

Oxygen Permeation and Thermo-Chemical Stability of Oxygen Separation Membrane Materials for the Oxyfuel Process

Anna Judith Ellett



Forschungszentrum Jülich GmbH Institute of Energy Research (IEF) Microstructure and properties of materials (IEF-2)

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Abstract

The reduction of CO_2 emissions, generally held to be one of the most significant contributors to global warming, is a major technological issue. CO_2 Capture and Storage (CCS) techniques applied to large stationary sources such as coal-fired power plants could efficiently contribute to the global carbon mitigation effort. The oxyfuel process, which consists in the burning of coal in an oxygen-rich atmosphere to produce a flue gas highly concentrated in CO_2 , is a technology considered for zero CO_2 emission coal-fired power plants. The production of this O_2 -rich combustion gas from air can be carried out using high purity oxygen separation membranes. Some of the most promising materials for this application are mixed ionic-electronic conducting (MIEC) materials with perovskite and K_2NiF_4 perovskite-related structures.

The present work examines the selection of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF58), $La_2NiO_{4+\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58) and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF50) as membrane materials for the separation of O_2 and N_2 in the framework of the oxyfuel process with flue gas recycling. Annealing experiments were carried out on pellets exposed to CO_2 , water vapour, O_2 and Cr_2O_3 in order to determine the thermo-chemical resistance to the atmospheres and the high temperature conditions present during membrane operation in a coal-fired power plant. The degradation of their microstructure was investigated using Scanning Electron Microscopy (SEM) in combination with electron dispersive spectroscopy (EDS) as well as X-Ray Diffraction (XRD). Also, the oxygen permeation fluxes of selected membranes were investigated as a function of temperature. The membrane materials selected were characterised using thermo-analytical techniques such as precision thermogravimetric analysis (TGA) and thermo mechanical analysis (TMA).

An increase in thermal expansion and oxygen permeation associated with an increase in oxygen vacancy concentration, observed also in the TGA curves, occurs during heating. BSCF50 exhibits permeation fluxes well above those of LSCF58, PSCF58 and La₂NiO_{4+ δ}, which are quite similar to each other. After exposure, no degradation of LSCF58, La₂NiO_{4+ δ} and PSCF58 occurs. On the other hand BSCF50 is found to be unstable in CO₂- and/or H₂O-containing atmospheres and also to exhibit a chemical demixing. The thermo-chemical stability and the oxygen permeation performances are both crucial factors in the selection of high purity oxygen separation membranes for the oxyfuel process, thus making LSCF58, PSCF58 and La₂NiO_{4+ δ} in this study the most suitable materials for this application. Serious issues arise, however, from the fact that secondary non-ion conducting oxide phases are formed in the bulk of every material, forming obstacles for oxygen ion migration, and also that a reaction with chromia occurs, preventing their use without protection.

Zusammenfassung

Kohlendioxid wird für das am stärksten zur globalen Erderwärmung beitragende Gas gehalten. Die Reduktion der CO₂ Emissionen durch technologische Maßnahmen ist daher ein sehr wichtiger Ansatz. Die Abtrennung und Speicherung von CO₂ aus Abgasen großer stationärer Anlagen, wie zum Beispiel fossiler Kraftwerke, kann hierbei einen effektiven Beitrag leisten. Ein mögliches Verfahren zum Betrieb CO₂- emissionsfreier Kraftweke ermöglicht der Oxyfuel Prozess. Hierbei wird der fossile Brennstoff in sauerstoffreicher und stickstoffarmer Atmosphäre umgesetzt, wobei ein Rauchgas mit hoher CO₂ Konzentration erzeugt wird. Eine Möglichkeit zur Erzeugung dieses O₂-reichen Gases kann der Einsatz von sauerstoff- trennenden Membranen sein. Mögliche Materialien für solche Membranen stellen Sauerstoff- Mischionenleiter aus Perowskiten und perowskitähnlichen Werkstoffen wie K₂NiF₄ dar. In der hier vorliegenden Arbeit wird der Fokus auf die Materialien La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF58), La₂NiO_{4+δ}, Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (PSCF58) und Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} (BSCF50) als Membranmaterialien für die Trennung von O₂ und N₂ im Rahmen des Oxyfuel Prozesses mit Rauchgasrückführung gelegt.

Zur Untersuchung der thermo-chemischen Stabilität der Materialien gegenüber Temperaturen und Atmosphären, wie sie in kohlegefeuerten Kraftwerken herrschen, wurden Auslagerungsversuche unter definierten Bedingungen durchgeführt, wobei die Proben in CO₂-, wasserdampf- und sauerstoffhaltigen Atmosphären ausgelagert wurden. Weiterhin wurden Versuche durchgeführt, die die Chromabdampfung aus Rohrleitungen und Wärmetauschern simulieren. Veränderungen der Mikrostruktur der untersuchten Proben wurden mithilfe der Rasterelektronenmikroskopie und analytischen Verfahren der Energie-dispersiven Röngenanalytik und der Röntgendiffrakometrie untersucht.

Die Sauerstoffpermeationsraten ausgewählter Membranen aus den oben genannten Materialien wurden in Abhängigkeit der Temperatur gemessen. Die Werkstoffe wurden mithilfe hochpräziser Thermogravimetrie und das Ausdehnungsverhalten mit Dilatometrie untersucht.

Ein Anstieg der thermischen Expansion und auch der Sauerstoffpermeation kann mit einer Erhöhung der Sauerstoff-Leerstellenkonzentration korreliert werden, die ebenfalls mit Hilfe der Thermogravimetrie bestimmt werden kann.

BSCF50 erreicht deutlich höherer Permeatflüsse als LSCF58, PSCF58 und La₂NiO_{4+ δ}. Bei den Auslagerungsversuchen konnten keine Degradationseffekte bei LSCF58, La₂NiO_{4+ δ} und PSCF58 nachgewiesen werden. BSCF50 erweist sich as instabil gegenüber CO₂- sowie wasserdampfhaltigen Atmosphären. Weiterhin wurden Entmischungen beobachtet.

Sowohl die thermo-chemische Stabilität, als auch die Permeationseigenschaften der untersuchten Materialien sind kritische Faktoren für eine Bewertung sauerstoffleitender Membranen. Hierbei scheinen von den untersuchten Werkstoffen LSCF58, PSCF58 und La₂NiO_{4+ δ} die am besten geeigneten Materialien. Allerdings ist zu beobachten, dass sich nicht leitende oxidische Sekundärphasen bilden können, welche den Sauerstofftransport blockieren. Die unter bestimmten Bedingungen beobachtete Bildung einer dichten Cr₂O₃ Schicht blockiert ebenfalls die Permeation des Sauerstoffs durch die Membran, so dass zusammenfassend gesagt werden kann, ein Einsatz der untersuchten Materialien als Membranwerkstoffe ist nur möglich mit zusätzlichen Maßnahmen zum Korrosionsschutz.

TABLE OF CONTENTS

1	INTRODUCTION		
	1.1	Kyoto protocol	1
	1.2	Coal-fired power plants	1
	1.3	CO ₂ capture concepts	1
	1.3	1 The post-combustion process	2
	1.3	2 The pre-combustion process	2
	1.3	3 The oxyfuel process	3
	1.3	 Economic viability Gas separation membranes for CCS 	4 4
	1.4	MIEC membranes for O_2/N_2 separation	
2	SCO		6
2	BAG	YEROUND	0 7
5	2 1	MIEC materials for avugan normashla membranas	יייייייייייייייייייייייייייייייייי
	5.1 2.1	The percondite structure	/ ح
	3.1 3.1	The Perfovskile structure	/
	3.1	The rudule such r opper phase, R_2 in $\frac{1}{4}$ type subctate $(R_2 D O_{4+0})$	12
	3.2	1 Bulk transport	15
	3.2	2 Surface processes	
	3.3	Oxyfuel process	19
	3.3	1 Oxycombustion	19
	3.3	2 Flue gas recycling	20
	3.3	3 Flue gas composition	20
	3.3	4 Combustion	21
4	СЦ.		
4		X and liferation to hair and (VDD)	25
	4.1	A-ray dilifaction technique (XRD)	23
	4.2 4 3	Thermal Analysis	24 24
	4.3	1 Differential Thermal Analysis combined with thermogravimetry (DTA/TG)	25
	4.3	 Precision Thermogravimetric Analysis (TGA). 	25
	4.3	3 Thermo Mechanical Analysis (TMA)	26
	4.4	Mass spectrometry	26
	4.5	Density measurements	28
	4.6	ICP-OES	29
	4.7	Hot gas extraction	29
5	MA	TERIALS SELECTED FOR THIS STUDY	30
	5.1	Mixed conducting acceptor-doped perovskites	30
	5.1	$1 \qquad La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} (LSCF58)$	30
	5.1	2 $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58)	31
	5.1	$3 Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta} (BSCF50)$	31
	5.2	Perovskite-related oxides	33

5.2	2.1 $La_2NiO_{4+\delta}$	
5.3	Sample preparation	34
5.3	3.1 Pressing	34
5.3	3.2 Sintering	34
6 DE	VELOPMENT OF THE PERMEATION TEST SET-UP	36
6.1	Module 1: The gas mixing unit	36
6.2	Module 2: The membrane testing unit	37
6.2	2.1 The heating unit:	
6.2	2.2 The recipient:	
6.3	Module 3: The analytical unit	
0.4	Development of the memorane recipient for dense ceramic memoranes	
0.4 6 5	4.1 Sealing technology	43
0.5	Over permeeting measurements	
0.0		43
7 TH	ERMO-CHEMICAL STABILITY INVESTIGATION SET-UP	48
7.1	CO ₂ and H ₂ O vapour influence on stability	48
7.2	Experimental set-up	49
7.3	Annealing conditions	52
7.4	Sample preparation	53
8 CH	IARACTERISATION OF THE MEMBRANE MATERIALS SELECTED	55
8.1	Chemical analysis of the calcined powders	55
8.2	Phase composition of the calcined powders	56
8.3	Sintering of the pellets for the annealing experiments	58
8.4	Density of the sintered samples	64
8.5	Precision thermogravimetric analysis	64
8.6	Dilatometric measurements	70
9 OX	YGEN PERMEATION THROUGH MIEC MEMBRANES	78
9.1	Thickness dependence of oxygen permeation fluxes	79
9.2	Comparison of the oxygen permeation fluxes through selected 1 mm membranes .	87
9.3	Conclusion	94
10 TH	ERMO-CHEMICAL STABILITY INVESTIGATION	95
10.1	Annealing in air	96
10.2	Annealing in CO ₂ -containing atmospheres	98
10	0.2.1 Air plus 10%CO ₂	104
10	0.2.2 1% O ₂ , 99% N ₂ plus 10% CO ₂	
10	$12.3 43\%O_2, 43\%CO_2 \text{ and } 14\%N_2 \dots$	109
10 3	EactSage TM thermo-chemical calculations	112
10.3 10.4	Annealing in water vapour-containing atmospheres	110
10.4	141 - 55 mol% CO ₂ 28 mol% O ₂ 12 mol% H ₂ O and 5 mol% N ₂	121
10	$0.4.2 50 \text{ mol}\% \text{ CO}_2, 25 \text{ mol}\% \text{ O}_2, 12 \text{ mol}\% \text{ H}_2\text{O} \text{ and } 5 \text{ mol}\% \text{ N}_2$	
10	0.4.3 25 mol% O_2 , 20 mol% H_2O , 55 mol% N_2	136

10.5	Volatilisation of chromium species	
10.5	1 Theory	
10.5	2 Results	
10.5	3 Discussion	
10.6	Co enrichment at the grain boundaries	
10.7	Phase analysis	148
10.7	1 Results	
10.7	2 FactSage TM thermo-chemical calculations	
10.7	3 Discussion	
10.8	Conclusion	
11 CON	CLUSION	
12 REFI	ERENCES	

1 Introduction

1.1 Kyoto protocol

Global warming is a major issue for our modern industrial societies. The observable effects of increasing levels of greenhouse gases, such as carbon dioxide (CO₂), released into the atmosphere have led to the signing of the Kyoto protocol by which countries commit to the reduction of greenhouse gas emissions worldwide. Since 1997 it has been ratified by more than 170 countries.

1.2 Coal-fired power plants

Carbon dioxide is generally held to be one of the most significant contributors to global warming. Fossil fuel-fired power plants are responsible for more than one third of the total global CO_2 emissions [1]. A 1000 MW pulverized coal-fired power plant emits between 6 and 8 Mt of CO_2 per year. Moreover the burning of fossil fuels provides more than 85% of the world's commercial energy needs [2]. Coal-fired power plants represent more than 20% of the world's total energy production [1] and over 40% of Germany's total domestic energy production [3]. With the rise of the global demand for electricity and also the abundance of coal resources, coal-fired power plants are and will remain an important source of energy in the foreseeable future. The major challenge is to decrease CO_2 emissions from large stationary sources. Therefore coal-fired power plants are prime candidates for the application of CO_2 Capture and Storage (CCS) techniques.

1.3 CO₂ capture concepts

 CO_2 capture technologies have been used for decades to produce a pure stream of CO_2 from natural or industrial CO_2 emissions for use in the food processing and chemical industries. The captured CO_2 is used for various industrial and commercial processes such as foam blowing, the production of urea, dry ice production and carbonated beverages. This work will focus on CO_2 capture in coal-fired power plants, for which three main processes are available at different stages:

- Post-combustion
- Pre-combustion
- Oxyfuel

1.3.1 The post-combustion process

The post-combustion process consists in the de-carbonisation of the flue gas. CO_2 is captured from the exhaust gas produced during combustion. The state of the art process to separate CO_2 from a flue gas is chemical absorption [4] which is a solvent process in which CO_2 reacts with an absorption liquid e.g. amine-based solvents or alkaline salt solutions. Amine scrubbing is the most commonly applied technique for CO_2 separation and the most widely used absorbent is monoethanolamine (MEA) [1,5,6]. This process is suitable for conventional power stations. Polymeric membranes are also used commercially for CO_2 removal from natural gas. However the lower CO_2 partial pressures of the exhaust gas from a coal-fired power plant results in having to compress the flue gas and thus in higher energy penalties.

1.3.2 The pre-combustion process

The pre-combustion process (Figure 1.1) consists in a de-carbonisation of the fuel gas. This process has been used for more than 50 years for hydrogen production in chemical and refining industries [7]. It is possible with Integrated Gasification Combined Cycle (IGCC) [8] and involves three steps [7]:

- Hydrocarbon conversion by partial oxidation, which is a partial combustion of coal in air, oxygen or oxygen-enriched air to produce a syngas mixture containing H₂ and CO.
- The conversion of the mixture to CO₂ and H₂. The thermo-dynamically controlled reaction which takes place is the water gas-shift reaction:

 $CO + H_2O(g) \rightarrow CO_2 + H_2$

H₂ removal will shift the overall reaction to the product side.

• The separation of CO_2 and H_2 to produce a hydrogen-rich stream. Technologies to remove CO_2 from the flue gas stream include chemical absorption described above, pressure swing adsorption (PSA) onto adsorbents such as zeolites which act as molecular sieves. Cryogenic separation in which CO_2 is physically separated from the syngas by condensing it to produce liquid CO_2 ready for storage, and physical absorption using solvents such as dimethylether of polyethylene glycol so-called Selexol or Rectisol (cold methanol) are other developed techniques [7]. Membrane separation is also commercially applied for H_2 separation but the selectivity of commercially available membranes for CO_2/H_2 separation is too low [1,8,7].



Figure 1.1. Schematic representation of the pre-combustion process

1.3.3 The oxyfuel process

The oxyfuel process (Figure 1.2) is a de-nitrogenation of the combustion gas (air). It consists in the burning of coal in an oxygen-rich atmosphere to produce a flue gas highly concentrated in CO₂. When coal is combusted in air the fraction of CO₂ in the flue gas is between 10% and 14% for a Pulverised Fuel-fired (PF) station. [9,10,4,11] Capture is easier at higher CO₂ concentrations, which can be achieved by using pure or enriched oxygen instead of air for coal combustion. The oxyfuel alternative will allow the flue gas to be composed of relatively clean exhaust gases, steam and CO₂ (80% to 85%). Water vapour can be readily condensed and separated from CO₂. Cryogenic fractionation with the use of an air separation unit (ASU) is the most commonly used method for the separation of oxygen from air. Pressure swing adsorption and gas separation membranes are more flexible options. This process will be discussed in further detail in Chapter 3.3.



Figure 1.2. Schematic representation of the oxyfuel process

1.3.4 Economic viability

The reduction of CO_2 emissions is a major technological issue. The economic viability of the different solutions also has to be considered. Conventional coal-fired power plants generate high volumes of flue gas with low CO_2 concentrations. The very high capital costs of installing a post-combustion separation system needed to process massive volumes of flue gases is a major impediment to post-combustion capture. A key to achieving lower capture costs lies in the production of a more concentrated stream of CO_2 . This can be done through the pre-combustion or oxyfuel processes.

However most processes considered to capture CO_2 from flue gas are capital and energy intensive. The air separation unit alone may consume about 15% of a power plant's electric output [12]. The absorption and adsorption routes also have high electricity costs. The release of CO_2 from solvents or from solid adsorbents after separation requires a large amount of additional energy. On the other hand gas separation membranes have relatively low energy consumption and their integration into membrane reactors is very promising. They are therefore excellent candidates for gas separation in coal-fired power plants.

1.3.5 Gas separation membranes for CCS

Three types of membrane are currently available for gas separation applications and are being considered for use in the processes for CO_2 capture:

- Organic porous polymer membranes
- · Inorganic porous membranes, amorphous or crystalline
- Inorganic dense membranes, metallic or ceramic

Polymeric membranes show excellent CO_2 separation potential from N_2 for the post-combustion process. They can also be used for H_2/CO_2 separation for the pre-combustion process and O_2/N_2 separation for the oxyfuel process. However they exhibit a low thermal stability and will not be considered for these processes that involve high temperatures and pressures [13]. Therefore porous crystalline inorganic membranes such as zeolites which are chemically, thermally and mechanically stable are favoured for all three concepts [14]. Dense inorganic membranes are also excellent candidates for H_2/CO_2 and O_2/N_2 separation. This work will consider the viability of the application of dense inorganic membranes for the separation of O_2 and N_2 in the framework of the oxyfuel process.

1.4 MIEC membranes for O₂/N₂ separation

Since the 1980s considerable interest has been shown in dense ceramic membranes for high purity oxygen separation. The use of mixed ionic-electronic conductor (MIEC) materials as oxygen separation membranes from air is regarded as a clean, cost-effective, stable and versatile technology. These membranes are dense materials with no detectable pores meaning that the molecular oxygen is not able to pass through them. Dense membranes derive their capability for oxygen separation from the presence of oxygen vacancies in the crystal lattice of the membrane material. These vacancies can be created in the lattice by doping of the material. They enable ionic oxygen to be selectively transported from one side of the membrane to the other, through the lattice, via a hopping mechanism.

This mechanism is only possible provided that the oxygen anions have enough thermal energy to overcome the thermal energy barrier to hop from one crystal lattice site to the other. As a result high temperatures are required for this application. Above 600°C oxygen vacancies become available for transport. Temperatures ranging typically between 700°C and 1000°C are required for oxygen separation membranes with infinite perm-selectivity [15]. Moreover, since oxygen anions are transported, a counter-balancing transport of electrons (e⁻) is present in order to maintain electroneutrality in the membrane material. There is no need of applying a voltage to generate oxygen transfer. Indeed, the driving force for this ion transport mechanism is an oxygen chemical potential gradient through the membrane.

This thesis will focus on mixed ionic and electronic conductors (MIEC), oxygen permeable ceramics, which exhibit both a high ionic and electronic conductivity thus allowing high oxygen fluxes [16].

2 Scope of the work

This work considers the viability of the application of selected dense inorganic Mixed Ionic-Electronic Conductor (MIEC) membranes for the separation of O_2 and N_2 in the framework of the oxyfuel process with flue gas recycling. The membrane, operating at temperatures ranging typically between 600°C and 1000°C will be exposed on its feed-side to air and on its sweep-side to high concentrations of CO_2 and water. Therefore, the membrane material will have to be stable at high temperatures and in the gaseous atmosphere of the flue gas.

The present study deals with the development of a test set-up and a membrane recipient designed and built to measure the oxygen permeation performance of membranes as a function of temperature and using different feed and sweep gas compositions. The oxygen permeation fluxes of selected MIEC membranes with perovskite and K₂NiF₄ perovskite-related structures i.e. $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ will be investigated as a function of temperature and membrane thickness.

In this work, the MIEC membrane materials selected are to be characterised using thermo-analytical techniques such as differential thermal analysis combined with thermogravimetry (DTA/TG), precision thermogravimetric analysis (TGA) and thermo mechanical analysis (TMA) in order to determine the thermal expansion properties as well as the change in oxygen stoichiometry.

Thermo-chemical stability tests will be carried out in order to determine whether these MIEC membrane materials can withstand the atmosphere and temperature conditions present during operation in a coal-fired power plant. Pellets of selected materials will be exposed to CO_2 , water vapour, O_2 and Cr_2O_3 , after which the degradation of their microstructure will be investigated using Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) in combination with Electron Dispersive Spectroscopy (EDS) as well as X-Ray Diffraction (XRD).

3.1 MIEC materials for oxygen permeable membranes

For their application as oxygen separation membranes, mixed ionic-electronic conducting (MIEC) materials must provide a high total conductivity i.e. a high oxygen flux. The total conductivity is the sum of the ionic and electronic conductivities. The ionic and electronic conductivity of MIECs are temperature dependant and can reach values of 1 S cm⁻¹ [17] and 10³ S cm⁻¹ [18], respectively, at high temperatures.

3.1.1 The perovskite structure

The term perovskite is used to describe a mineral with the same crystal structure as calcium titanium oxide (CaTiO₃). This mineral was first discovered in 1839 in the Ural Mountains of Russia by Gustav Rose, who named it after Russian mineralogist Lev Aleksevich von Perovski (1792–1856). The silicate-based perovskite Al-(Mg,Fe)SiO₃ is the main component of the lower earth mantel (70% to 80%) and is considered the most abundant phase on earth. Perovskites have a wide range of attractive properties such as ferroelectricity, superconductivity and also electronic and ionic conductivity.

The general structure of the perovskite mineral is ABX₃, where A and B are cations and X, most commonly, oxygen anions. However, perovskites are not necessarily oxides as fluoride, chloride, carbide, nitride, hydride and sulphide perovskites are also found. In the ABO₃ structure, A is generally a large alkaline earth, alkali or rare earth cation and B is a transition metal or a rare earth metal. The ideal perovskite has a close-packed cubic structure. In the cubic unit cell, the larger A-site cation occupies the body centre of the cube. The smaller B-site cations occupy the corner positions of the cube and are octahedrally coordinated to the oxygen anions in the mid-edge positions of the cube (Figure 3.1). The A- and B-site cations have a 12-fold and 6-fold anion coordination respectively. The total charge of A and B equals +6. A is usually of valence +2 and B of valence +4.



Figure 3.1. Representation of the ideal ABO₃ perovskite structure.

Although the cubic symmetry is the ideal structure, most perovskites have distorted structures due to rotation or tilting of the BO_6 octahedra caused by the relative radius difference between the A- and B-site cations. The most common distortion is the tilting of the BO_6 octahedra to accommodate the radius difference.

In order to study the stability of perovskites, Goldschmidt established, in the early 1920s, the tolerance factor, t, which describes the degree of distortion in perovskite structures and can be determined using the following equation [19]:

$$t = \frac{\left(r_A + r_o\right)}{\sqrt{2}\left(r_B + r_o\right)} \tag{Equation 3.1}$$

where r_A , r_B and r_O are the ionic radii of the A-site cation, the B-site cation and the oxygen anion respectively.

In general, for stable perovskites, t ranges from 0.75 to 1.00 [20]. When t equals unity, the perovskite is expected to adopt the ideal cubic structure while lower values of t correspond to lower symmetry. In the case of a tolerance factor higher than unity, the perovskite structure becomes hexagonal [21]. However, Goldschmidt found that most cubic perovskites have a tolerance factor ranging between 0.8 and 0.9 [22]. If 0.9<t<1, the perovskite will present distortions to rhombohedral symmetry [20]. For values of t between 0.8 and 1.00, the perovskite structure can present several symmetries e.g. cubic, orthorhombic, rhombohedric and quadratic.

Other stability criteria were found to be necessary to determine the possibility of formation of a perovskite structure such as the octahedral factor, which is the ratio of the ionic radii of the B-site cation and the oxygen anion (r_B/r_O). In the case of the ideal perovskite structure, r_B/r_O equals 0.425 [22]. The bond length is another criterion for the formation of a perovskite. For an ideal perovskite

structure, the bond lengths ratio must concur with the following equation [22,23]:

 $D(A-O) = \sqrt{2}D(B-O)$ (Equation 3.2) where D(A-O) and D(B-O) are the bond lengths of A-O bond and B-O bond respectively.

Oxygen migration in oxygen-deficient perovskite oxides ABO_{3-δ}

Among MIEC membranes, perovskite-type ceramic membranes exhibit the highest oxygen permeability due to their high ionic and electronic conductivities. Teraoka et al. [18] showed that the oxygen semipermeability of perovskite-type oxides is linked to the MIEC property of exhibiting very high electronic conductivity and lower ionic conductivity. In the $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ series, the oxygen permeation fluxes were found to be roughly proportional to the ionic conductivity of the perovskite [18]. On the one hand, the ionic conductivity, which controls the oxygen permeation rate [18], is generated by the introduction of oxygen vacancies in the perovskite lattice. This allows the vacancy hopping mechanism of oxygen ions to occur. On the other hand, electronic conductivity is generated by the formation of electron holes which allows the electron hopping mechanism between metal cations of the lattice, counter-balancing the oxygen ion conduction.

Oxygen anion mobility requires crystal defects in the direct vicinity of the lattice site occupied by the ion considered. When no intrinsic defects are present in the perovskite structure, the material does not exhibit ionic conductivity. In order to use this material as a MIEC membrane material, it is therefore necessary to introduce defects in the lattice, most commonly vacancies. They can also be impurities, ions displaced in interstitial sites or lattice ions in valence states such that the total charge of A and B is different from +6 [24]. These crystal defects are usually present in low concentrations at low temperatures. However, high temperatures induce an increase in defect concentration and ion activity, which in turn increase the ionic conductivity of the perovskites [25].

The creation of oxygen vacancies (Vö), which provide a path for oxygen anion transport in the lattice of the perovskite material, is represented by the oxygen non-stoichiometry (3- δ) where (Vö= δ). The degree of non-stoichiometry ranges usually between 0 and 1 [24]. A high vacancy concentration is necessary but the presence of a too large number of vacancies will affect the structural stability of the perovskite.

The oxygen non-stoichiometry results either from the reduction of a mixed valence B-site cation or from the substitution of A- and B-site cations with other cations of lower oxidation state. The introduction of multivalent cations in the B-sites of perovskites leads to the formation of electron holes, while the decrease in total charge of A- and B-sites is compensated by the formation of oxygen

vacancies. Charge defects must be counter-balanced by one of equal magnitude and opposite sign in order for the lattice to remain electronically neutral. Two charge compensation mechanisms are possible: the first one is the formation of oxygen vacancies, the second is the increase in valence state of the transition metal at the B-site. Temperature and oxygen partial pressure conditions will influence the charge defect compensation mechanism.

The valence of A-site cations is usually partially changed from 3+ to 2+ by doping of the perovskite material. If the A cation changes valence two compensation mechanisms are possible. In the first one, the surrounding oxygen anions counter-balance the valence charges by creating vacancies. If an oxygen vacancy is formed, the B-site cations will adjust their valence state and their coordination number [20]. The second one involves, on the one hand, part of the B-site cations modifying their valence state from 3+ to 4+ to balance the local charge. The valence of the A-site cations will not be easily modified since they have a strong ionic bonding with adjacent oxygen anions [20]. As a consequence, the valence of the B-site cations generally depends on the oxidation state of A [26]. On the other hand, as a result of some B-site cations being reduced, thus decreasing their valence state from 3+ to 2+, oxygen vacancies are created to compensate the excess negative charge [20].

The migration of oxygen ions was proven [27] to occur through a saddle point configuration, which is the triangle defined by two A-site cations and one B-site cation. The radius of a circle just touching the radii of these three cations is defined as the critical radius r_c by the relation [28]:

$$r_{c} = \frac{(r_{A})^{2} + 3/4(a_{o})^{2} - \sqrt{2}(a_{o})(r_{B}) + (r_{B})^{2}}{2(r_{A}) + \sqrt{2}(a_{o}) - 2(r_{B})}$$
(Equation 3.3)

where r_A and r_B are the radii of A- and B-site cations, a₀ is the lattice parameter of the unit cell.

Migration of anions having a radius smaller than r_c will pass through this opening without disturbing the boundary cations. A lattice vibration must occur, enlarging r_c , for mobile anions larger than r_c to pass the saddle point configuration [28]. Moreover, the size proportion of A and B is of importance in oxygen transport in the perovskite-type ABO₃ structure. The energy barrier for migration decreases with increasing size of B-site cations and decreasing size of A-site cations [27].

For fast oxide ion conductivity in perovskite materials, the following conditions are necessary [21,28]:

- High concentration of mobile charge carriers: O²⁻
- Sufficient crystallographic sites for the charge carriers i.e. high oxygen vacancy concentration
- · Low mean value of metal-oxygen bonding energy of the perovskite lattice,
- An open structure, i.e. a high lattice free volume, facilitating oxygen ion mobility,

• A critical cation saddle point for O²⁻ migration as large as possible.

Doping and tuning of perovskite properties

Perovskite properties are believed to derive from the non-stoichiometry of cations and anions, lattice distortion and cationic mixed valence, all of which can be tuned by appropriate cation doping. The perovskite structure has great chemical and geometrical flexibility. It can adapt easily to the relative sizes of the ions forming the compound. It can accommodate both high dopant concentrations, with a wide range of cation radii and also a high degree of oxygen non-stoichiometry.

Perovskite-type oxides can be doped by substituting a fraction of the A-site and/or B-site cations by cations with different atomic radii. This property is very interesting as it enables a tuning of the properties of these materials for a wide range of applications. Moreover, the fact that both A- and B-sites are available for substitutions provides a wide range of new possible perovskite materials with new interesting properties.

A typical example of cation substitution is the one of strontium for lanthanum in $LaCoO_{3-8}$. The best dopant among alkaline-earth cations for lanthanum A-site cations is considered to be Sr^{2+} , as it increases considerably the ionic and electronic conductivity. La^{3+} and Sr^{2+} cations have similar ionic radii so no significant distortion is observed. Lattice substitution between La^{3+} and Sr^{2+} is possible since the site distribution of O^{2-} anions around both cations is equivalent. The loss of local charge is balanced by creating oxygen vacancies as well as by the partial conversion of Co^{3+} to Co^{4+} [16,20,18,29].

