ANODES BASED ON MOLYBDENUM-DOPED CERIA FOR CARBON-AIR FUEL CELL APPLICATIONS

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Molybdenum (Mo)-doped ceria (CMO) nanoparticles were synthesized by the combustion method with three different Mo concentrations: 5 wt.%, 7 wt.% and 10 wt.%. The catalytic activity of CMO for wet gasification of carbon was studied in a fluidized bed reactor, while the mechanical and electrical properties of this material were characterized using dense sintered CMO pellets. The Young’s modulus increases with the Mo content; the highest measured value is 340.3 GPa for CMO with 10 wt.% Mo. Measurements of Vickers microhardness demonstrate that an increase in the Mo content produces a decrease in the microhardness of the material, suggesting that Mo confers semimetallic characteristics to CMO. The highest fracture toughness value, determined by the Niihara equation, is 4.65 MPa m$^{0.5}$ for CMO with 10 wt.% Mo. In addition, an increase in the molybdenum content produces an increase in the electrical conductivity under air and H$_2$ atmospheres. The maximum electrical conductivities under air and H$_2$ are found for CMO with 10 wt.% Mo at 800 °C: 1.87·10$^{-3}$ S cm$^{-1}$ and 9.37·10$^{-1}$ S cm$^{-1}$, correspondingly. Therefore, CMO with 10 wt.% Mo shows good catalytic activity during carbon gasification.

Based on its mechanical, electrical and catalytic properties, CMO 10 wt.% Mo was selected to perform electrochemical impedance spectroscopy (EIS) measurements in symmetric-cells with CMO-based electrodes, and polarization curve measurements in SOFCs with CMO anode, YSZ electrolyte and LSM cathode. The area specific polarization resistance (ASPR) values measured in air and hydrogen-water atmospheres are 6.76 Ω cm$^2$ and 5.68 Ω cm$^2$ at 800 °C, respectively. These APR values are lower than those reported in the literature for the same system under study, which was related to the improve synthesis method proposed in this work (combustion method). The diffusion of gaseous oxygen was related to a Knudsen-type mechanism, while the diffusion of hydrogen-water was related to a mixed mechanism between molecular and Knudsen-type diffusion. The maximum electrical power density obtained in the SOFC (using CMO-YSZ as cell anode) was 48.9 mW cm$^{-2}$. This low value was related to cathode problems and inadequate SOFC fabrication procedures.

The addition of molybdenum to cerium oxide improves its mechanical, electrical and catalytic properties, while the CMO anode in this work shows a lower polarization resistance compared to the results reported in the literature. These results show that the CMO is a good candidate for use as a carbon-air solid oxide fuel cell (CA-SOFC) anode. However, it is necessary to improve the SOFC fabrication method to determine if it is the reason for the low electrical power density obtained.
Nanopartículas de ceria dopada con molibdeno (CMO) fueron sintetizadas a través del método de combustión con tres concentraciones diferentes de molibdeno: 5 % p/p, 7 % p/p y 10 % p/p. La actividad catalítica del CMO en la gasificación húmeda de carbón fue estudiada en un reactor de lecho fluidizado, mientras que las propiedades mecánicas y eléctricas de este material fueron caracterizadas usando pellets densos de CMO sinterizado. El módulo de Young aumenta con el incremento del contenido de Mo; el mayor valor medido es 340.3 GPa para CMO con 10 % p/p de Mo. Mediciones de la microdureza Vickers demuestran que un incremento en el contenido de Mo produce una disminución en la microdureza del material, sugiriendo que el Mo confiere características semi-métalicas al CMO. El mayor valor de tenacidad a la fractura, determinado a través de la ecuación de Niihara, es 4.65 MPa m$^{0.5}$ para CMO con 10 % p/p de Mo. Además, un incremento en el contenido de molibdeno produce un aumento en la conductividad eléctrica medida bajo atmósferas de aire e hidrógeno. Las conductividades eléctricas máximas medidas en aire e hidrógeno fueron encontradas para CMO con 10 % p/p de Mo a 800 °C: $1.87 \times 10^{-3}$ S cm$^{-1}$ y $9.37 \times 10^{-1}$ S cm$^{-1}$, correspondientemente. Además, CMO con 10 % p/p de Mo muestra buena actividad catalítica para la reacción de gasificación de carbón.

En base a sus propiedades mecánicas, eléctricas y catalíticas, CMO con 10 % p/p de Mo fue seleccionado para llevar a cabo mediciones de espectroscopia de impedancia electroquímica (EIS) en celdas simétricas con electrodos basados en CMO, y para las mediciones de polarización en SOFCs con ánodo basado en CMO, YSZ como electrolito y LSM como cátodo. Los valores de resistencia a la polarización específica por área (ASPR) medidos en atmósferas de aire e hidrógeno húmedo son 6.76 Ω cm$^2$ y 5.68 Ω cm$^2$ a 800 °C, respectivamente. Estos valores de ASPR son menores que los reportados en la literatura para el mismo sistema en estudio, lo cual fue relacionado a la mejora en el método de síntesis propuesto en este trabajo (método de combustión). La difusión de oxígeno gaseoso fue relacionada a un mecanismo tipo Knudsen, mientras que la difusión de hidrógeno húmedo fue relacionada a un mecanismo mixto entre difusión molecular y tipo Knudsen. La máxima densidad de potencia eléctrica obtenida en la SOFC (usando CMO-YSZ como ánodo de la celda) fue de 48.9 mW cm$^{-2}$. Este bajo valor fue relacionado con problemas en el cátodo y un procedimiento inadecuado de fabricación de la SOFC.

La incorporación de molibdeno a la ceria mejora sus propiedades mecánicas, eléctricas y catalíticas, mientras que el ánodo de CMO, en este trabajo, muestra una menor resistencia a la polarización comparado con los resultados reportados en la literatura. Estos resultados muestran que el CMO es un buen candidato para ser usado como ánodo en celdas de combustible del tipo carbón-aire (CA-SOFC). Sin embargo, es necesario mejorar la fabricación de la SOFC para determinar si este factor es el responsable de la baja densidad de potencia eléctrica obtenida.
Dedicated to my parents, Lucía and José, my brother Hans and Mariana who supported and encouraged me during these long five years.

“creo que he visto una luz, al otro lado del río (...) sobretodo creo que no todo está perdido (...) oigo una voz que me llama, casi un suspiro: rema! rema! rema!”

Jorge Drexler, ‘Al Otro Lado del Río’
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<td>7.3.2 SEM micrograph and XRD of cathode surface after SOFC tests</td>
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</tr>
</tbody>
</table>
Nomenclature

