic conductivity. Therefore, if there was a less phase interdiffusion, more LBSFZ perovskite phase was preserved and then more oxygen species were released during temperature rising; and vice versa. Based on the above discussion, it can be concluded that the phase compatibility in the composites were important for their oxidation properties.

![Figure 7.4 O₂-TPD profiles of CGO-LBSFZ composites sintered at 1400 °C.](image)
Chapter 7 Development of tubular CGO-LBSFZ MEIC membrane reactor to combine oxygen separation with POM
The exterior surface morphologies of fresh CGO-LBSFZ membranes are shown in Fig. 7.5. It was noted that all these three CGO-LBSFZ membranes showed a dense surface with clear grain-boundary structures. Compared with the surface morphologies of LBSFZ oxides, CGO-LBSFZ composites had a smaller grain size caused by the addition of CGO phase, which would limit the growth of LBSFZ crystallites. The more grain boundary structures in CGO-LBSFZ composites may impede the oxygen ionic transport in the membrane and then reduce the oxygen permeation flux through the membrane.
Figure 7.6 Oxygen permeation fluxes of CGO-LBSFZ membranes as a function of temperature.

Oxygen permeation fluxes of the tubular CGO-LBSFZ composite membranes were tested as a function of temperature (Fig. 7.6). CGO-LBSFZ-2 membrane has an oxygen permeation flux as high as 0.513 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 °C. It displayed a relative higher oxygen permeation flux than CGO-LBSFZ-4 and CGO-LBSFZ-6 membranes in the temperature range from 800 to 950 °C. This result can be perfectly explained by the result of O$_2$-TPD test, that is CGO-LBSFZ-2 composite has a higher concentration of oxygen vacancies and then a greater oxygen ionic conductivity than CGO-LBSFZ-4 and CGO-LBSFZ-6 oxides. In order to evaluate the block effect of impurity phase Ba(CeO$_3$) in CGO-LBSFZ composite membranes, the theoretical oxygen permeation fluxes were calculated using the method described in section 5.3.4 of chapter 5, as seen in Table 7.2. The value of $J_{O_2,exp}$/
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\( J_{O_2,\text{cal}} \) was used to measure the block degree of impurity phase on the oxygen ionic transport in the CGO-LBSFZ membranes. Based on the calculations, CGO-LBSFZ-6 had the highest theoretical oxygen permeation flux and CGO-LBSFZ-2 had the lowest value. However, it turned out the opposite for the experimental values. The results demonstrated that CGO-LBSFZ-2 had a much lower block degree than CGO-LBSFZ-4 and CGO-LBSFZ-6, which is the reason why it has a higher oxygen permeation flux.

### Table 7.2 Oxygen permeation flux of CGO-LBSFZ composite membrane at 950 °C

<table>
<thead>
<tr>
<th>Material</th>
<th>Shape</th>
<th>Thickness (mm)</th>
<th>( \ln \left( \frac{p_2}{p_{O_2}} \right) )</th>
<th>( J_{O_2,\text{exp}} ) (cm³·cm⁻²·min⁻¹)</th>
<th>( J_{O_2,\text{cal}} ) (cm³·cm⁻²·min⁻¹)</th>
<th>( \frac{J_{O_2,\text{exp}}}{J_{O_2,\text{cal}}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CGO-LBSFZ-2</td>
<td>Tube</td>
<td>1.0</td>
<td>1.922</td>
<td>0.513</td>
<td>0.576</td>
<td>0.961</td>
</tr>
<tr>
<td>CGO-LBSFZ-4</td>
<td>Tube</td>
<td>1.0</td>
<td>2.029</td>
<td>0.370</td>
<td>0.667</td>
<td>0.526</td>
</tr>
<tr>
<td>CGO-LBSFZ-6</td>
<td>Tube</td>
<td>1.0</td>
<td>2.110</td>
<td>0.330</td>
<td>0.696</td>
<td>0.410</td>
</tr>
</tbody>
</table>