 $La_{1-x}Sr_xCoO_{3-\delta}$ strontium-doped lanthanum cobaltite exhibits some of the highest oxygen permeation fluxes. However this material shows low stability. Extensive research [16,30,31,32,33] has been conducted on acceptor-doped oxides with the generic formula $Ln_{1-x}A_xCo_{1-y}B_yO_{3-\delta}$ (with A=Sr, Ba, Ca and B=Fe, Cu, Ni; Ln with Ln=La, Pr, Nd, Sm or another lanthanide element). These materials, in which a precise composition can be tailored for a specific application, are considered to be among the most promising for oxygen separation membranes. The widely studied $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ (LSCF) [30,34,31,35] series has been found to be more stable and to exhibit only slightly lower ionic conductivity than the strontium-doped lanthanum cobaltite. The doping of iron was found to be necessary to preserve the stability of the perovskite even at high strontium concentrations [16].

In the LSCF series, the oxygen flux increases with cobalt and strontium content and decreases with increasing iron content [16,18], the highest flux being for $SrCo_{0.8}Fe_{0.2}O_{3-8}$. The partial substitution of Sr^{2+} for La³⁺ creates oxygen vacancies. [16] The increase in oxygen permeation is linked to the increase

in oxygen vacancies in the lattice of perovskite-type membranes. The increase of oxygen flux with the increase in Co^{3+} content is linked to the fact that O^{2-} diffusion is facilitated since Co^{3+} has a smaller ionic radius as well as smaller bonding energy to oxide ions than Fe^{3+} . The substitution of La^{3+} by Sr^{2+} is compensated predominantly by the formation of p-type carriers Fe^{4+} at high oxygen partial pressure (PO₂) (in oxidising atmosphere) and oxygen vacancies at decreasing PO₂. Oxygen vacancies created by further lowering PO₂ (in reducing atmosphere) are charge compensated by reduction of Fe^{3+} to Fe^{2+} leading to an n-type electronic conductivity [36].

The increasing substitution of A-site cation for lower valence metal ions usually causes, on the one hand, an increase in the oxygen permeation flux due to the increase in oxygen vacancy concentration and, on the other hand, a decrease in the phase stability. A compromise between high electronic and ionic conductivity, i.e. high oxygen permeation, and stability of the membrane material is therefore necessary.

3.1.2 The Ruddlesden-Popper phase, K_2NiF_4 -type structure ($A_2BO_{4+\delta}$)

In recent years much attention has been drawn to a different class of mixed ionic-electronic conductors (MIEC) with the K_2NiF_4 perovskite-related structure for application as ceramic membranes for high purity oxygen separation.

The crystal lattice of the K_2NiF_4 -type structure has the general composition $A_2BO_{4+\delta}$, where A is a rare earth cation and B a transition element. It can be described as a succession of perovskite layers ABO₃ alternating with rock salt AO layers in the cdirection (Figure 3.2) [37,38]. Oxygen ionic conduction in K_2NiF_4 -type materials is believed to occur via diffusion of oxygen interstitials in the rock-salt-type layers and also via a vacancy mechanism in the perovskite layers [39,40,41]. In the K_2NiF_4 type structure, the interstitial oxygen atoms are in a tetrahedral environment of A-cations.



Figure 3.2. Representation of the perovskite-like $A_2BO_{4+\delta}$ structure.

One of the most promising K₂NiF₄-type compounds is lanthanum nickelate (La₂NiO_{4+ δ}) considered to have good permeation properties and high stability [42,43]. La₂NiO_{4+ δ} exhibits a wide range of oxygen hyperstoichiometry ($0 \le \delta \le 0.25$), which determines the phase composition, structure and the transport and magnetic properties [40,37]. Oxygen excess in La₂NiO_{4+ δ} is associated with the incorporation of oxygen anions in the rock salt layers LaO, which have sufficient flexibility to accommodate oxygen as interstitial species. The oxygen ion excess is incorporated into the lattice as interstitial O²⁻ or O⁻ ions which are charge compensated for by oxidation of Ni²⁺ to Ni³⁺ or by a combination of oxidised oxygen ion O⁻ and oxidised nickel ion Ni³⁺ [40]. This high concentration of oxygen interstitials leaves a favourable pathway for oxygen mobility in the ab-plane, thus offering the possibility of rapid oxygen transport through the ceramic material [44]. Oxygen diffusion measurements showed that the diffusivity of this material is high and as a consequence that it has highly mobile oxygen interstitials [45]. Moreover, oxide ion diffusion was measured to be 10⁻⁷ cm²s⁻¹ at 750°C [46].

This interstitial oxide ion conduction is an attractive alternative to the vacancy-based conduction mechanism present in the perovskite-type oxides, where the dopant-vacancy interactions can limit the observed conductivity. Skinner et al. have shown that the oxide ion diffusion at temperatures of between 500°C and 800°C of La₂NiO_{4+ δ} is competitive with the usual perovskite materials [44]. It has been proposed that the mobility of the oxide ions occurs mainly through an interstitialcy mechanism in the ab-plane [40], although more recent work [47] has reported a lower activation energy for the diffusion in the c-direction. However, oxygen ion diffusion in the c direction is significantly slower. Even though it is considerably reduced by the limited mobility in the oxygen stoichiometric layers (c-direction), the overall conductivity is high enough to produce competitive oxide ion diffusion compatible with high purity oxygen separation.

 $La_2NiO_{4+\delta}$ appears to be a likely substitute for the usual perovskite materials, e.g. LSCF [48]. It has relatively high values of both ionic and electronic conductivities which makes significant oxygen permeability likely [49]. Moreover its thermal expansion properties and its stability together with its mixed conductivity make it a material competitive with the usual perovskite materials.

3.2 Theory of oxygen transport

In the case of MIEC membranes, the driving force for oxygen transport is the differential oxygen partial pressure across the membrane. On the high oxygen partial pressure (PO₂) side - the feed-side - molecular oxygen is reduced into oxygen anions O^{2-} which are incorporated in the lattice and released at the low PO₂ side - the permeate side - where they recombine to form oxygen molecules.

Higher fluxes are obtained when either or both electronic and ionic conductivity are increased. At a fixed total conductivity, the flux is maximum when ionic and electronic transference numbers are equal, i.e. 0.5. It is therefore important to maximise the product of mobility and concentration of ionic and electronic charge carriers in the appropriate ranges of temperature and oxygen partial pressures for the application considered [50].

The permeation rate through dense oxygen permeable membranes is essentially controlled by two factors: one is the rate of solid state diffusion within the membrane material and the other is the rate of interfacial oxygen exchange on both sides of the membrane [50,15]. A membrane is divided into a central bulk diffusion controlled zone (Wagner) and adjacent interfacial zones, between the gas phase and the oxide, where surface kinetics are predominant, as shown in Figure 3.3. Diffusion is rate determining if the membrane is above a certain thickness. When this thickness is reduced, the transfer of oxygen across the interfaces becomes the limiting factor for the oxygen flux.



Figure 3.3. Diagram representing the chemical potential drop across an MIEC membrane.

The oxygen flux through a membrane can be increased by decreasing its thickness as long as the oxygen permeation is controlled by bulk transport (as shown in Wagner's equation (Equation 3.14)). When the thickness of the membrane reaches a characteristic membrane thickness value, L_c , the permeation is controlled by both surface exchange and bulk diffusion kinetics. For thicknesses smaller than $2L_c$, the oxygen flux is independent of the membrane thickness, L. The characteristic membrane thickness L_c is determined by the ratio of the oxygen self diffusivity and surface exchange coefficient for predominant electronic conductors such as perovskites like LSCF [50,15]. To observe a high increase of the oxygen flux it is possible to decrease the thickness of the membrane to values in the μ m range i.e. thin film techniques [15].

Oxygen transport is also influenced by effects related to microstructure such as grain boundary diffusion and order-disorder phenomena, roughness or porosity of the membrane surface. Teraoka et al. [16] were the first to report the high oxygen fluxes of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ in the range 800-900°C. However conflicting values for the flux through $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ membranes have been measured by other groups, which reflects the influence of many parameters on the permeation flux, such as the characteristics of the sample measured (preparation method, grain size, etc.) and the experimental conditions (PO₂ gradient across the membrane, temperature, etc.)

3.2.1 Bulk transport

In the bulk transport theory it is assumed that the overall oxygen permeation is rate limited by diffusion of oxygen anions or transport of electronic charge carriers (electrons and electron holes) through the bulk oxide. Oxygen diffusion through MIEC oxides is done via an oxygen vacancy transport mechanism as described previously (Chapter 3.1).

The reaction of oxygen ion transport (reaction between the gaseous oxygen and the oxide lattice) is described by the following equation (Equation 3.4) using the Kröger-Vink notation [51]:

$$O_2 + 2V_0^* + 4e' \leftrightarrow 2O_0^x$$
 (Equation 3.4)

where oxygen vacancies V_o^{-} are assumed to be mobile ionic defects and to be fully ionised.

The reaction between electrons and electron holes can be expressed by:

$$nil \leftrightarrow e' + h'$$
 (Equation 3.5)

From Equation 3.4 and Equation 3.5 and assuming equilibrium, the chemical potential gradients of individual species can be expressed by the relations:

$$\frac{1}{2}\nabla\mu_{o_2} + \nabla\mu_{v_o} + 2\nabla\mu_{e'} = 0$$
 (Equation 3.6)

$$\nabla \mu_{\nu} + 2\nabla \mu_{e'} = 0 \qquad (Equation 3.7)$$

where $\mu_{V_o^-}$ is the chemical potential of an oxygen vacancy, μ_{e^-} and μ_{h^-} the chemical potential of electrons and electron holes respectively.

The single particle flux of charged carriers under an electrochemical potential gradient, when cross terms between fluxes are neglected, is given by [52]:

$$j_i = -\frac{\sigma_i}{z_i^2 F^2} \nabla \eta_i \qquad (Equation \ 3.8)$$

In this equation, σ_i is the conductivity, z_i the charge number, F is the Faraday constant. The gradient in electrochemical potential $\nabla \eta$ of the charge carrier *i* is given by:

$$\nabla \eta_i = \nabla \mu_i + z_i F \nabla \phi \qquad (Equation 3.9)$$

where $\nabla \mu_i$ and $\nabla \phi$ represent, respectively, the gradients in chemical and electrical potential.

Under steady-state conditions, no charge accumulation occurs. The flux of electronic charge carriers and ionic defects are related to each other by the charge balance:

$$2j_{v_{e}} = j_{e'} - j_{h'}$$
 (Equation 3.10)

By combining Equation 3.6 to Equation 3.10 and using the relationship $j_{o_2} = \frac{1}{2} j_{v_o^-}$, the oxygen flux across the membrane can be expressed:

$$j_{O_2} = -\frac{1}{16F^2} \frac{(\sigma_{e'} + \sigma_{h'})\sigma_{V_O}}{(\sigma_{e'} + \sigma_{h'}) + \sigma_{V_O}} \nabla \mu_{O_2}$$
(Equation 3.11)

where $\sigma_{e'} + \sigma_{h} = \sigma_{el}$ and $\sigma_{V_0} = \sigma_{ion}$.

Equation 3.11 can be expressed in a more generalised form:

$$j_{o_2} = -\frac{RT}{16F^2} \frac{\sigma_{el}\sigma_{ion}}{\sigma_{el} + \sigma_{ion}} \nabla \mu_{o_2}$$
 (Equation 3.12)

 σ_{el} and σ_{ion} are the partial conductivities provided by oxygen ionic and electronic defects, respectively. Integrating Equation 3.12 over the membrane thickness L using the relation:

$$\nabla \mu_{o_2} = RT \frac{\partial \ln P_{o_2}}{\partial x}$$
 (Equation 3.13)

where R is the gas constant, T the temperature, P_{O_2} the oxygen partial pressure, and x the distance coordinate yields the Wagner equation in its usual form:

$$j_{O_2} = -\frac{RT}{16F^2 L} \int_{\ln P_{O_2}}^{\ln P_{O_2}} \frac{\sigma_{el} \sigma_{ion}}{\sigma_{el} + \sigma_{ion}} d\ln P_{O_2}$$
(Equation 3.14)

where L is the membrane thickness, P_{o_2} and $P_{o_2}^{"}$ represent the oxygen partial pressure at the high- and lean- P_{o_2} side of the membrane respectively.

The Nernst-Einstein relation expresses the ionic conductivity as a function of the diffusion coefficient Dv and of the concentration Cv of mobile oxygen vacancies:

$$\sigma_{ion} = \frac{4F^2 C v D v}{RT}$$
 (Equation 3.15)

The temperature dependence of the diffusion coefficient of oxygen vacancies derived from Fick's law is represented by the relation:

$$Dv = Dv^{0} \exp\left(-\frac{Ea}{RT}\right)$$
 (Equation 3.16)

where Dv^0 is the diffusion coefficient of the oxygen vacancies at infinite temperature and Ea is the activation energy of bulk diffusion.

3.2.2 Surface processes

The oxygen exchange reaction between oxide surfaces and the gas phase involves a number of reaction steps, each step of which can be rate determining. These steps include molecular oxygen adsorption on the oxide surface, dissociation, charge transfer, surface diffusion of intermediate species (e.g. O_{ads} , O_{ads}^{-} and O_{ads}^{2-}) and incorporation into the lattice in the near-surface layer [15]. It is generally assumed that these reactions apply to the re-oxidation of oxygen anions in the reverse direction [53].

Wagner's equation is only valid when bulk transport is the limiting factor for oxygen diffusion across the membrane. However, the surface processes might have a great influence over the rate of oxygen permeation. The gradient in oxygen chemical potential will be consumed partially by the surface exchange kinetics at the interfacial zones of the membrane and partially by the bulk diffusion in the middle-zone [54]. For sufficiently thick membranes, oxygen permeation will be controlled by diffusion in the bulk. A mixed control will occur when the membrane thickness is decreased. For very thin membranes, surface reactions will govern oxygen permeation through the membrane.

Considering near-equilibrium conditions, the oxygen flux through the gas/ceramic interface is given by the Onsager equation:

$$J_{O_2} = -j_{ex}^{o'} \frac{\Delta \mu_{O_2}}{RT} = -j_{ex}^{o'} \frac{\Delta \mu_{O_2}}{RT}$$
(Equation 3.17)

where $\Delta \mu_{o_2}$ and $\Delta \mu_{o_2}$ represent the driving force across the two interfacial zones of the membrane.

Moreover, $\Delta \mu_{O_2} \approx \Delta \mu_{O_2}^{"}$, j_{ex}^{0} is the balanced exchange rate in the absence of an oxygen chemical potential gradient, the value of which can be readily determined using the ¹⁸O-¹⁶O isotopic exchange technique. It is linked to the surface exchange coefficient k_s, which is used to describe the rate of surface exchange, by the relation:

$$j_{ex}^{o} = \frac{1}{4}k_{s}c_{o} \qquad (Equation \ 3.18)$$

where c_o is the concentration of oxygen anions at equilibrium.

It was shown [55,56] that the high oxygen fluxes through cobaltite perovskites seem to be limited by surface exchange. The ratio $h=k/D^*$ was introduced, where k is the surface exchange coefficient and D* the tracer diffusion coefficient. This ratio has been considered a convenient parameter to determine the contribution of surface exchange in oxygen permeation kinetics. The small h values correspond to a high contribution to the total oxygen permeation resistance relative to bulk diffusion.

Determination of the Characteristic Membrane Thickness Lc

 L_c was introduced by Bouwmeester et al. in order to distinguish whether bulk diffusion or surface exchange govern the kinetics of oxygen permeation [50,15]. L_c is equal to the reciprocal of the ratio h. When both processes share the kinetics, L_c can be defined as:

$$L_{c} = \frac{RT}{16F^{2}} \frac{\overline{t_{el}\sigma_{ion}}}{j_{ex}^{o}}$$
(Equation 3.19)

where t_{el} is the electronic transference number and $\overline{t_{el}\sigma_{ion}}$ is the average value of the product of t_{el} and σ_{ion} .

 L_c can only be calculated at small PO₂ gradients across the membrane [54]. By combining Equation 3.17 and Equation 3.19, the total flux equation can be written as:

$$j_{o_2} = \frac{1}{1 + 2L_c/L} \frac{\overline{t_{el}\sigma_{ion}}}{16F^2} \frac{\Delta \mu_{o_2}^{total}}{L}$$
(Equation 3.20)

For membranes with high thickness values, Equation 3.20 equals Wagner's equation (Equation 3.14). When the thickness of the membrane is much lower than $2L_c$, the oxygen flux is independent of the thickness of the membrane. A value of 100µm is often quoted as the characteristic membrane thickness for perovskite structures although the L_c value can be much higher, up to 3000µm [50,54]. Calculations show that L_c can vary from the µm range to the mm range [15].

The characteristic thickness is represented by:

$$L_c = \frac{D}{k} = \frac{D^*}{k}$$
 (Equation 3.21)

where D is the self-diffusion coefficient of oxygen anions. If correlation effects can be neglected, $D=D^*$ [15].

3.3 Oxyfuel process

The oxyfuel process consists in the burning of coal in an oxygen-rich atmosphere to produce a flue gas highly concentrated in CO₂. This will allow the flue gas to be composed of relatively clean exhaust gases, steam and CO₂ (80% to 85%). In this process, the flue gas will be used to sweep the permeate side of the membrane in order to collect the molecular oxygen released from its surface.

Combustion in pure oxygen is a technology that has been used for years in the glass and metal manufacturing industries. Today, the cryogenic air separation technique is the only proven option for the oxyfuel process on an industrial scale [5]. From a technical point of view, the oxyfuel process can be applied to retrofits to existing coal-fired power plants as well as new ones [57]. Large scale applications of oxygen permeable membranes have not yet been developed. However, laboratory scale experiments have been performed [58,59,60,61,62], which enables an estimate of the flue gas composition and temperature. Moreover, several aspects of the oxyfuel process for use in coal-fired power plants, e.g. boiler design, combustion reactions and kinetics, gas cleaning technology etc., need to be further investigated in test pilot plants. The world's first pilot coal-fired power plant with CO_2 capture was inaugurated in September 2008 at Schwarze Pumpe in Germany by Vattenfall AB. It has a thermal capacity of 30 MW [63]. This project will improve understanding of the processes involved in oxyfuel combustion capture. Several aspects of the oxyfuel combustion process need clarifying, such as the combustion (reactions, ignition and flame stability), heat transfer and emission levels.

3.3.1 Oxycombustion

The combustion gas used for the oxyfuel process should have a 95% to 99% oxygen purity, the rest being mainly argon and nitrogen [64,65]. A 5% to 15% [58,65,66,57] excess of oxygen supplied to the boiler is necessary in order to obtain a stoichiometric and homogenous combustion of the coal. The flue gas is composed mainly of CO_2 but also water vapour, and small concentrations of impurities such as NO_x , SO_x , O_2 (from the oxygen excess), noble gases, metals and particulates [31]. The flue gas from the boiler is sent through a gas clean up process to remove particulates and acid gases. A DeNOx treatment unit is unlikely to be necessary in the oxyfuel process since NO_x should not be formed during the combustion in pure O_2 . However, the boiler air in-leakage (8%-16%) [64] could lead to the formation of small amounts of NO_x . A reduction of up to between 60% and 70% of NO_x emissions between combustion in air and oxy-combustion has been reported [10]. Other studies show much lower decreases of around 7.5% [43]. The concentration of SO_x on the other hand has been proven to be higher than for combustion in air since it is not diluted by the N_2 in air. Increases to over 200 ppmv

have been reported [11]. DeSOx might therefore be necessary to avoid building up sulphur inside the boiler. [10,11]. Another option would be the co-storage of SO₂ together with CO₂ (and possibly NO_x) since they have similar physical properties [64]. After complete dehumidification of the flue gas, it is estimated to have a CO₂ purity ranging between 80% and 95% [58,66,5]. The final step in this process is the compression and storage of the CO₂-rich stream.

3.3.2 Flue gas recycling

Flue gas recycling is necessary in the oxyfuel process for several reasons. The percentage of flue gas to be recycled has been determined in order that the combustion temperature remains the same as for a conventional air-fired power plant. Since combustion in pure oxygen leads to very high temperatures, around two thirds of the flue gas needs to be recycled into the boiler in order to control the combustion temperature [57]. It also compensates for the volume of missing N_2 so that the volume of gas to carry the heat through the boiler is sufficient [58,65-66,57]. Flue gas recycling also provides an increase in the concentration of CO_2 in the flue gas, which will be beneficial for the separation process of CO_2 from the rest of the flue gas [11]. This flue gas recycling will replace the effect of nitrogen as a heat sink that limits the temperature to about 2000°C under stoichiometric conditions. Moreover, the recycled flue gas stream is used to sweep the permeate side of the membrane thus lowering the oxygen partial pressure of that side of the membrane and allowing for the gradient in oxygen partial pressure to remain across the membrane. Additionally, sweeping the membrane with the recycled flue gas collects the oxygen ions released from its surface.

3.3.3 Flue gas composition

Simulations [65] have shown that the flue gas composition at the boiler exit is approximately 66w% CO_2 and 19w% H_2O ; N_2 and Ar accounting for 8w% and O_2 for 1w%. The study of a pilot-scale 1.5MW_t boiler [10] resulted in the determination of a dry flue gas composition of around 80vol% CO_2 , 3vol% O_2 and 17vol% N_2 . Without air infiltration into the boiler, the CO_2 content would reach 94vol% to 95vol%. Studies [58,66] found an estimated 89 vol% CO_2 purity of the flue gas. A simulation study of the boiler of a western Canadian pulverised coal-fired power plant of 400 MWe calculated that the purity of the dry flue gas was 91% CO_2 . It was assumed that the combustion took place in pure oxygen with flue gas recycling, at a ratio of 30/70 respectively. Moreover, the composition of the flue gas on a wet basis was found to be around 4%N₂, 3%O₂, 19%H₂O and 74%CO₂ [5].

The emission characteristics of CO₂, SO₂ and NO_x in the flue gas of coal combustion were investigated by varying the compositions and concentrations of the feed gas (O₂/CO₂/N₂) and the ratios of recycled flue gas. These studies suggest that the ideal O_2/CO_2 ratio in the feed is 30/70 with 40% or 50% recycled flue gas since it leads to the highest possible CO_2 purity in the flue gas of more than 95% [60,61,11].

3.3.4 Combustion

Coal combustion in the oxyfuel process is expected to be different from conventional air-combustion since CO_2 has a larger specific heat than N_2 [11]. The flue gas density is increased as CO_2 has a higher molecular weight than N_2 , i.e. 44 and 28 respectively. The flue gas volume in the oxyfuel process is decreased 4- to 5-fold compared to burning in air [10], since there is no dilution with nitrogen. This leads to a higher boiler efficiency. Moreover, the high concentrations of CO_2 and H_2O result in higher radiative and convective heat transfer compared to air-fired power plants [65].

3.3.5 Combustion gas composition

Little information is available concerning the feed gas composition in the oxyfuel process. However, a literature study of the oxyfuel process [57] assessed its characteristics to be a high proportion of O_2 in the feed gas, typically around 30% and a flue gas recycling of about 60% to 70%. Combustion studies of coal in different feed gas compositions [59,62] showed that a feed gas concentration of 28 vol% O_2 with the rest being mainly CO₂ produced slightly lower heat flux characteristics compared to air-fired combustion. The study of a 20 KW down-fired coal combustor [11] confirms that to reach the gas temperature in the combustion chamber of an air-fired plant, the oxygen concentration in the feed gas must be 30% or higher. A feed gas with a composition of 30% O_2 and 70% CO₂ enables a combustion with similar temperature profiles to those of conventional air-fired power plants. A 3 MW pilot scale study of coal oxyfuel combustion carried out by the Energy and Environmental Research Corporation (EERC) determined that with wet recycling, around 24% oxygen in the feed gas is necessary to reach the overall heat transfer obtained in an air-fired plant and that 27% is needed with dry recycling [67].

Research in the oxyfuel combustion process is currently considering two mechanisms for flue gas recycling as sweep gas over the permeate side of the membrane. In the first one, so-called "wet recycling", the flue gas is recycled directly after the clean up process that removes of particulates and acid gases. The gas swept over the membrane surface will be composed mainly of water and CO₂. In the second mechanism, so-called "dry-recycling", water is eliminated from the flue gas by condensation. However, a complete removal of water by simple condensing is not possible. Indeed, the use of molecular sieves is the only technology available to completely eliminate water from the flue gas

[66]. The sweep gas will be highly concentrated in CO_2 . Schematic representations of the two possible oxyfuel paths together with the estimated flue gas composition are shown in Figure 3.4 and Figure 3.5.

The operating conditions in the oxyfuel process are very aggressive. Therefore, the membrane materials that will be used in coal-fired power plants for the oxyfuel process have to be stable in the gaseous atmosphere of the flue gas.



Figure 3.4. Schematic representation of the oxyfuel process with water condensation.



Figure 3.5. Schematic representation of the oxyfuel process without water condensation.

4 Characterisation techniques

In order to characterise the changes in microstructure of the materials, a series of analytical techniques were used, namely, X-Ray Diffraction (XRD), light microscopy, Scanning Electron Microscopy (SEM) and Transmission Electron Microscopy (TEM) in combination with Electron Dispersive Spectrometry (EDS). Thermal analysis techniques e.g. Differential Thermal Analysis (DTA), Thermo mechanical Analysis (TMA), Thermogravimetric Analysis (TGA) were also used to characterise the properties of the different materials.

4.1 X-ray diffraction technique (XRD)

X-ray diffraction is an analytical technique that uses x-rays to characterise the phases present in a sample. This technique is used to determine the crystalline structure and composition of materials by their interference pattern of scattered x-rays. In x-ray tubes, a beam of electrons generated by a heated tungsten filament is accelerated towards a metal target, commonly molybdenum and copper. The high energy electrons produced can eject core electrons from the metal. When an outer shell electron fills an inner shell vacancy, an x-ray photon with the characteristic energy of the target material will be emitted. When an incident beam of x-rays strikes the surface of a crystal, the angle of the scattered beam can be used to determine the distance between layers of atoms in a sample using Bragg's law:

$$2d\sin(\vartheta) = n\lambda \qquad (Equation 4.1)$$

where d is the lattice spacing (nm), θ is the angle of incidence of x-rays (rad), λ is the wavelength of x-rays (m) and n is an integer. The peaks in an x-ray diffraction pattern are directly related to the atomic distances in a material.

In this work, XRD measurements of the surface of pellets or of powdered samples were carried out. The crystalline structure of the specimens was determined using a Siemens D500 diffractometer (Siemens AG, Karlsruhe, Germany) equipped with a monochromated Cu-K α radiation source. The diffraction patterns were recorded in the 2 θ angle range of between 15° and 85° at room temperature, with steps of 0.02°, a counting time of 1s per step and a resolution of (1/100)°. The voltage and current of the X-ray generator were 40 kV and 40 mA respectively.
4.2 Scanning electron microscopy (SEM)

Scanning electron microscopy (SEM) is a method for high-resolution imaging of surfaces that uses electrons for imaging when light microscopy uses visible light. The SEM has great magnification (up to 1000000×) and great depth of field which allows a large area of the sample to be in focus at one time. An incident beam of monochromatic electrons is raster-scanned across the sample's surface, and the resulting electrons emitted from the sample are collected to form an image of the surface. The electron beam is generated by a tungsten filament on which a voltage is applied thus causing it to heat up to approximately 2500°C. The electrons are accelerated toward the anode, which is positively charged with respect to the filament, and therefore forms powerful attractive forces for electrons. An electron detector is used with the SEM to convert the radiation of interest into an electrical signal for manipulation.

Energy dispersive x-ray spectroscopy (EDS) is a qualitative and quantitative chemical microanalysis technique performed in conjunction with a scanning electron microscope. It is an analytical technique that uses the x-rays that are emitted from the sample during bombardment by the electron beam to characterise the elemental composition of the volume analysed. Features or phases as small as about $1\mu m$ can be analysed. The minimum detection limits vary from about 0.1 weight percent to a few percent depending on the element and matrix [68].

Using SEM in combination with EDS makes it possible to observe the surface morphology and the cross-section of samples as well as to identify the composition of the different phases formed. Two SEM devices were used to carry out the investigations, namely the Stereoscan LEO440 (Cambridge, U.K.) with an acceleration voltage (EHT) of 20 kV and the Zeiss Supra50VP with an acceleration voltage of 15 kV. The EDS analyses were made with type ISIS 300 (Enysham, U.K.). The micrographs of the cross section were taken in the backscattered electron mode (BSE). The interpretation of the x-ray pattern was performed using the Software INCAEnergy/Wave. Furthermore, SEM requires the sample to be conductive in order to avoid charging effects. This is achieved by coating the sample in vacuum with platinum using a sputter coater.

4.3 Thermal Analysis

Thermal analysis techniques explore various aspects of changes occurring in a sample. Phenomena evolving during the reactions on heating or cooling under a temperature programme in a controlled atmosphere are observed.

4.3.1 Differential Thermal Analysis combined with thermogravimetry (DTA/TG)

DTA measurements provide information about transformations, either exothermic or endothermic, in the material that have occurred, relative to an inert reference, as a function of temperature and time. The main applications of DTA are to study phenomena occurring in materials such as transition, chemical reaction, adsorption, crystallisation, melting, and sublimation. It is possible to measure the heat of reaction and determine kinetic parameters.

In differential thermal analysis, two cells are used, one containing the sample under investigation and the other a reference material of thermally inert behaviour. The sample and the reference placed in alumina crucibles are subjected to identical heating and cooling conditions, in a furnace in a controlled atmosphere. The difference in temperature that develops between the sample and the reference material is measured while both are subjected to the same programmed increase or decrease in temperature [69,70,71].

The DTA/TG device used was a STA 449C Jupiter, Netzsch, (Germany). The cells can be heated to a maximum temperature of 1650°C and the sample investigated can weigh up to 5g. The resolution of the device is 0.1µm and 0.1µW for TG and DTA respectively. The investigation of powdered samples was carried out over the temperature range of 20°C to 1500°C with a heating and cooling rate of 5K/min.

4.3.2 Precision Thermogravimetric Analysis (TGA)

The TGA technique provides information about the chemical and thermal stability of materials and is commonly used to investigate decomposition, dehydration, oxidation reactions, reaction pathways, kinetics of reaction and quantity of specific component. The TG device, also called a thermobalance, records changes in mass of a specimen as a function of temperature, time, as well as atmosphere. The sample is placed in the thermobalance and is subjected to programmed heating and cooling cycles by a furnace in which the gaseous atmosphere can be varied. The mass change is accompanied by various physical and chemical processes which are detected [69,70,71].

In the current study, the thermobalance was used to monitor changes in oxygen non-stoichiometry. The TG device was a UMTS-5 from Mettler-Toledo (Giessen, Germany). Samples weighing up to 5g can be measured with an accuracy of $0.1\mu g$ [72]. This thermobalance was used in conjunction with a high temperature furnace that can achieve temperatures of up to 1600°C. Different gases are available, such as O₂, N₂, Ar, Ar/4%H₂. The sintered pellets were analysed in an atmosphere containing 20 vol% O₂

and 80 vol% Ar, in the temperature range of between 20°C and 1100°C, with heating and cooling rates of 0.625K/min.

4.3.3 Thermo Mechanical Analysis (TMA)

Dilatometry is the measurement of dimensional changes of a sample while subjected to a programmed heating or cooling in a controlled atmosphere. The TMA technique is commonly used to determine softening, sintering and glass transition temperatures of materials, as well as sintering temperatures of ceramics [69,70]. The device used in the current study measured the linear expansion or contraction of a specimen as a function of temperature and time under negligible loads.