\( T \) : Absolute temperature / K
\( E_A \) : Activation energy / eV
\( a_i \) : Activity of specie \( i \)
\( I_0 \) : Amplitude of electrical current sinusoidal response / A
\( E_0 \) : Amplitude of potential sinusoidal signal / V
\( \omega \) : Angular frequency / radians
\( A \) : Area of electrolyte / m\(^2\)
\( \text{ASPR} \) : Area specific polarization resistance / Ω cm\(^2\)
\( A_V \) : Average middle-length of the diagonal of the Vickers marks / m
\( d_V \) : Average of the diagonal length in the Vickers marks / m
\( N_A \) : Avogadro’s number / \( 6.0221367 \times 10^{23} \) particles mol\(^{-1}\)
\( \theta \) : Bragg angle / degrees
\( C \) : Capacitance / F
\( Y_0 \) : Capacitance value in the constant phase element (CPE) / F s\(^{\alpha -1}\)
\( E \) : Cell potential / V
\( \Delta H_T \) : Change of enthalpy at temperature \( T \) / J mol\(^{-1}\)
\( \Delta S_T \) : Change of entropy at temperature \( T \) / J mol\(^{-1}\) K\(^{-1}\)
\( \Delta G_T \) : Change of Gibbs free energy at temperature \( T \) / J mol\(^{-1}\)
\( \alpha_k \) : Charge transfer coefficient
\( R_{ct} \) : Charge transfer resistance / Ω
\( \sigma_{i,j} \) : Collision diameter between \( i \) and \( j \) species / Å
\( \Omega_{i,j} \) : Collision integral parameter of Chapman-Enskog model
\( C_i^* \) : Concentration in the bulk of specie \( i \) / mol l\(^{-1}\)
\( \alpha \) : Constant phase element coefficient
\( Z_{\text{CPE}} \) : Constant phase element impedance / Ω
\( l_c \) : Radial crack length / m
\( A \) : Cross sectional area / m\(^2\)
\( D \) : Crystallite size / nm
\( I \) : Current / A
\( j \) : Current density / A m\(^{-2}\)
\( \rho \) : Density / kg m\(^{-3}\)
\( \delta \) : Diffusion layer thickness / cm
\( d_i \) : Diameter of molecule of specie \( i \) / nm
\( d_{\text{pore}} \) : Diameter of pores / µm
\( D_i^{\text{eff}} \) : Effective diffusion coefficient of specie \( i \) / cm\(^2\) s\(^{-1}\)
\( E_Y \) : Elastic modulus / Pa
\( E_0 \) : Elastic modulus at zero porosity / Pa
\begin{center}
<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
</thead>
<tbody>
<tr>
<td>(e)</td>
<td>Electrical charge of electron / (-1.602 \times 10^{-19}) C</td>
</tr>
<tr>
<td>(\sigma)</td>
<td>Electrical conductivity / S m(^{-1})</td>
</tr>
<tr>
<td>(P_{\text{elec}})</td>
<td>Electrical power density / W m(^{-2})</td>
</tr>
<tr>
<td>(\delta)</td>
<td>Electronic path length or diffusion layer thickness / m</td>
</tr>
<tr>
<td>(R)</td>
<td>Electrical resistance / (\Omega)</td>
</tr>
<tr>
<td>(l)</td>
<td>Electrolyte thickness / m</td>
</tr>
<tr>
<td>(\Delta H_{i,T})</td>
<td>Enthalpy of species (i) at temperature (T) / J mol(^{-1})</td>
</tr>
<tr>
<td>(\Delta S_{r,T})</td>
<td>Entropy of the reaction at temperature (T) / J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(\Delta S_{i,T})</td>
<td>Entropy of species (i) at temperature (T) / J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(J_0)</td>
<td>Exchange current / A m(^{-2})</td>
</tr>
<tr>
<td>(F)</td>
<td>Faraday’'s constant / 96 485 C mol-equiv(^{-1})</td>
</tr>
<tr>
<td>(K_{IC})</td>
<td>Fracture toughness / Pa m(^{0.5})</td>
</tr>
<tr>
<td>(X_f)</td>
<td>Fuel utilization</td>
</tr>
<tr>
<td>(\beta)</td>
<td>Full width at half maximum (FWHM) of diffractogram peaks / degrees</td>
</tr>
<tr>
<td>(R)</td>
<td>Gas constant / 8.314 J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(c_{p,i})</td>
<td>Heat capacity of (i) species / J mol(^{-1}) K(^{-1})</td>
</tr>
<tr>
<td>(\Delta H_{CP,i})</td>
<td>Heat of change of phase / J mol(^{-1})</td>
</tr>
<tr>
<td>(\dot{Q})</td>
<td>Heat flow / W</td>
</tr>
<tr>
<td>(\text{HHV})</td>
<td>Higher heating value / kJ kg(^{-1})</td>
</tr>
<tr>
<td>(Z_{Im})</td>
<td>Imaginary component in impedance expression / (\Omega)</td>
</tr>
<tr>
<td>(r_{Im})</td>
<td>Imaginary part radius of the semicircle in the Nyquist plot / (\Omega)</td>
</tr>
<tr>
<td>(Z)</td>
<td>Impedance / (\Omega) or (\Omega) cm(^2) (corrected by area)</td>
</tr>
<tr>
<td>(L)</td>
<td>Inductance / H</td>
</tr>
<tr>
<td>(K_n)</td>
<td>Knudsen number</td>
</tr>
<tr>
<td>(a)</td>
<td>Lattice parameter / nm</td>
</tr>
<tr>
<td>(j_l)</td>
<td>Limiting current density / A m(^{-2})</td>
</tr>
<tr>
<td>(P_V)</td>
<td>Load applied by Vickers indenter / N</td>
</tr>
<tr>
<td>(\Lambda)</td>
<td>Mean free path / (\mu)m</td>
</tr>
<tr>
<td>(x_i)</td>
<td>Molar fraction</td>
</tr>
<tr>
<td>(M_i)</td>
<td>Molar weight of specie (i) / g mol(^{-1})</td>
</tr>
<tr>
<td>(\nu_e)</td>
<td>Number of electrons involved in electrochemical reaction</td>
</tr>
<tr>
<td>(E_N)</td>
<td>Nernst potential / V</td>
</tr>
<tr>
<td>(\text{OCV})</td>
<td>Open circuit voltage / V</td>
</tr>
<tr>
<td>(\Phi_{\text{SOFC}})</td>
<td>Overall SOFC efficiency</td>
</tr>
<tr>
<td>(\eta)</td>
<td>Overpotential / V</td>
</tr>
<tr>
<td>(P_i)</td>
<td>Partial pressure of specie (i) / atm</td>
</tr>
<tr>
<td>(\phi)</td>
<td>Phase angle / degrees</td>
</tr>
<tr>
<td>(\nu)</td>
<td>Poisson’s ratio</td>
</tr>
<tr>
<td>(\varepsilon_p)</td>
<td>Porosity</td>
</tr>
<tr>
<td>(Z_{Re})</td>
<td>Real component in impedance expression / (\Omega)</td>
</tr>
<tr>
<td>(r_{Re})</td>
<td>Real part radius of the semicircle in the Nyquist plot / (\Omega)</td>
</tr>
<tr>
<td>(r)</td>
<td>Radius of the circular sample (impulse essay) / m</td>
</tr>
<tr>
<td>(\rho_e)</td>
<td>Electrical resistivity / (\Omega) m</td>
</tr>
<tr>
<td>(f_{20})</td>
<td>Resonance frequency obtained by excitation in the border of the disc sample / Hz</td>
</tr>
<tr>
<td>(W_{\text{elec,rev}})</td>
<td>Reversible electrical work / J mol(^{-1})</td>
</tr>
<tr>
<td>(Q_{\text{rev}})</td>
<td>Reversible heat / J mol(^{-1})</td>
</tr>
</tbody>
</table>
\( E_{\text{rev},T} \): Reversible potential at temperature \( T / \text{V} \)

\( W_{\text{rev}} \): Reversible work / J mol\(^{-1}\)

\( \Delta H_{i,T^o}^o \): Standard enthalpy of species \( i \) at \( T^o = 298.15 \text{ K} / \text{J mol}^{-1} \)

\( \Delta S_{i,T^o}^o \): Standard entropy of species \( i \) at \( T^o = 298.15 \text{ K} / \text{J mol}^{-1} \text{K}^{-1} \)

\( P^o \): Standard pressure / 1 bar

\( \epsilon \): Strain

\( \nu_i \): Stoichiometric coefficient of reactants \( i \)

\( \nu_j \): Stoichiometric coefficient of products \( j \)

\( T_{\text{CP},i} \): Temperature of change of phase / K

\( \Phi_{\text{Th}} \): Thermodynamic efficiency (Maximum theoretical efficiency)

\( h \): Thickness of the sample / m

\( \tau \): Time constant / s

\( \tau_p \): Tortuosity

\( \Delta \varphi_{IR}^{\text{total}} \): Total ohmic losses / V

\( \Phi_V \): Voltage efficiency

\( Z_W \): Warburg impedance / \( \Omega \)

\( \lambda \): Wavelength of radiation / \( \text{Å} \)

\( x_{C,\text{coal}} \): Weight fraction of carbon in coal

Kröger–Vink notation:

\( A_B^\text{X} \): an A ion sitting on a B lattice site, with neutral charge.

