Table of contents

1. SCOPE OF THE THESIS & OBJECTIVES 9

1.1 References 15

2. RESUMEN/SUMMARY/RESUM 17

2.1. Resumen 19

2.2. Summary 22

2.3. Resum 24

3. INTRODUCTION 27

3.1. Introduction to the membrane reactors 29

3.2. Membrane assemblies based on ionic ceramic conductors 34

3.2.1. Pure oxygen ion conductors 42

3.2.2. Pure proton conductors 45

3.2.3. Mixed ion – electronic conductors 49

3.3. Membrane reactor using high temperature ceramic materials 54

3.3.1. Hydrogen production 54

3.3.2. Syngas production 56

3.3.3. Higher hydrocarbons production 57

3.3.4. Methane production 60

3.3.5. Ammonia production 61

3.4. Electrodes for protonic conducting ceramics 62

3.5. Finite elements for high temperature membrane reactors .. 63

3.6. References 66

4. EXPERIMENTAL METHODOLOGY 77

4.1. Materials synthesis 79

4.1.1. Sol-gel method 79

4.1.2. Solid state reaction 81

4.1.3. Co-precipitation method 82

4.2. Deposition techniques 83

4.2.1. Tubular support tested 83

4.2.2. Dip-coating 84

4.2.3. Sputtering 85

4.2.4. Screen-printing 87

4.3. Structural characterization 88

4.3.1. X-ray powder diffraction 88

4.3.2. Scanning electron microscope 91

4.3.3. Field emission scanning electron microscope 93

4.4. Chemical characterization 94

4.4.1. Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) 94

4.5. Electrochemical characterization 94

4.5.1. Electrochemical Impedance Spectroscopy (EIS) 94

4.6. References 101

5. DIP-COATING METHOD TO DEVELOP COPPER BASED ANODES FOR HIGH TEMPERATURE MEMBRANE REACTORS 103

5.1. Introduction 105

5.2. Results 107

5.2.1. Characterization of synthesized materials 107

5.2.2. Optimization of the dip-coating methodology 110

5.2.3. Effect of the sintering process in the cermet microstructure 116

5.2.4. Effect of the dipping conditions 120

5.2.5. Electrochemical characterization 122

5.2.6. Stability of the cermet electrode 127

5.2.7. Dip-coating on asymmetric initially reduced tubes 128

5.3. Summary 131

5.4. References 132

6. COPPER SPUTTERED ANODES FOR MEMBRANE REACTORS AT HIGH TEMPERATURE 135

6.1. Introduction 137

6.2. Results 138

6.2.1. Sputtering at room temperature 139

6.2.2. Sputtering at high temperature 141

6.3. Future works 147

6.4. Summary 147

6.5. References 148

7. CHARACTERIZATION OF OXYGEN TRANSPORT ON BSCF MEMBRANES ASSISTED BY FLUID DYNAMIC SIMULATIONS 151

7.1. Introduction 153

7.2. Methods 156

7.3.1. Experimental procedure 156

7.3.2. Modelling 158

7.3.3. Fitting procedure 165

7.3.4. Description of the simulation studies 167

7.3. Results 171

7.3.5. Fitting results 171

7.3.6. Results of the CFD simulations of the 3D permeation setup 173

7.4. Summary 191

7.5. References 195

8. ENERGETIC EVALUATION OF SOLID OXIDE ELECTROLYSER USING PROTONIC CONDUCTORS 205

8.1. Introduction 208

8.2. Methods 210

8.2.1. Methodology to evaluate the thermofluid dynamic of the electrolysis process by finite elements 210

8.2.2.Methodology to evaluate the efficiency of the electrolysis process 221

8.3. Results 227

8.3.1.Evaluation of the thermofluid dynamic of electrolysis based on protonic conducting materials at high temperature 227

8.3.2.Evaluation of the efficiency of electrolysis process based on protonic conducting materials at high temperature 244

8.4. Summary 254

8.5. References 257

9. THERMOFLUID DYNAMIC EVALUATION OF THE HYDROGEN EXTRACTION IN A PROTONIC MEMBRANE REFORMER 261

9.1. Introduction 264

9.2. Objectives 266

9.3. Methods 267

9.3.1. Description of the process 267

9.3.2. Experimental procedure 268

9.3.3. Geometry 268

9.3.4. Physics equations 270

9.3.5. Studies performed and conditions 281

9.3.6. Effect of the radiation in the heat transference 288

9.3.7. Meshing and solver 289

9.4. Results 290

9.4.1. Brief description of the experimental results 290

9.4.2. Validation of the finite element model..... 294

9.4.3. Analysis of the PMR in adiabatic conditions 307

9.5. Summary 323

9.6. References..... 327

10. FLUID DYNAMIC EVALUATION OF THE HYDROGEN EXTRACTION IN METHANE DEHYDROAROMATIZATION REACTOR 333

10.1. Introduction 335

10.2. Methods..... 338

10.2.1. Experimental setup and reference conditions..... 338

10.2.2. Model implementation 339

10.2.3. Fitting of the kinetic model to experimental data..... 346

10.2.4. Studies performed 346

10.3. Results 348

10.3.1. Fitting the kinetics to the experimental data 349

10.3.2. Spatial distribution of the reaction rates..... 350

10.3.3. Hydrogen extraction analysis 353

10.3.4. Influence of gas inlet velocity 356

10.3.5. Influence of reactor geometry 359

10.3.6. Influence of catalyst bed porosity 363

10.3.7. Influence of the ethylene formation kinetics 364

10.4. Summary 366

10.5. References 369

11. GENERAL REMARKS AND CONCLUSION 373

11. General conclusions 375

12. Acronyms 379

13. Figure list 381

14. Table list 399

15. Scientific contribution 401