The thermal expansion coefficient (TEC), α , can be determined from dilatometric data using the relation:

$$\alpha = \frac{1}{L_0} \cdot \frac{\Delta L}{\Delta T}$$
 (Equation 4.2)

where ΔL and ΔT are the variations of sample length and time respectively and L_0 is the original length of the sample before experimentation.

The dilatometer used was a Setsys Evolution, Setaram (France), in which the maximum temperature is 1600°C. The measurement range to be selected is either up to 200µm or up to 2000µm. The dimensions of the specimen can be up to 20mm in height and 10mm in diameter. However, this technique requires the samples being measured to have a minimum height of between 6mm and 10mm in order to detect significant changes in length. The resolution of the device is 0.2nm. The measurements were carried out in air under a load of 5g, The samples were heated from 20°C to 1100°C where they were kept for a dwelling time of 1 hour and then cooled down to 20°C with heating and cooling rates of 3K/min. The samples need to have plane-parallel surfaces, which is why they were sanded on SiC grinding paper.

4.4 Mass spectrometry

Mass spectrometry is a micro-analytical technique used for the quantitative determination of the elemental composition of a specimen, which is done through the experimental measurement of the mass of gas phase ions produced from the ionisation of the molecules and atoms of a specimen. These ions are separated according to their mass to charge ratio (m/z) and then detected.

The three functional modules of a mass spectrometer, represented in Figure 4.1 are:

- The ioniser
- The mass analyser
- The detector



Figure 4.1. Schematic representation of Mass spectrometer.

Electron ionisation (EI) produces molecular ions from a gas phase specimen in the ionisation chamber. These molecular ions fragment in a reproducible and unique way enabling their identification. Ionisation and fragmentation of gas phase molecules occur from their interaction with ionising low energy electrons, which are generated from an electrically heated filament (the cathode) to a temperature at which it emits free electrons. The electrons emitted are accelerated through an electric field and attracted to a trap (the anode) located opposite the cathode in the ionisation chamber, which pressure is around 10^{-1} Pa in order to minimise the collisions between ions and molecules.

The mass analyser used in this work was an ion trap quadrupole, which separates the ions produced by the ionisation process according to their mass to charge ratio (m/z). A high frequency electric field is created between two pairs of opposing hyperbolic rod electrodes. The voltage between the rod electrodes consists of a direct voltage, onto which is superimposed a high frequency alternating voltage. This electric field, corresponding to a certain value of voltage, frequency and field radius, traps ions of all m/z values and only the ions of interest with a specific m/z ration are accelerated towards the ion detector, where they are electrically detected. The trapped ions are neutralised and filtered out [73]. Quadrupole mass spectrometers require high vacuum, the total pressure used is less than 10^{-5} mbar

A quadrupole mass spectrometer OmniStarTM from Pfeifer (Germany) was used in this work to analyse the composition and purity of the different gas streams of the permeation set-up. The detection threshold of this device is as low as 1ppm. Twelve gas lines are connected to the mass spectrometer through temperature controlled steel capillaries. The control and evaluation software QuadStarTM 32-bit enables switching of the gas stream analysed.

4.5 Density measurements

The density of the samples was determined by the Buoyancy method based on the Archimedean Principle. The apparent weight of the sample, i.e. the weight reduced by the buoyancy force, in a reference liquid was measured by a precision balance. The value of the weight of the sample in air combined with the weight of the sample in the reference liquid was used to calculate the density of the sample. Ethanol was used as the reference liquid for the measurements. The density of ethanol was determined using a quartz glass reference cylinder. The density measurements were carried out at least five times to average out the variation in values measured.

The volume that the sample occupies in air and the volume of liquid displaced by immersing the sample are the same, which gives:

$$V_l = \frac{m_l}{\rho_l} = V_s = \frac{m_s}{\rho_s}$$
(Equation 4.3)

with m_l and m_s the weight of the sample weighed in liquid and in air respectively and the density of the sample and the density of the liquid. The mass of the liquid ml is yielded by the difference between the weights of the sample in air ma and in liquid ml, the apparent immersed weight:

$$m_{liquid} = m_s - m_l \qquad (Equation \ 4.4)$$

This leads to:

$$\rho_s = \rho_l \frac{m_s}{m_s - m_l} \tag{Equation 4.5}$$

The relative density (in %) is given by:

$$\frac{\rho}{\rho_0} \times 100 \qquad (Equation \ 4.6)$$

where ρ and ρ_0 are the actual and the theoretical densities respectively.

The theoretical density (ρ_0) is determined by:

$$\rho_0 = \frac{Mz}{N_a V_{el}}$$
(Equation 4.7)

where M is the molar mass of the material considered, N_a is the Avogadro constant, z is the number of atoms per unit cell and V_{el} is the elementary cell volume.

4.6 ICP-OES

Inductively Coupled Plasma-Optical Emission Spectroscopy is a qualitative and quantitative technique for chemical analysis which enables the determination of the composition of metals, minerals, ashes, glasses, ceramics, oils, mixed oxides and perovskites. The inductively coupled plasma is used to produce excited atoms and ions. This property is used to determine the composition of samples from the release of radiations at wavelengths characteristic of each element. The intensity of this emission indicates the concentration of the element within the sample. Standard calibration solutions of known concentration are used to determine the concentration of each element in the solution [74].

The stoichiometry of powders was controlled by optical emission spectroscopy, IRIS from Thermo (TJA). 10mg of sample was dissolved in a mixture of 3ml HCl/1ml H₂O₂, filled to 50ml with distilled water. In ICP-OES analysis, the liquid sample is atomised in a nebuliser system and introduced into the inductively generated argon plasma, where it is ionised. The spectrum emitted is transferred into a spectrometer where it is decomposed into the individual wavelengths and evaluated. The intensities of the spectral lines are measured by CID semiconductor detectors. The relative error for the measured elements is of $\pm/-3\%$.

4.7 Hot gas extraction

The analysis of the oxygen content in a specimen was conducted by heating the specimen in a gaseous stream of helium, in a graphite crucible, by means of resistance heating. Oxygen is determined by infrared detection of the content of CO_2 , resulting from the reaction of oxygen and graphite. This method is suitable for the determination of the nitrogen, oxygen and hydrogen content in metals, minerals, rock, ceramic materials and perovskites, etc. High accuracy and reproducibility of the analysis results from using calibration standards (RSD: 1-3%) The analysis was carried out with the Leco TCH 600 nitrogen/oxygen/hydrogen determinator. The instrumental detection limit is $0.5 \ \mu g \ g^{-1}$ [75].

5 Materials selected for this study

Gas separation membranes are considered to be an efficient technology for the future generation of zero CO_2 -emission power plants. To be a promising oxygen separation membrane material, it must satisfy important criteria. The material must exhibit high oxygen permeability as well as a stable lattice structure under oxygen partial pressure gradients. Moreover, the minimum electronic conductivity required for use as oxygen permeable membrane was defined as being 100 S cm⁻¹ [31].

For this work, four MIEC oxides were selected for their interesting properties:

- $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF58)
- $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58)
- Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃₋₈ (BSCF50)
- $La_2NiO_{4+\delta}$

The LSCF58 and PSCF58 materials were synthesised at Forschungszentrum Jülich, at the partner institute (IEF-1), by the spray-drying process using aqueous nitrate solutions of the different cations. The lanthanum nickelate and BSCF50 powders used in this work were purchased from Treibacher Industrie AG, Austria.

The mixed conducting acceptor-doped perovskite and perovskite-related oxides selected for this work, together with their main properties, are described below:

5.1 Mixed conducting acceptor-doped perovskites

MIEC oxides have attracted great attention since they exhibit high levels of electronic and ionic conductivity as well as a high degree of stability [34]. Teraoka et al. [16] measured permeation rates of perovskite-type oxides one or two orders of magnitude higher than those of stabilized zirconia.

5.1.1 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF58)

LSCF58 has been developed as one of the standard reference materials for solid oxide fuel cell (SOFC) cathodes. The electronic conductivity of these materials is extremely high, typically in the range 10^2 S cm⁻¹ to 10^3 S cm⁻¹, with the materials not containing iron (y=0) exhibiting the highest values [18,76]. Moreover, the electronic conduction in perovskite materials remains predominant in usual ranges of temperature and oxygen partial pressure [50]. Indeed, the ionic conductivity of LSCF ranges

between 1 S cm⁻¹ and 10⁻² S cm⁻¹ at 800°C [18,76]. Membranes of the LSCF series were found to exhibit oxygen semipermeability at temperatures above 500°C and high oxygen permeation fluxes [16]. The study of a tubular $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-8}$ membrane found permeation fluxes of about 0.21 cm³/cm² min at 900°C [77]. The electronic conductivity of the well-studied $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-8}$ was found to be relatively high, i.e. 333 S cm⁻¹ at 800°C [30] and approximately 250 S cm⁻¹ at 800°C) [31]. The ionic conductivity was found to be several orders of magnitude lower than the electronic conductivity, i.e. 10^{-2} S cm⁻¹ at 800°C [31].

5.1.2 $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58)

In the present study, praseodymium was chosen as a substitute for lanthanum in the LSCF58 perovskite material as an attempt to increase the oxygen permeability. It was found [16] that for A-site substitution, the oxygen permeation flux increased with a decrease in ionic radius, which seems to lower the potential energy barrier for oxide ion migration. In the series $Ln_{0.6}Sr_{0.4}CoO_{3-6}$ (with Ln=lanthanide such as La, Pr, Nd, Sm and Gd), the oxygen flux was found to increase with decreasing radius of the lanthanide ion [78]. Praseodymium, which has a lower ionic radius than lanthanum, was therefore judged to be a good candidate as a replacement for lanthanum in LSCF. Moreover praseodymium oxide (PrO_x) has a high electrocatalytic activity in electrochemical reactions involving oxygen [79]. It was found [80] that applying a layer of PrO_x as activating agent on the surface of lanthanum nickelate based membranes enhanced the oxygen permeation fluxes at high PO₂ gradients. The ionic conductivity in $Pr_{1-x}Sr_xCo_{1-y}Fe_yO_{3-6}$ (PSCF) is expected to be higher than that of LSCF because of the possibility of a valence change from Pr^{3+} to Pr^{4+} which would result in the increase in oxygen vacancy formation. For the $Pr_{1-x}Sr_xCo_{0.8}Fe_{0.2}O_{3-6}$ series, the electrical conductivity was found to be at least higher than 279 S cm⁻¹ between 600K and 900 K [90].

Lanthanum and Praseodymium deficiencies were introduced into the membrane material in order to enhance the oxygen permeation fluxes. A cation non-stoichiometry will introduce additional oxygen vacancies into the lattice due to a shift in the charge balance between cations and anions. The creation of oxygen vacancies increases the concentration of charge carriers and could improve the electrical and ionic conductivity of the material.

5.1.3 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF50)

 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was chosen in this study because this MIEC material exhibits some of the highest oxygen permeation fluxes and has a high structural stability. The barium cation (Ba^{2+}) was

found [78] to be the most effective A-site dopant in $LnCoO_{3-8}$ (Ln=lanthanide such as La, Pr, Nd, Sm and Gd). The use of barium cations instead of lanthanum cations (La³⁺) at the A-site in $SrCo_{0.8}Fe_{0.2}O_{3-8}$ was reported to increase the structural stability of the perovskite material by preventing oxidation of the B-site cation i.e. Co^{3+} to Co^{4+} and Fe^{3+} to Fe^{4+} [24,81,82]. Doping the A-sites of $SrCo_{0.8}Fe_{0.2}O_{3-8}$ with barium cations, which have a larger ionic radius than strontium cations (Sr^{2+}), was found [81] to increase the phase stability of the membrane material while keeping the oxygen flux levels constant. The substitution of Sr^{2+} by Ba^{2+} results in the reduction of the repulsive interaction generated from oxygen ion migration through the saddle point configuration as well as the increase in mobility of oxygen ions [82]. Furthermore, it was found [81] that the substitution of Ba^{2+} for La^{3+} at the A-site of $SrCo_{0.8}Fe_{0.2}O_{3-8}$ also slightly improved the oxygen permeation flux.

The oxygen permeation fluxes of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes were investigated in numerous studies [81,83,84,82,85,86,87,88], which measured very high flux values. Indeed, for disk shaped membranes, fluxes of up to 1.4 ml.cm⁻².min⁻¹ at 950°C [81,83], 3 ml.cm⁻².min⁻¹ at 850°C [85], 1.9 ml.cm⁻².min⁻¹ at 875°C [86] and 10⁻⁶ mol.cm⁻².s⁻¹ at 900°C [87] were reported. Fluxes as high as 3 ml.cm⁻².min⁻¹ at 900°C [82] were reported for a tubular BSCF50 membrane. A flux of 1.12 ml.cm⁻².min⁻¹ at 875°C for 150 hours continuous operation was measured which demonstrates the good stability and excellent permeability of the BSCF50 membrane material [82]. Moreover, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was reported to exhibit a stable oxygen permeation flux under an air/He partial pressure gradient for 1000 hours operation as oxygen separation membrane at 850°C [81].

The cobalt-rich MIEC materials usually exhibit high thermal expansion coefficients (TECs) [89] which is partially caused by the large variations of the ionic radius of cobalt in the material deriving from the oxidation of Co^{3+} to Co^{4+} . Thermal expansion mismatch would be a serious issue when combining membrane and construction materials in the heated areas of a coal-fired power plant. The membrane materials should have TECs close to that of the construction materials to avoid mechanical stresses and possible cracking of the membrane.

La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- $\delta}} was found to exhibit a high TEC value of 17.4 10⁻⁶ K⁻¹ in the temperature range 30°C-1000°C [90], which is very close to the TEC value of 17.5 10⁻⁶ K⁻¹ measured for La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}$ [30]. In the Ln_{1-x}Sr_xMn_{1-y}Co_yO_{3- δ} series, with Ln=lanthanide, the TECs of the perovskite material were measured to decrease with decreasing ionic radius of the lanthanide ion i.e. for Ln=Pr the TEC was lower than for Ln=La [91]. The TEC of Pr_{0.6}Sr_{0.4}Co_{0.8}Fe_{0.2}O_{3- δ} was found to be as high as 19.7 10⁻⁶ K⁻¹ in the range 30°C-850°C [92]. However, the cation non-stoichiometric material, Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} (PSCF58), was found to exhibit lower TEC, as linear TECs of 13.4 10⁻⁶ K⁻¹ at 700°C and of 15 10⁻⁶ K⁻¹ at 850°C were measured [93]. Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} was found to have the}</sub>

highest thermal expansion coefficient among the selected materials. Indeed, TEC values of up to 19.8 10^{-6} K^{-1} [94], 18 10^{-6} K^{-1} in the temperature range of between 25°C and 1000°C [85] and 16 10^{-6} K^{-1} and 31 10^{-6} K^{-1} in the range 20°C to 600°C and 600°C to 1100°C respectively [95] were found. TEC values for BSCF50 derived from high temperature XRD data were reported to be as high as 21 10^{-6} K^{-1} in the temperature range of between 20°C and 1000°C [96]. However, lower TEC values were also measured e.g. 11.5 10^{-6} K^{-1} in the range 30°C-1000°C [97].

5.2 Perovskite-related oxides

5.2.1 $La_2NiO_{4+\delta}$

La₂NiO_{4+ δ} has been reported to possess relatively high values of both ionic and electronic conductivity. The electronic conductivity was found to be as high as 100 S cm⁻¹ at 700°C [9,13,98,99,47] 103 S cm⁻¹ at 450°C , 76 S cm⁻¹ at 800°C [72 100], 60 S cm⁻¹ at 700°C [68 101], 48 at 700°C [73 102]). The ionic conductivity, which is several orders of magnitude lower than the electrical conductivity, was measured to be 1.5 10⁻² S cm⁻¹ [47]. La₂NiO_{4+ δ} was found to exhibit high permeation fluxes, comparable to those measured for the materials of the La_{1-x}Sr_xCo_{1-y}Fe_yO_{3- δ} series. Fluxes of up to around 4.10⁻⁷ mol.cm⁻².s⁻¹ at 950°C [43], 2.5 10⁻⁹ mol.cm⁻².s⁻¹ at 1000°C [103], 4 10⁻⁸ mol.cm⁻².s⁻¹ [104] and 3.4 10⁻⁷ mol.cm⁻².s⁻¹ [105] were reported.

Moreover, the A_2BO_4 structure has higher thermo-chemical stability than the perovskite-type structure. Both structures undergo a partial reduction/oxidation reaction resulting in oxygen vacancy and electron hole defects. However, at high temperature and low oxygen partial pressures, the ABO₃ phase becomes unstable and undergoes a reaction to A_2BO_4 [101]. The oxygen transport properties of $La_2NiO_{4+\delta}$, e.g. tracer diffusion and surface exchange coefficients, were found to be close to current MIEC materials such as LSCF [44,39,40].

In contrast to perovskite-type membranes, the thermal expansion coefficient of $La_2NiO_{4+\delta}$ is relatively low (around 13.0 10⁶ K⁻¹ [9,1,98,39,106,119] and as low as 11.6 10⁶ K⁻¹ [101], and 13.8 10⁶ K⁻¹ [42]), which is an advantage when upgrading the membrane test set-up to an industrial scale. Moreover, its relatively low thermal expansion coefficient and high structural stability [42] together with its mixed conduction properties make $La_2NiO_{4+\delta}$ an excellent option for use as a gas separation membrane in the framework of the oxyfuel process in coal-fired power plants.

5.3 Sample preparation

5.3.1 Pressing

Samples for the annealing experiments:

The powder was shaped into pellets by applying around 125 MPa in a uniaxial cylindrical press at room temperature. An aqueous solution of around 1% carboxymethyl cellulose (CMC) was used as binder to improve bonding of the powdered material. The green-bodies weighed around 0.5g and were 8mm in diameter.

Samples for the permeation experiments:

Disk membranes were uniaxially pressed at room temperature at a pressure of around 100 MPa from powdered material.

5.3.2 Sintering

Sintering is a thermally activated process which involves coarsening and densification of the powdered samples. In the first stage of sintering, a physical reaction takes place which results in the formation of necks between the grains which are in contact with each other. Small particles merge into larger ones, resulting in greater mean pore size. In the second stage of sintering, as the temperature increases, the necks broaden and shrinkage occurs which changes the microstructure of the packing. The driving force for sintering is a decrease of the surface energy of the system with solid state diffusion from areas with relatively large convex curvature (high Gibbs free energy) to areas with small concave curvature (low Gibbs free energy) [50].

Samples for the annealing experiments:

The pressed green-bodies were sintered in alumina crucibles. A bed of powder was placed between the pellets and the alumina crucible to prevent chemical interactions. The crucibles were covered in order to avoid evaporation of elements from the surface of the material.

The temperature programme used is described below:

The samples were first heated to 400°C with a heating rate of 3K/min in order for the binder to evaporate slowly to prevent the formation of cracks in the bulk material. A fast heating rate of 8K/min was used to heat the samples up to 950°C. Between 950°C and the sintering temperature of each

specimen, a heating rate of 3K/min was used in order to limit the formation of pores. A holding step at the sintering temperature was performed. A slow cooling to room temperature with a cooling rate of 5K/min was allowed.

The sintering temperatures and holding times listed in Table 5.1 were different depending on the sample composition:

Material	Sintering temperature (°C)	Holding time (h)
La ₂ NiO ₄	1400	3
LSCF58	1200	5
PSCF58	1200	5
BSCF50	1100	5

Table 5.1. Temperatures and holding times for the sintering of materials selected for annealing experiments

Samples for the oxygen permeation experiments:

The pressed green-bodies were sintered with a heating and cooling rate of 5K/min using different sintering temperatures and holding times, listed in Table 5.2, according to the material. The membranes were cut to the final sizes of 10mm and 15mm in diameter using a grinding technique developed in Forschungszentrum Jülich at the partner institute ZAT (Central Technology Division). The exact desired membrane thicknesses of 0.5mm, 1mm and 1.5mm were obtained by grinding the samples on silicon carbide (SiC) abrasive paper. The membranes to be measured were polished with successive grades of SiC grinding paper to ensure flat reproducible surfaces.

 Table 5.2. Temperatures and holding times for the sintering of materials selected for oxygen permeation experiments

 Material
 Sintering temperature (°C)

 Holding time (h)

Material	Sintering temperature (°C)	Holding time (h)	
La ₂ NiO ₄	1400	10	
LSCF58	1200	5	
PSCF58	1200	10	
BSCF50	1100	10	

6 Development of the permeation test set-up

The permeation set-up, shown in Figure 6.1, was designed and built to measure oxygen permeation fluxes and perm-selectivities of membranes as a function of temperature using different feed and sweep gas compositions. One important feature of the test facility is its modularity. This modular construction with several functional groups allows variations in the set-up to be performed easily.



Figure 6.1. Membrane oxygen permeation test set-up.

The test set-up is composed of three independent modules:

- The gas mixing unit
- The membrane testing unit
- The analytical unit

6.1 Module 1: The gas mixing unit

The available gases are: Synthetic air (79% N_2 and 21% O_2), He, Ar, N_2 , CO₂ and a mixture of Ar and H_2 of 95% and 5% respectively. It is possible to mix all gases in the appropriate ratio in order to obtain a desired composition. The gas flow rates were controlled by mass-flow meters (Brooks, Holland) in

the range of 0 L_n/h to 60 L_n/h , calibrated specifically for each gas line. A maximum gas flow rate of 1 L_n/min can be achieved in the testing facility. The permeation set-up features a stainless steel gas mixing chamber (Swagelok, USA) containing stainless steel balls used to obtain a homogenous mixture of the gas stream. Steel was chosen for the tubing.

A water reservoir is incorporated into the permeation test set-up, thus allowing measurements with water vapour to be carried out. A coil heating element for water gasification and gas preheating is integrated in the test facility behind the mixing chamber. The coil and the tubing past it can be heated to a maximum temperature of 270° C, which corresponds to the dew point of water at 30 bar, in order to vaporise the liquid water and prevent oxygen adsorption and condensation problems in the tubing. Barometers installed in the test facility, on the feed and the sweep-side of the membrane, regulate the pressure in the tubing before and after the membrane. Moreover, ultrasound-flow rate controllers (ADM-2000, Agilent Technologies, USA) operating in the measurement range of between 0 and 1 L_n/min were used in order to check the volume flow in the different streams. This configuration has the main advantage that the volume flow can be determined independently of the gas specie. In order to prevent back diffusion of air from the gas outlets into the system, the exhaust gases exited through silicon oil glass bubblers, which were integrated into the retentate and permeate gas lines.

6.2 Module 2: The membrane testing unit

The testing unit comprises a heating device and a recipient for the incorporation of membranes to be investigated. The operation limits for the permeation test facility are:

- Maximum temperature: 1000°C,
- Maximum pressure: 30 bars
- Maximum gas flow: 1 L_n/min
 - 6.2.1 The heating unit:

It consists of a two-zone vertical furnace from Prüfer, Germany, which can be operated up to 1200°C with a steady-state control accuracy of +/-5 K. The heating coil inside the furnace increases the temperature of the feed and sweep gas streams flowing through the recipient tubing before they reach the membrane. The length of the membrane recipient is therefore of great importance, as it has to allow sufficient heating time. This is particularly necessary in the case of measurements with water vapour which has a higher heat capacity than the other gases in use.

6.2.2 The recipient:

The permeation test set-up was configured in order to allow permeation measurements of dense and also porous membranes for use in the pre-combustion, the post-combustion and the oxyfuel process. The measuring conditions of these two types of membrane are very different from each other. They vary from the point of view of sample geometry, gas composition and temperature range. Two different recipients for the incorporation of the membranes investigated were therefore designed.

The temperature range for the measuring of porous membranes is between 200°C and 550°C. A stainless steel sample holder represented in Figure 6.2 was developed. The use of stainless steel allows for high pressures, up to 30 bars, to be used. The sample holder was designed for disk-shaped membranes with a diameter of 40mm and a thickness ranging between 0.3mm and 5mm.



Figure 6.2. 3D representation of the stainless steel recipient for porous membrane. (Source: ZAT)

Dense membranes, however, need to be measured in the temperature range 600°C to 1000°C. Stainless steel is not suitable for such high temperatures, which is why quartz glass was preferred. A recipient made of a quartz glass cell and tubing was designed for disk-shaped membranes with a diameter of 10mm and 15mm and a thickness of between 0.3mm and 5mm. A maximum total pressure of around 2 bars can be applied when using the quartz glass recipient configuration. However, a maximum pressure of 1 bar was used during measurements. Figure 6.3 below shows the gas streams on each side of the membrane. (See Figure 6.6 for the schematic representation of the dense membrane recipient.)



Figure 6.3. Principle of the dense membrane recipient. The membrane, sealed to the quartz glass tubing, is located between the feed/retentate and permeate/sweep gas chambers.

6.3 Module 3: The analytical unit

In the analytical unit, the composition of the different gas streams involved in a permeation measurement is monitored by mass spectrometry. However, a gas chromatograph could also be connected. A fraction of the stream to be analysed is directed to a quadrupole mass spectrometer (described in Chapter 4.4), which can analyse alternately the feed, the sweep, the permeate and the retentate stream. The composition of the gas stream after preheating in the coil can also be analysed in order to detect and identify possible contamination and impurities from corrosion of the tubing.

The main purpose of the mass spectrometer is the determination of the oxygen concentration in the permeate stream, from which it is possible to calculate the oxygen permeation flux for every experimental condition.

The gas streams to be analysed together with the main measuring and regulation facilities are shown in Figure 6.4.

Development of the permeation test set-up



Figure 6.4. Schematic representation of the oxygen permeation test facility, with 1) the gas bottles, 2) the mass-flow meters, 3) the gas mixing chamber, 4) the water reservoir, 5) the heating coil, 6) the mass spectrometer, 7) the computer, 8) the furnace, 9) the dense membrane recipient.

A process monitoring software (Figure 6.5) for the operation of the permeation test set-up was developed by ZAT. It allows the operator to select the operating conditions desired for each experiment carried out. The test facility features a computer supported gas mixing system in which the gas stream composition and flux can be varied for the feed- and for the sweep-side of the membrane. The pressure on each side of the membrane can be set to different values. Moreover, the furnace temperature and temperature programme as well as the temperature of the coil heating element are regulated by this software.

Development of the permeation test set-up



Figure 6.5. Screen shot of the process monitoring software.

The permeation test set-up has great flexibility in respect to temperature, gas composition, sample geometry and membrane type. Indeed, it is possible to measure dense inorganic as well as porous membranes. The compositions of the feed and sweep gases are adapted according to the membrane type being measured. This chapter will focus mainly on the description of the permeation set-up designed for dense MIEC membranes for the separation of oxygen from air.

The experimental conditions for the investigation of dense ceramic membranes in the permeation test facility are listed below:

- Feed gas: synthetic air
- Sweep gas available: Ar or He
- Maximum temperature: 1000°C
- Pressure: 1 bar

6.4 Development of the membrane recipient for dense ceramic membranes

Several versions of the dense membrane recipient were designed, tested and improved for optimal experimental conditions and precision of results. All the recipients were produced by the glassblowing department of ZAT, in Forschungszentrum Jülich.

The first version of the dense membrane recipient consisted of a quartz glass outer recipient, a quartz glass tube to be sealed to the membrane positioned in a membrane holder on which were hooked two quartz glass rods. These rods were connected to the top part of the recipient by springs intended to apply a load on the membrane holder sufficient to allow a sealing between the glass tube and the membrane to be performed. In this design, the springs were located inside the furnace and subjected to the high temperature conditions of a permeation measurement. The spring load was, therefore, greatly impaired and therefore insufficient to deform the selected gasket and seal it to the quartz glass tube. Another design needed to be adopted with springs further away from the heat source. At a lower temperature, the spring load would be less affected and the spring performance improved.

The second version of the dense membrane recipient is represented in Figure 6.6. The membrane is positioned between an inner quartz glass tube and an outer quartz glass tube with a curved rim at its lower extremity on which the membrane is rested. Sealing between the membrane and each of the tubes is provided by the use of a screw cap that applies pressure on a spring positioned at the upper extremity of the inner tube. The design allows contact-pressure sealing with the application of a constant pressure even at high temperatures.

Development of the permeation test set-up



Figure 6.6. Schematic representation of the recipient for dense membranes.

6.4.1 Sealing technology

The operating temperature of these MIEC membranes ranges typically between 600°C and 1000°C. Oring seals are not suitable for this application since their upper operation temperature limit is only 400°C. Sealants with high melting points are required for use as sealing material for dense ceramic membranes to be measured at high temperatures. Sealing materials such as glass (Duran), and precious metals (silver and gold) were considered. However, the melting temperature of silver at 961°C is too low for this application as permeation fluxes are measured at up to 1000°C.

Glass sealing

The softening point of Duran glass is 815°C [107]. Wetting tests of the surface of LSCF58 membranes with Duran glass were conducted at 900°C, resulting in good wetting of the surface of the ceramic. However, sealing experiments, using the first version of the recipient and a Duran glass ring of 1cm diameter, 1mm width and flattened on its sides, were carried out. The assembly was heated to 900°C and kept for 60 min, and then heated to 950°C and kept for 60 min, without achieving the sealing of the

membrane to the glass tube. Moreover, a permeation study of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ [35] showed that glass sealants can react with the membrane material resulting in a change of composition in the membrane. A diffusion of the seal over the surface of the membrane was also observed causing a decrease in the membrane's effective surface area. This caused a significant decrease in oxygen permeation through the membrane, reaching a 13.6% decrease after 160 hours. Because of the interfacial reaction between the glass sealant and the perovskite membrane, this sealing technique can not be considered as an option for long term operation in the permeation test set-up.

Gold sealing

Gold has chemical inertness towards perovskite-type membrane materials. The melting temperature of gold is 1064°C, which is compatible for its use as sealing material in this application. However, melted metals have bad wetting properties on ceramics due to incompatibility of surface tension.

Sealing tests using the first variant of the recipient and a flat gold ring were conducted by heating the assembly up to 980°C and holding the temperature for 60 min. Ineffective adherence of the gold to the membrane and the tube was observed. A gold ring of 1mm thickness was therefore preferred as it allows bigger deformation of the material with the load applied and therefore better bonding. A second sealing test was carried out by heating the assembly up to 980°C for 60 min. No melting or deformation of the ring was observed as the spring load was not sufficient.

Sealing tests using the second variant of the dense membrane recipient were more successful as the 1mm-thick gold ring provided reliable gas-tight sealing of dense membranes at high temperatures. Furthermore, the bonding of the gold gaskets to the ceramic surface and the quartz glass tubes was so strong that it could not be removed without damage to the membrane or the sample recipient.

6.5 Testing the set-up

A series of measurements was carried out in order to optimise the operation of the test facility and the precision of measurements.

Originally, Teflon tubing was used to carry the gas streams to and from the membrane recipient during permeation measurements. A series of measurements were performed in that configuration. However, oxygen was found to permeate through Teflon [108]. The amount of oxygen that permeated through the Teflon tubing was corrected for each test by a "zero measurement" of the gas composition in the system at a temperature where no apparent permeation through the membrane was observed, i.e. around

500°C. Despite the difficulty of connecting steel tubes to glass, the Teflon tubing was finally replaced by steel, which is impermeable to oxygen.

