

TABLE OF CONTENTS

1	INTRODUCTION	1
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
1.3.4	Economic viability	4
1.3.5	Gas separation membranes for CCS	4
1.4	MIEC membranes for O ₂ /N ₂ separation	5
2	SCOPE OF THE WORK	6
3	BACKGROUND	7
3.1	MIEC materials for oxygen permeable membranes	7
3.1.1	The perovskite structure	7
3.1.2	The Ruddlesden-Popper phase, K ₂ NiF ₄ -type structure (A ₂ BO _{4+δ})	12
3.2	Theory of oxygen transport	13
3.2.1	Bulk transport	15
3.2.2	Surface processes	17
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
3.3.5	Combustion gas composition	21
4	CHARACTERISATION TECHNIQUES	23
4.1	X-ray diffraction technique (XRD)	23
4.2	Scanning electron microscopy (SEM)	24
4.3	Thermal Analysis	24
4.3.1	Differential Thermal Analysis combined with thermogravimetry (DTA/TG)	25
4.3.2	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	MATERIALS SELECTED FOR THIS STUDY	30
5.1	Mixed conducting acceptor-doped perovskites	30
5.1.1	La _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (LSCF58)	30
5.1.2	Pr _{0.58} Sr _{0.4} Co _{0.2} Fe _{0.8} O _{3-δ} (PSCF58)	31
5.1.3	Ba _{0.5} Sr _{0.5} Co _{0.8} Fe _{0.2} O _{3-δ} (BSCF50)	31
5.2	Perovskite-related oxides	33

5.2.1	La ₂ NiO _{4+δ}	33
5.3	Sample preparation	34
5.3.1	Pressing.....	34
5.3.2	Sintering.....	34
6	DEVELOPMENT 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
6.2.1	The heating unit:	37
6.2.2	The recipient:	38
6.3	Module 3: The analytical unit.....	39
6.4	Development of the membrane recipient for dense ceramic membranes	42
6.4.1	Sealing technology.....	43
6.5	Testing the set-up.....	44
6.6	Oxygen permeation measurements.....	45
7	THERMO-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	CHARACTERISATION 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	OXYGEN 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	THERMO-CHEMICAL STABILITY INVESTIGATION.....	95
10.1	Annealing in air	96
10.2	Annealing in CO ₂ -containing atmospheres.....	98
10.2.1	Air plus 10%CO ₂	104
10.2.2	1% O ₂ , 99%N ₂ plus 10%CO ₂	107
10.2.3	43%O ₂ , 43%CO ₂ and 14%N ₂	109
10.2.4	67 mol% CO ₂ , 25 mol% O ₂ and 8 mol% N ₂	112
10.3	FactSage TM thermo-chemical calculations.....	116
10.4	Annealing in water vapour-containing atmospheres	121
10.4.1	55 mol% CO ₂ , 28 mol% O ₂ , 12 mol% H ₂ O and 5 mol% N ₂	123
10.4.2	50 mol% CO ₂ , 25 mol% O ₂ , 20 ol% H ₂ O, 5 mol% N ₂	127
10.4.3	25 mol% O ₂ , 20 mol% H ₂ O, 55 mol% N ₂	136

10.5	Volatilisation of chromium species	137
10.5.1	Theory	137
10.5.2	Results.....	138
10.5.3	Discussion.....	144
10.6	Co enrichment at the grain boundaries	145
10.7	Phase analysis	148
10.7.1	Results.....	149
10.7.2	FactSage TM thermo-chemical calculations.....	159
10.7.3	Discussion.....	162
10.8	Conclusion	162
11	CONCLUSION.....	165
12	REFERENCES	169