

Outline

| | |
|---|-----------|
| 1. Context and scope of the thesis..... | 11 |
| 1.1. References | 15 |
| 2. Resumen/Summary/Resum | 19 |
| 2.1. Resumen | 19 |
| 2.2. Summary | 21 |
| 2.3. Resum | 23 |
| 3. Introduction..... | 27 |
| 3.1. Technologies | 27 |
| 3.1.1. Power-to-Power: fuel cells..... | 27 |
| 3.1.1.1. Types of fuel cells..... | 28 |
| 3.1.1.2. Solid oxide fuel cells..... | 31 |
| 3.1.1.3. Phosphate-based fuel cells | 33 |
| 3.1.2. Power-to-Hydrogen: Electrolyzer | 34 |
| 3.1.2.1. Solid oxide electrolyzer | 35 |
| 3.1.2.2. Phosphate-based electrolyzer | 36 |
| 3.1.3. Power-to-Gas | 37 |
| 3.2. Conductivity | 40 |
| 3.2.1. Intrinsic defects..... | 42 |
| 3.2.1.1. Ionic defects | 42 |
| 3.2.1.2. Electronic defects..... | 44 |
| 3.2.2. Extrinsic defects: mixed conductivity..... | 45 |
| 3.2.3. Diffusion mechanisms..... | 51 |
| 3.3. Cell components and material | 53 |
| 3.3.1. Electrolyte | 53 |
| 3.3.1.1. Materials | 54 |

| | | |
|--------------|--|-----------|
| 3.3.1.1.1. | Ionic conductors..... | 54 |
| 3.3.1.1.2. | Protonic conductors..... | 56 |
| 3.3.1.1.2.1. | High temperature | 56 |
| 3.3.1.1.2.2. | Low temperature | 58 |
| 3.3.2. | Electrodes | 59 |
| 3.3.2.1. | Materials | 60 |
| 3.3.2.1.1. | High temperature | 60 |
| 3.3.2.1.1.1. | Perovskites..... | 60 |
| 3.3.2.1.1.2. | Ruddlesden-Popper | 62 |
| 3.3.2.2. | Electrode configuration | 63 |
| 3.3.2.2.1. | Electrochemical activation of oxygen | 65 |
| 3.3.2.2.2. | Electrochemical activation of hydrogen | 67 |
| 3.4. | Appendix: Defect chemistry and mechanisms..... | 68 |
| 3.5. | References | 68 |
| 4. | Methodology | 75 |
| 4.1. | Material synthesis..... | 75 |
| 4.1.1. | Solid state reaction (SSR) | 75 |
| 4.1.2. | Pechini..... | 77 |
| 4.1.3. | Co-precipitation | 78 |
| 4.2. | Materials summary | 79 |
| 4.3. | Structural characterization | 81 |
| 4.3.1. | X-Ray Diffraction (XRD) | 81 |
| 4.3.2. | Scanning Electron Microscopy (SEM) | 84 |
| 4.3.3. | Transmission Electron Microscopy (TEM)..... | 86 |
| 4.3.4. | Thermogravimetric Analysis (TGA) | 87 |
| 4.4. | Sample preparation | 89 |
| 4.4.1. | Dense samples | 89 |

| | | |
|------------|--|------------|
| 4.4.2. | Electrodes preparation | 91 |
| 4.5. | Electrochemical characterization..... | 94 |
| 4.5.1. | DC total electrical conductivity | 94 |
| 4.5.2. | Electrochemical Impedance Spectroscopy (EIS) | 96 |
| 4.5.3. | Fuel cell mode | 100 |
| 4.5.4. | Electrolyzer mode | 102 |
| 4.5.5. | High temperature set-up | 104 |
| 4.5.6. | Low temperature set-up | 107 |
| 4.5.7. | Gas chromatography..... | 109 |
| 4.5.8. | Mass spectrometry | 110 |
| 4.6. | Summary | 110 |
| 4.7. | References | 111 |
| 5. | Improvement of BSCF performance by B site dopants | 115 |
| 5.1. | Introduction | 115 |
| 5.2. | Results and discussion | 116 |
| 5.2.1. | Structural characterization | 116 |
| 5.2.1.1. | X-Ray diffraction..... | 116 |
| 5.2.1.2. | Thermogravimetric analysis in CO ₂ atmosphere | 118 |
| 5.2.1.3. | Total DC electrical conductivity | 120 |
| 5.2.2. | Symmetrical cells characterization | 121 |
| 5.2.2.1. | Electrode microstructure | 121 |
| 5.2.2.2. | Polarization resistance | 123 |
| 5.2.2.2.1. | Operation temperature influence | 123 |
| 5.2.2.2.2. | Oxygen partial pressure influence on the cell performance | 131 |
| 5.2.2.2.3. | CO ₂ containing atmosphere influence on the cell performance | 134 |