\( V_O^{\bullet\bullet} \): an oxygen vacancy, with double positive charge.

\( A_i^{\bullet\bullet} \): an A interstitial ion, with double positive charge.

\( C_i'' \): a C anion on an interstitial site, with single negative charge.

\( O_i'''' \): an oxygen anion on an interstitial site, with double negative charge.

\( e_i' \): an electron. No site is normally specified.
Chapter 1

Introduction

1.1 Global and Chile Energy Scenario

Electricity is the flow of electrical power or charge. It is the most flexible, convenient and widely used form of energy. The electricity that we use is a secondary energy source because it is produced by converting primary sources of energy such as coal, natural gas, nuclear energy, solar energy, and wind energy into electrical power. It is also referred to as an energy carrier, which means it can be converted to other forms of energy such as mechanical energy or heat. Currently, fossil fuels cover more than 80% of the energy used by mankind and about 60% of the electricity is produced starting from this primary energy form [1].

In 2015, according to data from the International Energy Agency (IEA), of a total of 23 332 TWh of electrical power produced worldwide, a 41.3% is generated from coal, as shown in figure 1.1.1 [2]. Figure 1.1.2 shows a strong growth on the global demand of coal of approximately 4.5 billion metric tons per year in 2000 to 6.9 billion metric tons per year in 2018 [3, 4]. It is expected that this trend in coal consumption will increase due to the high dependence on this fuel in USA and China. In addition, according to the IEA, to 2030 the world demand for electrical power will grow between 46 and 58%, so coal appears as a cheap and abundant source of primary energy to produce this electrical power [5].

![Figure 1.1.1: World total electricity generation by source in 2015. Other includes geothermal, solar, wind, biofuels and waste, and heat [2].](image-url)
The production of electricity in the world has been carried out mainly in thermoelectric plants. Thermoelectric plants burn fossil fuels in a furnace and the heat generated is used for steam generation. The high pressure steam is expanded against a turbine associated with an electric generator, a device capable of converting mechanical energy into electrical energy. This fossil fuel-fired plants present a conversion efficiency of thermal to electrical energy of \( \text{ca.} \ 45\% \) in the case of newer technologies such as combined cycle power plants. The low energy efficiency of this technology leads to the release of large amounts of carbon dioxide into the atmosphere per unit of energy produced. In addition in these generation plants other gases from the burning of fossil fuels are emitted such as nitrogen oxides and sulfur oxides, which have very harmful effects on human health and ecosystems.

In Chile, the production of electrical power is also carried out mainly in thermoelectric plants. The net installed generation capacity per month amounts to 22,535 MW (up to December 2017), which is composed of 66.1\% of thermoelectric production, 15.1\% of conventional hydroelectric production and 18.8\% of non-conventional renewable energies (NCRE) [6] as shown in Figure 1.1.3. However, since Chile is a country with a great potential in conventional and non-conventional renewable energies\[1\], the long-term commitment in our country is focused on promoting adequate conditions for the development of the use of renewable energies (particularly, solar, wind and geothermal). As a sign of this new energy policy and in an effort to avoid the adverse effects of electricity generation in thermoelectric plants, the State of Chile has approved 38 electric generation projects (only four of them correspond to thermoelectric plants) to be built between November 2017 and March 2024. It is estimated that these new 38 projects will contribute with a total of 2,408 MW per month by the year 2024, of which only 20\% will come from the burning of fossil fuels, as shown in Figure 1.1.4. Figure 1.1.5 shows the accumulated energy contribution up to the year 2024 and the individual contribution of the projects approved by the State of Chile since 2017. This projection shows an

---

\[1\] Within conventional renewable energies, the most widespread is hydraulic energy on a large scale, while non-conventional, correspond to those that have a great potential for development such as geothermal, wind, solar, biomass and mini-hydro.
important contribution of the NCRE projects between 2017 and 2018, however since 2019 the additional electric power generation projected is dominated by the conventional hydroelectric projects.

Figure 1.1.3: Composition of net installed generation capacity in Chile up to December 2017 [6].

Figure 1.1.4: Estimation of the electric power that will be added to the Chilean electricity system between the years 2017 and 2024 [6].

Figure 1.1.5: Cumulative production of electrical power, by source, projected up to 2024 [6].

As a method of comparison between different electricity generation technologies, economists have reached consensus on the use of the Levelized Costs of Energy (LCOE) indicator. This indicator
considers the costs of construction, operation and maintenance of the generation system, in addition to considering the costs of pollutant emissions from the electrical power production method under study. The LCOE can also be regarded as the average minimum cost at which electricity must be sold in order to break-even over the lifetime of the project. The data published in November 2017 by the Investment Bank Lazard in New York, compares the LCOE value for many different technologies of generation. This data, showed in Table 1.1.1 demonstrates the low cost of electrical energy when this is produced by fossil fuels-fired power plants.

Table 1.1.1: Comparison of LCOE value for different electricity generation technologies [7].

<table>
<thead>
<tr>
<th>Generation type</th>
<th>LCOE value /US$ MWh⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solar photovoltaic</td>
<td>85</td>
</tr>
<tr>
<td>Geothermal</td>
<td>77</td>
</tr>
<tr>
<td>Wind</td>
<td>30</td>
</tr>
<tr>
<td>Gas-combined cycle</td>
<td>68</td>
</tr>
<tr>
<td>Coal</td>
<td>60</td>
</tr>
<tr>
<td>Nuclear</td>
<td>112</td>
</tr>
</tbody>
</table>

According to projections of the U.S. Energy Information Administration (EIA) prices of electricity production through NCRE will be lower and competitive in the next 30 years, even being lower than the prices of electricity produced from fossil fuels. This decrease is expected for the technological improvements that these technologies will experience, which are still in development [8].

In the current scenario, in which the price of electricity generation is lower using technologies based on fossil fuels such as coal or natural gas and technologies based on renewable energy are not yet competitive enough, to ensure energy supply in a carbon-constrained world there is pending urgency in developing new technologies for coal or gas conversion that offer significantly higher conversion efficiencies than 30 - 35% (current efficiencies for coal-based power technologies), and thus lower greenhouse gases emissions [9]. Carbon-air solid oxide fuel cells appear as a solution for the generation of electrical power more efficiently compared to traditional carbon-based technologies and with a lower environmental impact.