At first, an unsteady permeation flux was observed after a change in temperature of the membrane or a change in sweep flux for each measurement. Several hours were needed for a steady state condition to be reached. However, this time was recorded to be shorter at high sweep gas stream fluxes and at high temperatures. In order to decrease this time, improvements in the permeation test set-up such as shortening of the tubing and decreasing the unnecessary dead volume of the membrane recipient were carried out.

6.6 Oxygen permeation measurements

The determination of the oxygen permeation flux through dense ceramic membranes was carried out by imposing an oxygen partial pressure gradient across the specimen. An oxygen-rich gas stream and oxygen-lean gas stream (an inert gas) are supplied to the feed- and the sweep-side of a sealed ceramic disk respectively. The number of moles of oxygen permeating per unit of time through a unit of membrane surface area is measured downstream using mass spectrometry from which the oxygen permeation flux is calculated. The mass spectrometer was calibrated frequently using a standard calibration gas composed of 5000 ppm O_2 , 500 ppm N_2 and 99.45% Ar.

Oxygen transport through a membrane is controlled by both surface kinetics and bulk diffusion to a degree that varies according to the membrane type and geometry. Moreover, the oxygen separation rates depend mainly on the temperature, the thickness of the sample, the properties (i.e. electronic and ionic conductivities) of the membrane material and the oxygen partial pressure gradient applied to the membrane.

Membrane performance and operational life can be affected by different parameters, i.e. the chemical stability of the material at high temperatures, the effects induced by the presence of an oxygen potential gradient (e.g. the segregation of impurities to the surface of the membrane and to grain boundaries, kinetic demixing and kinetic decomposition of the membrane material [109]).



Figure 6.7. Quartz glass membrane recipient showing a successful sealing of a membrane

In this work, the oxygen permeation fluxes through LSCF58, PSCF58, BSCF50 and La₂Ni0_{4+ δ} dense MIEC membranes were measured as a function of temperature and membrane thickness (0.5mm, 1mm and 1.5mm). The polished membrane disks were sealed between two quartz glass tubes using gold gaskets of 1mm in thickness and 15mm in diameter. Since the thicknesses of the membranes were small compared to their diameters, radial diffusion could be discounted. To ensure gas-tightness, the assembly (Figure 6.7) was compressed by a spring load system and heated to a temperature close to the melting point of gold in a vertical tube furnace. The heating and cooling rates were 7K/min and 1K/min respectively. The cooling rate used was lower than the heating rate in order to prevent crack formation due to thermal stresses.

Synthetic air was supplied to the feed-side of the membrane and argon (99,5% purity) was flushed over the permeate side. The gas flow rates, controlled by mass-flow meters, were 100 ml/min and 50 ml/min on the feed-side and on the sweep-side of the membrane respectively. Using a quadrupole mass spectrometer the oxygen permeation rate was measured from 1000°C to the temperature where the membrane cracked. The monitoring of the membrane temperature was done by an N-type thermocouple positioned near the membrane surface, on the feed-side. However, interactions between the membrane material and the chromium were observed. A difference of 3K was found between the temperature measured by this thermocouple and the one measured by the furnace thermocouple. The measurement error of the thermocouple being higher than 3K (standard tolerance of $\pm/-0,75\%$), monitoring of the temperature by the thermocouple present in the furnace was considered to be sufficient.

Dense membranes for oxygen separation must be free of cracks and connected-through porosity. Gas leakage through cracks or pores of the disk and through the gold sealing was monitored by mass

spectrometry. The leakage was determined by the amount of N_2 in the permeate stream and deducted from the O_2 concentration measured.

The correction for leakage of the permeating oxygen is calculated as follows:

$$C = C_o - C_N \frac{0.2095}{0.7811}$$
 (Equation 6.1)

where C_0 and C_N are the concentrations of oxygen and nitrogen in the sweep gas stream respectively.

The resulting oxygen permeation flux, Jo_2 (ml cm⁻² min⁻¹) was calculated according to Equation 6.2:

$$j_{o_2} = \frac{FC}{S}$$
 (Equation 6.2)

where C is the permeating oxygen concentration in the argon stream (ppm) after correction for leakage; F, the argon stream flow rate (ml min⁻¹); S, the membrane effective surface area (cm²).

7 Thermo-chemical stability investigation set-up

7.1 CO₂ and H₂O vapour influence on stability

One of the most important factors for the selection of materials for use in the oxyfuel process of coalfired power plants is the long-term stability of the ceramic material under the operating conditions of the process. Such an oxygen-separation unit will be operating at high temperature (above 600°C), under an aggressive atmosphere of CO₂, water vapour and O₂ at the sweep-side of the membrane and will be subject to a high partial pressure gradient from the high to the low oxygen partial pressure side [110]. Corrosion issues due to the presence of CO₂ and H₂O could also greatly affect the performance of the membrane.

It is known that acceptor-doped perovskites can incorporate water [50] and that CO_2 can adsorb on their surface [111], which can lead to a partial poisoning of the membrane as CO_2 would decrease the number of free active sites available for oxygen adsorption and desorption. Moreover, a reaction zone on the surface of perovskite membranes could act as a protective layer, thus preventing oxygen permeation. Most perovskite-containing alkaline-earth elements can react with CO_2 gas species as they tend to form carbonates [112,86]. Studies [112,110] showed that oxygen fluxes through Ba- and Srdoped perovskites ($La_{0.2}Ba_{0.8}Co_{0.8}Fe_{0.2}O_{2.6}$ and $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{2.6}$) deteriorated over time when the membranes were in contact with gaseous mixtures containing CO_2 and H_2O . However the fluxes were found to be restored to their initial values after raising the temperature above 700°C [110] and 810°C [112] in an oxygen-containing atmosphere, for $La_{0.2}Sr_{0.8}Co_{0.8}Fe_{0.2}O_{2.6}$ and $La_{0.2}Ba_{0.8}Co_{0.8}Fe_{0.2}O_{2.6}$ respectively. Although it was not mentioned, carbonates might have been formed.

The study of $SrCo_{0.8}Fe_{0.2}O_{3-\delta}$ tubular membranes for partial oxidation of methane to synthesis gas (syngas), i.e. CO and H₂, demonstrated that after a prolonged exposure to such a reducing environment, a chemical decomposition of the perovskite material towards strontium carbonate (SrCO₃) and elemental cobalt and iron occurred [113]. The study [114] of the ageing of La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} in a gaseous atmosphere containing H₂O, CO₂ and O₂, in the ratio 2:1:1, at a temperature of 750°C and total pressures of 1 and 5 atm for up to 1000 hours showed that a modification of the surface of the ceramic occurred. SrCrO₄ and LaCrO₄, originating from a chromia contamination, were found on the surface of the samples. Moreover, SrCO₃ was found on the surface of the samples after annealing for only 1 week [114].

Furthermore, after long-term operation at 850°C, barium carbonate (BaCO₃) was formed on the surface of $La_{0.2}Ba_{0.8}Fe_{0.8}Co_{0.2}O_{3-8}$ membranes used for the partial oxidation of methane to syngas [32]. The study [115] of a $La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.5}O_{3-8}$ membrane used for the production of an oxygen enriched carbon dioxide stream through air separation with CO₂ as sweep gas showed that flushing the membrane with CO₂ altered its surface. Indeed $La_{0.1}Sr_{0.9}Co_{0.5}Fe_{0.5}O_{3-8}$ underwent a carbonation reaction leading to the formation of strontium carbonate and lanthanum, iron and cobalt oxides [115].

 $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ is known to form carbonates and hydrates when in contact with CO₂ and water vapour. Oxygen permeation experiments [86], in which a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane was swept periodically with pure CO₂ and pure helium, were performed. An immediate and total disappearance of the oxygen flux upon switching to CO₂ on the sweep-side of the membrane was observed. However this phenomenon was reversible as the fluxes were restored when switching back to helium. A degradation of the structure of the perovskite material was reported. On the surface of the samples, a mixed strontium enriched carbonate (Ba_xSr_{1-x})CO₃ was formed. Under this phase, a plate-like structure, which was thought to be a novel mixed oxide of the form $(Ba,Sr)_x(Co,Fe)_yO_z$, was present. Furthermore, after sweeping the surface of the samples with pure He for 100 min, the plate-like structure disappeared.

Moreover, even minor amounts of CO₂ and water vapour can affect the chemical stability of the membrane material. It was reported [81] that the use of ambient air for oxygen permeation measurements through $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes caused a gradual decrease of the flux due to the small amounts, in the ppm range, of water vapour and CO₂ present in the feed gas stream, which indicates that these minor impurities might contribute to surface segregation of the material. Another study [96] of the permeation of oxygen through $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes reported that the permeation fluxes were found to decrease by 37% when only 0.012 atm of CO₂ were added to He on the sweep-side of the membrane.

7.2 Experimental set-up

In the oxyfuel process, the flue gas will be used to sweep the permeate side of the membrane in order to collect the molecular oxygen released from its surface. Consequently, the membrane material has to be stable in the gaseous atmosphere of the flue gas. Moreover, the oxygen permeation membrane will need to operate for several thousand hours at high temperatures. It is therefore important to ascertain to which degree the selected membrane material will be altered from exposure to the sweep gas at operating temperatures and for long periods of time. It was not possible to carry out long term

permeation experiments with CO_2 and water vapour in the permeation test facility as these measurements are time consuming. This is why long term annealing experiments were conducted in a furnace (Figure 7.1) on pellet samples exposed to near-operating conditions. Although the membrane material is not subjected to an oxygen partial pressure gradient, which is known to influence the degradation of the material [109], it is essential to determine the possible reactions between the sweep gas and the MIEC materials selected.

In this work, the determination of the thermo-chemical stability of selected MIEC oxygen separation membrane materials for CO_2 capture in the oxyfuel process was carried out in a dual set-up (Figure 7.2). The annealing test facility consists of a gas mixing apparatus and of two three-zone horizontal tube furnaces from Prüfer GmbH (Germany) that can operate at up to 1000°C, allowing two independent experiments to be run in parallel. A quartz glass tube of 120cm in length and 8cm in diameter is located in the annealing tube furnace. A quartz glass cap is sealed on each side of the quartz glass tube using O-rings. Two openings are located on each cap, which act as gas and liquid water inlet and outlet. The specimens to be investigated are placed in quartz glass sample holders of 10cm in length and 3cm in diameter. Quartz glass was chosen as it can withstand high temperatures and is not known to interact with the materials in the experimental temperature range.

The operating gases are: N_2 , O_2 and CO_2 and water vapour. The gas flow rates were controlled by mass-flow meters (Brooks, The Netherlands) in the range of 0 ml_n/h to 50 ml_n/h, calibrated specifically for each gas line. Humidification of the gas stream is conducted by direct introduction of liquid water, through a quartz glass capillary, in the hot zone of the furnace, where it is vaporised. This technique was chosen to minimise the cost of the set-up. The water flow rate was controlled by a water-flow meter Fl Ω mega (Brooks instruments B.V, The Netherlands) in the range of 0 g/h to 15 g/h. In order to prevent back diffusion of air from the gas outlets into the system, the exhaust gases exited through silicon oil glass bubblers. A glass bubbler was also used to collect the water exiting the system.

Thermo-chemical stability investigation set-up



Figure 7.1. Stability test set-up

An estimated composition for the sweep and permeate gas streams was determined from discussions with E. Riensche (Forschungszentum Jülich, IEF-3) and from the overview of the oxyfuel process provided in Chapter 3.3. The flue gas is assumed to be composed of about 89mol% CO₂, on a dry basis, or 66mol% CO₂ and 26mol% water vapour, on a humid basis. The permeate stream would consist of about 25% permeating O₂ and 75% recycled flue gas. These compositions were used for the annealing experiments performed in near operation conditions.



Figure 7.2. Schematic representation of the stability test set-up, with 1) the gas bottles, 2) the massflow meters, 3) the water-flow meter, 4) the water container, 5) the flow controller unit, 6) the quartz glass sample holder, 7) the gas bubblers, 8) the tube furnace and 9) the quartz glass tubes.

7.3 Annealing conditions

The materials selected for the thermo-chemical stability investigation are listed below:

- La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₈ (LSCF58)
- $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58)
- Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O₃₋₈ (BSCF50)
- $La_2NiO_{4+\delta}$

The pellets, placed in quartz glass sample holders in the test facility, were annealed in the temperature range of between 600°C and 900°C and exposed to a continuous stream of gases flowing at 50ml/min for 200 hours, 500 hours or 1000 hours, after which the samples were quenched to room temperature in air. The composition of the gas stream was varied to investigate the influence of different gases on the

stability of the selected MIEC membrane materials. The annealing experiments were carried out in the atmospheres and over the dwelling times listed in the table below (Table 7.1).

	Annealing conditions		
Atmosphere (in mol%)	Temperatures (°C)	Dwelling times (hours)	
Air	600, 700, 800	200, 500	
Air +10% CO ₂	600, 700, 800, 900	200	
(1% O ₂ , 99%N ₂) +10%CO ₂	600, 700, 800	200	
43%O ₂ , 14%N ₂ , 43%CO ₂	600, 700, 800	200	
25% O ₂ , 8% N ₂ , 67% CO ₂	600, 700, 800	200, 500	
28% O ₂ , 5% N ₂ , 55% CO ₂ , 12% H ₂ O	600, 700, 800	200	
25% O ₂ , 50% CO ₂ , 5% N ₂ , 20% H ₂ O	600, 700, 800	200, 500	
25% O ₂ , 45% N ₂ , 20% H ₂ O	600, 700, 800	200	
Air next to a Cr ₂ O ₃ disk	800	1000	

Table 7.1. Atmospheres and annealing conditions for $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets

7.4 Sample preparation

Due to the small depth of field obtained from an optical microscope it is essential that the surface of the specimen to be examined is optically flat and level, acting as a perfect mirror. Metallographic preparation was conducted in order to study the cross-section of samples after the annealing experiments.

The annealed samples were embedded in an epoxy resin to prepare a cross section of the pellets. The first step of sample preparation is grinding, which refers to abrasion of the sample surface by coarse abrasive particles. Grinding was performed by using rotating discs covered with different grades of silicon carbide paper. Grinding was continued until all the blemishes were removed, the sample surface was flat, and all the scratches were in a single orientation. The objective of each grinding step is to obtain a plane surface with minimal damage that can be removed easily during polishing in the shortest possible time.

The second step is polishing of the specimen, which is the abrasion of the sample surface by fine abrasive particles which are usually suspended in water or another solvent. Diamond is used as an

Thermo-chemical stability investigation set-up

abrasive to accomplish the fastest material removal and the best smoothness possible. Normally a final polishing step is performed with water-based lubricants with high viscosity and very fine abrasive particles. The final result of the grinding and polishing operations is a smooth mirror-like surface.

A preparation method without water was chosen for the samples to be observed since the carbonates which are expected to be formed on the surface of the materials were found to be sensitive to water and to decompose. This dry grinding process was performed until a final step of P4000 grinding paper grade. The surface of the samples was observed to be relatively scratch-free after grinding on such fine particle grinding paper. The polishing step was performed with 1µm diamond powder in mineral oil (Bühler). The final polishing step could not be performed since water could not be used in this preparation process.

This method produced relatively poor final results with many scratches as the different preparation steps usually require the use of water or water-based solutions. Moreover a lot of loose particles detached from the pellets during the polishing process and scratched the polished surface of the sample.

8 Characterisation of the membrane materials selected

8.1 Chemical analysis of the calcined powders

The cation and the oxygen content of the calcined powders of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF58) and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (PSCF58) received from IEF-1, as well as $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ (BSCF50) and $La_2NiO_{4+\delta}$ received from Treibacher, were determined by ICP-OES and hot gas extraction (Chapter 4) respectively. The precise weight percentage of the elements composing each material investigated is reported in the following table (Table 8.1).

Table 8.1. Chemical composition (in weight%) of LSCF58, PSCF58, BSCF50 and $La_2NiO_{4+\delta}$ calcined
powders.

Flomont	Material			
Element	$La_2NiO_{4+\delta}$	BSCF50	LSCF58	PSCF58
La	68.9 ±2.1		36.8 ± 11.0	
Ni	14.9 ± 0.45			
Ba		31.4 ±0.94		
Pr				36.9 ± 11.1
Sr		20.5 ± 0.61	16.0 ± 0.48	15.9 ± 0.48
Со		21.5 ±0.64	5.3 ±0.16	5.4 ±0.16
Fe		5.5 ±0.16	20.5 ±0.61	20.6 ±0.62
0	16.76 ±0.12	20.68 ±0.21	21.7 ±0.37	21.46 ±0.37

This chemical analysis determined the precise chemical composition of each material studied, (shown in Table 8.2). Considering the experimental error, these results correlate well with the desired chemical compositions. The oxygen non-stoichiometry measured for each material is also consistent with values found in the literature (Chapter 3.1).

Desired chemical composition	Actual chemical composition
$La_2NiO_{4+\delta}$	La _{1.98} Ni _{1.016} O _{4.19}
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	$Ba_{0.50}Sr_{0.511}Co_{0.798}Fe_{0.215}O_{2.82}$
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\text{-}\delta}$	$La_{0.583}Sr_{0.402}Co_{0.198}Fe_{0.808}O_{2.98}$
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3-\delta}$	$Pr_{0.579}Sr_{0.401}Co_{0.202}Fe_{0.816}O_{2.96}$

Table 8.2. Chemical composition LSCF58, PSCF58, BSCF50 and $La_2NiO_{4+\delta}$ calcined powders.

In this work, the oxygen non-stoichiometry of BSCF50 was measured to be 0.18. An oxygen content of 2.79 for the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material at room temperature was determined by thermogravimetric analysis (TGA) [82,116]. However, an oxygen non stoichiometry of 0.318 was measured by iodometric

titration for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ [96]. Moreover, an oxygen excess of 0.19 was measured for $La_2NiO_{4+\delta}$ in this work. The oxygen excess for $La_2NiO_{4+\delta}$ was determined at 0.14 +/- 0.01 [101] by TGA as well as iodometric and cerimetric titration. Oxygen excess values of 0.18 [117] as well as 0.14 and 0.16, by iodometric titration and by TGA respectively [118], were determined. TGA and iodometric titration studies of the oxygen excess of $La_2NiO_{4+\delta}$ [119] determined a mean value of 0.13. No information about the oxygen non-stoichiometry of LSCF58 and PSCF58 could be found. However, the oxygen content of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ was measured to be 2.974 and 2.966 with iodometric titration and TGA respectively [31], which is coherent with the oxygen content of 2.98 measured for the LSCF58 material in this study.

8.2 Phase composition of the calcined powders

The phase purity of a MIEC powder to be used as oxygen permeation membranes is essential for maximal performance. Moreover, the higher the content of secondary phases, the higher the probability of shrinkage effects due to chemical reactions during sintering. The calcined powders received were therefore investigated with X-ray diffraction (XRD) in order to check their phase purity. The X-ray diffraction patterns of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ can be seen in Figure 8.1.



Figure 8.1. XRD diagrams of the calcined powders (A): $La_2NiO_{4+\delta}$, (B): $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (C): $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (D): $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.

The XRD patterns of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ present the characteristic peaks of the perovskite structure (Figure 8.1). However, the peaks of the diffraction patterns of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ were found to be relatively wide. The XRD patterns of the LSCF58 and PSCF58 materials can be indexed in a trigonal and orthorhombic symmetry respectively. Moreover, the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ calcined powder received from IEF-1 was found to exhibit a considerable amount of secondary phases. The main phase, i.e. PSCF58, represented around 85% of the specimen, the rest being praseodymium oxide (PrO₂). The $La_2NiO_{4+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ calcined powders purchased from Treibacher were found to be single phased. The XRD patterns of the $La_2NiO_{4+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ materials can be indexed in an orthorhombic and pseudo-cubic symmetry respectively.



Figure 8.2. XRD diagrams of the sintered pellets (A): $La_2NiO_{4+\delta}$, (B): $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (C): $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (D): $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.

After the sintering step, all powders were found to be single phased (Figure 8.2). The characteristic peaks of PrO_2 were no longer present. Moreover, a narrowing of the diffraction peaks characteristic of the perovskite structure was observed for the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ materials. The sintering conditions to which the LSCF58 and PSCF58 samples were subjected enabled the formation of the final desired product. The calcination process of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ powders should, therefore, have been carried out for a longer time in order to obtain the single phased final product which was nevertheless produced after the sintering step.

Secondary phases were found in each sintered sample as will be discussed in Chapter 10.7 . However, no secondary phases were detected by XRD. This indicates that the amount of secondary phases is very low, below the detection limit of impurities for the XRD device, which is of about 5 weight%. An optical analysis needs therefore to be carried out with the software "analysis pro" from Olympus Soft Imaging Solutions GmbH (Germany) in order to determine the amount of secondary phases present in each sintered pellet studied.

8.3 Sintering of the pellets for the annealing experiments

The sintering step is a crucial part of the specimen preparation as it determines the density of the samples. It is therefore important to select the sintering conditions with great care. In order to determine the optimal sintering temperature and dwelling time for each material, a literature study as well as DTA/TG and dilatometric studies were conducted. DTA in combination with TG investigations were carried out on the calcined powdered samples in order to determine whether any melting or phase transformation of the materials to be sintered occurred in the temperature range considered for sintering. Furthermore, a dilatometric investigation was conducted to study the shrinkage of unsintered specimens as a function of temperature.

8.3.1
$$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$$

Studies of the sintering conditions of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ disk shaped membranes determined that the ideal sintering temperature and dwelling time were around 1100°C for between 7 and 8 hours [83] and 1150°C for 5 hours [83,86,120]. Other sintering conditions were also used for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane disks, e.g. 1150°C for 8 hours [121] and 1100°C for 10 hours [122]. A temperature range of between 1100°C and 1150°C and a dwelling time of between 5 and 10 hours can therefore be considered for the sintering of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets.

Characterisation of the membrane materials selected



The DTA/TG investigation of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ calcined powder was carried out in the temperature range of between room temperature and 1200°C. The DTA/TG curve (Figure 8.3), exhibits an endothermic and an exothermic peak upon heating and upon cooling, respectively, at the temperatures of approximately 1050°C and 1035°C respectively. The temperature related to these peaks corresponds to the melting temperature of the material. The release of oxygen started at around 500°C. The weight decreased continuously over the temperature range 500°C to 1200°C to reach a weight change of about 1.35 mass%.

Having assessed the sintering conditions used in other studies and the DTA investigation carried out, a sintering temperature of 1100°C was chosen for the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets to ensure that no melting of the material would occur.

$8.3.2 \qquad La_2NiO_{4+\delta}$

Different studies of the properties of $La_2NiO_{4+\delta}$ material showed that different sintering temperatures and dwelling times were used for the preparation of $La_2NiO_{4+\delta}$ samples. Indeed, $La_2NiO_{4+\delta}$ membranes were sintered at 1400°C for 20 hours [118], 1300°C for 4 hours, obtaining a density of 93.3% of the theoretical density [123] and 1350°C for 3 hours, obtaining less than 5% porosity [103]. Moreover, rectangular bars of $La_2NiO_{4+\delta}$ were found to be sintered at 1370°C for 5 hours [124]. A temperature
range of between 1300°C and 1400°C and a dwelling time of between 3 hours and 20 hours can, therefore, be considered for the sintering of $La_2NiO_{4+\delta}$ pellets.



The DTA/TG investigation of the La₂NiO_{4+ δ} was carried out in the temperature range of between room temperature and 1500°C. The DTA curve of La₂NiO_{4+ δ} calcined powder (Figure 8.4) showed that no melting of the material occurred up to 1500°C. The release of oxygen started at around 400°C. The weight decreased continuously over the temperature range 400°C to 1500°C to reach a weight change of about 0.35 mass%.



Figure 8.5. Shrinkage curve of an unsintered pellet of $La_2NiO_{4+\delta}$.

The TMA investigation of an unsintered La₂NiO_{4+ δ} pellet was carried out in the temperature range of between room temperature and 1500°C (Figure 8.5). In the first stage of the measurement, a slight expansion of the sample occurred up to 1000°C. The shrinkage of the La₂NiO_{4+ δ} pellet started at around 1000°C to reach 0.56mm at 1500°C. The slope of the shrinkage curve is the steepest between 1250°C and 1400°C.

Having reviewed the sintering conditions used in other studies as well as these DTA/TG and TMA investigations carried out, a dwelling time of 3 hours and the two sintering temperatures of 1350°C and 1400°C were chosen for the preparation of $La_2NiO_{4+\delta}$ pellets.

In order to determine the best sintering conditions to be used, density measurements were carried out on the samples sintered at these two different temperatures. The density of three samples sintered at each temperature was measured in order to have valid statistics. The density of the pellets sintered at the temperature of 1400°C was higher than that of the pellets sintered at 1350°C, as shown in Table 8.3. The sintering conditions finally chosen for the preparation of $La_2NiO_{4+\delta}$ pellets are therefore a sintering temperature of 1400°C and a dwelling time of 3 hours.

Material	Sintering temperature	Measured density
$La_2NiO_{4+\delta}$	1400°C	6.55
$La_2NiO_{4+\delta}$	1350°C	6.384

Table 8.3. Density of the La₂NiO_{4+ δ} pellets as a function of sintering temperature.

8.3.3 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

No information about the sintering conditions of either PSCF58 or LSCF58 samples was found in the literature. However, much information is provided about the preparation of $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ (LSCF60) samples. The sintering temperature and dwelling time for the preparation of rectangular bars of LSCF60 were found to be 1200°C for 4 hours [125] and 1250°C for 5 hours [126]. Moreover, $La_{0.6}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets were sintered at 1200°C for 8 hours, obtaining a density of 95% of theoretical density [114]. Tubular LSCF60 membranes were sintered at 1250°C for 5 hours, obtaining a density of at least 90% of the theoretical density [77]. Therefore a temperature range of between 1200°C and 1250°C and a dwelling time of between 4 and 8 hours can be considered for the sintering of LSCF58 pellets.



The DTA/TG investigation of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O₃₋₆ was carried out in the temperature range of between room temperature and 1200°C. The DTA/TG curve of LSCF58 calcined powder (Figure 8.6) showed that no melting of the material occurred up to 1200°C. The release of oxygen started at around 450°C. The weight decreased continuously over the temperature range 450°C to 1200°C to reach a weight change of about 1.1 mass%.

Characterisation of the membrane materials selected



Figure 8.7. Shrinkage curve of an unsintered pellet of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}.

The shrinkage curve of an unsintered $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellet in the temperature range of between 100°C and 1200°C is shown in Figure 8.7. In the first stage of the measurement up to 780°C, a slight expansion occurred. The shrinkage of the sample started at around 780°C to reach 0.8mm at 1200°C. The slope of the shrinkage curve is the steepest in the temperature range of between 1000°C and 1200°C.

Having checked the sintering conditions used in other studies and these DTA/TG and TMA investigations carried out, a sintering temperature of 1200° C and a dwelling time of 5 hours were chosen for the preparation of LSCF58 pellets. As $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ have similar properties (Chapter 5.1), the same temperature programme was applied for the sintering of PSCF58 pellets.

The following table (Table 8.4) summarises the sintering conditions used for each material selected for annealing experiments.

Material	Sintering temperature (°C)	Dwelling time (h)
$La_2NiO_{4+\delta}$	1400	3
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	1100	5
La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}	1200	5
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3\text{-}\delta}$	1200	5

Table 8.4. Temperatures and dwelling times for the sintering of LSCF58, PSCF58, BSCF50 and $La_2NiO_{4,5}$ pellets

8.4 Density of the sintered samples

For annealing experiments, as opposed to the oxygen permeation measurements, a perfectly dense pellet is not required. However, the sample should be free of cracks and open porosity to avoid the infiltration of gases throughout the material, which could affect the results of the stability investigation as much greater reaction areas would result. Samples with a density of above 90% of the theoretical density are sufficient for this study. The crystallographic densities of the sintered pellets were calculated from the lattice parameters determined by X-ray diffraction of the powdered materials selected for this study.

The lattice parameters together with the cell symmetry of the powdered materials selected for this study are given in Table 8.5.

Material	Symmetry	Lattice parameters		
		a (A)	b (A)	c (A)
$La_2NiO_{4+\delta}$	orthorhombic	5.4567	5,467	12.6738
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	cubic	3.9839	-	-
La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	trigonal	5,493	-	13,409
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3-\delta}$	orthorhombic	5.499	7.715	5.458

Table 8.5. Lattice parameters and cell symmetry of LSCF58, PSCF58, BSCF50 and $La_2NiO_{4+\delta}$.

The average density of the sintered pellets, measured by the buoyancy method, as well as their theoretical density and also the percentage of theoretical density is listed in Table 8.6. A measured density of above 90% of the theoretical crystallographic density, which is the minimum density required, was found for each material.

Table 8.6. Theoretical and measured densities of LSCF58, PSCF58, BSCF50 and La₂NiO_{4+ δ} pellets.

Material	Theoretical density	Measured density	Percentage of theoretical density
$La_2NiO_{4+\delta}$	7,037	6,55	93,1
Ba0.5Sr0.5Co0.8Fe0.2O 3-8	5,746	5,42	94,3
La0.58Sr0.4Co0.2Fe0.8O3-8	6,258	5,66	90,4
Pr0.58Sr0.4C00.2Fe0.88O3-6	6,346	5,72	90,1

8.5 Precision thermogravimetric analysis

TGA was used to determine the mass change of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$. In these measurements, the temperature is the only variable. The partial pressure of oxygen, which is the only factor that can influence the oxygen stoichiometry of the material, is kept constant. The oxygen stoichiometry change of the material can be determined from the TG measurement knowing the molar mass of the compound investigated.

Dense sintered pellets of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ were submitted to a thermally programmed cycle in an atmosphere composed of 20% O₂ and 80% Ar since it is not probable that argon will react with the ceramic materials. The measurements were conducted in the temperature range of between 200°C and 1100°C. The heating and cooling rates used were 0.625K/min. This provides for the measurement to take place under quasi-equilibrium conditions.

First, the samples were heated to 1100°C with a relatively fast heating rate of 8.75K/min and kept at that temperature for 6 hours. This was to ensure a state of equilibrium in respect to the oxygen stoichiometry. Secondly, the changes in oxygen stoichiometry were measured during the cooling from 1100°C to 200°C, at which latter temperature there was a dwelling of 6 hours, and also during a subsequent re-heating to 1100°C with a further dwelling of 6 hours. These isotherm dwelling segments were carried out to ensure that the measured samples and the TGA test set-up were in thermal equilibrium in order to obtain stable values. The incorporation and loss of oxygen into and out of the lattice of MIEC materials are reversible processes. The mass of the samples should therefore remain constant after the thermal cycling as no phase change should occur in the material.

The temperature programme used for the TGA measurements is shown in Figure 8.8 below:



Figure 8.8. Temperature programme for the TGA measurements.

The TGA curves of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ as a function of temperature exhibit a weight loss during heating as well as a hysteresis

between the heating and cooling curves. The observed weight loss of the samples investigated during heating is due to the loss of oxygen from the lattice. With increasing temperature the oxidation state of the B-site metal cations decreases, which results in the formation of oxygen vacancies to compensate for this phenomenon. The existence of a hysteresis between the heating and cooling curves suggests a low surface exchange coefficient of oxygen or a low diffusion of oxygen in the material.