#### 7.3.3 Performance of CGO-LBSFZ-2/Ni-based catalyst membrane reactor

As CGO-LBSFZ-2 membrane exhibited the highest oxygen permeation flux, it was selected to fabricate membrane reactor with a commercial Ni-based catalyst for POM into syngas. Fig. 7.7 displayed the oxygen permeation flux, CO selectivity and \( \text{CH}_4 \) conversion as a function of temperature, where 20 % CH\(_4\)/He was used as the feed gas. It was noted that the oxygen permeation flux under POM atmosphere was...
greatly improved, compared with the flux under helium atmosphere, due to the increase of oxygen partial pressure gradient. The CGO-LBSFZ-2 membrane can have an oxygen permeation flux as high as 2.69 cm$^3$·cm$^{-2}$·min$^{-1}$. The conversion of methane rose gradually with temperate and achieved nearly 100 % at 950 °C, while the CO selectivity dropped from 80.4 % at 800 °C to 49.2 % at 950 °C. This can be explained by the changing of O$_2$/CH$_4$ ratio at different temperatures. The ratio of O$_2$/CH$_4$ will become greater with the elevation of temperature and then cause excessive oxygen in the POM reaction, which will lead the oxidation of CO to CO$_2$ and then reduce the CO selectivity. In the case of 50 % CH$_4$/He as the feed gas (Fig. 7.8), the oxygen permeation flux was further improved and can achieve 6.14 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 °C. The conversion of methane was greater than 97 % in the temperature range of 800 to 950 °C. The CO selectivity was nearly kept the same from 800 to 850 °C and displayed a different trend, compared with that in Fig. 7.7. This was caused by the excess of methane relative to oxygen. The excessive methane will thermally decomposed on catalyst to form surface carbon as explained by the direct POM mechanism, so the increased oxygen from 800 to 850 °C will mainly react with the surface carbon and will not cause the drop of CO selectivity.
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Figure 7.7 POM reaction of CGO-LBSFZ-2 membrane at 950 °C with 20% CH₄-He feed gas.

Figure 7.8 POM reaction of CGO-LBSFZ-2 membrane at 950 °C with 50% CH₄-He feed gas.
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Figure 7.9 XRD patterns of CGO-LBSFZ-2 membrane before and after POM reaction for 50 h.
The crystal structure of CGO-LBSFZ-2 membrane after POM was examined by XRD, as seen in Fig. 7.9. It was found that the XRD pattern of used membrane was similar with the pattern of fresh membrane and there was no new impurity phases formed. The diffraction peaks of LBSFZ perovskite phase in the composite shifted to lower angle due to the reduction of iron by CH$_4$ and CO. It was concluded that CGO-LBSFZ composite membrane had the enough chemical stability under POM reducing atmosphere. The micrographs of CGO-LBSFZ-2 after POM reaction were shown in Fig. 7.10. It was observed that the exterior surface of CGO-LBSFZ-2 membrane became very rough after reaction, which was caused by the adjustment of
Chapter 7 Development of tubular CGO-LBSFZ MEIC membrane reactor to combine oxygen separation with POM

crystal structure under reducing atmosphere. However, the CGO and LBSFZ-2 grains in the composite membrane still packed together tightly, which ensured the membrane in a dense form, through the observation of cross-section view.

7.4 Conclusions

The addition of CGO phase can improve the membranes’ chemical stability under reducing atmosphere and mechanical strength. The XRD and TPR results reveal that CGO-LBSFZ-2 perovskite oxide has the best phase compatibility and chemical stability among CGO-LBSFZ samples. Although LBSFZ-2 membrane shows a lower oxygen permeation flux than the other LBSFZ membranes in chapter 6, the CGO-LBSFZ-2 composite membrane exhibits a higher oxygen permeation flux than the other composite membranes due to the less phase interdiffusion. A membrane reactor composed of CGO-LBSFZ-2 membrane and commercial Ni-based catalyst was successfully fabricated. Its oxygen permeation flux can achieve 6.14 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 °C when 50 % CH$_4$/He was used as the feed gas. After POM reaction, the XRD result and morphologies of CGO-LBSFZ-2 membrane demonstrated that the phase stability and mechanical strength were still in good conditions.
Chapter 8 Conclusions and recommendations

8.1 Conclusions

This PhD thesis focuses on the two important concerns of MEIC membrane reactor for methane into syngas: one is the removal of sulphur-containing compounds by carbon adsorbents; the other is the development of MEIC membrane suitable for oxygen separation under POM atmosphere. The achievements of this study are summarized in the following sections.