1.2 Carbon-Air Solid Oxide Fuel Cells (CA-SOFCs)

Fuel cells are electrochemical devices capable of converting the chemical energy of fuels into electrical energy directly by the reaction of the fuel and an oxidant on the surface of electrodes. These electrochemical systems are more efficient because they are not subject to Carnot cycle efficiency restrictions such as thermal generation cycles [9]. Unlike thermoelectric plants, whose conversion efficiencies are between 30 - 45%, fuel cells can achieve efficiencies even higher than 60%. The fuel cells are typically classified according to the type of electrolyte they use, the fuel supplied to the system and the working temperature. Table 1.2.1 shows a summary of the more studied fuel cells existing.
### Types of fuel cells and main characteristics

<table>
<thead>
<tr>
<th>Fuel cell technology</th>
<th>Ionic conductor (electrolyte)</th>
<th>Operating temperature</th>
<th>Efficiency</th>
<th>Generation Capacity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Proton exchange membrane (PEMFC)</td>
<td>Solid polymeric membrane</td>
<td>50 - 100 °C</td>
<td>40 - 50%</td>
<td>0.03 - 250 kW</td>
</tr>
<tr>
<td>Direct methanol (DMFC)</td>
<td>Solid polymeric membrane</td>
<td>60 - 200 °C</td>
<td>40%</td>
<td>0.001 - 100 kW</td>
</tr>
<tr>
<td>Alkaline (AFC)</td>
<td>KOH solution</td>
<td>50 - 200 °C</td>
<td>ca. 50%</td>
<td>10 - 100 kW</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>Phosphoric acid</td>
<td>ca. 200 °C</td>
<td>40%</td>
<td>100 - 1 300 kW</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>Lithium and potassium carbonate eutectic</td>
<td>ca. 650 °C</td>
<td>&gt;50%</td>
<td>155 - 2 000 kW</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>Yttria stabilized zirconia</td>
<td>800 - 1 000 °C</td>
<td>&gt;50%</td>
<td>1 - 1 700 kW</td>
</tr>
</tbody>
</table>

In Table 1.2.1, it is possible to observe that the fuel cells with proton exchange membrane, alkaline and phosphoric acid electrolyte work at low temperature (lower than 200 °C), which represents an advantage from the energy point of view (less energy is required to reach the operational temperature) and the thermal stability of the materials. However, its conversion efficiencies do not exceed 50% and its generation capacities are also lower compared to other technologies such as molten carbonate fuel cells and solid oxide fuel cells [10].

Solid oxide fuel cells (SOFCs) have become one of the most attractive alternatives for large-scale electricity generation, due to their high conversion efficiency and also for their high electrical generation capacity [11]. The SOFCs are formed by a solid and dense electrolyte composed of complex metal oxides. This electrolyte has the ability to work as an ion conductor and act as an impermeable barrier to the gases. The electrolyte is sandwiched by two electrodes, anode and cathode, also formed by complex metal oxides. The electrodes must be porous to allow the diffusion of gases and the materials must have the appropriate catalytic activity to allow oxidation (anode) or reduction (cathode) depending on the case. In Figure 1.2.1 a schematic of a SOFC is shown, which is fed with hydrogen as fuel and oxygen as oxidant. Oxygen is reduced at the surface of the cathode to produce oxide ions (O\(^{2-}\)), which are conducted through the electrolyte. The fuel is oxidized on the triple phase boundaries (TPBs) in the presence of these oxide ions, and as a product of this oxidation an electric current is produced. The flow of electrons produced is conducted to the cathode, where they participate in the reduction of oxygen, thus forming a cycle of reduction-oxidation reactions which are expressed in reactions 1.2.1 and 1.2.2. The sum of both equations results in the global reaction 1.2.3.

\[
\frac{1}{2}O_2(g) + 2e^- \rightarrow O^{2-}_{\text{(electrolyte)}} \quad (1.2.1)
\]
The high operating temperatures (800 - 1000 °C) of the SOFCs promote the electrocatalysis of the oxidation and reduction half-reactions even without the presence of precious metals, increases the electrical and ionic conductivity of the materials, making them less resistive, and also due to the exothermicity of the chemical reactions, the co-generated heat can be recovered (combined heat and power-CHP-system) obtaining global energy production efficiencies close to 90% [12,13].

A subclass of SOFCs are the so-called carbon-air solid oxide fuel cells (CA-SOFCs), which use coal or biomass as fuel. The thermodynamics of these systems show that at high temperatures (above 900 °C) the theoretical efficiency of chemical to electrical energy conversion in a CA-SOFC is close to 100%. On the other hand, the fuel and products are distinct separate phases (solid and gas) making their separation and recycling of unspent fuel easier. Thus the fuel utilization can be almost 100% [14]. The compartments of the fuel and the oxidant are separated (unlike the traditional thermoelectric plants), subsequently concentrated flows of flue gas are obtained. This reduces the volume of by-product gas because it is not mixed with air, reducing the emissions of polluting gases.

The predicted high theoretical efficiency for carbon electro-oxidation makes it an attractive alternative to use in SOFC. However, the major problem in its use in solid oxide fuel cells is the physical contact between the fuel and the anode (electrode where oxidation occurs). Some proposed solutions to these problems is to improve the contact between the anode and the fuel using molten salts [9,15] as electrolyte or through the previous gasification of the coal [16,17] (which will be described with more detail in Chapter 3). In addition to these drawbacks, coal carries impurities such as sulfur and many materials are susceptible to sulfur contamination, together with deactivation by carbon deposition. Due to these reasons, several efforts are being carried out to develop new materials more resistant than the conventional SOFC anode materials (e.g. nickel-yttria stabilized zirconia) to the demanding operational conditions of a CA-SOFC.
1.3 Project Aim

The increase in global electricity demand reflected in future projections, encourages finding more efficient and sustainable electricity generation technologies over time. Carbon-air solid oxide fuel cells (CA-SOFCs) appear to be a promising alternative to conventional carbon-based power plants to produce electrical energy through the electro-oxidation of coal or carbonaceous fuels, with higher conversion efficiencies and lower environmental impact.

This PhD research project aimed to synthesize, characterize and test a new anode material for CA-SOFCs with electrical and mechanical properties comparable to that of conventional SOFCs anode materials.
Chapter 2

Fundamentals of Electrochemistry

A solid oxide fuel cell (SOFC) is an electrochemical device which converts the Gibbs free energy of the combustion reaction between a fuel and an oxidant, fed into the cell, as far as possible directly into electricity and heat (losses). Using thermodynamics, it is possible to relate the Gibbs free energy of reaction with a reversible electrical work and the heat that is reversibly transferred to the surrounding environment [18].

During the operation of a fuel cell two effects are identified to reduce the electrical power produced: the first is the ohmic resistance which generates heat, and the second is the irreversible mixing of gases which causes a voltage drop. Generally, this means that a SOFC is not able to convert completely the fuel. In a real SOFC system, heat is exchanged within the SOFC in several ways including fuel processing, air preheating, flue gas cooling, etc. Excess air is commonly required to prevent overheating, while the conversion of hydrocarbons into hydrogen and carbon monoxide often absorbs heat [18].

Before a revision of the literature on materials, fuels and types of solid oxide fuel cells, it is necessary to provide the thermodynamic and kinetic bases of the fuel cells for a better understanding of concepts that will be referenced in the subsequent chapters and sections.