For $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ the mass change is totally reversible which confirms that it is only linked to the gain and loss of oxygen in the lattice of the material. Moreover, the evaporation of elements from the samples was negligible.



8.5.1 TGA of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Figure 8.9. Temperature dependence of the oxygen stoichiometry change in $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$.

In Figure 8.9 above, upon heating, no change in oxygen stoichiometry is observed under the temperature of 300°C for the BSCF50 sample. A slight increase in oxygen stoichiometry of $|\Delta\delta|=0.003$ is found between 300°C and 400°C after which a continuous non-linear decrease in oxygen stoichiometry is seen with the temperature increasing up to 1100°C. The maximum oxygen stoichiometry change is of $|\Delta\delta|=0.176$ at 1100°C.

The increase in oxygen stoichiometry in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ sample in the temperature range of between 200°C and 300°C can be explained by the fact that the cooling rate was too high and that the sample was not in equilibrium at 200°C. This oxygen gain could also result from the oxidation of the cobalt and iron cations, which adopt the initial valence state of 3+ at low temperature (Fe³⁺ and Co³⁺),

to Fe^{4+} and Co^{4+} cations during heating. The resulting charge loss was compensated for by the incorporation of oxygen ions into the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ perovskite lattice.

With the increase in temperature, the oxidation state +4 became thermodynamically unstable and a reduction of Fe^{4+} and Co^{4+} cations to Fe^{3+} and Co^{3+} occurred, accompanied by the loss of lattice oxygen to compensate for the charge gain. Higher temperatures led to the partial reduction of Fe^{3+} and Co^{3+} to Fe^{2+} and Co^{2+} , which was followed by a further loss of oxygen. The reverse process should occur on cooling of the material. However, only the oxidation of Fe^{2+} and Co^{2+} to Fe^{3+} and Co^{3+} is observed on the TGA curve (Figure 8.9).

A hysteresis between the heating and cooling curves of the TG measurement of BSCF50 can be observed in the temperature range of between 230°C and 980°C. The maximum oxygen stoichiometry difference between the heating and cooling curves is of $|\Delta\delta|=0.014$.



8.5.2 TGA of La₂NiO_{4+ δ}

Figure 8.10. Temperature dependence of the oxygen stoichiometry change in $La_2NiO_{4+\delta}$

In the TGA curve of the La₂NiO_{4+ δ} sample (Figure 8.10), there is no change in oxygen stoichiometry when heated up to the temperature of 300°C. A continuous non-linear decrease in oxygen stoichiometry is observed with the temperature increasing up to 760°C, after which a linear decrease up to 1100°C is found. The maximum oxygen stoichiometry change is of $|\Delta\delta|=0.078$ at 1100°C.

In this material, nickel adopts the initial valence state of 2+ at 200°C. At higher temperatures nickel is partially reduced to Ni⁺. The decrease in oxygen stoichiometry originated from the formation of oxygen

vacancies which compensates for this charge gain. The reverse process occurred on cooling with the oxidation of Ni^+ to Ni^{2+} .

There is a hysteresis between the heating and cooling curves of the TG measurement of La₂NiO_{4+ δ} observed over the whole temperature range of the measurement, i.e. between 200°C and 1100°C. The maximum oxygen stoichiometry difference between the heating and cooling curves is of $|\Delta\delta|=0.0024$. This hysteresis between the heating and cooling curves could however be an artefact of the measurement. Moreover, the original oxygen stoichiometry was not recovered. The heating and cooling rates might have been too high to reach equilibrium conditions in the temperature range 200°C to 350°C.



8.5.3 TGA of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Figure 8.11. Temperature dependence of the oxygen stoichiometry change in LSCF58

The temperature dependence of the oxygen stoichiometry change in LSCF58 is shown in Figure 8.11. Upon heating, no change in oxygen stoichiometry appears for this $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ sample under the temperature of 600°C. There is a continuous non-linear decrease in oxygen stoichiometry with the temperature increasing up to 950°C, after which a linear decrease up to 1100°C can be found. The maximum oxygen stoichiometry change is of $|\Delta\delta|=0.111$ at 1100°C.

A hysteresis between the heating and cooling curves of the TG measurement of LSCF58 is seen in the temperature range of between 500°C and 975°C. The maximum oxygen stoichiometry difference between the heating and cooling curves is of $|\Delta\delta|=0.0057$.

8.5.4 TGA of $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$



Figure 8.12. Temperature dependence of the oxygen stoichiometry change in $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

The temperature dependence of the oxygen stoichiometry change in $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ is shown in Figure 8.12. Here the oxygen stoichiometry of the PSCF58 sample begins to change from a temperature of 550°C. A continuous non-linear decrease in oxygen stoichiometry is observed as the temperature rises to 780°C, after which there is a linear decrease up to 920°C. In the temperature range of between 920°C and 1100°C, a non-linear decrease of the oxygen stoichiometry is observed. The maximum oxygen stoichiometry change is of $|\Delta\delta|=0.135$ at 1100°C.

For this sample the hysteresis between the heating and cooling curves of the TGA measurement is found between 500°C and 970°C. The maximum oxygen stoichiometry difference between the heating and cooling curves is of $|\Delta\delta|=0.0044$.

8.5.5 Discussion

The TGA curves of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- $\delta}$ and Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- $\delta}$ are very similar. The explanation for the oxygen stoichiometry change $\Delta\delta$ in both these materials is that Co and Fe adopt the initial valence state of 3+ at low temperatures. Higher temperatures led to the partial reduction of Fe³⁺ to Fe²⁺ and Co³⁺ to Co²⁺, which was followed by a loss of oxygen and the formation of oxygen vacancies to compensate for the charge gain. The reverse process occurred on cooling of the LSCF58 and PSCF58 samples with the oxidation of Fe²⁺ to Fe³⁺ and Co²⁺ to Co³⁺.}}

Characterisation of the membrane materials selected

Matarial	Hysteresis	
Waterial	Temperature range (°C)	Maximum Δδ (10 ⁻²)
$La_2NiO_{4+\delta}$	200 to 1100	0.24
$Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$	230 to 980	1.4
La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ}	500 to 975	0.57
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3\text{-}\delta}$	500 to 970	0.44

Table 8.7. Characteristics of the hysteresis between the heating and cooling TGA curves of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$.

On the one hand, as seen in Table 8.7 and Table 8.8, the sample with the narrowest hysteresis as well as the lowest change in oxygen stoichiometry at 1100° C, which is an indication of the stability of a material, is La₂NiO_{4+δ}. On the other hand Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} presents the largest hysteresis as well as the maximum oxygen stoichiometry change at 1100° C. A relatively small hysteresis is observed for the LSCF58 and PSCF58 samples. Furthermore, the substitution of praseodymium for lanthanum in Ln_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ}, with Ln=La or Pr, increased the loss of lattice oxygen in the perovskite structure.

Table 8.8. Oxygen stoichiometry change $\Delta\delta$ at 1100°C for LSCF58, PSCF58, BSCF50 and La₂NiO_{4+ δ}.

Material	Δδ at 1100°C (10 ⁻²)
$La_2NiO_{4+\delta}$	7.8
$Ba_{0.5}Sr_{0.5}Co_{0.\ 8}Fe_{0.2}O_{\ 3\text{-}\delta}$	17.6
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3\text{-}\delta}$	11.1
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3-\delta}$	13.5

8.6 Dilatometric measurements

The thermal expansion, described by the thermal expansion coefficient (TEC), represents a serious obstacle to the integration of membranes into the construction materials in the heated parts of a coalfired power plant. It is important to determine the TEC of each material to be used as an oxygen permeation membrane in order to check their compatibility with the materials they will be combined with. A thermal expansion mismatch could severely damage the membrane assembly causing stresses and even cracks.

The thermal expansion behaviour of dense sintered pellets of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ of 5.4mm, 5.755mm, 5.58mm and 5.275mm high respectively was measured in air between 20°C and 1100°C. The TMA curves in the temperature range of 200°C to 1000°C are shown in the following graphs, Figure 8.13 to Figure 8.20.



8.6.1 Thermal expansion of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Figure 8.13. Temperature dependence of the thermal expansion coefficient of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

Here (Figure 8.13) the measurement is unstable up to 300°C, but the increase in TEC is quasi linear between 300°C and 530°C. An inflexion point is observed at a temperature of between 530°C and 600°C. Then a linear increase with a steep slope is present up to 650°C. The increase of TEC up to 900°C is linear and has a more gradual slope. Finally, a decrease of the slope of the TEC curve is observed in the temperature range of between 900°C and 1000°C. The thermal expansion coefficient of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3.\delta}$ between 20°C and 1000°C was measured to be 20.5 10⁻⁶ K⁻¹.

Characterisation of the membrane materials selected



Figure 8.14. Temperature dependence of the relative expansion of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

A linear increase of the relative expansion of the BSCF50 pellet is observed in the temperature range of between 200°C and 550°C (Figure 8.14). An inflexion point is apparent between 550°C and 650°C. At higher temperatures, between 650°C and 1000°C, the increase is linear with a steeper slope and reaches 2.02% at 1000°C.



8.6.2 Thermal expansion of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

In Figure 8.15, a non-linear increase of the TEC of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ with increasing temperature is observed up to 700°C, after which an inflexion point is found at a temperature of between 700°C and 770°C. At higher temperatures, a linear increase with a steep slope is present up to 1000°C. A dent is

observed at around 920°C which could be explained by the reorganisation of the perovskite structure of LSCF58. The thermal expansion coefficient of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ between 20°C and 1000°C was measured as 17.9 10⁻⁶ K⁻¹.



Figure 8.16. Temperature dependence of the relative expansion of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$.

Figure 8.16 shows a linear increase of the relative expansion of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in the temperature range of between 200°C and 700°C. An inflexion point is apparent between 700°C and 800°C. At higher temperatures, between 800°C and 1000°C, the increase is linear with a steeper slope reaching 1.74% at 1000°C.



8.6.3 Thermal expansion of $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

Here (Figure 8.17) there is a non-linear increase of the TEC of $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.\delta}$ with temperatures increasing up to 700°C, after which an inflexion point is found at a temperature of between 700°C and 770°C. At higher temperatures, a linear increase with a steep slope is present up to 1000°C. The thermal expansion coefficient of PSCF58 between 20°C and 1000°C was measured as 18.2 10⁻⁶ K⁻¹.



Figure 8.18. Temperature dependence of the relative expansion of $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$.

The relative expansion of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellet (Figure 8.18) shows a linear increase in the temperature range of between 200°C and 660°C. An inflexion point is apparent between 660°C and

760°C. At higher temperatures, between 760°C and 1000°C, the increase is linear with a steeper slope and reaches 1.78% at 1000°C.

8.6.4 Thermal expansion of $La_2NiO_{4+\delta}$



Figure 8.19. Temperature dependence of the thermal expansion coefficient of $La_2NiO_{4+\delta}$

This measurement was found to be unstable between 100°C and 500°C, in which temperature range a non-linear increase of the TEC of $La_2NiO_{4+\delta}$ is observed as the temperature rises (Figure 8.19). At higher temperatures, i.e. between 600°C and 1000°C, the increase is linear and gradual. The thermal expansion coefficient of $La_2NiO_{4+\delta}$ between 20°C and 1000°C was measured as 14.9 10⁻⁶ K⁻¹.



Figure 8.20. Temperature dependence of the relative expansion of $La_2NiO_{4+\delta}$.

A linear increase of the relative expansion of the $La_2NiO_{4+\delta}$ pellet is observed over the whole temperature range of the measurement, reaching 1.45% at 1000°C, as seen in Figure 8.20.

Material	TEC (10 ⁻⁶ K ⁻¹)	Relative expansion (%)
$La_2NiO_{4+\delta}$	14.9	1.45
$La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$	17.9	1.74
$Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.88}O_{3\text{-}\delta}$	18.2	1.78
Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ}	20.5	2.02

 Table 8.9. Thermal expansion coefficient (TEC) and relative expansion in the temperature range of between 20°C and 1000°C

As seen in the above table (Table 8.9), the TECs measured in this work are coherent with the values reported in the literature study in Chapter 5. On the one hand, $La_2NiO_{4+\delta}$ is the sample with the lowest thermal expansion up to 1000°C. On the other hand $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ presents the highest expansion coefficient up to 1000°C. Furthermore, the substitution of praseodymium for lanthanum in $Ln_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, with Ln=La or Pr, increased very slightly the thermal expansion.

8.6.5 Discussion

For all samples, an increase in thermal expansion, which is associated with a loss of lattice oxygen leading to an increase in oxygen vacancy concentration [127,128], is observed during heating. The formation of these oxygen vacancies is related to the reduction of the B-site cations during heating, which can cause a decrease in the B–O electrostatic bond strength according to Pauling's second rule. Therefore, the size of the BO₆ octahedra increases, which leads to an increased lattice expansion. The increase in thermal expansion could also be caused by a disordering of the crystal lattice during heating [129].

Three types of expansion can be distinguished i.e. the total, the chemical and the thermal expansions [122]. The change in slope observed for all materials is caused by the cumulative effect of the chemical expansion (described by the chemical expansion coefficient: CEC) with the thermal expansion. The chemical expansion is associated with the release of oxygen from the lattice of the materials studied.

There also appears to be a correlation between the oxygen non-stoichiometry and the thermal expansion of the materials studied. For all samples, the change in slope of the TMA curves took place in the same temperature range where the oxygen stoichiometry change is observed in the TGA curves. The thermal expansion and decrease in oxygen stoichiometry of each material follow the same trend. In fact, the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material exhibits the greatest change in oxygen stoichiometry as well as

the greatest thermal expansion. And the $La_2NiO_{4+\delta}$ material exhibits the least change in oxygen stoichiometry as well as the lowest thermal expansion.

9 Oxygen permeation through MIEC membranes

One of the main criteria for the selection of materials as oxygen separation membranes in the framework of the oxyfuel process of coal-fired power plants is the magnitude of the oxygen permeation flux. Bredesen and Sogge [130] reported that membranes need to exhibit oxygen permeation fluxes of at least 10 ml min⁻¹ cm⁻² in order to be competitive with the traditional high purity oxygen separation processes.

In this work, the oxygen transport kinetics through selected dense MIEC membrane materials, i.e. $La_2NiO_{4+\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ were investigated in the temperature range of between 700°C and 950°C. Membrane disks of 15mm in diameter were prepared free of cracks and connected through porosity. Although it is impossible to achieve theoretical density, membranes must be prepared with the highest attainable relative density. All sintered samples exhibited densities higher than 90% of their theoretical density which is considered the lower limit for oxygen separation membranes.

The membrane disks were polished on both sides with successive grades of silicon carbide grinding paper (up to P1200) to ensure flat reproducible surfaces. The membrane disks were then sealed between two quartz glass tubes using two gold gaskets of 1mm in diameter. To ensure gas-tightness, the assembly was compressed by a spring load system and heated in a vertical tube furnace to a temperature close to the melting point of gold. Synthetic air was fed to the feed-side of the membrane and argon (99.5% purity) to the permeate side. The gas flow rates were 100 ml min⁻¹ and 50 ml min⁻¹ on the feed-side and on the sweep-side of the membrane respectively.

At first the membranes were heated to 1000°C, at which temperature an unsteady permeation flux was observed. This was caused by the time needed for the atmosphere to change within the whole permeation test set-up and also for the gradient of oxygen partial pressure to establish across the membrane until a steady state was reached. Then the oxygen permeation of each membrane was measured on cooling with steps of 50°C, down to 700°C. At each temperature step, an unsteady permeation flux was observed at first before reaching a steady state. This can be attributed to the decrease in oxygen vacancy concentration when cooling the membrane material as was discussed in Chapter 8.5. Improvements in the permeation test set-up such as shortening of the tubing and decreasing the unnecessary dead volume of the membrane recipient allowed for a decrease of the time needed to reach a steady state condition. This time was dependent on the membrane material and ranged between two and three hours. Cracking of the membrane was observed on cooling due to

stresses induced by a thermal expansion mismatch between the membrane material, the gold gasket and the quartz glass recipient.

The oxygen permeation rate was measured by mass spectrometry. The leakage was determined by the amount of N_2 in the permeate stream and deducted from the measured O_2 concentration. The resulting oxygen permeation flux density, Jo_2 (ml cm⁻² min⁻¹) was calculated according to Equation 9.1:

$$j_{o_2} = \frac{FC}{S}$$
 (Equation 9.1)

where C is the permeating oxygen concentration in the argon stream (ppm) after correction for leakage; F the argon stream flow rate (ml min⁻¹); and S the membrane effective surface area (cm²).

9.1 Thickness dependence of oxygen permeation fluxes

In order to determine whether the kinetics of oxygen permeation are rate limited by bulk diffusion or by surface exchange, oxygen permeation fluxes were measured through $La_2NiO_{4+\delta}$, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes of three different thicknesses, i.e. 0.5mm, 1mm and 1.5mm, as a function of temperature (700°C to 950°C). When bulk diffusion is the rate limiting factor, the flux is proportional to the inverse of the thickness of the membrane measured, which corresponds to Wagner's equation (Equation 9.2) that describes the oxygen flux (*jo*₂) when bulk diffusion controls oxygen permeation.

$$j_{o_2} = -\frac{RT}{16F^2L} \int_{\ln p_{O_2}}^{\ln p_{O_2}} \frac{\sigma_i \sigma_e}{\sigma_i + \sigma_e} d\ln(p_{O_2})$$
(Equation 9.2)

where σ_i and σ_e are the ionic and electronic conductivities respectively; F the Faraday constant; R the gas constant; T the temperature; L the membrane thickness; pO_2 and pO_2 the partial pressure on the oxygen-rich and oxygen-lean side respectively.

9.1.1 La₂NiO_{4+δ}

The temperature dependence of the permeation fluxes of $La_2NiO_{4+\delta}$ in the temperature range of between 700°C and 950°C, as a function of membrane thickness, is shown in Figure 9.1. The permeation fluxes were seen to increase with increasing temperature and with decreasing membrane thickness. However, in the temperature range of between 700°C and 800°C, the permeation flux for the 0.5mm membrane is lower than for the 1mm membrane.

Moreover, the increase in permeation flux with membrane thickness was not measured to be proportional to the inverse of the membrane thickness. The surface exchange influence on the oxygen permeation through La₂NiO_{4+ δ} membranes under 1.5mm can, therefore, not be neglected. This confirms the findings of V.V. Kharton et al. and D.M. Bochkov et al. [131,132] who determined that surface exchange limitations to the oxygen permeation fluxes through La₂NiO_{4+ δ} -based ceramics must be taken into account. Moreover, the oxygen permeation of La₂NiO_{4+ δ} membranes was found to be limited by both bulk transport and surface exchange rates when the membrane thickness is less than 1.5mm [131,80,132].



Figure 9.1: Temperature dependence of oxygen permeation fluxes through $La_2NiO_{4+\delta}$ membranes

In order to check the stability of the $La_2NiO_{4+\delta}$ membrane material under an oxygen partial pressure gradient, a long-term permeation measurement was conducted on a 1.5mm membrane kept at 800°C for 400 hours. The oxygen permeation flux of this membrane was measured initially, after a 150-hour dwelling time at 800°C as well as after a 400-hour dwelling time.

Time (h)	C (mol%)		
	at 800°C	at 900°C	
0	0.6	1	
150	0.28	0.53	
400	0.24	0.48	

Table 9.1. Evolution of the oxygen concentration in the permeate stream (C).

Figure 9.1 shows the decrease of the oxygen permeation flux between the initial measurement and after 150 hours. Table 9.1 gives the evolution of the decrease in oxygen concentration in the permeate stream of the La₂NiO_{4+ δ} membrane measured at 800°C and 900°C. A decrease in oxygen concentration of more than 50% occurred between the first 800°C measurement and the one after 150 hours. The oxygen concentration was found to be more stable between 150 hours and 400 hours as the oxygen concentration drop was of less than 15%. A similar decrease was observed for the oxygen concentration in the permeate stream of the membrane measured at 900°C as the decrease was less than 50% between the first measurement and the one after 150 hours and less than 10% between the measurement after 150 hours and the one after 400 hours.



Figure 9.2. SEM micrographs of the surface of the feed-side of a $La_2NiO_{4+\delta}$ membrane after a 400-hour operation.

In order to determine what caused the permeation rate to suffer such a fast and drastic decrease, an investigation of the microstructure of the membrane was carried out. No degradation of the surface of the sweep-side of the membrane was observed. EDS analysis of the surface of the feed-side of the membrane showed the presence of a chromium layer (Figure 9.2). This layer appeared to be a lanthanum, nickel and chromium-based oxide. XRD analysis of the surface of $La_2NiO_{4+\delta}$ pellets annealed for 1000 hours next to a chromia pellet showed that $LaCrO_3$ and $NiCr_2O_4$ were formed, as further described in Chapter 10.5.

Oxygen permeation through MIEC membranes



Figure 9.3. SEM micrograph and elemental mapping of the cross fracture of the feed-side of a $La_2NiO_{4+\delta}$ membrane after 400-hour operation.

An elemental mapping of the cross fracture of the feed-side surface of a $La_2NiO_{4+\delta}$ membrane subjected to a gradient in oxygen partial pressure for 400 hours was carried out with SEM in combination with EDS, as seen in Figure 9.3. The distribution of lanthanum and nickel seems to be homogenous over the chromium-containing layer covering the entire surface of the feed-side of the membrane. The chromium layer of homogenously distributed LaCrO₃ and NiCr₂O₄ was found up to a depth of 1,5µm in the sample. Moreover, a nickel oxide inclusion, corresponding to a bright area in the elemental mapping of nickel and a dark area in that of lanthanum, is also observed less than 4μ m below the surface of the membrane.

The source of chromium contamination was found to be the thermocouple used in the set-up to monitor the temperature next to the membrane. At high temperature, the volatile chromium species from the thermocouple were transported through the test set-up to the feed-side of the membrane where a reaction occurred. This result is of importance considering that the high temperature components in coal-fired power plants are made of chromium steel. The fact that the oxygen permeation flux decreases so fast, after only 150 hours, when $La_2NiO_{4+\delta}$ reacts with chromium makes it a material incompatible for use in power plants, at least not without appropriate protection.

9.1.2 $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

The temperature dependence of the oxygen permeation fluxes of $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in the temperature range of between 700°C and 950°C, for the three different membrane thicknesses (0.5, 1 and 1.5mm) is shown in Figure 9.4. The oxygen permeation fluxes were observed to increase with increasing temperature and with decreasing membrane thickness. There seems to be a proportional increase of the fluxes of the three membranes with different thicknesses in the temperature range of the measurement. A deviation from this trend occurred for the 1mm membrane measured in the temperature range of between 700°C and 800°C. However, the increase is not proportional to the inverse of the thickness. Therefore the kinetics of oxygen permeation through $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ perovskite-type membranes are not governed by bulk diffusion. Surface exchange has also to be taken into account.



Figure 9.4. Temperature dependence of the oxygen permeation fluxes through $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ membranes



Figure 9.5. SEM micrographs of the surface of the sweep-side of a $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane after an oxygen permeation experiment of approximately 100 hours.

After a permeation measurement of approximately 100 hours, an EDS analysis of the surface of the feed- and sweep-sides of the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ membrane was carried out. Figure 9.5 shows the presence of a chromium layer on the surface of the sweep-side of this sample. This layer appeared to be a strontium- and chromium-containing oxide. Chromium oxide particles are observed to nucleate and grow out of the surface of these pellets. XRD analysis of the surface of a $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellet annealed for 1000 hours next to a chromia pellet showed that strontium chromate (SrCrO₄) and cobalt chromite (CoCr₂O₄) spinel were formed, as further described in Chapter 10.5. As for the La₂NiO_{4+ δ} membrane, the source of chromium contamination was the thermocouple used in the set-up to monitor

the temperature next to the membrane. However, the position of the thermocouple in the membrane recipient was different. And although it was placed on the low oxygen partial pressure side of the membrane, namely the sweep-side, volatile species were formed and reacted on the surface of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane.



Figure 9.6. SEM micrographs of the surface of the feed-side of a $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane after an oxygen permeation experiment of approximately 100 hours.

Figure 9.6 shows the presence of secondary phase inclusions on the surface of the feed-side of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane after an oxygen permeation experiment of approximately 100 hours. EDS point analysis measurements were carried out in order to determine the chemical composition of the secondary phases present. These phases seemed to be cobalt oxide in which iron was dissolved. They were identified as being $Co_{3-x}Fe_xO_4$ inclusions. The formation of these cobalt and iron oxide phases on the surface of the membrane suggests that a kinetic demixing of the membrane material occurred during the permeation measurement. These phases were formed by the reaction of migrating cations with gaseous oxygen on the surface of the oxygen-rich side of the membrane. This is a serious concern since a demixing of the material will lead to the development of secondary non-ion-conducting phases which can considerably decrease the oxygen permeation flux of oxygen separation membranes.

9.1.3 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

The temperature dependence of the oxygen permeation fluxes of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in the temperature range of between 700°C and 950°C, for the three different membrane thicknesses (0.5, 1 and 1.5mm) is shown in Figure 9.7. The oxygen permeation value of the 0.5mm thick sample at 700°C does not figure in the graph since the membrane cracked during the measurement, after the temperature of 750°C. The values of the oxygen permeation fluxes of the three membranes were very similar to each other over the whole temperature range of the measurement. The fluxes increased with increasing temperature and with decreasing membrane thickness. There seems to be a proportional increase of the

fluxes of the three membranes with different thicknesses in the temperature range of the measurement. A significant deviation from this trend occurred for the 1.5mm membrane measured in the temperature range of between 850°C and 950°C. However, the increase is not proportional to the inverse of the thickness. Consequently, the influence of surface exchange and of bulk diffusion on the kinetics of oxygen permeation through $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ perovskite-type membranes has to be considered.



Figure 9.7. Temperature dependence of oxygen permeation fluxes through $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ membranes

Bouwmeester et al. [50,15] calculated the characteristic thicknesses of several $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ perovskite oxides to be in the range of between 20µm and 500µm at 900°C. The membranes measured in this work were above 0,5mm, which is at the limit of that range. Moreover, oxygen permeation fluxes measured through a $La_{0,6}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ ceramic disk 0.96mm thick [133] showed that both bulk diffusion and surface exchange seem to control the overall oxygen permeation. Oxygen permeation in $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-\delta}$ membranes seems to be governed by bulk diffusion. However, surface exchange kinetics might contribute to the control of oxygen transport.



Figure 9.8. SEM micrographs of the surface of (A) the sweep-side and (B) the feed-side of a $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.\delta}$ membrane after a permeation experiment of approximately 100 hours.

After a permeation measurement of approximately 100 hours, an EDS analysis of the surface of the feed- and sweep-sides of the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} membrane was carried out. Figure 9.8 (A) shows the presence of a chromium layer on the surface of the sweep-side of this sample. This layer appeared to be a strontium- and chromium-containing oxide. Chromium oxide particles are found to nucleate and grow out of the surface of the sweep-side of the membrane. XRD analysis of the surface of a La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} pellet annealed for 1000 hours next to a chromia pellet showed that strontium chromate (SrCrO₄) and the iron cobalt chromite (FeCoCrO₄) spinel were formed, as further described in Chapter 10.5. As for the Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} membrane, the source of chromium contamination was the thermocouple used in the set-up to monitor the temperature next to the membrane, on the sweep-side.

Here also, $Co_{3-x}Fe_xO_4$ inclusions were found on the surface of the feed-side of the same $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane after a permeation experiment of approximately 100 hours, as seen in Figure 9.8 (B). The formation of these cobalt and iron oxide phases on the surface of the membrane suggests that a kinetic demixing of the membrane material occurred during the permeation measurement, which is of as great a concern as for the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes.

9.2 Comparison of the oxygen permeation fluxes through selected 1 mm membranes

In order to compare the oxygen permeation fluxes of the membrane materials selected for this study, i.e. $La_2NiO_{4+\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, permeation experiments were carried out on 1mm-thick membranes measured in the temperature range of between 700°C and 950°C. The temperature dependences of the oxygen permeation fluxes of these membranes are given in graphs Figure 9.9 to Figure 9.12.

In the temperature range measured, the oxygen permeation fluxes increased with increasing temperature. This phenomenon can be explained by an increase in the mobility and the concentration of the lattice oxygen vacancies with increasing temperature [33]. The temperature dependency of the loss of lattice oxygen related to the concentration in oxygen vacancies was reported previously, in Chapter 8.5.

9.2.1 Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ}

The Arrhenius plots of the oxygen permeation flux density of a 1mm $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membrane in the temperature range of between 950°C and 700°C is shown in Figure 9.9. An increase of the permeation flux density was observed with increasing temperature. The maximum permeation flux for $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ was measured as 1.5 10⁻⁶ mol cm⁻² s⁻¹ at 950°C. The decrease was almost linear down to 800°C, after which temperature, the slope of the curve steepened gradually down to 700°C. At this temperature, the permeation flux was measured to be 0.4 10⁻⁶ mol cm⁻² s⁻¹.



Figure 9.9. Temperature dependence of the oxygen permeation flux of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$

9.2.2 $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

Figure 9.10 gives the Arrhenius plots of the oxygen permeation flux density of a 1mm $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane in the temperature range of between 950°C and 700°C. The oxygen permeation fluxes were found to increase with increasing temperature. The maximum flux density was recorded at 950°C as 0.4 10⁻⁶ mol cm⁻² s⁻¹. A linear decrease in flux was observed in the temperature

range of between 950°C and 850°C, after which the decrease was almost linear down to 700°C, where a 0.2 10^{-7} mol cm⁻² s⁻¹ permeation flux was measured. The slope of the curve representing the oxygen permeation flux density steepened in the temperature range of between 850°C and 700°C compared to the curve in the temperature range of between 950°C and 850°C.



Figure 9.10. Temperature dependence of the oxygen permeation flux of $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

9.2.3 $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$

The Arrhenius plots of the oxygen permeation flux density of a 1mm La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} membrane in the temperature range of between 950°C and 700°C is given in Figure 9.11. At 950°C, the permeation flux reached a maximum value of 0.3 10⁻⁶ mol cm⁻² s⁻¹. A linear decrease in flux was observed between 950°C and 850°C and also between 850° and 700°C, the slope of the curve being steeper in the temperature range of between 850°C and 700°C than in the temperature range of between 950°C and 850°C and 700°C than in the temperature range of between 950°C and 850°C. At 700°C, the permeation flux density was measured to be 0.2 10⁻⁷ mol cm⁻² s⁻¹. A behaviour similar to the one of the 1mm $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ sample was observed for the oxygen permeation flux density of this La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} membrane. However the slope of the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} sample and in the temperature range of between 850°C and 850°C and 850°C cond 850°C cond 850°C cond 850°C cond 850°C cond 850°C, is steeper for the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} sample and in the temperature range of between 850°C cond 850°C c



Figure 9.11. Temperature dependence of the oxygen permeation flux of $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

9.2.4 $La_2NiO_{4+\delta}$

The Arrhenius plots of the oxygen permeation flux density of a 1mm La₂NiO_{4+ δ} membrane in the temperature range of between 950°C and 700°C is shown in Figure 9.12. A maximum permeation flux of 0.3 10⁻⁶ mol cm⁻² s⁻¹ was measured at 950°C. A continuous decrease in the oxygen permeation flux was recorded over the temperature range of between 950°C and 700°C, at which temperature the flux was of 0.3 10⁻⁷ mol cm⁻² s⁻¹. The slope of the curve increased gradually as the temperature decreased over the whole temperature range of the measurement.

