

OUTLINE

0. Preamble	15
Summary	15
Resumen	17
Resum	19
Context and scope of the Thesis	21
1. Introduction	25
1.1. Gas separation membranes	25
1.2. Mixed ionic-electronic conduction	26
1.2.1. Fluorites	27
1.2.2. Perovskites	27
1.2.3. Composite materials	28
1.3. Oxygen transport mechanisms	29
1.3.1. Bulk diffusion	30
1.3.2. Surface exchange reactions	32
1.4. Performance optimization	33
1.4.1. Material properties	34
1.4.2. Operation conditions	34
1.4.3. Thickness reduction	35
1.4.4. Surface modification	36
1.4.5. Protective layers	36
1.5. Applications of Oxygen Transport Membranes	37
1.5.1. Available technologies for the production of oxygen	37
1.5.2. Application of OTMs in Power Generation and CCS: Oxyfuel and Gasification technologies	39
1.5.3. Chemical Industry Applications	42
1.7. References	46
2. Experimental	57
2.1. Material synthesis	57
2.1.1. Co-precipitation	57
2.1.2. Pechini or sol-gel route	58
2.2. Material processing. Sample preparation	58
2.2.1. Membranes and electrolytes	58
2.2.2. Production of LSCF porous supports by freeze-casting	59

2.2.3. Rectangular bars.	60
2.2.4. Catalytic layer/Electrode deposition.	60
2.3. Structural characterization.	61
2.3.1. Scanning Electron Microscopy.	61
2.3.2. X-Ray Diffraction.	62
2.3.4. Raman spectroscopy.	63
2.4. Thermal analysis.	64
2.4.1. Thermo-gravimetry (TG).	64
2.5. Electrochemical characterization.	64
2.5.1. DC total electrical conductivity.	64
2.5.2. Electrochemical Impedance Spectroscopy (EIS).	65
2.6. Membrane performance characterization.	68
2.6.1. Experimental set-up. Planar membranes.	68
2.6.2. Experimental set-up. Capillary membranes.	70
2.6.3. Oxygen flux calculation.	72
2.6.4. Conversion, selectivity and yield calculation.	73
2.7. References.	74
3. Permeation studies on BSCF membranes.	77
3.1. Introduction.	77
3.2. Planar membranes.	78
3.2.1. Membrane microstructure.	78
3.2.2. Oxygen permeation: thickness variation.	80
3.2.3. Oxygen permeation: catalytic activation.	85
3.2.4. Oxidative De-Hydrogenation of Ethane (ODHE) on BSCF membrane reactors.	90
3.3. Tubular membranes.	96
3.3.1. Capillary membrane description.	97
3.3.2. Oxygen permeation.	99
3.3.3. Oxidative Coupling of Methane.	102
3.4. Conclusions.	116
3.5. References.	118
4. Permeation studies on LSCF membranes.	125
4.1. Introduction.	125
4.2. Tape-cast supported LSCF membranes.	126
4.2.1. Characterization of the membrane assembly microstructure.	126

4.2.2. Effect of sweep gas flux on the oxygen permeation.	126
4.2.3. Effect of oxygen partial pressure in feed on the oxygen permeation.	129
4.2.4. Effect of catalytic layer on the oxygen permeation.	134
4.2.5. Effect of CO ₂ content in sweep stream on the oxygen permeation. .	136
4.3. Freeze-cast supported LSCF membranes.....	138
4.3.1. Production of porous supports by means of freeze casting.	138
4.3.2. Effect of the freeze-cast porous support.	140
4.3.3. Effect of membrane catalytic activation.....	146
4.4. Conclusions.....	153
4.5. References.....	155
5. Oxygen permeation on an Asymmetric CGO-Co membrane.....	163
5.1. Introduction.	163
5.2. Membrane assembly microstructure.....	164
5.3. Oxygen permeation tests.	166
5.3.1. Temperature and sweep gas dependence.....	166
5.3.2. Effect of oxygen partial pressure in feed stream.....	168
5.3.3. Effect of CO ₂ content in sweep stream.	169
5.3.4. Effect of CH ₄ content in sweep stream.....	171
5.3.5. Carbon dioxide stability test.	172
5.4. Conclusions.....	178
5.5. References.....	179
6. Composite oxygen-transport membranes for operation in CO ₂ /SO ₂ -rich gas environments.	185
6.1. Introduction.	185
6.2. Oxygen permeation and stability of dual-phase bulk membranes.....	186
6.2.1. Microstructural characterization.	186
6.2.2. EC measurements.....	188
6.2.3. Oxygen permeation characterization.	189
6.3. Catalytic study on the activation of the system 60NFO-40CTO.	196
6.3.1. Electrochemical characterization of reference case.....	197
6.3.2. Electrochemical characterization of activated cases.	199
6.3.3. Oxygen permeation tests.	204
6.4. Oxygen permeation in thin supported dual-phase membranes.....	208
6.4.1. Chemical compatibility.....	208
6.4.2. Microstructural study	209

6.4.3. Oxygen permeation tests.	211
6.5. Conclusions.....	216
6.6. References.....	218
7. Conclusions and remarks.....	227
8. Scientific contribution.....	233
8.1. Publications.....	233
8.2. Patents.....	234
8.3. Congress participations.....	234
Oral presentations.....	234
Selected posters presentations.....	235
9. Acronyms and symbols.....	237
10. Figures and Tables list.....	239
10.1. Figures.....	239
10.2. Tables.....	247