2.1 Thermodynamics Principles

The first and the second law of thermodynamics allow the description of a reversible fuel cell, whereas in particular the second law of thermodynamics governs the reversibility of the transport processes. The fuel and the air are separated within the fuel cell as non-mixed gases consisting of the different components. The assumption of a reversible operating fuel cell presupposes that the chemical potentials of the fluids at the anode and the cathode are converted into electrical potentials at each specific gas composition. The Figure 2.1.1 describe that the reactants (fuel and oxidant) deliver its total enthalpy \( \sum_i \nu_i \Delta H_{i,T} \) to the fuel cell and the total enthalpy of the products \( \sum_j \nu_j \Delta H_{j,T} \) leaves the cell, where \( \nu_i \) and \( \nu_j \) correspond to stoichiometric coefficients for reactants and products correspondingly while \( \Delta H_{i,T} \) and \( \Delta H_{j,T} \) are the reactants and products enthalpy values correspondingly, at certain \( T \) temperature.

The first law of thermodynamics for open systems is given by the expression of the energy balance
Figure 2.1.1: Energy balance in a reversible fuel cell.

\[
\Delta H = \sum_j \nu_j \Delta H_{j,T} - \sum_i \nu_i \Delta H_{i,T} = Q_{\text{rev}} + W_{\text{rev}} \quad (2.1.1)
\]

The change of enthalpy, \( \Delta H \), is the maximum energy possible to obtain if the fuel is totally oxidized. From expression 2.1.1 it is possible to observe that this enthalpy change consist of work and heat. The second law of thermodynamics applied on reversible systems gives:

\[
Q_{\text{rev}} = T \cdot \Delta S_T \quad (2.1.2)
\]

Replacing equation 2.1.2 into equation 2.1.1 it is obtained an expression of enthalpy change in function of temperature of process, entropy change and reversible work:

\[
\Delta H_T = T \cdot \Delta S_T + W_{\text{rev}} \quad (2.1.3)
\]

The reversible work is the electrical work in a fuel cell. From equation 2.1.3 and the Gibbs free energy definition (equation 2.1.4), it is possible to obtain the reversible electrical work (\( W_{\text{elec,rev}} \)) from the free energy of the system:

\[
\Delta G_T = \Delta H_T - T \cdot \Delta S_T \quad (2.1.4)
\]

\[
\Delta G_T = W_{\text{rev}} = W_{\text{elec,rev}} \quad (2.1.5)
\]

Considering that one mole of fuel produce \( \nu_e \) moles of electrons, so one mole of fuel produce \( \nu_e \cdot N_A \) electrons pass round the external circuit, where \( N_A \) is Avogadro’s number. If \(-e\) is the electron charge of one electron, then the charge that flows is:

\[
-\nu_e \cdot N_A \cdot e = -\nu_e \cdot F \quad (2.1.6)
\]
where $F$ is the Faraday constant, or the charge of one mole of electrons.

If $E$ is the voltage of the fuel cell, then the electrical work done moving this charge round the circuit is:

$$W_{\text{elec}} = -\nu_e \cdot F \cdot E$$

(2.1.7)

If the system is reversible (or has no losses) and operates at a constant temperature $T$, then this reversible electrical work, $W_{\text{elec,rev}}$, done will be equal to the Gibbs free energy released. So,

$$\Delta G_T = -\nu_e \cdot F \cdot E_{\text{rev},T}$$

(2.1.8)

Thus,

$$E_{\text{rev},T} = -\frac{\Delta G_T}{\nu_e \cdot F}$$

(2.1.9)

Considering that it will not be considered the contribution for expansion work ($\Delta V = 0$) and also that the change of enthalpy represents the maximum energy produced by the chemical reactions, it is possible to obtain an expression of the thermodynamic or maximum theoretical efficiency, as the ratio between the reversible electrical work output of the system and the enthalpy of chemical reactions:

$$\Phi_{\text{Th},\text{elec}} = -\frac{\Delta G_T}{\Delta H_T} = -\frac{W_{\text{elec,rev}}}{\Delta H_T}$$

(2.1.10)

In the following subsections, the mathematical expressions for the calculation of the thermodynamic variables studied in fuel cells and the expression for the calculation of the open circuit potential will be presented.

### 2.1.1 Enthalpy of Reaction

The enthalpy of reaction $\Delta H_T$ represents the total energy produced by the chemical reactions involved in the fuel cell system. The enthalpy of the system depends on the enthalpy of each “$i$” component of the chemical reaction, $\Delta H_{i,T}$, which can be calculated with the following mathematical expression:

$$\Delta H_{i,T} = \Delta H_{i,T^o} + \int_{T^o}^{T} c_{p,i}(T) dT$$

(2.1.11)

where, $\Delta H_{i,T^o}$ and $c_{p,i}$ are the standard enthalpy and the heat capacity of species “$i$” respectively.

If change of phase of the species “$i$” occurs the mathematical expression must include the heat of change of phase, $\Delta H_{CP,i}$, and the heat capacities of phase 1, $c_{p,i}^{\text{Phase1}}$ (before the change of phase)

$^1$This means that the property was measured at standard conditions ($P^o = 1 \text{ bar}, T^o = 298.15 \text{ K}$).
and phase 2, $c_{p,i}^{\text{Phase2}}$ (after the change of phase) as shown in the equation 2.1.12

$$\Delta H_{i,T} = \Delta H_{i,T}^o + \int_{T_o}^{T_{CP,i}} c_{p,i}^{\text{Phase1}}(T) dT + \Delta H_{CP,i}^o + \int_{T_{CP,i}}^{T} c_{p,i}^{\text{Phase2}}(T) dT$$ (2.1.12)

### 2.1.2 Entropy of Reaction

The entropy of reaction $\Delta S_T$ is related to the heat produced by the fuel cell when it operates reversibly, as shown in equation 2.1.2. This thermodynamic variable is calculated in a similar way to the enthalpy and depends on the entropy of each species “i” of the chemical reaction, which is calculated according to the following mathematical expression:

$$\Delta S_{i,T} = \Delta S_{i,T}^o + \int_{T_o}^{T} \frac{c_{p,i}(T)}{T} dT$$ (2.1.13)

where $\Delta S_{i,T}^o$ is the standard entropy of species “i”. If change of phase of species “i” occurs, the equation 2.1.13 adopts the following form:

$$\Delta S_{i,T} = \Delta S_{i,T}^o + \int_{T_o}^{T_{CP,i}} \frac{c_{p,i}^{\text{Phase1}}(T)}{T} dT + \frac{\Delta H_{CP,i}}{T_{CP,i}} + \int_{T_{CP,i}}^{T} \frac{c_{p,i}^{\text{Phase2}}(T)}{T} dT$$ (2.1.14)

### 2.1.3 Gibbs Free Energy

The Gibbs free energy $\Delta G_T$ represents the electrical work produced by the fuel cell, as shown in equation 2.1.3. The value of Gibbs free energy is obtained from the equation 2.1.4 in which the values of $\Delta H_T$ and $\Delta S_T$ can be calculated by obtaining the values of enthalpy and entropy of each of the reaction components, using equations 2.1.11 to 2.1.14. Once these enthalpy and entropy values of each species have been obtained, the enthalpy and entropy of the reaction can be calculated by means of the following expressions:

$$\Delta H_T = \sum_j \nu_j \Delta H_{j,T} - \sum_i \nu_i \Delta H_{i,T}$$ (2.1.15)

$$\Delta S_T = \sum_j \nu_j \Delta S_{j,T} - \sum_i \nu_i \Delta S_{i,T}$$ (2.1.16)

where the subscripts $j$ and $i$ refer to products and reactant of the chemical reaction involved in the fuel cell, respectively.
2.1.4 Open Circuit Voltage (OCV) or Nernst Potential

The reversible potential, expressed in equation 2.1.9, shows the potential as a function of the Gibbs free energy, which is expressed in equation 2.1.4 as a function dependent on temperature. This potential is a simplification, which considers that the system operates under standard conditions respect to the activities of the species involved in chemical reactions ($a_i = 1.0$ for all species). Each of the reactants, and the products, has an associated activity. It is beyond the scope of this thesis work to give a thorough description of activity. However, in the case of gases behaving as ideal gases, it can be expressed as:

$$a_i = \frac{P_i}{P^o} \quad (2.1.17)$$

where $P_i$ is the partial pressure of the $i$ gaseous specie, $P^o$ is the standard pressure (1 bar).