Oxygen permeation through MIEC membranes



Figure 9.12. Temperature dependence of the oxygen permeation flux of $La_2NiO_{4+\delta}$



Figure 9.13. Temperature dependence of the oxygen permeation flux density of 1mm-thick $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ membranes The oxygen permeation flux density through the 1mm thick $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ membrane is clearly well above the fluxes of all three other materials, as can be seen in Figure 9.13. In the temperature range of between 700°C and 800°C, the permeation curves of $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ almost coincide. An increase of the permeation flux of $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

after 800°C compared to the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- $\delta}} curve was observed. The fact that the Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-<math>\delta}$ flux is higher than the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- $\delta}$} flux can be explained by the substitution of Pr for La, which has a lower ionic radius than La. The decrease in ionic radius seems to lower the potential energy barrier for oxygen ion migration through the material lattice. Similar results were found in the series Ln_{0.6}Sr_{0.4}CoO_{3- $\delta}$} (with Ln=lanthanide such as La, Pr, Nd, Sm and Gd), in which the oxygen flux was found to increase with decreasing radius of the lanthanide ion [78]. This result also corroborates the finding that the substitution of Pr for La increased the loss of lattice oxygen (Chapter 8.5) and thus the concentration of oxygen vacancies, responsible for the permeation of oxygen through the lattice of MIEC perovskite materials. The oxygen permeation flux density through La₂NiO_{4+ $\delta}} is higher than that of Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} is higher than that of Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} is higher than that of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-<math>\delta}$ is higher than that of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and L}}</sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub></sub>

At high temperatures, oxygen vacancies become available for oxygen transport through the perovskitebased membranes. In the La₂NiO_{4+ δ} membrane material, related to the K₂NiF₄-type structure, oxygen transport is based on the oxygen vacancy hopping mechanism as well as on an interstitial diffusion. In the perovskite-type membrane materials, such as $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and Pr0.58Sr0.4Co0.2Fe0.8O3-6, oxygen transport is solely based on the oxygen vacancy hopping mechanism. The increase in concentration of oxygen vacancies might therefore have a greater influence on the oxygen permeation fluxes of La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ}, Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes than those of $La_2NiO_{4+\delta}$ membranes. This could be the reason why the slope of the oxygen permeation flux density curves of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and Pr0.58Sr0.4Co0.2Fe0.8O3-6 1mm membranes increased after 800°C whereas it decreased for La2NiO4+6 membranes. The slope of the oxygen permeation flux through the 1mm Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3.6} membrane decreased after 800°C. However, the slopes of the TGA curves (Chapter 8.5) representing the oxygen loss of the lattice were steeper for the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ materials after 800°C than for the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material. A rapid increase of the concentration of oxygen vacancies in the La0,58Sr0,4Co0,2Fe0,8O3-6 and Pr0,58Sr0,4Co0,2Fe0,8O3-6 materials might have induced this increase of the oxygen permeation flux observed after 800°C.

9.2.5 Activation energies for oxygen permeation

Table 9.2 lists the activation energies (Ea) for oxygen permeation of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ membranes calculated from the oxygen permeation data as a function of temperature. As expected, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ exhibits the lowest activation

energy of 48 kJ/mol as its oxygen permeation fluxes are the highest. The activation energies are found to follow the same trend as oxygen permeation flux densities.

Material	Ea (kJ/mol)
Ba _{0,5} Sr _{0,5} Co _{0,8} Fe _{0,2} O _{3-δ}	48
$La_2NiO_{4+\delta}$	88
$La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3\text{-}\delta}$	101
$Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$	124

Table 9.2. Activation energies (in KJ/mol) for oxygen permeation through 1mm $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes.

9.2.6 Discusion

The oxygen permeation fluxes measured in this work coincide with the range of values found in the literature. Conflicting values for the flux through MIEC membranes have been measured by different groups, which reflects the influence of many parameters on the oxygen permeation results. Indeed, the performance of membranes can be affected by many factors such as the preparation technique of the membrane material (powder synthesis [134], shaping and sintering techniques [135], the microstructure of the sample (e.g. grain size, porosity) [136], the configuration the permeation test set-up as well as the experimental conditions (e.g. feed and sweep gas fluxes). Different oxygen permeation fluxes were found for Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ}, membranes prepared with the solid state reaction and with the EDTA-citric acid complexing synthesis method [84]:

Another study [134] measured different oxygen permeation fluxes for $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, membranes prepared with different powder preparation techniques, namely solid state reaction, modified citrate and citrate-EDTA complexing methods. The highest permeation values were found for the samples where powder was prepared with the solid state reaction. These samples exhibited the biggest grain size and the densest microstructure, which would suggest that grain boundaries hinder oxygen ion transport and that oxygen transport is faster through grain bulk than along the grain boundaries [134]. Moreover, the oxygen permeation fluxes of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ membranes sintered at different temperatures and for different dwelling times were found to increase considerably with increasing grain size [83]. These observations could be the result of a time and temperature dependent cobalt enrichment at the grain boundaries, which was studied in Chapter 10.6 of this work.

9.3 Conclusion

Oxygen permeation through MIEC membranes is a thermally activated process directly related to the concentration and the mobility of oxygen vacancies in the lattice of the material. Oxygen permeation through $La_2NiO_{4+\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes, whose thicknesses range between 0.5mm and 1.5mm, seems to be governed by surface exchange as well as bulk diffusion. However, a decrease in membrane thickness caused an increase in oxygen permeation flux for all membranes. A kinetic demixion of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane materials was observed after an approximately 100-hour operation. It would be interesting to investigate the microstructure of $La_2NiO_{4+\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes after operation in order to determine whether a kinetic demixion also occurs.

The maximum oxygen permeation fluxes were measured for 1mm $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ membranes over the whole temperature range investigated. The fluxes for 1mm $La_2NiO_{4+\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membranes are well below the values of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ one and are also of the same order of magnitude, $La_2NiO_{4+\delta}$ being slightly higher in the temperature range of between 700°C and 850°C and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ higher after 850°C.

The maximal temperature considered for the application is 800°C for energy and cost efficiency reasons. At this temperature the highest oxygen permeation flux obtained was of about 1.4 ml min⁻¹ cm⁻² for the 1mm Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} membrane. The fluxes of La₂NiO_{4+ δ}, Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} 1mm membranes are between 0.1 ml min⁻¹ cm⁻² and 0.2 ml min⁻¹ cm⁻². Considering that the minimum oxygen permeation flux for the selection of a material as a high purity oxygen separation membrane is 10 ml min⁻¹ cm⁻², a lot of work still needs to be done in order to improve the oxygen permeation of these materials. Membrane surface modification and the development of thin film membrane technology are options currently being considered.

10 Thermo-chemical stability investigation

The thermo-chemical stability of MIEC materials is an important concern for their selection as high purity oxygen separation membranes in the oxyfuel process of coal-fired power plants. The oxyfuel process consists in the burning of coal in an oxygen-rich atmosphere to produce a flue gas highly concentrated in CO₂. This will allow the flue gas to be composed of relatively clean exhaust gases, steam and CO₂. The production of this combustion gas highly concentrated in oxygen from air can be carried out using oxygen permeable MIEC membranes. A concept for the oxyfuel process with membrane technology is to recycle the flue gas to sweep the permeate side of the membrane, exposing it to high concentrations of CO₂ and water. Therefore, the La₂NiO_{4+ δ}, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ}, La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} membrane materials have to be stable in the gaseous atmosphere of the flue gas. The literature study in Chapter 3.3 and discussions with E. Riensche (Forschungszentum Jülich, IEF-3) determined that the atmosphere that is believed to be the closest to the flue gas composition is about 89 mol% CO₂ on a dry basis, or 66 mol% CO₂ and 26 mol% water vapour, on a humid basis. Moreover, it was estimated in Chapter 3.3 that the permeate gas stream would consist of about 25% permeating O₂ and 75% flue gas.

As described in Chapter 7.2, the experimental set-up is composed of a quartz glass tube placed in a three-zone horizontal tube furnace. The sintered pellets of La₂NiO_{4+ δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ}, Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} were placed in a quartz glass sample holder and annealed at 600°C, 700°C and 800°C for 200 hours and 500 hours. This temperature range was chosen for the annealing experiments because 600°C is the minimum operating temperature for perovskite-type membranes and 800°C is the maximum temperature considered for this application. Operating membranes above 800°C would not be cost and energy efficient. Two dwelling times of 200 hours and 500 hours were selected in order to have a detectable reaction in the bulk material or on the surface if a reaction were to occur. The 500-hour dwelling time was only applied to the samples annealed in the atmospheres believed to be the closest to operating conditions on the feed and the permeate sides of a high purity oxygen separation membrane for the oxyfuel process. The atmospheres used for the annealing experiments are listed in the table (Table 10.1) below:
Atmosphere (in mol9/)	Annealing conditions	
Atmosphere (m mor%)	Temperatures (°C)	Dwelling times (hours)
Air	600, 700, 800	200, 500
Air +10% CO ₂	600, 700, 800, 900	200
(1% O ₂ , 99%N ₂) +10%CO ₂	600, 700, 800	200
43%O ₂ , 14%N ₂ , 43%CO ₂	600, 700, 800	200
25% O ₂ , 8% N ₂ , 67% CO ₂	600, 700, 800	200, 500
28% O ₂ , 5% N ₂ , 55% CO ₂ , 12% H ₂ O	600, 700, 800	200
25% O ₂ , 50% CO ₂ , 5% N ₂ , 20% H ₂ O	600, 700, 800	200, 500
25% O ₂ , 45% N ₂ , 20% H ₂ O	600, 700, 800	200

 Table 10.1. Atmospheres and annealing conditions for $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets

Furthermore, given that the high temperature components in coal-fired power plants are made of chromium-containing ferritic and austenitic steels, it is of considerable importance to determine whether an interaction will occur between the construction materials and the membrane materials selected. Thus, a long term annealing experiment was carried out in which $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets were placed next to a Cr_2O_3 disk at a distance of 1cm in order to observe any reaction that might occur on the surface of the samples exposed.

10.1 Annealing in air

Air will be supplied to the feed-side of the MIEC membranes considered for the separation of oxygen from air in the framework of the oxyfuel process in coal-fired power plants. Thus it is essential to assess the stability of the materials selected in this study i.e. $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in air at high temperatures. These annealing experiments were carried out at 600°C, 700°C and 800°C for 200 hours and 500 hours.

After annealing in air, no phase change was observed on the surface of all samples studied after annealing at every temperature and exposure time. However, secondary phases were observed throughout the material of all samples at all temperatures. EDS analysis determined that cobalt oxide inclusions were formed in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets (Figure 10.1), nickel oxide inclusions in the $La_2NiO_{4+\delta}$ pellets (Figure 10.2) and a mixture of cobalt and iron oxide inclusions in the

 $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ as well as the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets (Figure 10.2). These secondary phases present in all samples will be discussed in greater detail later in this chapter.



Figure 10.1. (A) SEM micrograph of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air at 700°C for 200 hours and (B) light microscopy picture of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air at 800°C for 500 hours.





 $\begin{array}{l} Figure \ 10.2 \ . \ SEM \ micrograph \ of \ the \ cross \ section \ of \ pellets \ annealed \ in \ air: \ (A) \\ La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} \ (C) \ Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} \ and \ (E) \ La_2NiO_{4+\delta} \ at \ 800^{\circ}C \ for \ 200 \ hours \ and \ light \ microscopy \ picture \ of \ the \ cross \ section \ of: \ (B) \ La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} \ (D) \\ Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta} \ and \ (F) \ La_2NiO_{4+\delta} \ at \ 600^{\circ}C \ for \ 500 \ hours. \end{array}$

10.2 Annealing in CO₂-containing atmospheres

In the "dry recycling" option of the oxyfuel process, the permeate side of MIEC membranes will be in contact with CO₂ from the recycled flue gas. In order to assess the stability of the materials selected in this study i.e. $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ in CO₂-containing atmospheres, a series of annealing experiments was conducted at high temperatures.

• The first annealing atmosphere, air (79%N₂ and 21%O₂) plus 10%CO₂ added, was chosen in order to test the stability of these materials in an atmosphere with a relatively low CO₂ concentration. These annealing experiments were carried out at 600°C, 700°C, 800°C and 900°C for 200 hours.

• A second atmosphere of 1% O_2 , 99% N_2 plus 10% CO_2 added was selected to determine the influence of oxygen on the reaction with CO_2 . These annealing experiments were carried out at 600°C, 700°C and 800°C for 200 hours.

• The third annealing condition selected had higher contents of CO₂ and O₂, i.e. 43%O₂, 43%CO₂ and 14%N₂. These annealing experiments were carried out at 600°C, 700°C and 800°C for 200 hours.

• For the last annealing experiment in CO_2 -containing atmospheres, the atmosphere believed to be the closest to operating conditions, on a dry basis, i.e. 67 mol% CO_2 , 25 mol% O_2 and 8 mol% N_2 was chosen. This series of annealing experiments was carried out at 600°C, 700°C and 800°C for 200 hours and 500 hours.

For each annealing condition in CO₂-containing atmospheres, cobalt oxide inclusions were formed in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, pellets, nickel oxide (NiO) inclusions in the $La_2NiO_{4+\delta}$ pellets and a mixture of cobalt and iron oxide inclusions in both the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ as well as the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets.



Figure 10.3. SEM micrograph of the $(Ba_xSr_{1-x})CO_3$ layer on the surface of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed at 800°C for 200 hours in air +10 mol% CO₂.

After annealing in CO₂-containing atmospheres, no phase change was observed on the surface of the La₂NiO_{4+ δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} samples studied. However, a reaction zone was observed on the surface of all Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} samples at all annealing temperatures and dwelling times. A top layer, which was determined to be composed of barium and strontium by EDS analysis, was found on the surface of all samples, as seen in Figure 10.3 above. Under this layer, a needle-like structure layer was formed in all Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} samples, as seen in Figure 10.4 and Figure 10.7.

Carbon can not be measured precisely with SEM analysis as it is present in the vacuum chamber. Carbon deposition occurs on the surface of the samples measured with this technique. The longer the measuring time, the longer the electron beam remains on the point measured, the more carbon will be deposited. Therefore, in order to check whether the top layer contained carbon, a line scan of the cross fracture of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ sample annealed in air +10%CO₂ at 800°C for 200 hours was carried out starting from the surface over the needle-like structure and down to the matrix $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material (Figure 10.4). The cross fracture of the sample was analysed in order to rule out any degradation of the surface that might have been caused by the metallographic technique used to prepare it for microscopic observation. The intensity of the carbon spectrum is much higher in the top layer than in the rest of the pellet, as seen in Figure 10.4. Likewise, the barium and strontium contents are clearly higher in the top layer. The intensities of the iron and cobalt spectra are very low in

the top layer and increase greatly in the needle-like structure. This layer was, therefore, determined to be a mixed barium and strontium carbonate of the form $(Ba_xSr_{1-x})CO_3$.



Figure 10.4. SEM micrograph and EDS line scan of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air +10% CO2 for 200 hours at 800°C.

A carbonate layer, which can prevent O_2 -adsorption on the surface of oxygen permeation membranes, had built up over the entire surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed at 700°C and 800°C for all dwelling times. But, after annealing at 600°C, only part of the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets is covered as the kinetics of the carbonisation seem to be much slower at this temperature.

EDS and XRD analyses (Figure 10.5) show that this layer is a mixed barium and strontium carbonate with the chemical composition (Ba_xSr_{1-x})CO₃. In order to determine the composition of this mixed carbonate layer EDS point analysis measurements of three areas in a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5%N₂ at 800°C for 500 hours (Figure 10.6) were conducted in order to have valid statistics. The elemental composition in mass% of the mixed carbonate layer is shown in Table 10.2. By averaging the values obtained from these three measurements, the composition $Ba_{0.43}Sr_{0.57}CO_3$ was determined for the mixed carbonate. A substantial experimental error is always present for the quantification of carbon and oxygen with the EDS analysis since this technique does not allow for the precise detection of light elements, and carbon is deposited on the surface of the samples during the measurements. Therefore, the fact that these measurements are not normalised should be taken into account when considering the precision of the results. Although the experimental error is considerable, the estimation of the ratio between barium and strontium contents is workable.



Figure 10.5. Powder XRD spectra of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O₂, 8%N₂ at 800°C for 200 hours.



Figure 10.6. SEM micrograph showing the 3 areas measured in the $(Ba_xSr_{1-x})CO_3$ layer of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5%N₂ at 800°C for 500 hours.

Table 10.2. Chemical composition (in atomic%) of the mixed barium and strontium carbonate measured in three different areas of the layer.

Element	Area 1	Area 2	Area 3
Ba	8.8	9	9.1
Sr	11.3	12.1	11.9
С	24	24	22.7
0	55	55	56.4

In addition to the carbonate layer, a needle-like structure was formed under it in all $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples, as seen in Figure 10.10. EDS and XRD analyses could not determine the composition of this layer precisely. However, it seemed to be a (Ba, Sr, Co, Fe)-containing perovskite. As each individual needle in the needle-like structure layer has a maximum width of around 1µm after annealing at 800°C, a transmission electron microscopy (TEM) investigation of the microstructure was conducted in order to determine its composition more precisely (Figure 10.7). The $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ sample annealed in 67% CO₂, 25% O₂ and 8% N₂ at 800°C for 500 hours was selected for this investigation as it presented a needle-like structure layer thick enough to enable the FIB lamellae to be cut. It is important to mention that, in TEM analysis, the composition of the area measured has to be single phased over the entire thickness of the FIB lamellae in order to measure the desired phase.



Figure 10.7. TEM micrograph of the needle-like structure of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O₂ and 8% N₂ at 800°C for 500 hours.

Element	Needle	Matrix material
Ba	21.09	25.18
Sr	4.64	26.86
Со	65.36	32.13
Fe	8.91	15.83

Table 10.3. Chemical composition (in atomic%) of a needle and of the matrix material.

The chemical compositions of the needles as well as the matrix (Table 10.3) were determined by EDS with a 5% error. The phases present are Ba, Sr, Co and Fe oxides with two different chemical compositions. The needles appear to be oxides with the composition $Ba_{0,38}Sr_{0,05}Co_{0,5}Fe_{0,07}O_z$ and the matrix a perovskite with the composition $Ba_{0,494}Sr_{0,506}Co_{0,68}Fe_{0,32}O_z$. The composition of the matrix is very similar to the original $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material. Taking into account the experimental error, the barium and strontium contents are unchanged. The cobalt content is lower and the iron content is higher than the cobalt and iron contents of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material respectively.

An elemental mapping of an area in the needle-like structure of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O₂ and 8% N₂ at 800°C for 500 hours was carried out with TEM (Figure 10.8). Three distinct areas are apparent in the sample. The first area corresponds to the needles, which present high contents of barium and cobalt and low contents of strontium and iron. The second area corresponds to the matrix material which has lower contents of barium and cobalt than the needles as well as much higher contents of strontium and iron. The third area seems to be an area, where both the matrix and needles were present over the thickness of the FIB lamellae, and which has approximately the same amounts of barium and cobalt as the BSCF50 matrix but lower strontium and iron contents. A depletion of the concentration of barium and strontium in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material may possibly have caused these needles to build up at its interface with the mixed barium and strontium carbonate layer.



Figure 10.8. TEM micrograph and elemental mapping of the needle-like structure of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O₂ and 8% N₂ at 800°C for 500 hours.

10.2.1 Air plus 10%CO₂

After annealing in air +10%CO₂ for 200 hours, the cross sections of La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ}, La₂NiO_{4+ δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} pellets, shown in Figure 10.9. below, do not present any degradation of their surface. However, secondary oxide phases are found in the bulk of all samples investigated after every annealing time.



Figure 10.9. SEM micrographs of the cross section of pellets annealed in air $+10\%CO_2$ for 200 hours: $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ (A) at 800°C and (B) at 600°C, $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ (C) at 800°C and (D) at 600°C, $La_2NiO_{4+\delta}$ (E) at 800°C and (F) at 600°C.

After annealing the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets in air +10%CO₂ for 200 hours, a mixed barium and strontium carbonate layer and a needle-like structure layer were formed on their surface (Figure 10.10). As seen in Table 10.4, the thicknesses of both the mixed carbonate layer and the needle-like structure layer were found to increase with increasing temperature. The thicknesses of the (Ba_xSr_{1-x})CO₃ and

needle-like structure layers could not be determined for the sample annealed for 600 hours because too many scratches were present near the surface of the pellet after the metallographic preparation. Both layers were four times thicker after annealing at 800°C than at 700°C. Between 800°C and 900°C, a further increase in thickness of 50% and 10% was measured for the mixed carbonate and the needle-like structure layer respectively.

Table 10.4. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$ and needle-like structure layers as a function of annealing temperature of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in air $+10\%CO_2$ for 200 hours.

Annealing	Thickness (Ba _x Sr _{1-x})CO ₃ layer Needle-like structur (µm) layer (µm)	
temperature (°C)		
700	0,7	3,5
800	3	15
900	4,5	16,5

Moreover, cobalt oxide inclusions can be observed in the needle-like structure in the samples annealed at 700°C, 800°C and 900°C. In the sample annealed at 900°C, these inclusions seem to be building a layer at the interface between the mixed carbonate and the needle-like structure layers. This sample also exhibits a much thicker needle-like formation than the samples annealed at temperatures of under 800°C. An increase in annealing temperature also induced an increase in needle thickness.





Figure 10.10. SEM micrographs of the cross section of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in air +10%CO₂ for 200 hours: (A) at 600°C, (B) 700°C, (C) 800°C and (D) 900°C.

10.2.2 1% O₂, 99%N₂ plus 10%CO₂

No change in the microstructure of the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets annealed in 1% O₂, 99%N₂ +10%CO₂ for 200 hours, is observed in the SEM micrographs of their cross section (Figure 10.11). However, secondary oxide phases were present in the bulk of all samples after annealing at every temperature.





Figure 10.11. SEM micrographs of the cross section of pellets annealed in $1\%O_2$, $99\%N_2 + 10\%CO_2$ for 200 hours at 800° C: (A) $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (B) $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (C) $La_2NiO_{4+\delta}$.

A barium strontium carbonate layer, under which the needle-like structure layer was present, was formed on the surface of all the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 1% O₂, 99%N₂ +10%CO₂ for 200 hours at every temperature (Figure 10.12). At 600°C, this layer did not cover the entire surface of the pellets. A continuous mixed carbonate layer was observed on the surface of the samples annealed at 700°C and 800°C. The thickness of both the carbonate and the needle-like structure layer after annealing in this atmosphere are given in the table (Table 10.5) below.

Table 10.5. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$ and needle-like structure layers as a function of annealing temperature of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in $1\%O_2$, $99\%N_2 + 10\%CO_2$ for 200 hours.

Annealing	Thickness (Ba _x Sr _{1-x})CO ₃ layer Needle-like structure (µm) layer (µm)	
temperature (°C)		
700	0,7	4,5
800	4,5	16,5

The thicknesses of both layers were found to increase with increasing temperature, as seen in Table 10.5. The mixed carbonate layer was measured to be six times thicker in the sample annealed at 800°C than the one annealed at 700°C. And the needle-like structure was more than 3 times thicker. Cobalt oxide inclusions can also be observed in the needle-like structure layer. An increase in annealing temperature also caused an increase in needle thickness.



Figure 10.12. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in $1\%O_2$, $99\%N_2 + 10\%CO_2$ for 200 hours: (A) at 700°C and (B) at 800°C.

Moreover, a decrease in oxygen partial pressure caused only a slight increase of both the mixed carbonate and needle-like structure layers. A 30% and a 10% increase in thickness of the needle-like structure layer occurred between the samples annealed in air +10%CO₂ and in 1%O₂, 99%N₂ +10%CO₂ for 200 hours at 700°C and 800°C respectively. As for the mixed carbonate layer, a 50% increase in thickness was measured between these same samples. The samples annealed at 700°C, however, had the same thickness.

10.2.3 43%O₂, 43%CO₂ and 14%N₂

An increase in CO₂ and oxygen content in the annealing atmosphere did not cause a change in the microstructure of the surface of the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- $\delta}$}, Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- $\delta}$} and La₂NiO_{4+ δ} pellets annealed in 43%O₂, 43%CO₂ and 14%N₂ for 200 hours, as seen in Figure 10.13. But the previously mentioned mixed barium and strontium carbonate as well as the needle-like structure layers were formed on the surface of the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} pellets at all temperatures (Figure 10.14 and Figure 10.15).



Figure 10.13. SEM micrographs of the cross section of pellets annealed in 43%O₂, 43%CO₂ and 14%N₂ for 200 hours at 800°C: (A) $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (B) $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (C) $La_2NiO_{4+\delta}$.

An increase in the thicknesses of both the mixed barium and strontium carbonate layer and the needle-like structure layer was found with increasing temperature, as seen in Table 10.6, Figure 10.14 and Figure 10.15. The thickness of the mixed carbonate layer doubled between the samples annealed at 600°C and the ones annealed at 700°C. The thickness of this layer was a further five times thicker after annealing at 800°C than at 700°C. As for the thickness of the needle-like structure layer, it tripled between the sample annealed at 700°C and the one annealed at 800°C. The preparation of the sample annealed at 600°C did not allow for its thickness to be measured. Moreover, cobalt oxide inclusions are seen in the needle-like structure layer as well as at the interface between this layer and the mixed carbonate layer Figure 10.14 (B). An increase in annealing temperature also led to an increase in needle thickness.

Table 10.6. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$ and needle-like structure layers as a function of annealing temperature of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 43% O_2 , 43% CO_2 , 14% N_2 for 200 hours.

Annealing	Thic	kness
temperature (°C)	(Ba _x Sr _{1-x})CO ₃ layer Needle-like struct (µm) layer (µm)	
700	0,9	5,7
800	5	18



Figure 10.14. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in $43\%O_2$, $43\%CO_2$ and $14\%N_2$ for 200 hours: (A) at 700°C and (B) at 800°C.



*Figure 10.15. SEM micrograph of the cross-fractions of Ba*_{0,5}*Sr*_{0,5}*Co*_{0,8}*Fe*_{0,2}*O*_{3-δ} *pellets annealed for 200 hours in 43%O*₂, 43%CO₂ and 14%N₂ at 600°C, 700°C and 800°C, from left to right.

10.2.4 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂

In the "dry recycling" option of the oxyfuel process, the flue gas will be recycled onto the permeate side of the MIEC membrane after separating the water vapour present from the rest of the gas stream. The atmosphere with the composition of 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ is supposed to be close to the composition of this recycled flue gas stream. After annealing in this CO₂–rich atmosphere, EDS and XRD analysis did not detect carbonates on the surface of the La_{0,58}Sr_{0,4}CO_{0,2}Fe_{0,8}O_{3-δ} pellets annealed at 600°C, 700°C or 800°C for 200 hours and 500 hours. Although no degradation of the microstructure of the surface of these samples was observed, secondary oxide phases were found in all samples annealed at all temperatures and annealing times.

An SEM investigation of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ samples annealed in 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ for 500 hours was carried out in order to determine with absolute certainty whether a change in the surface of the pellets had occurred. The cross fracture of the samples was analysed without metallographic preparation to rule out any degradation of the reaction zone the preparation technique might have caused. No reaction was detected even after annealing in such a CO₂–rich atmosphere for the long annealing time of 500 hours as can be seen in Figure 10.16.







Figure 10.16. SEM micrographs and light microscopy pictures of pellets annealed in 67% CO₂, 25% O_2 , 8% N_2 at 800°C for 500 hours: (A) $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (B) $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (C) $La_2NiO_{4+\delta}$.

Table 10.7 as well as Figure 10.18 and Figure 10.17 show that the thicknesses of both the mixed barium and strontium carbonate layer as well as the needle-like structure layer increase with increasing temperature. A 50% increase of the mixed carbonate layer was measured between the sample annealed at 600°C and the one annealed at 700°C. The carbonate layer was five times thicker on the surface of the sample annealed at 800°C than the one annealed at 700°C. The thickness of the needle-like structure layer more than tripled between the sample annealed at 600°C and the one annealed at 700°C. A further doubling of the thickness of that layer occurred between the sample annealed at 700°C and the ones annealed at 800°C.

Table 10.7. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$ and needle-like structure layers as a function of annealing temperature of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 67 mol% CO_2 , 25 mol% O_2 and 8 mol% N_2 for 200 hours.

Annealing	Thickness		
temperature (°C)	(Ba _x Sr _{1-x})CO ₃ layer Needle-like structure (µm) layer (µm)		
600	0,7	2,5	
700	1	9	
800	5,5	22	

Here also, cobalt oxide inclusions are observed in the needle-like structure in all samples. In the sample annealed at 600°C Figure 10.17 (A), these inclusions are very large and are found near the surface of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet. The two different cobalt oxide phases present in this inclusion, i.e. CoO in the centre of Co_3O_4 (as discussed in Chapter 10.7), are distinctly visible. Mixed barium and strontium carbonate phases are also found in the needle-like structure layer for the sample annealed at 800°C, as seen in Figure 10.18 (B). This might be due to the fact that, during annealing, the reaction zone did not stop at the interface between the needle-like structure and the mixed carbonate layer and that carbonates formed within the perovskite matrix material of the needle-like structure.



Figure 10.17. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 67% CO₂, 25% O₂ and 8% N₂ for 200 hours: (A) at 600°C and (B) at 700°C.



Figure 10.18. SEM micrographs of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O₂ and 8% N₂ at 800°C for 200 hours.

The thicknesses of both the mixed barium and strontium carbonate layer and the needle-like structure layer of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ for 500 hours were found to increase with increasing temperature, as seen in Table 10.8 and Figure 10.17. The thickness of the mixed carbonate layer of the sample annealed at 800°C was measured to be six times thicker than that of the sample annealed at 700°C, and the needle-like structure layer more than twice as thick. Furthermore, cobalt oxide inclusions can be observed in the needle-like structure in all samples and also at the interface between the needle-like structure and the mixed carbonate layer in the sample annealed at 800°C (Figure 10.19 (B)).

Table 10.8. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$ and needle-like structure layers as a function of annealing temperature of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 67 mol% CO_2 , 25 mol% O_2 and 8 mol% N_2 for 500 hours.

Annealing	Thickness	
temperature (°C)	(Ba _x Sr _{1-x})CO ₃ layer (µm)	Needle-like structure layer (µm)
700	1,5	13
800	9	33



Figure 10.19. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 67% CO₂, 25% O₂ and 8% N₂ for 500 hours: (A) at 700°C and (B) at 800°C.

The thicknesses of the mixed barium and strontium carbonate layer as well as the needle-like structure layer were found to increase also with increasing annealing time. An increase in thickness of around 50% for the needle-like structure layer and around 60% for the mixed carbonate layer were measured between the sample annealed in 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ at 800°C for 200 hours and the one annealed for 500 hours. A 50% increase of both layers was observed between the samples annealed at 700°C for 200 hours and the ones annealed for 500 hours. Likewise, an increase in needle thickness was induced by an increase in annealing temperature and time.