8.1.1 Conclusions for carbon adsorbents

As micro/mesoporous activated carbon (AC) was expected to have the best porous structure for adsorption, the preparation of this kind of AC was systematically studied in this work, which includes the selection of carbonaceous precursor and its modification.

Four cellulose-based precursors (ALC, MEC, CAC and HEC), which bear different types of side chain group, are selected to investigate the effects of pendant side-chain groups on the porous structures of resulting ACs. After carbonization under argon atmosphere and subsequent activation under CO$_2$ atmosphere, ACs were obtained from these cellulose precursors. It was proved that the products after carbonization were essentially a mixture of PAHs as characterized by FT-IR and XPS. During the pyrolysis, these pendant groups of the celluloses affect the structures of PAHs through: (1) the sizes; (2) distribution of thermally derived oxy-groups that
include carboxyl, quinonoid, phenol, and ether; and (3) the presence of saturated hydrocarbon moieties. The carbonization product AC_HEC40 presents the desired structures of PAHs. As far as the activation is concerned, its effectiveness depends on the use of a proper temperature. The presence of stable oxy-groups between PAH flakes assists CO₂ to access reactive sites. The BET results show that AC_HEC47 has the largest surface area as high as 1297 m²/g and the highest mesopore volume up to 0.487 cm³/g in all AC samples examined.

Based on the above results obtained, HEC as the precursor was further studied to make the porous structures of AC more controllable. The polymer chains of HEC were covalently crosslinked with carboxylic acids (SCA, TPA, BZA and PMA) by the esterification reaction. The insights gained from this study provide the evidence that the esterified polymer precursor affects the substitution and sizes of PAH rings as well as the formation of aliphatic carbons constituting the pyrolysis products. When the benzene-borne polyprotic acids, i.e. TPA and PMA, were used, the increase in crosslinking degree from 1 wt.% to 5 wt.% caused an optimal outcome that happens at ca. 3 wt%. FT-IR and ¹³C-NMR spectral studies, in correlation with the BET surface analysis, show that this outcome originates from an optimal sizes and regular substitution of PAHs. The complicated substitution, big sizes of PAHs, and the presence of aliphatic carbons in the carbonization products do not favour graphitization of these PAHs, which in turn sacrifice both micro- and mesopores and surface area. On the other hand, smaller PAHs although allow ready local graphitization, they stifle the extension of micropore channels. With the aim of
examining local crosslinking density, 4-arm PMA was used to crosslink HEC. In contrast to TPA, PMA brings about complex PAHs and higher aliphatic carbon contents, they virtually impedes the development of mesopores as a result of hindrance to graphitization.

The adsorption capacities of obtained AC adsorbents were evaluated by the removal of H$_2$S tests. It was found that not only the porous structure of AC, such as specific surface area, the total pore volume and the portion of mesopore volume, but also the surface basicity will affect its adsorption capacity. It was also observed that there was a cooperative relationship between micropores and mesopores existing in the adsorption process of H$_2$S, and that the former structural trait is more influential.

8.1.2 Conclusions for MEIC membrane reactor

Tubular dual-phase MEIC membranes made of ionic conductor and mixed conductor were investigated. Mixed conductive phase LBFZ was combined with oxygen ionic conductive phase CGO and YSZ. It was found that Ba$^{2+}$ cations in LBFZ phase were easy diffusing into CGO and YSZ lattices to form Ba(CeO$_3$) and BaZrO$_3$, respectively. CGO as the ionic conductor shows much better phase compatibility with LBFZ than YSZ. The TPR tests revealed that CGO-LBFZ composite had a better chemical stability than pure LBFZ under reducing atmosphere and the LBFZ phase in the composite could keep its perovskite structure after TPR. The addition of CGO phase can reinforce the mechanical strength of CGO-LBFZ composite membrane to survive under high oxygen partial pressure.
gradient at high temperatures. The effects of relative content of CGO and LBFZ phases on the performances of the composite membrane were also investigated. It was found that the oxygen permeation flux didn’t increase proportionally with the content of LBFZ due to the phase interdiffusion. The CGO40-LBFZ60 membrane can achieve an oxygen flux of 0.84 cm$^3$·cm$^{-2}$·min$^{-1}$ at an oxygen partial gradient of 21 kPa/1.1 kPa at 950 ºC.