The high temperature of operation of a SOFC, produces a deviation of the value of the activities of the species respect to the standard state, for which it is necessary to correct the mathematical expression of the reversible potential. The activities of the reactants and products modify the Gibbs free energy change of the reaction, and this thermodynamic function can be expressed as:

$$\Delta G_{T,P} = \Delta G_T + RT \ln \left( \frac{\prod_j P_j^{\nu_j}}{\prod_i P_i^{\nu_i}} \right) \quad (2.1.18)$$

where the subscripts $j$ and $i$ refer to products and reactant of the chemical reaction involved in the fuel cell, respectively and $\nu$ represents the stoichiometric coefficients of each species involved in the chemical reaction.

Modifying the equation in the same way that equation 2.1.9 a new expression of electrical potential is obtained:

$$E_{N,T} = \Delta E_{rev,T} + \frac{RT}{\nu_e F} \ln \left( \frac{\prod_i P_i^{\nu_i}}{\prod_j P_j^{\nu_j}} \right) \quad (2.1.19)$$

Equation 2.1.19 is called Nernst equation and the potential $E_{N,T}$ is known as Nernst potential, also frequently referred to as open circuit voltage (OCV).

2.2 Kinetic Principles

If there is no electrical component connected to the fuel cell, the potential of the cell is the open circuit voltage (OCV) or Nernst potential. When an electrical component is connected to the elec-
trodes of the fuel cell, the electric circuit is closed and a potential difference is established between the electrodes of the cell, consequently, an electric current flow (commonly expressed as electrical current density) appears. The intensity of the potential difference, when the fuel cell is operating, depends on several physical and chemical phenomena that occur within the cell, called polarization losses. It is possible to define a potential applied to the system, considering the polarization losses as shown below:

\[
E = E_{N,T} - \eta^{\text{act}}_{\text{an}} - \left| \eta^{\text{conc}}_{\text{ca}} - \eta^{\text{conc}}_{\text{an}} \right| - \Delta \phi^{\text{IR}}_{\text{total}}
\]  

(2.2.1)

where \( \eta^{\text{act}}_k \) and \( \eta^{\text{conc}}_k \) correspond to the anodic or cathodic \((k = an, ca)\) activation and concentration polarization, respectively, and \( \phi^{\text{IR}}_{\text{total}} \) are the total ohmic losses which include the electrolyte, electrodes and current collector resistances.

In the following subsections, a brief description of each polarization loss and the mathematical expressions that describe them will be presented. Finally, the equations that describe the fuel consumption, the electrical power produced and the heat generated by the fuel cell will be presented as a function of kinetic and thermodynamic parameters.

### 2.2.1 Activation Overpotential

Electrode reactions involve charge transfer as a fundamental step, in which neutral species are converted into an ion, or an ion is converted into a neutral species. Both reactions thus involve electron transfer. Considering the chemical reactions that occur in the fuel cell schematized in Figure 1.2.1, it is possible to observe that in the cathode, the charge transfer reaction involves the conversion of an oxygen molecule \( \text{O}_2 \) into oxide ions \( \text{O}^{2-} \), while in the anode the process of oxidation of the hydrogen produce an electrical current which is conducted to the cathode, producing the reduction of the oxygen. A portion of the fuel cell potential is lost to overcome the activation energy barrier related to reaction that transfers the electrons to or from the electrode and the electrode|electrolyte interfaces.

This process, apparently depends only on the ability of the electrodes to carry out the charge transfer reactions, however the transport of gases also plays a very important role (in this case, \( \text{H}_2 \) at the anode, \( \text{O}_2 \) at the cathode) which must be correctly distributed to the porous electrodes. In the case that there are no diffusional problems, the mathematical equation that relates the activation overpotential \( \eta^{\text{act}}_k \) \((k = an, ca)\) with the current density \( j \) can be expressed by the Butler-Volmer equation:

\[
\begin{align*}
    j &= j_{0,k} \left[ \exp \left( \frac{\alpha_k \nu_e F \eta^{\text{act}}_k}{RT} \right) - \exp \left( - \frac{(1 - \alpha_k) \nu_e F \eta^{\text{act}}_k}{RT} \right) \right] \\
    \end{align*}
\]  

(2.2.2)

where \( j_{0,k} \) is the exchange current density, \( \alpha_k \) is the charge transfer coefficient, \( \nu_e \) are the number of electrons involved in the electrochemical reactions give by stoichiometry, \( F \) is the Faraday constant, \( R \) is the gas constant, and \( T \) is the operating temperature.
The constant $\alpha_k$ is called the charge transfer coefficient and is the proportion of the electrical energy applied that is harnessed in changing the rate of an electrochemical reaction. Its value depends on the reaction involved and the material the electrode is made of and must be in the range 0 to 1.0.

The exchange current density, $j_{0,k}$, is a measure of the rate of charge transfer process and depends on the materials properties, microstructure, temperature and also the atmosphere. This kinetic parameter is an indicator of the electrocatalytic activity of the material. Large values of $j_{0,k}$ mean that the electrode reactions are fast and large current densities can be obtained with small activation overpotentials.

As it has been explained so far, the exchange current density is a crucial factor in improving fuel cell performance. An increase of this parameter can be achieved in the following ways:

- Raising the cell temperature: The exchange current density is dependent of the temperature. Thermal energy allows overcome the activation energy barrier.
- Using more effective catalysts: The catalysts decreases the activation energy barrier of the reactions.
- Increasing the roughness of the electrodes: The increase of real surface area of each nominal area unit of electrode increase the $j_{0,k}$ value.
- Increasing the reactant concentration and pressure of gases: Use pure oxygen instead of air in the cathode or increase the gases feeding pressure, produce an increasing catalyst site occupancy.

### 2.2.2 Concentration Overpotential

Considering that the oxygen at the cathode of the fuel cell is supplied in the form of air, during the fuel cell operation a slight reduction in the concentration of the oxygen in the region of the electrode is observed, as the oxygen is consumed. The extent of this change in concentration will depend on the current being taken from the fuel cell, and on physical factors relating to how well the air around the cathode can circulate, and how quickly the oxygen can be replenished. This change in concentration will cause a reduction in the partial pressure of the oxygen.

The same phenomenon occurs at the anode of the fuel cell, supplied with hydrogen, which will experience a slight drop in pressure while this fuel is consumed during the operation of the cell. In addition, as hydrogen is consumed, water appears as a product of the hydrogen oxidation reaction. The appearance of water in the fuel stream that feeds the anode, produces the dilution of the hydrogen stream, gradually decreasing its partial pressure.