10.3 FactSageTM thermo-chemical calculations

The FactSageTM thermo-chemical software and databases [137], by Thermfact/CRCT (Montreal, Canada) and GTT-Technologies (Aachen, Germany), was used to predict phase formations on the surface of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets exposed to one of the annealing atmospheres selected for this work, i.e. 67 mol% CO₂, 25 mol% O₂ and 8 mol%. No data concerning these materials was available in the FactSageTM thermodynamic databases, therefore the individual components of these materials were used to predict the thermodynamic equilibriums in the systems investigated.

In a first step, the partial pressure of oxygen in the system was determined at each annealing temperature, i.e. 600° C, 700° C and 800° C. This PO₂ value, corresponding to the atmosphere present at the surface of the pellets, was determined to be $log(PO_2)=-0.65$ in the atmosphere 67% CO₂, 25% O₂ and 8% N₂ respectively in the temperature range of between 600° C and 800° C. The surface of each material is demarcated on the graphs showing the activities of the different phases formed as a function of the oxygen partial pressure in the system (Figure 10.20 to Figure 10.25).

Figure 10.20 shows the activities of the phases formed in the $La_2NiO_{4+\delta}$ material, in an atmosphere composed of 67% CO₂, 25% O₂ and 8% N₂ at 800°C, calculated by FactSage as a function of the oxygen partial pressure in the system. The lanthanum and nickel carbonates were not found to be stable in the conditions selected, which is in agreement with the experimental results. FactSage predicted the formation of nickel oxide (NiO) and lanthanum oxide (La₂O₃). However, only the NiO was found in the pellets after annealing in all conditions, which shows the limits of theoretical calculations.



Figure 10.20. Oxygen partial pressure dependence of the activities of the phases formed in $La_2NiO_{4+\delta}$ in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 800°C.

The activities of the phases formed in the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets, in the atmosphere 67% CO₂, 25% O₂ and 8% N₂ at 800°C, calculated by FactSage as a function of oxygen partial pressure are shown in Figure 10.21. The lanthanum, cobalt and iron carbonates were found to be unstable in the conditions selected, which corroborates the experimental results. However, FactSage predicted the formation of strontium carbonate, which was not observed on the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ samples after the annealing experiments. Likewise, lanthanum oxide (La_2O_3) was expected to be formed from the FactSage calculation but was not present in the annealed pellets.



Figure 10.21. Oxygen partial pressure dependence of the activities of the phases formed in $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 800°C.

The FactSage software was used to determine the activities of the phases formed in the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets in the atmosphere 67% CO₂, 25% O₂ and 8% N₂ at 800°C as a function of oxygen partial pressure, as shown in Figure 10.22. The lanthanum, cobalt and iron carbonates were found to be unstable in the conditions selected, again in agreement with the experimental results. However, FactSage predicted the formation of strontium carbonate, which was not present on the surface of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ specimens after the annealing experiments. Likewise, praseodymium oxide (PrO₂), which was expected to be formed from the FactSage calculations, was not observed.



Figure 10.22. Oxygen partial pressure dependence of the activities of the phases formed in $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 800°C.

FactSage predicted the formation of both barium and strontium carbonates on the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets at all temperatures (Figure 10.23, Figure 10.24 and Figure 10.25). With decreasing PO₂, which corresponds to a gradual progression into the material from the surface of the samples, the activity of these carbonates decreased, leading to the formation of barium and strontium oxides. Although no data about the $(Ba_{1-x}Sr_x)CO_3$ formed on the surface of the samples during the annealing experiments was available in the FactSage thermodynamic databases, it can be assumed that the activity of this compound is found between the activities of the individual carbonates (BaCO₃ and SrCO₃), the data of which is available.



Figure 10.23. Oxygen partial pressure dependence of the activities of the phases formed in Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 600°C.



Figure 10.24. Oxygen partial pressure dependence of the activities of the phases formed in Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 700°C.



Figure 10.25. Oxygen partial pressure dependence of the activities of the phases formed in Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} in the atmosphere 67% CO₂, 25% O₂, 8% N₂ at 800°C.

10.4 Annealing in water vapour-containing atmospheres

In the "wet recycling" option of the oxyfuel process, the permeate side of the MIEC membrane will be in contact with CO₂ as well as water vapour from the recycled flue gas. In order to assess the stability of the materials selected in this work i.e. $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in CO₂- and H₂O-containing atmospheres, a series of annealing experiments was conducted at high temperatures. At first, the atmosphere 55 mol% CO₂, 28 mol% O₂, 12 mol% H₂O and 5 mol% N₂ was chosen in order to test the stability of the material selected in an atmosphere with a relatively low water vapour concentration. These annealing experiments were carried out at 600°C, 700°C and 800°C for 200 hours. For the second annealing experiment in CO₂and H₂O-containing atmospheres, the atmosphere believed to be the closest to operating conditions, on a humid basis, i.e. 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O and 5 mol% N₂ was selected. These annealing experiments were carried out at 600°C, 700°C and 800°C for 200 hours.

After annealing $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ pellets in CO₂- and H₂O-containing atmospheres, a silicate layer was formed on the surface of all the samples. A reaction with silica (SiO₂) occurred on the surface of the pellets to form silicates. The contamination source was found to be the quartz glass tube and sample holder from which silica

evaporated due to the high partial pressure of water vapour and high temperature conditions. Moreover, silica volatile species are known to react with metal oxides. After oxygen permeation experiments on $La_{0,60}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ [138], the surface of the membrane was contaminated with silica. The origin of this contamination was identified as being siloxane-containing grease used in the manual valves of the set-up. As siloxanes evaporate very easily, they were transported towards the surface of the membrane with the gas flow.

Volatile silicon based species are formed from the quartz glass components of the annealing test set-up when exposed to high water vapour-containing atmospheres at high temperatures. This process is directly related to the partial pressure of water vapour as seen in Equation 10.1 and Equation 10.2 below giving the volatilisation reaction [139,140].

$$SiO_{2(s)} + 2H_2O_{(g)} \leftrightarrow Si(OH)_{4(g)}$$
 (Equation 10.1)

$$SiO_{2(s)} + H_2O_{(g)} \leftrightarrow SiO(OH)_{2(g)}$$
 (Equation 10.2)

Si(OH)₄ is the predominant specie formed below the temperature of 1100° C, above which SiO(OH)₂ is predominantly formed [140]. Si(OH)₄, formed when water vapour was present, reacted with the perovskite-type membrane material to form a silicate layer, which constitutes a diffusion barrier preventing oxygen adsorption on the surface of the high purity oxygen separation membrane and hampers further permeation through the membrane. The poisoning of perovskite-type membrane materials by silica rules out the use of silicon based gaskets for their sealing in the gas separation device. Moreover, some coal types (e.g. brown and black coal) contain significant amounts of silica. The concentration of silica in brown coal and in black coal ranges between 6.10⁻³ weight% and 1,5 weight% and between approximately 1 weight% and 6 weight% respectively [141]. In the option for the oxyfuel process with flue gas recycling, the silica present in the fly ash after combustion of these silica-containing coal grades could be deposited on the sweep-side of the oxygen permeation membranes. This could represent an important issue for the stability of these MIEC membrane materials.

No reaction other than that with silica occurred on the surface of the La₂NiO_{4+ δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} pellets. However, after annealing the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} samples in CO₂- and H₂O-containing atmospheres, the mixed barium and strontium carbonate as well as the needle-like structure layers were again present as after annealing in CO₂-containing atmospheres (Figure 10.28).

10.4.1 55 mol% CO₂, 28 mol% O₂, 12 mol% H₂O and 5 mol% N₂

Figure 10.26. shows the cross section of the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ pellets annealed in 55 mol% CO₂, 28 mol% O₂, 12 mol% H₂O and 5 mol% N₂ at 800°C for 200 hours. Although no degradation of the microstructure of their surface was observed, secondary oxide phases were present throughout all samples annealed at every temperature.



Figure 10.26. SEM micrographs of the cross section of pellets annealed in 55%CO₂, 28%O₂, 12%H₂O, 5%N₂ at 800°C for 200 hours: (A) $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, (B) $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and (C) $La_2NiO_{4+\delta}$.

Table 5.19 and Figure 10.27 show that the thicknesses of the barium and strontium carbonate layer, the needle-like structure layer as well as the silicate layer of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed in 55 mol% CO₂, 28 mol% O₂, 12 mol% H₂O and 5 mol% N₂ for 200 hours all increase with increasing temperature. After annealing at 800°C, the mixed carbonate layer was three times thicker and the needle-like structure layer five times thicker than after annealing at 700°C. A 50% increase of the silicate layer was measured between the sample annealed at 700°C and the one annealed at 800°C.

Table 10.9. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$, the needle-like structure as well as the barium and strontium silicate layers as a function of annealing temperature of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in 55 mol% CO_2 , 28 mol% O_2 , 12 mol% H_2O and 5 mol% N_2 at 800°C for 200 hours.

Annealing	Thickness (Ba _x Sr _{1-x})CO ₃ Needle-like structure layer (μm) Silicate lay (μm)		
temperature (°C)			Silicate layer (µm)
700	23	2,5	1
800	67	12	1,5

An increase in annealing temperature also induced an increase in needle thickness. Moreover, barium and strontium carbonate phases are present in the needle-like structure of the samples annealed at 800°C, as seen in Figure 10.27. Cobalt oxide inclusions can also be observed in the needle-like structure of all samples. An increase in the concentration of these inclusions seems to occur near the mixed carbonate layer of the sample annealed at 800°C as seen in Figure 10.28. A 0.5µm thick cobalt oxide layer was formed at the interface between the needle-like structure and the mixed carbonate layer in the sample annealed at 800°C.



Figure 10.27. SEM micrographs of the cross section of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in 55%CO₂, 28%O₂, 12%H₂O, 5%N₂ for 200 hours: (A) at 700°C and (B) at 800°C.



Figure 10.28. SEM micrograph of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 55%CO₂, 28%O₂, 12%H₂O, 5%N₂ at 800°C for 200 hours.

It should be noted that the interfaces between the silicate and carbonate layers and between the carbonate and needle-like structure layers are no longer clearly demarcated, as seen in Figure 10.27 (B). Silicate phases as well as needles are present in the mixed carbonate layer. It seems that the silicate layer originates from the reaction of silica with the mixed barium and strontium carbonate located on the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets. The perovskite matrix material between the needles also seems to react with CO₂, thus increasing the thickness of the $(Ba_xSr_{1-x})CO_3$ layer within the needle-like structure layer. Moreover, it appears that a decomposition of the needles, which offer a high surface area, occurs leading to the formation of cobalt oxide and mixed barium and strontium carbonate. This would explain the high concentration of cobalt oxide inclusions and the low concentration of needles under the cobalt oxide layer.



Figure 10.29. SEM micrograph and elemental mapping of the cross section of a Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} pellet annealed in 55%CO₂, 28%O₂, 12%H₂O, 5%N₂ at 800°C for 200 hours.

An elemental mapping of the cross section of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed in 55 mol% CO₂, 28 mol% O₂, 12 mol% H₂O and 5 mol% N₂ at 800°C for 200 hours was carried out with SEM in order to determine the distribution of the elements present, i.e. Ba, Sr, Co, Fe, C and O. The three distinct areas of the surface of the sample, i.e. the silicate, the carbonate and the needle-like structure layers, can be distinguished in the elemental mapping (Figure 10.29). The top layer of the specimen, corresponding to the silicate layer, exhibits high strontium, barium and oxygen contents. Under this layer, high contents of barium, strontium as well as carbon are found in the mixed carbonate layer. The intensity of barium is stronger in the mixed carbonate layer than in the silicate layer, whereas the intensity of strontium is stronger in the silicate layer. In the needle-like structure, two separate phases seem to be present i.e. the bright areas corresponding to cobalt oxide inclusions, the darker area the matrix material. The cobalt oxide layer formed under the mixed carbonate layer can also be seen clearly.

10.4.2 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂

In the "wet recycling" option of the oxyfuel process, the flue gas will be re-circulated onto the permeate side of the MIEC membrane without separating the water vapour present from the rest of the gas stream. The composition of this flue gas is believed to be close to the composition selected for this annealing experiment, i.e. 50 mol% CO_2 , 25 mol% O_2 , 20 mol% water vapour, 5 mol% N_2 .

After annealing $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ pellets in this atmosphere for 200 hours and 500 hours at 600°C, 700°C and 800°C, a silicate layer was present on the surface of each sample. Besides, the mixed barium and strontium carbonate as well as the needle-like structure layer were also observed in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples.

A homogenous silicate layer, the composition of which could not be determined precisely, was built on the surface of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets, as can be seen in Figure 10.30 and Figure 10.31. However, the EDS spectrum of each sample exhibits the peaks corresponding to the elements constituting these materials as well as silicon. It is difficult to identify the composition of the silicate layer as its thickness is very low i.e. below 1µm after annealing for 500 hours at 800°C, and the measurement might include peaks corresponding to the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ base material present under this layer. Moreover, cobalt and iron oxide inclusions were found in every $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ specimen after annealing at every temperature and dwelling time.



Figure 10.30. SEM micrographs and light microscopy pictures of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ at 800°C: (A), (B) and (C) for 500 hours and (D) for 200 hours.





Figure 10.31. SEM micrographs and light microscopy pictures of Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} pellets annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂: at 700°C (A) for 200 hours and (B) for 500 hours; (C) and (D) at 800°C for 500 hours.

The silicate layer covering the surface of the La₂NiO_{4+ δ} pellets was determined to be lanthanum silicate by XRD analysis (Figure 10.32) and identified as La₁₀(SiO₄)₆O₃. Figure 10.33 (B) shows a lanthanum silicate crystal growing out of the surface of the La₂NiO_{4+ δ} material. The EDS spectra of the rest of the silicate layer present on the surface exhibits peaks corresponding to lanthanum and nickel silicate. The presence of the nickel peak, which has a relatively low intensity, could originate from the La₂NiO_{4+ δ} material under this layer. Nickel oxide inclusions are found throughout the material as seen in Figure 10.33 (D).



Figure 10.32. Powder XRD spectra of the La₂NiO_{4+ δ} pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ at 800°C for 200 hours.



Figure 10.33. (A), (B) and (C) SEM micrographs and (D) light microscopy picture of a $La_2NiO_{4+\delta}$ pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ at 800°C for 500 hours.

The thickness of the silicate layers formed on the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ pellets annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ for 200 hours and 500 hours at 600°C, 700°C and 800°C could not be measured precisely by light microscopy observation. However it was estimated to be approximately 1µm. The thickness of the silicate layer formed on the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets was found to be considerably higher, as can be seen in Table 10.10 and Table 10.11.

Table 10.10. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$, the needle-like structure as well as the barium and strontium silicate layers as a function of annealing temperature of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 50% CO_2 , 25% O_2 , 20% H_2O , 5% N_2 for 200 hours.

Annealing	Thickness		
temperature (°C)	(Ba _x Sr _{1-x})CO ₃ layer (µm)	Needle-like structure layer (µm)	Silicate layer (µm)
700	4	15	2
800	18	61	2,4



Figure 10.34. Light microscopy picture and SEM micrograph of the cross section of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ for 200 hours at: (A) 600°C, (B) 700°C and (C) 800°C.

An EDS analysis of the layer covering the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets detected barium, strontium and silicon peaks. The composition of this layer could not be determined by XRD as the peaks corresponding to the silicate formed could not be identified. The mixed barium and strontium carbonate as well as the needle-like structure layers were found under this silicate layer. The thickness of these layers was found to increase with increasing temperature as can be seen in Table 10.10 and Figure 10.34. An increase in annealing temperature also induced an increase in needle thickness. The carbonate and needle-like structure layers of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ specimen annealed in 50 mol% CO_2 , 25 mol% O_2 , 20 mol% water vapour, 5 mol% N_2 for 200 hours were four times thicker after annealing at 800°C than at 700°C. A 25% increase was measured between the thickness of the silicate layer of the sample annealed at 700°C and the one annealed at 800°C.
Furthermore, the interfaces between the silicate and carbonate layers and between the carbonate and needle-like structure layers are not clearly defined, as seen in Figure 10.34 (C). Silicate phases as well as needles are present in the mixed carbonate layer. A reaction between CO_2 and the perovskite matrix material of the needle-like structure also occurs, thus increasing the thickness of the $(Ba_xSr_{1-x})CO_3$ layer within the needle-like structure layer. Besides, cobalt oxide inclusions can be observed in the needle-like structure in all samples. A cobalt oxide layer was formed at the interface between the needle-like structure and the mixed carbonate layer in the sample annealed at 800°C (Figure 10.34 (C)).







Figure 10.35. SEM micrograph and light microscopy picture of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ for 500 hours at: (A) 600°C, (B) 700°C and (C) 800°C.

As seen in Table 10.11 and Figure 10.35, the thicknesses of the mixed barium and strontium carbonate layer, the needle-like structure layer as well as the silicate layer of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ for 500 hours were found to increase with increasing temperature. A 55% increase of the mixed carbonate layer was measured between the sample annealed at 700°C and the one annealed at 800°C. The needle-like structure layer of the sample annealed at 800°C was more than five times thicker than the one annealed at 700°C. Likewise, the silicate layer was four times thicker. Although cobalt oxide inclusions were observed throughout all the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples, the cobalt oxide layer present in the previous samples was no longer observed after annealing at 800°C for 500 hours.

Table 10.11. Maximum thickness of the $(Ba_xSr_{1-x})CO_3$, the needle-like structure as well as the barium and strontium silicate layers as a function of annealing temperature of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂at 800°C for 500 hours.

Annealing	Thickness		
temperature (°C)	(Ba _x Sr _{1-x})CO ₃ Needle-like structureSiliclayer (μm)layer (μm)		Silicate layer (µm)
700	14	16	2,5
800	21	90	10

Additionally, an increase in annealing time caused an increase in the thicknesses of the mixed barium and strontium carbonate layer, the needle-like structure layer as well as the silicate layer. In the case of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ at 700°C for 500 hours, the carbonate layer was more than four times thicker than that of the sample annealed for 200 hours (Table 10.10 and Table 10.11). The thickness of the needle-like structure layer was almost constant as the increase was of less than 1%. The silicate layer showed a 25% increase. As for the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed at 800°C, a 15% and a 50% increase of the mixed carbonate layer and needle-like structure layer respectively were measured between the samples annealed for 200 hours and those annealed for 500 hours. Likewise, the silicate layer was four times thicker after annealing for 500 hours than after annealing for 200 hours.



Figure 10.36. SEM micrograph of the cross section of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ at 800°C for 500 hours.

The top layer found on the surface of all $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples was determined to be composed of barium and strontium silicate by EDS analysis. As seen in Figure 10.36, the silicate layer is composed of two different phases. In order to determine the composition of these two phases precisely, EDS point analysis measurements of the barium and strontium silicate layer were carried out. The chemical composition of the mixed silicate layer was determined to be $Ba_{0,63}Sr_{0,37}SiO_4$ and $Ba_{0,46}Sr_{0,54}SiO_4$ for the bright white phase (phase 1) and the light grey phase (phase 2) respectively. The silicate layer was formed on top of the (Ba_xSr_{1-x})CO₃ layer.

Element	Phase 1	Phase 2
Ba	18,20	13,70
Sr	10,80	16,20
Si	13,70	14,30
0	56,90	55,70

Table 10.12. Chemical composition (in atomic%) of the two barium and strontium silicate phases.

After the formation of the carbonate layer started on the surface of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets, a reaction with silica (SiO₂) occurred, and a light grey silicate phase with the composition

 $Ba_{0,46}Sr_{0,54}SiO_4$ which is very close to the barium and strontium ratios of $Ba_{0,43}Sr_{0,57}CO_3$ as well as a bright white phase which has a higher barium content and a lower strontium content, were formed.

The SEM micrographs of the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ at 700°C and 800°C for 500 hours (Figure 10.37) show that the formation of the silicate layer occurs by the growth of nodules out of the surface of the specimen. The individual silicate crystals agglomerated into these nodules, the diameters and heights of which are seen to increase with increasing temperature.



Figure 10.37. SEM micrographs of the surface of a Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} pellet annealed in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ for 500 hours: (A) at 700°C and (B) at 800°C.

After annealing in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ at 700°C and 800°C for 200 hours as well as 500 hours, the barium and strontium silicate layer was observed to spall off the surface of the pellets, as observed in Figure 10.37 and Figure 10.38. Figure 10.38 shows two areas: Area 1 and Area 2 present on the surface of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed at 800°C for 500 hours, correspond to the mixed carbonate and silicate layer respectively. The silicate layer presents large cracks and spalled off a large area of the surface of the sample which reveals the carbonate layer

formed beneath the external silicate layer. In Figure 10.37 (B) of the surface of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed at 800°C for 500 hours, the silicate layer is detached from the mixed carbonate layer.



Figure 10.38. SEM micrograph of the surface of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet showing the spallation of the external silicate layer after annealing in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ at 800°C for 500 hours.

 $10.4.3 \qquad 25 \ mol\% \ O_2, \ 20 \ mol\% \ H_2O, \ 55 \ mol\% \ N_2$

In order to check whether water alone has an effect on the degradation of the materials selected, a series of 200-hour annealing experiments was carried out at 600°C, 700°C and 800°C in an atmosphere composed of 25 mol% O_2 , 20 mol% H_2O , 55 mol% N_2 . Although all the samples developed a silicate layer on their surface (Figure 10.39), no other degradation was observed. XRD analysis could not determine the composition of the barium and strontium silicate present on the surface of the BSCF50 samples or that of the silicate layer formed on the surface of the LSCF58 and PSCF58 samples.



Figure 10.39. SEM micrographs of the cross fracture of: (A) $La_2NiO_{4+\delta}$, (B) $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, (C) $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and (D) $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets annealed in 25% O_2 , 20% H_2O , 55% N_2 at 800°C for 200 hours.

10.5 Volatilisation of chromium species

10.5.1 Theory

Chromium is one of the main elements in steels and alloys used in high temperature applications such as construction materials in coal-fired power plants. When exposed to high temperatures in oxygencontaining atmospheres, a stable protective chromia (Cr_2O_3) scale, which increases the corrosion resistance of these chromium steel alloys, is built on the surface of the material. The volatilisation of chromium species becomes a significant issue when this chromia layer is exposed to high temperatures as well as atmospheres with a high oxygen partial pressure. This effect is even more pronounced in water vapour-containing atmospheres. At high Po_2 , the main volatile chromium specie formed from Cr_2O_3 at high oxygen partial pressure is $CrO_3(g)$. This process is linked to the oxygen partial pressure present, as seen in Equation 10.3 below [139].

$$\frac{1}{2}Cr_2O_{3(e)} + \frac{3}{4}O_{2(e)} \leftrightarrow CrO_{3(e)}$$
 (Equation 10.3)

The partial pressure of CrO_3 is directly related to the partial pressure of oxygen. The evaporation process of chromium species will be increased in oxygen-rich atmospheres. Thus, the evaporation rate of chromia will be higher on the feed-side of the membrane, which is the side with a high vapour pressure of oxygen.

Moreover, the presence of water vapour accelerates the degradation of chromia forming alloys. The evaporation rate of these volatile chromium species was proven to increase in water vapour-containing atmospheres [142]. This is due to the formation of oxy-hydroxydes e.g. CrO₂(OH)₂ in the presence of water vapour, as described by Equation 10.4 [143].

$$1/2 Cr_2 O_{3(s)} + 3/4 O_{2(g)} + H_2 O_{(g)} \leftrightarrow Cr O_2 (OH)_{2(g)}$$
 (Equation 10.4)

A long term annealing experiment was carried out in which the pellets of $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ were placed next to a Cr_2O_3 disk and annealed in air for 1000 hours in order to check whether an interaction would occur between the construction materials of a coal-fired power plant and the oxygen permeation membrane materials selected.

10.5.2 Results

During annealing, a chromium-containing layer was formed on the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ (Figure 10.42), $La_2NiO_{4+\delta}$ (Figure 10.46), $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ (Figure 10.44) and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ (Figure 10.40) pellets. EDS and XRD analysis enabled the chemical composition of this layer to be determined for each sample annealed. EDS point analysis measurements of the surface of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ sample detected barium chromium oxide phases, and which were found to be barium chromate (BaCrO₄) by XRD analysis (Figure 10.45). For the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ specimen, mainly strontium chromium oxide was detected by EDS. The reflexions of strontium chromate (SrCrO₄) and of the cobalt chromite (CoCr₂O₄) spinel were found in the XRD spectrum of the surface of the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellet (Figure 10.41). In the

 $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ specimen, EDS analysis also detected primarily strontium chromium oxide. The XRD spectrum of the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellet exhibited the reflexions of strontium chromate (SrCrO₄) and iron cobalt chromite (FeCoCrO₄) spinel (Figure 10.43). EDS point analysis measurements of the surface $La_2NiO_{4+\delta}$ sample detected lanthanum as well as nickel chromium oxide, which was determined to be lanthanum chromium oxide (LaCrO₃) and the nickel chromite (NiCr₂O₄) spinel by XRD analysis (Figure 10.47).



Figure 10.40. SEM micrographs of a Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} pellet annealed in air at 800°C for 1000h next to a Cr₂O₃ pressed pellet: (A) and (B) surface, (C) cross fracture and (D) light microscopy picture of the cross section.



Figure 10.41. Powder XRD spectra of the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellet annealed in air at 800°C next to a Cr_2O_3 disk in air for 1000 hours.



Figure 10.42. SEM micrographs of a $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellet annealed in air at 800°C for 1000h next to a Cr_2O_3 pressed pellet: (A) surface, (B) cross fracture and (C) light microscopy picture of the cross section.



Figure 10.43. Powder XRD spectra of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3.\delta}$ pellet annealed in air at 800°C next to a Cr_2O_3 disk in air for 1000 hours.

After annealing in air at 800°C for 1000 hours next to a Cr_2O_3 pressed pellet, the entire surface of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets was contaminated with chromium-containing oxides (Figure 10.420 and Figure 10.42). However, after 1000 hours, a continuous layer was not formed. Chromium oxide particles, which nucleate and grow out of the surface of these pellets, were observed.

A continuous barium chromate layer was formed over the entire surface of the BSCF50 pellet, after annealing in air at 800°C for 1000 hours next to a Cr_2O_3 pressed pellet (Figure 10.44). The chromium oxide particles are observed to nucleate and grow out of the surface of the specimen. There seems to be an increase in the thickness of the barium chromate layer on the grain boundaries, as can be seen in Figure 10.44 (C). Moreover, a needle-like structure is formed in the bulk of the BSCF50 pellet as seen in Figure 10.44 (D). An EDS investigation of the needles found them to be composed of a (Ba, Sr, Co and Fe)-containing oxide with no chromium incorporated and with a barium content lower than that of the original $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material. A depletion of the concentration of barium in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material seems to have caused these needles to build up at its interface with the barium chromate layer. Thermo-chemical stability investigation



FZLIEF/2008 EHT=16.00 kV Signal A= SE2 WD= 10 mm $2\mu m$ FZLIEF/2008 EHT=15.00 kV Signal A= BSD WD= 10 mm $10\mu m$ Figure 10.44. SEM micrographs of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air at 800°C for 1000h next to a Cr_2O_3 pressed pellet: (A) and (B) surface, (C) cross fracture and (D) cross section.



Figure 10.45. Powder XRD spectra of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air at 800°C next to a Cr_2O_3 disk in air for 1000 hours.



Figure 10.46. SEM micrographs of a $La_2NiO_{4+\delta}$ pellet annealed in air at 800°C for 1000h next to a Cr_2O_3 pressed pellet: (A) and (B) surface, (C) cross fracture and (D) cross section.

After annealing in air at 800°C for 1000 hours next to a Cr_2O_3 pressed pellet, a continuous layer of chromium-containing oxides was formed over the entire surface of the La₂NiO_{4+ δ} pellet (Figure 10.46). The analysed lanthanum chromium oxide and nickel chromite appear to grow into the specimen as seen in Figure 10.46 (C) and (D).

The maximum thickness of the chromium oxide layer on the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets can be found in Table 10.13 below. The BSCF50 specimen exhibits the thickest chromium oxide layer at 3µm. The thicknesses of the other layers were too thin to be measured precisely. They were, however, less than 1µm thick.



Figure 10.47. Powder XRD spectra of the $La_2NiO_{4+\delta}$ pellet annealed in air at 800°C next to a Cr_2O_3 disk in air for 1000 hours.

Table 10.13. Thickness of the chromium oxide layer on the surface of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $La_2NiO_{4+\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ pellets after annealing next to a Cr_2O_3 disk in air at 800°C for 1000 hours.

Sample	Thickness (µm)
$Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3\text{-}\delta}$	3
$La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$	<1
$Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$	<1
$La_2NiO_{4+\delta}$	<1

10.5.3 Discussion

The fact that all the materials investigated reacted with chromia demonstrates the potential problems of vaporisation and transport of chromium species from the chromia scale of the components of a coalfired power plant to the membrane. The reduction of gaseous chromium oxide and oxy-hydroxide species to solid Cr_2O_3 phase would be in competition with the reduction of O_2 on the surface of the MIEC membranes. Thus, the chromium-containing oxide layer formed on the surface of the membrane material during operation would constitute a diffusion barrier preventing oxygen permeation through the high purity oxygen separation membrane.

The degradation of the permeation performances of a membrane by chromium oxide deposition and poisoning is a serious issue for its use in coal-fired power plants. In this work the stability of materials selected in relation to chromium was investigated in a "dry" atmosphere. However, it would be interesting, in a further study, to investigate the stability of these materials when in contact with volatile oxy-hydroxides, in water vapour-containing atmospheres.

10.6 Co enrichment at the grain boundaries

After the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets were subjected to the thermo-chemical stability tests, a bright coloured secondary phase seemed to build on the grain boundaries of all samples annealed in every atmosphere, at every temperature and for every dwelling time. This phase, which was barely visible after annealing in air for 200 hours (Figure 10.48 (A)), was found to coarsen with increasing annealing time and temperature. Besides, this secondary phase seems to grow from the grain boundary inside the grain, as can be seen in Figure 10.48 (B) and Figure 10.49. Cobalt oxide inclusions are also observed mainly along the ground boundaries although they can also be found in the grains. Moreover, secondary phases are found around these cobalt oxide inclusions, as can been in Figure 10.49 and Figure 10.50.



Figure 10.48. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed: (A) in air at 600°C for 200 hours and (B) in 43%O₂, 43%CO₂ and 14%N₂ at 800°C for 200 hours.

Table 10.14 gives the chemical compositions, determined by EDS point analysis measurements, of the phases present on the grain boundary and of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ material of a sample annealed in 43%O₂, 43%CO₂ and 14%N₂ at 800°C for 200 hours. An increase in cobalt concentration of more than 12% and a decrease in iron content of more than 80% between the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ matrix material and the phase on the grain boundary was measured. Similar barium and strontium contents were found. As for the phase growing from the grain boundary into the grain, iron and cobalt contents similar to the phase on the grain boundary were found. A slight increase in barium and a decrease in strontium concentrations were, however, observed.

