## Development of high temperature MIEC catalytic reactors for energy conversion and storage applications

#### 0. Preamble

Summary	7
Resumen	8
Resum	10

#### 1. Introduction

1.1 Climate	e change and CO <sub>2</sub> as a greenhouse gas	17
1.2.1 0	CO <sub>2</sub> capture, storage and valorisation	18
1.2.2 0	Oxy-combustion processes for CO <sub>2</sub>	
capt	ure	21
1.2.3	Oxygen production	22
1.2 Mixed i	1.2 Mixed ionic and electronic conductivity materials	
(MIEC)	for oxygen production	
1.2.1 N	MIEC materials and oxygen transport	
mec	hanism	24
1.2.2 0	Oxygen permeability and stability in	
Pero	ovskite-type OTMs	27
1.2.3 I	Dual-phase materials for OTMs	31
1.3 CO <sub>2</sub> rev	valorisation	35
1.3.1	Thermosolar chemical looping	36
1.3.2 \$	Solid oxide electrolysis cells (SOEC)	38
1.4 Scope o	of the thesis	41
1.5 Referen	ices	41

#### 2. Methodology

2.1 Material synthesis	57
2.1.1. Modify Pechini Method	57
2.2 Sample preparation	59
2.2.1. Dense samples (MIEC membranes and	d
electrolytes	59
2.2.2. Porous layers (Electrodes and catalytic	c
layers)	61
2.3 Material characterization	63
2.3.1 X-ray diffraction technique	63
2.3.2 Scanning electron microscopy	64
2.3.3 Surface area BET	66
2.3.4 Total conductivity	66
2.4 Lab scale reactors	68
2.4.1. Fixed bed reactors	68
2.4.2. MIEC membrane reactors	70
2.4.3. Electrochemical reactors	71
2.5 References	75

# 3. Optimization of dual-phase electrodes for high-temperature membrane reactors

3.1 Introduction	79
3.2 Sample preparation and characterization	81
3.3 EIS study for different ratios in dual-phase	
electrodes	86
3.4 Influence of the catalytic layers on the oxygen	
permeation	93
3.5 Conclusions	
	96
3.6 References	98

4.	Novel dual-phase MIEC membranes for		
	catalytic membranes reactors		
	4.1.Introduction	105	
	4.2.Sample preparation	106	
	4.3. Physical characterization and total conductivity		
	4.3.1 Microstructural characterization	107	
	4.3.2 Total conductivity	108	
	4.4.Electrochemical studies	110	
	4.5.Oxygen permeation	116	
	4.6.Post-mortem characterization	123	
	4.7.Conclusions	126	
	4.8.Bibliography	127	

### 5. Lowering operation temperature in oxygen transport membrane reactors (OTMR) by membrane electrification

5.1 Catalytic membrane reactors based on oxygen	
transport membranes	133
5.2 Electrified OTM concept, device and calculation	18
	137
5.3 BSCF capillary membrane characterization	139
5.4 Oxygen permeation studies	140
5.5 Oxidative dehydrogenation of ethane in BSCF	
catalytic membrane Reactor	147
5.6 Post-mortem characterization	152
5.7 Conclusions	156
5.8 References	157

6.	Effect of conductivity in chemical looping	
	methane reforming using doped ceria as an	
	oxygen-carrier catalyst	
	6.1 Chemical looping methane reforming	167
	6.2 Sample preparation	169
	6.3 Structural properties of lanthanide-doped ceri	a 169
	6.4 Chemical looping test	172
	6.5 Impact of dopant ionic radius on the POM	
	reaction	181
	6.6 Impact of dopant ionic radius on the CO <sub>2</sub>	
	splitting reaction	184
	6.7 Characterization after chemical looping test	187
	6.8 Conclusions	190
	6.9 References	191
7.	<b>Conclusions and remarks</b>	
		199

8. Figure and table list

203