In both cases, the reduction in gas pressure will result in a reduction in the cell voltage. This potential loss is called concentration overpotential. This situation creates a concentration gradient of the species between the bulk stream and the electrode|electrolyte, thus the total concentration overpotential can be expressed as the equation 2.2.3 [18]:

$$ |\eta_{\text{total}}^{\text{conc}} | = \text{OCV}^{\text{react}} - \text{OCV}^{\text{bulk}} $$ (2.2.3)
where \textit{react} means the reaction zone of the electrode. The concentration overpotential \( \eta_{k}^{\text{conc}} \) of anode and cathode \((k = an, ca)\) can be estimated using the Nernst equation as follows:

\[
\eta_{an}^{\text{conc}} = \frac{RT}{2F} \ln \left( \frac{P_{H_2}^{\text{bulk}} P_{H_2}^{\text{react}}}{P_{H_2}^{\text{bulk}} P_{H_2}^{\text{react}}} \right)
\]

(2.2.4)

\[
|\eta_{ca}^{\text{conc}}| = \frac{RT}{2F} \ln \left( \left[ \frac{P_{O_2}^{\text{bulk}}}{P_{O_2}^{\text{react}}} \right]^{1/2} \right)
\]

(2.2.5)

The determination of the concentration overpotentials from equations [2.2.4] and [2.2.5] is a difficult work because it is complicated in practice to measure the partial pressure of gases at the reaction sites. Another formulation express these overpotentials as function of the limiting current [18, 19]. The limiting current density \((j_l)\) corresponds to the current density at which the partial pressure of the reacting species at the reaction sites tends to zero. The concentration overpotential as function of the limiting current is presented as follows [20]:

\[
\eta_{an}^{\text{conc}} = \frac{RT}{2F} \ln \left( \frac{1}{1 - \frac{j}{j_{l,H_2}}} \right)
\]

(2.2.6)

\[
|\eta_{ca}^{\text{conc}}| = \frac{RT}{4F} \ln \left( \frac{1}{1 - \frac{j}{j_{l,ca}}} \right)
\]

(2.2.7)

where \(j_{l,H_2}\) and \(j_{l,H_2O}\) are the limiting current densities of hydrogen and water in the anode and \(j_{l,ca}\) is the limiting current density of oxygen in the cathode. The limiting current densities of each component are expressed by the equations:

\[
\hat{j}_{l,H_2} = \frac{2FD_{H_2}^{\text{eff}} P_{H_2}^{\text{bulk}}}{RT \delta_{an}}
\]

(2.2.8)

\[
\hat{j}_{l,H_2O} = \frac{2FD_{H_2O}^{\text{eff}} P_{H_2O}^{\text{bulk}}}{RT \delta_{an}}
\]

(2.2.9)

\[
\hat{j}_{l,ca} = \frac{4FD_{O_2}^{\text{eff}} P_{O_2}^{\text{bulk}}}{RT \delta_{ca}}
\]

(2.2.10)

where \(D_{i}^{\text{eff}}\) is the effective diffusivity of the component \(i\), and \(\delta_{k} (k = ca, an)\) is the boundary layer thickness in the cathode or anode.
2.2.3 Ohmic Potential Losses

Ohmic losses are produced due to the electrical resistance of the electrodes (cathode and anode), other components of fuel cell (interconnectors, current collectors, etc), and the resistance to the flow of ions in the electrolyte. The ohmic potential drop, \( \Delta \phi^{IR}_{\text{total}} \), produced in a fuel cell of total resistance \( R_{\text{cell}} \), follows the Ohm’s law, being simply proportional to the current density:

\[
\Delta \phi^{IR}_{\text{total}} = I R_{\text{cell}}
\]  
(2.2.11)

Equation 2.2.11 can be re-written as function of electrical conductivity of the fuel cell components as follows:

\[
\Delta \phi^{IR}_{\text{total}} = I \sum_{i} \frac{\delta_i}{A_i \sigma_i}
\]  
(2.2.12)

where, \( \sigma_i \), \( \delta_i \) and \( A_i \) are the electrical conductivity of component \( i \) of the fuel cell, the path length of the fuel cell component and the cross sectional area of this component, correspondingly. In the most of fuel cells the resistance is mainly caused by the electrolyte, though the cell interconnects or current collectors can also be important [21]. From equation 2.2.12 it is easy to observe that a form to reduce the ohmic overpotential in a fuel cell is to use electrodes and electrical components with the highest possible electrical conductivities, make the electrolyte as thin as possible, increase the cross-sectional area of the cell components and decrease the path length of the components [21].

2.2.4 Fuel Cell Power Density and Heat Generation

The operating voltage of the fuel cell at a given current density can be determined by estimating the different potential losses at a given current density. Once the potential losses have been calculated, the potential of the cell is calculated with the equation 2.2.11. For each current density value, a cell voltage is obtained, then plotting this data, a polarization curve is obtained, as shown in Figure 2.2.1.a.

The electrical power density \( P_{\text{elec}} \) produced by the SOFC can be calculated from the operating cell potential and current density using the equation:

\[
P_{\text{elec}} = j \cdot E
\]  
(2.2.13)

Plotting the electrical power density at different current density values it is obtained a curve like that shown in Figure 2.2.1.b. From this curve, the maximum electrical power density value is obtained. This point represents the optimal operating current density.

The different irreversibilities present during the operation of a SOFC are transformed into heat. If this heat is added to the heat produced by entropic losses in the global fuel oxidation reaction (in
2.2.5 Voltage Efficiency, Fuel Utilization and SOFC Efficiency

The operating voltage of the fuel cell is different from the value of the open circuit potential, due to the different polarization losses that occur within the fuel cell as shown in Figure 2.2.1.a. Considering this, it is possible to define a fuel cell voltage efficiency $\Phi^V$, as the ratio between the operating voltage and the Nernst potential, as expressed below:

$$\Phi^V = \frac{E}{E_N}$$

(2.2.15)

On the other hand, the fuel that is fed to the fuel cell, may not be completely consumed within the fuel cell, due to kinetic or transport issues. Therefore, it is possible to define a fuel utilization $X_f$ as the ratio between the fuel consumed by the fuel cell and the fuel that was fed to the fuel cell, as follow:

$$X_f = \frac{x_{\text{in}}^{\text{fuel}} - x_{\text{out}}^{\text{fuel}}}{x_{\text{in}}^{\text{fuel}}}$$

(2.2.16)
where \( x_{\text{fuel}}^{\text{in}} \) and \( x_{\text{fuel}}^{\text{out}} \) represent the mole fraction of the fuel at the inlet and the exit of the fuel cell, respectively.

The overall SOFC efficiency \( \Phi_{\text{SOFC}} \) can be defined in terms of the thermodynamic efficiency \( \Phi_{\text{Th}}^{\text{elec}} \), the voltage efficiency \( \Phi^{\text{V}} \) and the fuel utilization \( X_f \), as follows:

\[
\Phi_{\text{SOFC}} = \Phi_{\text{Th}}^{\text{elec}} \cdot \Phi^{\text{V}} \cdot X_f \tag{2.2.17}
\]

### 2.3 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is used to identify the physical characteristics of a system. The method is to model the system using what is called an electrical equivalent circuit, where each element of the circuit is supposed to correspond to a physical characteristic of the system under study. Fitting the impedance data using an electrical model gives access to the values of the elements and hence of the physical characteristics.

In this section it is presented a brief overview about the concepts in EIS technique and the mathematical treatment used in this research work.

#### 2.3.1 Fundamentals of EIS

The electrical resistance is the ability of the circuit to resist the flow of electrical current. The resistance defined in terms of current and potential is expressed by the Ohm’s law (see equation 2.3.1).

\[
R = \frac{E}{I} \tag{2.3.1}
\]

The Ohm’s law represents the behavior of ideal resistors. An ideal resistor has several simplifying properties:

- It follows Ohm’s law at all current and voltage levels.
- Its resistance value is independent of frequency.
- AC current and voltage signals through a resistor are in phase with each other.