| | | |
|------------|---|------------|
| 5.2.3. | Fuel cell characterization | 136 |
| 5.2.3.1. | Influence of the operation temperature..... | 137 |
| 5.2.3.2. | Influence of pO_2 , pH_2 and pH_2O in the fuel cell performance 139 | |
| 5.2.3.3. | Total flow influence on the fuel cell performance..... | 143 |
| 5.2.3.4. | Stability on the cell performance..... | 144 |
| 5.2.4. | Electrolyzer characterization | 146 |
| 5.2.4.1. | Steam electrolysis | 146 |
| 5.2.4.2. | Co-electrolysis | 150 |
| 5.2.4.3. | Electrolysis and co-electrolysis comparison | 157 |
| 5.3. | Conclusions | 158 |
| 5.4. | References | 159 |
| 6. | $La_{2-x}A_xNi_{1-y}B_yO_{4+\delta}$ electrodes for ionic electrolytes..... | 165 |
| 6.1. | Introduction | 165 |
| 6.2. | Results and discussion | 166 |
| 6.2.1. | Characterization of $La_{2-x}A_xNi_{1-y}B_yO_{4+\delta}$ compounds | 166 |
| 6.2.1.1. | Cell parameters and δ determination..... | 166 |
| 6.2.1.2. | DC total conductivity measurement | 173 |
| 6.2.1.3. | Electrochemical impedance spectroscopy measurements 176 | |
| 6.2.1.3.1. | Temperature influence on EIS results..... | 176 |
| 6.2.1.3.2. | Co-doped influence on EIS results | 178 |
| 6.2.1.3.3. | LPNCO temperature influence on EIS results | 181 |
| 6.2.1.3.4. | LPNCO pO_2 influence on EIS results | 183 |
| 6.2.2. | Fully-assembled cell | 185 |
| 6.2.2.1. | SEM micrographs characterization | 185 |
| 6.2.2.2. | Fuel cell mode performance | 186 |

| | | |
|------------|--|------------|
| 6.2.2.3. | Electrolysis mode | 188 |
| 6.2.2.4. | Co-electrolysis mode..... | 189 |
| 6.2.2.5. | Thermodynamic simulation of co-electrolysis | 191 |
| 6.3. | Conclusions | 192 |
| 6.4. | References | 193 |
| 7. | LSM electrode improvement strategies | 199 |
| 7.1. | Introduction | 199 |
| 7.2. | Results and discussion | 199 |
| 7.2.1. | Symmetrical cells characterization | 200 |
| 7.2.1.1. | Phases compatibility | 200 |
| 7.2.1.2. | XRD and FE-SEM characterization..... | 201 |
| 7.2.1.3. | Polarization resistance determination..... | 204 |
| 7.2.1.3.1. | LSM and LSM-GDC cathode electrochemical performance 207 | |
| 7.2.1.3.2. | Stability of the infiltrated cathodes | 208 |
| 7.2.1.3.3. | Influence of oxygen partial pressure | 211 |
| 7.2.2. | Fully-assembled cell performance | 213 |
| 7.2.2.1. | Fuel cell mode performance | 213 |
| 7.2.2.2. | Electrolysis mode performance | 215 |
| 7.3. | Conclusions | 217 |
| 7.4. | References | 218 |
| 8. | La_{2-x}A_xNi_{1-y}B_yO_{4-δ} electrodes for protonic electrolytes..... | 223 |
| 8.1. | Introduction | 223 |
| 8.2. | Results and discussion | 224 |
| 8.2.1. | Electrodes characterization | 224 |
| 8.2.1.1. | Reactivity test..... | 224 |
| 8.2.1.2. | Electrochemical characterization..... | 225 |