Table 10.14. Chemical composition (in atomic%) determined by EDS analysis of the phases present in the bulk of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 43% O_2 , 43% CO_2 and 14% N_2 at 800°C for 200

hours.				
	Phase			
Element	On the grain boundary	BSCF50 matrix		
Ba	12.9	13.7	12.0	
Sr	11.7	10.6	11.5	
Со	19.0	19.3	16.9	
Fe	0.8	0.7	4.4	
0	55.7	55.7	55.2	



Figure 10.49. SEM micrographs of the cross section of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed: (A) in 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂ at 800°C for 500 hours and (B) in air at 800°C for 1000 hours next to a Cr_2O_3 disk..

Large cobalt oxide inclusions as well as a considerable amount of secondary phases growing from the grain boundaries are observed in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂ at 800°C for 500 hours (Figure 10.49 (A)) and in air at 800°C for 1000 hours next to a Cr₂O₃ disk (Figure 10.49 (B)). The EDS point analysis spectrum of the phase present on the grain boundaries of the sample annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂ at 800°C for 500 nous? (Co₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂ at 800°C for 500 nous analysis spectrum of the phase present on the grain boundaries of the sample annealed in 50 mol% CO₂, 25 mol% O₂, 20 mol% H₂O, 5 mol% N₂ at 800°C for 500 hours shows that this phase has a lower concentration of strontium and iron as well as a higher concentration of cobalt than the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material.

As seen in Table 10.14 and Table 10.15, the phase growing on the grain boundary of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in air at 800°C for 1000 hours next to a Cr_2O_3 disk presents the same cobalt concentration as the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 43%O₂, 43%CO₂ and 14%N₂ at 800°C for 200 hours as well as a very similar iron content. It seems that the growth of this

phase is not influenced by the annealing atmosphere and that its development seems to be temperature and time dependant.

	Phase		
Element	Growing from the boundary	BSCF50 matrix	
Ba	11.6	11.5	
Sr	12.6	11.7	
Со	19.0	16.9	
Fe	0.6	4.4	
0	56.2	55.5	

Table 10.15. Chemical compositions (in atomic%) determined by EDS analysis of the phases present in the bulk of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellet annealed in air at 800°C for 1000 hours next to a



*Figure 10.50. SEM micrograph of the surface of a Ba*_{0,5}*Sr*_{0,5}*Co*_{0,8}*Fe*_{0,2}*O*_{3-δ} *pellet annealed in 50% CO*₂, 25% *O*₂, 20% *H*₂*O*, 5% *N*₂ *at 800°C for 200 hours.*

After annealing in 50 mol% CO₂, 25 mol% O₂, 20 mol% water vapour, 5 mol% N₂ at 800°C for 200 hours, the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} sample exhibited bright coloured secondary phases on the grain boundaries (Table 10.16 phase 1), around the cobalt oxide inclusions (Table 10.16 phase 5) as well as inclusions inside the grain (Table 10.16 phase 2). A secondary phase (Table 10.16 phase 4) slightly darker than the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} material was also found near some of the bright coloured phases. The bright coloured phases seem to be a perovskite with a higher cobalt content and a lower iron content than the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} material (Table 10.16 phase 3). The barium and strontium concentrations vary within the range of the measurement error. The darker phase has a cobalt content similar to the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} material. However a 30% and a 23% increase of iron and strontium concentrations, respectively, were observed. A 20% decrease of barium content was also measured.

Table 10.16. Chemical compositions (in atomic%) determined by EDS analysis of the phases present in
the bulk of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 50% CO ₂ , 25% O ₂ , 20% water vapour, 5% N ₂ at
800°C for 200 hours.

Floment	Phase				
Liement	1	2	3	4	5
Ba	11.9	12.1	11.9	9.3	12.1
Sr	11.9	12.3	11.9	14.7	12.5
Со	18.9	19.0	16.1	16.0	19.6
Fe	1.3	1.5	4.4	5.7	1.0
0	56.1	55.2	55.7	54.3	54.8

The fact that the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ material exhibits a chemical demixing, which seems to be temperature and time dependent, is of great concern for its selection as a high purity oxygen separation membrane. Indeed, if this demixing occurs at such a fast rate during the annealing experiments, it will be even faster when applying a gradient of oxygen partial pressure across a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ membrane during operation.

When oxygen-ion-conducting perovskite-type oxides are subjected to oxygen chemical potential gradients, oxygen anions can migrate through the lattice. A simultaneous flow of electrons as well as mobile cations is established in the opposite direction to counterbalance the oxygen ion flow. However, cation diffusion in perovskite materials is many orders of magnitude lower than oxygen diffusion. A demixing of the material will occur if the cations have different diffusion coefficients [144].

After about 700 hours at 1150 C in an O_2/N_2 gradient [109], $La_{0.5}Sr_{0.5}Fe_{1-x}Co_xO_{3-\delta}$ (x=0, 0.5 and 1) membranes were found to exhibit a kinetic demixing near the surfaces in all samples. Moreover, the mobility of Co/Fe and La/Sr were found to be different, with Fe and Co being the most mobile cations.

10.7 Phase analysis

Secondary non-ion-conducting phases present in the bulk material can considerably decrease the oxygen permeation flux of high purity oxygen separation membranes since they form obstacles for oxygen ions migrating through the membrane. The formation of these secondary phases is, therefore, a serious concern for the selection of membrane materials. EDS and XRD analysis determined that secondary nickel oxide (NiO) phases were found in the La₂NiO_{4+δ} samples (Figure 10.57) after the sintering step as well as after each annealing experiment. Cobalt oxide inclusions were formed in the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} pellets (Figure 10.52), and a mixture of cobalt and iron oxide inclusions in the La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} as well as the Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} pellets (Figure 10.55).

These oxide inclusions were formed during the sintering step of the preparation of the pellets because of the high temperatures applied. The observation of light microscopy pictures of the cross section of the annealed pellets seems to indicate an increase of the amount and the size of these inclusions with increasing annealing time. A phase analysis of an area of about $5.10^4 \ \mu m^2$ in each of the samples selected was carried out in order to determine the percentage of secondary phases and to corroborate this apparent increase. Eight light microscopy pictures of the cross section of these specimens were taken next to each other randomly and studied with the software "analySIS pro" [145] from Olympus Soft Imaging Solutions GmbH (Germany). In order to observe a significant change in the concentration of the secondary oxide phases when comparing the sintered and the annealed pellets, the samples annealed for the longest times were selected for this phase analysis. The selected annealing conditions for the La₂NiO_{4+δ}, Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} samples are listed in Table 10.17 below.

Atmosphere (in mol9/)	Annealing conditions		
Atmosphere (m mor %)	Temperatures (°C)	Dwelling times (hours)	
Air	800	500	
25% O ₂ , 8% N ₂ , 67% CO ₂	800	500	
25% O ₂ , 50% CO ₂ , 5% N ₂ , 20% H ₂ O	800	500	
Air next to a Cr ₂ O ₃ pellet	800	1000	

Table 10.17. Annealing conditions for the samples selected for the phase analysis

The annealing atmosphere as well as the temperature might also have an influence on the growth of these secondary oxide phases, however, due to a lack of time only a selection of samples was chosen for the analysis of the secondary phases present in the samples after sintering and annealing.

10.7.1 Results

For the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ samples, the oxide inclusions were composed of two different phases, one in the centre of the other. When observed with light microscopy, the centre phase is seen as a dark grey phase around which a light grey phase is found. With SEM the phases appear to have two shades of grey, one being a dark grey phase at the centre of which a lighter grey phase is present.

BSCF50

For the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples, EDS analysis allowed for the determination of the chemical composition of both secondary oxide phases, as seen in Table 10.18. Phase 1, in the centre, had the chemical composition $Co_{0,98}O_{1,02}$ and phase 2 the composition $Co_{3,1}O_{3,9}$. The cobalt oxide phases formed in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples were therefore identified as being CoO and Co_3O_4 . Co_3O_4 is the phase at the centre of which CoO is found. In the SEM micrographs, the phase with the highest oxidation state is the darkest. In the cobalt oxide Co_3O_4 , cobalt has the oxidation state +2 and +3. And in CoO, cobalt adopts the lower oxidation state of +2. Thus the Co_3O_4 phase appears darker than the CoO phase.

Table 10.18. Chemical composition (in atomic%) determined by EDS analysis of the two cobalt oxide phases present in the bulk of a $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3.\delta}$ pellet annealed in 55% CO₂, 28% O₂, 12% H₂O, 5% N₂ at 600°C for 200 hours.

Element	Phase 1	Phase 2
Со	49,00	44,00
0	50,80	55,30

The XRD analysis of the ground pellets did not show CoO reflexions for any of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ annealed samples. However, Co_3O_4 was detected in all the samples except for the sintered one. Figure 10.51 shows the powder XRD spectra of a $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ at 800°C for 200 hours presenting the reflexions of Co_3O_4 . The phase analysis of selected $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples showed that cobalt oxide amounts for less than 1% of the sample (Table 10.19).



Figure 10.51, Powder XRD diagram of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellet annealed in 67% CO₂, 25% O_2 and 8% N_2 at 800°C for 200 hours.



Thermo-chemical stability investigation



*Figure 10.52. Light microscopy picture of Ba*_{0,5}*Sr*_{0,5}*Co*_{0,8}*Fe*_{0,2}*O*_{3-δ} *samples: (A) as sintered; (B) to (E) annealed: (B) in 25% O*₂, 50% *CO*₂, 5% *N*₂, 20% *H*₂*O*, (*C) in 25% O*₂, 8% *N*₂, 67% *CO*₂, (*D) in air at 800°C for 500 hours and (E) in air for 1000 hours.*

After annealing for 200 hours and 500 hours at 600°C as well as for 200 hours at 700°C in every atmosphere, both phases were present in the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-6}$ pellets. However, after annealing the pellets for 500 hours at 700°C and 800°C as well as at 800°C for 200 hours, only the Co₃O₄ phase was observed. The interface between the CoO centre phase and the Co₃O₄ phase is very irregular. It seems that the less stable CoO transforms gradually into Co₃O₄, more stable in this temperature range and partial pressure of oxygen [146].

An obvious increase in size of the cobalt oxide phases is observed between the sintered sample and the samples annealed in 50%CO₂ and for 1000 hours (Figure 10.52). An increase in the number of these phases seems to occur between the sintered sample and the annealed samples. Moreover, the determination of the concentration of the cobalt oxide inclusions by phase analysis showed an increased concentration in the annealed samples compared to the sintered sample.

Atmosphere	Amount of secondary phases (%)
Sintered	0,15
Air	0,55
67% CO ₂ , 25% O ₂ , 8% N ₂	0,4
50% CO ₂ , 25% O ₂ , 5% N ₂ , 20% H ₂ O	0,3
Air next to a Cr ₂ O ₃ pellet	0,5

 Table 10.19. Amount of secondary phases measured in a specific area of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$

 samples after annealing in different atmospheres.

LSCF58 and PSCF58

EDS point analysis of the cross section of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ sintered pellets determined the chemical composition of the secondary oxide phases present. Both phases have a similar cobalt and iron content, as seen in Table 10.20. The cobalt oxide phases formed in these samples were identified as CoO and Co₃O₄, with iron dissolved in each of these phases. $Co_{1-x}Fe_xO$ is found in the centre of the $Co_{3-x}Fe_xO_4$ phase.

Table 10.20. Chemical composition (in atomic%) determined by EDS analysis of the cobalt and iron oxide phase present in the bulk of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets sintered at 1200°C for 5 hours.

Element	LSCF58	PSCF58
Со	35,40	39,7
Fe	7,2	5,2
0	55,7	54,5

Here also, the XRD analysis of the ground pellets revealed the same results as for the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples above. No CoO reflexions for any of the annealed samples were present and Co_3O_4 was only detected in some of the annealed samples. When the Co_3O_4 reflexions were present they were within the experimental error range of the measurement of 5%. Cobalt and iron oxide phases therefore amount for less than 1% of the sample, as seen in Figure 10.53. This is confirmed by the phase analysis of selected $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ samples (Table 10.21 and Table 10.22).



Figure 10.53. Powder XRD diagram of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellet annealed in 67 mol% CO₂, 25 mol% O₂ and 8 mol% N₂ at 700°C for 500 hours.

After annealing for 200 hours at 600°C in every atmosphere, both phases were present. However, after annealing in air for 500 hours at all temperatures as well as at 800°C and 700°C for 200 hours, only the light grey phase $Co_{1-x}Fe_xO$ was observed in light microscopy pictures. In the same way, as described

for the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ specimens, the $Co_{1-x}Fe_xO$ phase gradually transformed into the more stable $Co_{3-x}Fe_xO_4$ phase at high temperatures.

$\underline{La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}}$

By observing the light microscopy pictures of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ samples (Figure 10.54), it seems that the size of the secondary oxide phases found in the annealed samples is greater than the size of the ones in the sintered sample. As seen in Table 10.21, an increase in the concentration of secondary phases between the sintered sample and the samples annealed was measured with the software "analySIS pro".





Figure 10.54. Light microscopy picture of La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-δ} samples: (A) as sintered;(B) to (E) annealed: (B) in 25% O₂, 50% CO₂, 5% N₂, 20% H₂O, (C) in 25% O₂, 8% N₂, 67% CO₂, (D) in air at 800°C for 500 hours and (E) in air for 1000 hours.

 Table 10.21. Amount of secondary phases measured in a specific area of the $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$

 samples after annealing in different atmospheres.

Atmosphere	Amount of secondary phases (%)
Sintered	0,3
Air	0,55
67% CO ₂ , 25% O ₂ , 8% N ₂	0,6
50% CO ₂ , 25% O ₂ , 5% N ₂ , 20% H ₂ O	0,65
Air next to a Cr ₂ O ₃ pellet	0,45

$\underline{Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}}$

Here also it seems that the secondary phases found in the samples annealed are greater in size than the ones found in the sintered sample (Figure 10.55). Moreover, Table 10.22 shows an increase in secondary phase concentration between the sintered sample and the annealed samples.



Thermo-chemical stability investigation



Figure 10.55. Light microscopy picture of $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ samples: (A) as sintered; (B) to (E) annealed: (B) in 25% O_2 , 50% CO_2 , 5% N_2 , 20% H_2O , (C) in 25% O_2 , 8% N_2 , 67% CO_2 , (D) in air at 800°C for 500 hours and (E) in air for 1000 hours.

Atmosphere	Amount of secondary phases (%)
Sintered	0,35
Air	0,4
67% CO ₂ , 25% O ₂ , 8% N ₂	0,8
50% CO ₂ , 25% O ₂ , 5% N ₂ , 20% H ₂ O	0,45
Air next to a Cr ₂ O ₃ pellet	0,95

Table 10.22. Amount of secondary phases measured in a specific area of the $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ samples after annealing in different atmospheres.

$La_2NiO_{4+\delta}$

When the nickel oxide reflexions were present they were within the experimental error range of the measurement of 5%. They amount, therefore, for less than 1% of the sample, as seen in Figure 10.57. This is confirmed by the phase analysis study of selected $La_2NiO_{4+\delta}$ samples (Table 10.23).



Figure 10.56. Powder XRD diagram of the $La_2NiO_{4+\delta}$ *pellet annealed in air at* 600°*C for 200 hours.*



Thermo-chemical stability investigation



*Figure 10.57. Light microscopy picture of La*₂*NiO*_{4+δ} *samples: (A) as sintered; (B) to (E) annealed:* (B) in 25% O₂, 50% CO₂, 5% N₂, 20% H₂O, (C) in 25% O₂, 8% N₂, 67% CO₂, (D) in air at 800°C for 500 hours and (E) in air for 1000 hours.

Observing the cross sections of the different samples (Figure 10.57), it seems that the sintered sample exhibits a greater amount of smaller secondary phases than the annealed samples. The determination of the concentration of secondary phases showed that an increase of nickel oxide phases between the sintered sample and the samples annealed occurred, as seen in Table 10.23.

Atmosphere	Amount of secondary phases (%)
Sintered	0,2
Air	0,4
67% CO ₂ , 25% O ₂ , 8% N ₂	0,25
50% CO ₂ , 25% O ₂ , 5% N ₂ , 20% H ₂ O	0,4
Air next to a Cr ₂ O ₃ pellet	0,3

Table 10.23. Amount of secondary phases measured in a specific area of the $La_2NiO_{4+\delta}$, samples after annealing in different atmospheres.

10.7.2 FactSageTM thermo-chemical calculations

The FactSageTM thermo-chemical software was used to predict the formation of oxide phases in the materials selected in this work. As no data concerning the La₂NiO_{4+ δ}, Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} materials was available in the FactSageTM thermodynamic databases, the individual components of these materials were used to predict the thermodynamic equilibrium in the system investigated.

The activity of the individual chemical components of $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ in air was calculated between 600°C and 1200°C. Figure 10.58 shows the activities of CoO, Co₃O₄, Co and O₂ calculated as a function of temperature. In the temperature range considered, the cobalt oxides were found to be the most stable compounds. Moreover, CoO appeared to be more stable than Co₃O₄ in air between 890°C and 1200°C. Whereas the spinel Co₃O₄ was found to be more stable in air under 890°C.

The temperature used to sinter the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets was 1100°C, at which temperature CoO is the most stable. It can be assumed that the CoO phase was formed during sintering and mostly during the 3-hour dwelling step at the temperature of 1100°C. Due to the slow cooling rate of 3K/min used in the sintering temperature programme, a phase transformation, which started at approximately 880°C, occurred during cooling, thus leading to the formation of Co_3O_4 around the CoO phases. This explains the presence of both cobalt oxide phases in the sintered $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ pellets (Figure 10.52).



Figure 10.58. Temperature dependence of the activities of cobalt and cobalt oxide in air

Both phases were found in the pellets annealed for 200 hours and 500 hours at 600°C as well as for 200 hours at 700°C in every atmosphere. And after annealing for 500 hours at 700°C and 800°C as well as at 800°C for 200 hours, the CoO is no longer observed and only the spinel, which is the most stable compound, remained. However, the plots of the activities of CoO and Co_3O_4 in the different annealing atmospheres showed that only the spinel was found to be stable in every condition. Figure 10.59 is one example of these plots showing the activity of the CoO and the Co_3O_4 spinel for the annealing condition 67% CO₂, 25% O₂, 8% N₂ at 600°C. Therefore, the phase transformation kinetics can be assumed to be relatively slow, leading to the complete disappearance of CoO only after several hundred hours for the samples annealed at 600°C and 700°C.



Figure 10.59. Temperature dependence of the activities of cobalt and cobalt oxide in 67% CO₂, 25% O_2 , 8% N_2 at 600°C.

No data about the oxide phases formed in the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ pellets was available in the FactSageTM thermodynamic databases. However, the phase formation process of $Co_{1-x}Fe_xO$ and of $Co_{3-x}Fe_xO_4$ is considered to be similar to that of the cobalt oxide phases formed in the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ pellets. The kinetics of the phase transformation seem, however, to be slightly faster as both phases were only present in the sintered samples and in the samples annealed at 600°C for 200 hours in all atmospheres, all other samples containing only the more stable $Co_{3-x}Fe_xO_4$ phase.

The activities of the individual chemical components of $La_2NiO_{4+\delta}$ in air were calculated between 600°C and 1500°C using FactSageTM. The plots of the activities of NiO, Ni and O₂ calculated as a function of temperature are shown in Figure 10.60. In the temperature range considered, nickel oxide was found to be the most stable compound. The predicted thermodynamic results support the experimental results in that NiO inclusions were observed in all $La_2NiO_{4+\delta}$ samples after sintering and annealing in all conditions.



Figure 10.60. Temperature dependence of the activities of nickel and nickel oxide in air

10.7.3 Discussion

Although no trend indicated that the annealing atmosphere could influence the growth of these secondary oxide phases, the concentration of these phases was found to increase during annealing. The amount of oxide inclusions was always lower in the sample sintered than in the samples annealed, which indicates that a progressive chemical demixing of the membrane material occurred during the annealing experiments. The development of these secondary non-ion-conducting phases in the bulk material can considerably decrease the oxygen permeation flux of high purity oxygen separation membranes. Moreover, during operation, the high oxygen partial pressure gradient present across the membrane could aggravate this secondary phase formation phenomenon, which would be a serious issue. It would, therefore, be interesting to study the phase formation process in membrane disks after long term permeation experiments.

10.8 Conclusion

On the one hand, after annealing $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$, $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ in air, no reaction was observed on the surface of any of the samples, which demonstrates their stability in this atmosphere. Moreover, $La_2NiO_{4+\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ were found to be very stable in CO₂-containing atmospheres. No reaction occurred on the surface of these samples even at high CO₂-concentrations, high temperatures and long

annealing times. Although no degradation of the $La_2NiO_{4+\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ material was observed after annealing these pellets in CO₂- and H₂O-containing as well as H₂O-containing atmospheres, a silicon contamination of their surface from the quartz glass components of the annealing test set-up occurred. This contamination was also present on the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples annealed in CO₂- and H₂O-containing atmospheres. The fact that these MIEC materials react with silicon definitely rules out the possibility of using glass gaskets to seal the membranes in the oxygen separation device. The presence of silica in the coal grades is also a significant issue when considering the oxyfuel process option with flue gas recycling.

On the other hand, a reaction zone composed of a mixed carbonate layer and a needle-like structure layer was observed on the surface of all $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples at all annealing temperatures and dwelling times. When comparing the results of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples annealed in all CO₂-containing atmospheres, an increase in the thicknesses of both the mixed barium and strontium carbonate layer and the needle-like structure layer were found with increasing CO₂-concentration. As stated previously, the thicknesses of both these layers increased also with increasing annealing time and temperature. These results demonstrate the low stability of $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ to CO₂ since carbonates were formed on the surface of all specimens even after short exposure times of only 200 hours to atmospheres with a relatively low CO₂ concentration.



Figure 10.61. Thicknesses of: (A) the needle-like structure layer and (B) the mixed carbonate layer of Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-δ} pellets annealed at 800°C in 50% CO₂, 25% O₂, 20% H₂O, 5% N₂ (CO₂/H₂O) and in 67% CO₂, 25% O₂ and 8% N₂ (CO₂) for 200 hours and 500 hours.

Additionally, although water vapour alone did not affect the samples, when combined with CO_2 , it seems to exacerbate the formation of the carbonate and needle-like structure layers as their thicknesses are higher when annealing at 800°C in an atmosphere composed of 50 mol% CO_2 , 25 mol% O_2 , 20 mol% water vapour and 5 mol% N_2 for 200 hours than in an atmosphere composed of 67 mol% CO_2 , 25 mol% O_2 and 8 mol% N_2 for 500 hours, as seen in Figure 10.61. Even though the concentration of CO_2 decreased by about 25 percent, the thickness of the carbonate layer doubled

(Table 10.7, Table 10.8, Table 10.10 and Table 10.11). Likewise, the thickness of the needle-like structure layer increased by around 90%.

The $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples also presented a cobalt enrichment at the grain boundaries as well as different inclusions in the grains, one enriched in cobalt and another enriched in iron and strontium. The fact that a demixing of this material occurred after such short annealing times and without applying a gradient of oxygen partial pressure, which would be present during membrane operation, is a serious drawback of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ membrane material for the oxyfuel process of coal-fired power plants.

Such a significant degradation of the surface of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples when annealed in CO_{2^-} as well as CO_{2^-} and H_2O -containing atmospheres makes it a membrane material that would need to be used either with a protective layer or in a concept for the oxyfuel process without flue gas recycling over the permeate side of the membrane. Such a process is currently being developed at Forschungszentrum Jülich. The "OXYVAC-JÜL" [147] pressure driven process consists in creating a partial pressure gradient of oxygen between the permeate- and the sweep-side of the oxygen permeation membrane by applying a vacuum on the permeate side. However, $La_2NiO_{4+\delta}$, $La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ and $Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3-\delta}$ are oxygen permeation membrane materials perfectly compatible with the flue gas recycling concept of the oxyfuel process. The "dry recycling" and the "wet recycling" options could be applied to these materials which are stable in CO_2 - as well as CO_2 - and H_2O -containing atmospheres.

An important issue arises from the fact that all these potential high purity oxygen separation membrane materials could react with volatile chromium species from chromia forming alloys used as construction materials in coal-fired power plants. Therefore, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ would be incompatible for use in coal-fired power plants in the framework of the oxyfuel process, at least not without a protective layer. The development of secondary non-ion conducting oxide phases in the bulk of $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, $La_2NiO_{4+\delta}$ and $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ could also be a problem as they form obstacles for oxygen ions migrating through the membrane. However, the amount of these phases was always measured to be below 1% after annealing. It is important to study the development of these phases after long-term permeation experiments since the gradient of oxygen partial pressure, which is the driving force for oxygen migration through the membrane, could enhance the chemical demixing of the MIEC material.

11 Conclusion

In this work, selected MIEC materials with perovskite and perovskite-related structures, i.e. $La_2NiO_{4+\delta}$, $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ considered for use as high purity oxygen separation membranes in the framework of the oxyfuel process with flue gas recycling were investigated in respect to their thermo-chemical stability and oxygen permeation performances, which are both crucial selection factors.

Chapter 8 characterised these membrane materials using thermo-analytical techniques such as precision thermogravimetric analysis (TGA) and thermo mechanical analysis (TMA). The La₂NiO_{4+ δ} material was found to exhibit the lowest change in oxygen stoichiometry with the narrowest hysteresis as well as the lowest thermal expansion, which is an indication of the stability of this material. On the other hand, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3- δ} showed the highest change in oxygen stoichiometry as well as the highest thermal expansion. The TGA curves of La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} and Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3- δ} are very similar. However, the substitution of praseodymium for lanthanum induced a slight increase in loss of lattice oxygen from the perovskite structure.

In Chapter 9, an investigation of the permeation performances of La₂NiO_{4+ δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ}, Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} membranes was carried out. The highest oxygen permeation fluxes measured were for 1mm BSCF50 membranes over the whole temperature range. The fluxes for 1mm La₂NiO_{4+ δ}, PSCF58 and LSCF58 membranes were well below the values of the Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3- δ} membrane and were also of the same order of magnitude, La₂NiO_{4+ δ} being slightly higher in the temperature range of between 700°C and 850°C and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} membranes, with thicknesses ranging between 0.5mm and 1.5mm, seemed to be governed by surface exchange as well as bulk diffusion. However, a decrease in membrane thickness caused an increase in oxygen permeation flux for all membranes.

There appears to be a correlation between the loss of oxygen from the lattice, associated to the increase in oxygen vacancy concentration in the MIEC materials studied in this work and measured with TGA, and the increase in thermal expansion as well as the increase in oxygen permeation observed with increasing temperature.

Chapter 10 dealt with the investigation of the thermo-chemical stability of the membrane materials selected for this study after exposure to CO_2 , water vapour, O_2 and Cr_2O_3 . After exposure to air no

Conclusion

reaction was observed on the surface of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$, samples. However, a carbonate layer and a needle-like structure layer were formed on the surface of all BSCF50 pellets when exposed to CO₂- as well as in CO₂- and H₂O-containing atmospheres at all annealing temperatures and dwelling times. Water vapour, when combined with CO₂, seemed to exacerbate the formation of the carbonate and needle-like structure layers. All $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples also developed cobalt enrichment at the grain boundaries as well as secondary phase inclusions in the grains and on the grain boundaries. These effects were related to a chemical demixing of the material. The temperature and time-related cobalt enrichment at the grain boundaries could result in a considerable decrease in oxygen permeation fluxes as the grain boundaries would hinder the transport of oxygen ions through the material.

After exposure to air, CO₂- and water vapour-containing atmospheres, no degradation of the surface of the $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$, $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_2NiO_{4+\delta}$ samples was observed. After exposure to water vapour-containing atmospheres, however, a silicon contamination of their surface from the quartz glass components of the annealing test set-up occurred. This contamination was also present on the surface of the $Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-\delta}$ samples. The fact that these MIEC materials react with silicon is a significant issue when considering the oxyfuel process option with flue gas recycling as silica is a component of coal grades. Additionally, all the materials investigated were found to react with chromia, which demonstrates the potential problems of vaporisation and transport of chromium species from the chromia scale of the steel components of a coal-fired power plant to the membrane.

Secondary non-ion conducting phases were formed in the bulk of all materials during sintering and their concentration was found to increase during annealing. The development of these phases, related to a progressive demixing of the membrane material, could considerably decrease the oxygen permeation fluxes of high purity oxygen separation membranes as they form obstacles for oxygen ion transport. However, the amount of these phases was always measured to be below 1%. During operation, the high oxygen partial pressure gradient present across the membrane, which is the driving force for oxygen migration through the membrane, could aggravate the demixing of these MIEC materials. Indeed, a kinetic demixion of the $Pr_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ and $La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-\delta}$ membrane materials was observed after an approximately 100-hour operation. It would, therefore, be interesting to study the secondary phase formation process in membrane disks after long term permeation experiments.

In conclusion, the significant degradation of the $Ba_{0,5}Sr_{0,5}Co_{0,8}Fe_{0,2}O_{3-\delta}$ samples when exposed to atmospheres reproducing close to operation conditions together with its temperature and time-related chemical demixing demonstrates the poor thermo-chemical stability of this material. This rules out its use as a high purity oxygen separation membrane in the framework of the oxyfuel process.

La₂NiO_{4+ δ}, La_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ} and Pr_{0,58}Sr_{0,4}Co_{0,2}Fe_{0,8}O_{3- δ}, stable in close to operation conditions, are oxygen permeation membrane materials perfectly compatible with the flue gas recycling concept of the oxyfuel process. The "dry recycling" and the "wet recycling" options could be applied to these materials stable in CO₂- as well as CO₂- and H₂O-containing atmospheres. However, an important issue arises from the fact that these potential high purity oxygen separation membrane materials could react with volatile chromium and silicon species. The silicon- and chromium-containing oxide layers formed on the surface of the membrane material during operation would constitute a diffusion barrier preventing oxygen permeation through the membrane. The degradation of the permeation performances of a membrane by chromium and silicon oxide deposition is a serious issue for its use in coal-fired power plants. The use of a protective layer on the surface of these membranes might therefore be required in order for them to be used in coal-fired power plants in the framework of the oxyfuel process.

Moreover, much work still needs to be done in order to improve the oxygen permeation properties of these materials, which do not reach the minimum oxygen permeation flux of 10 ml min⁻¹ cm⁻² required for the selection of a material as a high purity oxygen separation membrane. Membrane surface modification and the development of thin film membrane technology are options currently being considered.
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Abstract

Gas separation membranes are considered to be an efficient technology for the future generation of zero CO_2 -emission power plants. This work studies the oxygen permeation performances and stability in near-operation conditions of mixed ionic-electronic conducting membranes for high purity oxygen separation in the framework of the Oxyfuel process.

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Anna Ellett studied Chemistry at the University Pierre and Marie Curie in Paris, France. The author joined the Institute for Energy Research (IEF-2) in Forschungszentrum Jülich in 2005, where she worked on the development of oxygen permeation membrane materials in the framework of the Oxyfuel process. This dissertation was successfully approved by the Technical University of Aachen (RWTH) for the achievement of a Doctorate of Natural Sciences in June 2009.

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