In order to reduce the phase interdiffusion caused by Ba$^{2+}$, LBFZ perovskite oxide was modified by replacing part of Ba$^{2+}$ with Sr$^{2+}$. The effects of A-site dopants Ba$^{2+}$ and Sr$^{2+}$ on the properties of LBSFZ materials were studied. The tolerance factors of LBSFZ oxide get larger with the increase of Ba-doping level, but they are all in the range for a stable perovskite structure. All LBSFZ oxides had some extent of phase decomposition after treated by the 5 % H$_2$/N$_2$ stream. Through the characterizations of TPR and XRD, it was observed that Ba$^{2+}$ can stabilize the perovskite structure better than Sr$^{2+}$ under the reducing atmosphere due to its larger ionic radius. The oxygen permeation tests showed that LBSFZ membranes with higher Ba-doping level exhibited greater oxygen permeation flux from 800 to 950 ºC under an air/He gradient. In addition, O$_2$-TPD test manifested that LBSFZ perovskite oxide with higher Ba-doping level had lower activation energy for oxygen transport. LBSFZ-6 membrane could achieve an oxygen permeation flux of 1.07 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 ºC, but its mechanical strength was not sustainable for a long-time run.
Finally, LBSFZ perovskite oxides and CGO phase were selected to fabricate CGO-LBSFZ composite membranes. The addition of CGO phase can improve CGO-LBSFZ membranes’ mechanical strength and chemical stability under reducing atmosphere, which is same with CGO-LBFZ membranes. Through the adjustment of A-site composition of LBSFZ, CGO-LBSFZ-2 perovskite oxide showed the best phase compatibility and chemical stability among CGO-LBSFZ samples. CGO-LBSFZ-2 composite membrane exhibited a higher oxygen permeation flux than the other composite membranes due to the less phase interdiffusion, which let CGO-LBSFZ-2 have an oxygen permeation flux close to the theoretical value. A membrane reactor composed of CGO-LBSFZ-2 membrane and commercial Ni-based catalyst was successfully fabricated. Its oxygen permeation flux can achieve 6.14 cm$^3$·cm$^{-2}$·min$^{-1}$ at 950 °C when 50 % CH$_4$/He was used as the feed gas. The CGO-LBSFZ-2 membrane reactor can keep enough chemical endurance against syngas caused structural deterioration, as demonstrated by the XRD result and morphologies of used membrane.
8.2 Recommendations for the future work

Based on the conclusions of this study, the following suggestions are given for the future research on the development of carbon adsorbent and MEIC membrane reactor.

8.2.1 Surface modification of carbon adsorbent

The surface properties of carbon adsorbent are important to its adsorption capacity of specific adsorbates. They can be modified by oxidation/reduction of surface groups or impregnation with Na₂CO₃, KIO₃ and other metal salts. Although the mesoporous structure in carbon adsorbents didn’t show a greater contribution than microporous structure in this study, the mesopores can provide the enough space for the metal salts or other impregnants which may enhance the chemical interactions and surface complexing with adsorbates and then improve the adsorption capacity.

8.2.2 Development of asymmetric membrane reactor

For a specific MEIC material, the improvement of chemical and structural stability will commonly cause the degradation of its oxygen permeation flux. To solve this problem, one possible way is reducing the membrane thickness, because oxygen permeation flux is inversely proportional to the membrane thickness, when it is controlled by the bulk diffusion. Since the MEIC membrane layer needs to be very thin, it cannot be self-supported and need a porous substrate to support. The
phase and thermal expansion compatibility between the membrane material and the support material are the issues need to consider. The CGO-LBSFZ-2 membrane developed in this study can function as the MEIC layer to be coated on a porous ceria support and then get the asymmetric membrane, which should have satisfied phase compatibility.

8.2.3 Modification of membrane surface

In order to reduce the oxygen transport resistance limited by the surface exchange reaction, the membrane surface can be modified accordingly. One method is to increase the available membrane surface area for oxygen adsorption or desorption by coating a porous layer on membrane; the other way is to reduce the oxygen activation energy by coating a high oxygen ionic conductive porous layer on the membrane surface, in which the porous layer can be modified by noble metal or nanoparticles of active oxides.
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