| | | |
|--------------|---|------------|
| 8.2.1.2.1. | Influence of operation temperature..... | 225 |
| 8.2.1.3. | Influence of electrode sintering temperature | 233 |
| 8.2.1.3.1. | Influence of composite electrodes | 235 |
| 8.2.1.3.2. | Dry conditions and isotopic effect influence | 237 |
| 8.2.1.3.2.1. | $\text{La}_2\text{NiO}_{4+\delta}$ | 237 |
| 8.2.1.3.2.2. | $\text{La}_{1.5}\text{Pr}_{0.5}\text{Ni}_{0.8}\text{Co}_{0.2}\text{O}_{4+\delta}$ | 240 |
| 8.2.1.3.2.3. | $\text{La}_{1.5}\text{Pr}_{0.5}\text{NiO}_{4+\delta}$ | 242 |
| 8.2.1.3.2.4. | $\text{Nd}_2\text{NiO}_{4+\delta}$ | 243 |
| 8.2.1.3.2.5. | General remarks | 244 |
| 8.3. | Conclusions | 248 |
| 8.4. | References | 248 |
| 9. | Cer-cer cathodes for PC-SOFC..... | 253 |
| 9.1. | Introduction | 253 |
| 9.2. | Results and discussion | 255 |
| 9.2.1. | Compatibility test..... | 255 |
| 9.2.2. | Electrochemical characterization..... | 256 |
| 9.2.2.1. | Cathode sintering temperature influence | 256 |
| 9.2.2.1.1. | Microstructure characterization | 256 |
| 9.2.2.1.2. | Electrochemical analysis of cer-cer cathodes sintering temperature..... | 259 |
| 9.2.2.2. | Influence of volume ratio on the electrode performance 263 | |
| 9.2.2.3. | LSM/LWO 60/40 % v/v electrode limiting mechanisms .. | 266 |
| 9.2.2.4. | Infiltration of the electrode composite..... | 269 |
| 9.2.2.4.1. | XRD and FESEM characterization..... | 271 |
| 9.2.2.4.2. | Electrochemical characterization | 272 |
| 9.2.2.4.3. | Stability of SDC infiltrated sample | 276 |

| | | |
|-------------|--|------------|
| 9.2.2.5. | Fully-assembled fuel cell | 278 |
| 9.3. | Conclusions | 281 |
| 9.4. | References | 282 |
| 10. | CsH₂PO₄-based electrochemical cell..... | 287 |
| 10.1. | Introduction | 287 |
| 10.2. | Results and discussion | 289 |
| 10.2.1. | Structural characterization | 289 |
| 10.2.1.1. | XRD characterization..... | 289 |
| 10.2.1.2. | Conductivity characterization | 290 |
| 10.2.1.2.1. | Influence of temperature | 290 |
| 10.2.1.2.2. | Influence of water partial pressure | 291 |
| 10.2.2. | Electrochemical characterization of symmetrical cells..... | 293 |
| 10.2.2.1. | Symmetrical cell configuration | 293 |
| 10.2.2.1.1. | Influence of system pressure on the cell operation ... | 295 |
| 10.2.2.1.2. | Influence of steam content on the cell operation | 297 |
| 10.2.2.1.3. | Influence of temperature on the cell operation..... | 299 |
| 10.2.3. | Electrochemical characterization in asymmetrical cells | 303 |
| 10.2.3.1. | Electrolyte supported cell | 303 |
| 10.2.3.1.1. | Fuel cell mode..... | 303 |
| 10.2.3.1.2. | Electrolysis mode..... | 306 |
| 10.2.3.2. | Steel supported cell | 310 |
| 10.2.3.2.1. | Fuel cell mode..... | 311 |
| 10.2.3.2.2. | Electrolysis mode..... | 313 |
| 10.2.3.2.3. | FIB-SEM characterization..... | 316 |
| 10.2.4. | Tailoring the mechanical properties of CDP electrolyte | 317 |
| 10.2.4.1. | SEM and XRD electrolyte characterization | 319 |
| 10.2.4.2. | Electrochemical characterization of the electrolyte..... | 320 |

| | | |
|-------------|---|------------|
| 10.2.5. | Active electrode support –Ni sponge..... | 321 |
| 10.2.5.1. | SEM and XRD electrode characterization | 321 |
| 10.2.5.2. | Electrochemical characterization..... | 324 |
| 10.2.5.2.1. | Electrodes characterization by symmetrical cell configuration..... | 324 |
| 10.2.5.2.2. | Fuel cell characterization | 336 |
| 10.3. | Conclusions | 338 |
| 10.4. | References | 339 |
| 11. | General remarks..... | 343 |
| 12. | Acronyms..... | 349 |
| 13. | Figures list..... | 355 |
| 14. | Tables list..... | 371 |
| 15. | Scientific contribution | 373 |