However, there are other components of electrical circuits that do not follow Ohm’s law and in addition the applied AC voltage has a different phase than the current flowing through these electrical components; these types of electrical elements correspond to capacitors and inductors. The concept of resistance is not enough to describe the electrical behavior of those circuit elements that do not follow the Ohm’s law. The impedance is a more general concept, which is a measure of the ability of a circuit or circuit element to resist the flow of electrical current, but unlike the resistance, is not limited by the simplifying properties presented in an ideal resistor.
The electrochemical impedance can be measured by applying an AC potential to an electrochemical cell and measuring the AC current signal response. The magnitude of the AC potential signal is normally small. This is done so that the cell’s response is pseudo-linear. In a linear (or pseudo-linear) system, the current response to a sinusoidal potential will be a sinusoid at the same frequency but shifted in phase (see Figure 2.3.1).

![Figure 2.3.1: Sinusoidal current response in a linear system.](image)

The excitation potential signal, expressed as a function of the time, has the mathematical form of equation 2.3.2.

\[
E(t) = E_0 \sin(\omega t) \tag{2.3.2}
\]

where \(E(t)\) is the potential as function of the time \(t\), \(E_0\) is the amplitude of the perturbation signal, and \(\omega\) is the angular frequency. The relationship between the angular frequency \(\omega\) (expressed in radians/second) and the frequency (in Hz) is shown in equation 2.3.3.

\[
\omega = 2\pi f \tag{2.3.3}
\]

In a linear system, the current response signal \(I(t)\) is shifted in a phase angle \((\phi)\) and has a different amplitude \(I_0\). The current response signal is represented by equation 2.3.4.

\[
I(t) = I_0 \sin(\omega t + \phi) \tag{2.3.4}
\]
Then, it is possible to calculate the impedance of the system using an analogous Ohm’s law expression (equation 2.3.5).

\[
Z = \frac{E(t)}{I(t)} = \frac{E_0 \sin(\omega t)}{I_0 \sin(\omega t + \phi)} = Z_0 \frac{\sin(\omega t)}{\sin(\omega t + \phi)} \tag{2.3.5}
\]

With the Euler relationship it is possible to express the impedance of the electrochemical cell as a complex function. The potential and current response are expressed by equation 2.3.6 and 2.3.7 correspondingly.

\[
E(t) = E_0 \exp(i\omega t) \tag{2.3.6}
\]

\[
I(t) = I_0 \exp(i\omega t - \phi) \tag{2.3.7}
\]

The impedance is then represented as a complex number,

\[
Z(\omega) = \frac{E}{I} = Z_0 \exp(i\phi) = Z_0 (\cos(\phi) + i\sin(\phi)) \tag{2.3.8}
\]

The expression of \(Z(\omega)\) is composed of a real and an imaginary part. Plotting the real part in the X-axis and the imaginary part in the Y-axis, the Nyquist plot is obtained. The imaginary part in Nyquist plot is negative and each point of the curve is the impedance at one frequency (see Figure 2.3.2).

![Figure 2.3.2: Nyquist plot representation.](image)

Another representation method is the Bode plot. In the Bode plot, the impedance is plotted against the frequency value in a logarithmic-X-axis; in that case, the absolute value of the impedance vector \(|Z|\) (in logarithmic scale) and the phase angle shift are plotted in different Y-axis, as shown the Figure 2.3.3.
2.3.1.1 Linearity of the Systems

Electrical circuit theory distinguishes between linear and non-linear systems (circuits). Impedance analysis of linear circuits is much easier than analysis of non-linear ones.

A linear system is one that possesses the property of the superposition. If the input consists of the weighted sum of several signals, then the output is simply the superposition, that is, the weighted sum, of the responses of the system to each of the signals. Mathematically, let $y_1(t)$ be the response of a continuous time system to $x_1(t)$ and let $y_2(t)$ be the output corresponding to the input $x_2(t)$. Then the system is linear if:

- The response to $x_1(t) + x_s(t)$ is $y_1(t) + y_2(t)$.
- The response to $ax_1(t)$ is $ay_1(t)$.

For a potentiostated electrochemical cell (as is the case of fuel cells), the input is the potential and the output is the current.

Generally the electrochemical systems are not linear, however using a small portion of the current-voltage curve (I-V curve) is possible to achieve pseudo-linearity as is depicted in Figure 2.3.4.

In normal EIS practice, a small amplitude (1 to 10 mV) AC signal is applied to the cell. With such a small potential signal, the system is pseudo-linear. The small perturbation usually oscillates around the open circuit voltage (OCV). This feature prevents the polarization of the material since it has been reported that in some systems the polarization produces irreversible changes to the surface of the material and one of the characteristics of the EIS is that it is a non-destructive technique. A small perturbation around the OCV produces small changes that are reversible in the system [22].
2.3.1.2 Steady State Systems

Measuring an EIS spectrum takes time (often up to many hours). The system being measured must be at a steady state throughout the time required to measure the EIS spectrum. A common cause of problems in EIS measurements and analysis is drift in the system being measured.

In practice a steady state can be difficult to achieve. The cell can change through adsorption of impurities, growth of an oxide layer, coating degradation, or temperature changes, to list just a few factors.

Standard EIS analysis tools may give inaccurate results on a system that is not at steady state.

2.3.1.3 Electrical Circuit Elements

EIS data are commonly analyzed by fitting to an equivalent electrical circuit model. Most of the circuit elements in the model are common electrical elements such as resistors, capacitors, and inductors. To be useful, the elements in the model should have a basis in the physical electrochemistry of the system. As an example, most fuel cells models contain a resistor that models the Ohmic electrolyte resistance.

Table 2.3.1 lists the common circuit elements, the equation for their current versus voltage relationship, and their impedance.

<table>
<thead>
<tr>
<th>Component</th>
<th>Current-Voltage relation</th>
<th>Impedance expression</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistor</td>
<td>$E = IR$</td>
<td>$Z = R$</td>
</tr>
<tr>
<td>Capacitor</td>
<td>$I = CdE/dt$</td>
<td>$Z = 1/i\omega C$</td>
</tr>
<tr>
<td>Inductor</td>
<td>$E = LdI/dt$</td>
<td>$Z = i\omega L$</td>
</tr>
</tbody>
</table>

Notice that the impedance of a resistor is independent of frequency and has no imaginary compo-
The impedance of an inductor increases as frequency increases. Inductors have only an imaginary impedance component. As a result, the current through an inductor is phase-shifted -90 degrees with respect to the voltage.

The impedance versus frequency behavior of a capacitor is opposite to that of an inductor. A capacitor’s impedance decreases as the frequency is raised. Capacitors also have only an imaginary impedance component. The current through a capacitor is phase-shifted 90 degrees with respect to the voltage.

The different components of the circuit can be summed depending on the arrangement of the electrical connections. The elements can be connected in series (a) and parallel scheme (b) (see Figure 2.3.5).

![Figure 2.3.5: Scheme of different arrangements of connections of electrical circuit elements.](image)

The mathematical expression of the equivalent impedance ($Z_{eq}$) that represent the sum of the impedances of each circuit arrangement is shown in equation 2.3.9 for series connection and equation 2.3.10 for parallel connection.

$$Z_{eq} = Z_1 + Z_2 + Z_3 \quad (2.3.9)$$

$$\frac{1}{Z_{eq}} = \frac{1}{Z_1} + \frac{1}{Z_2} + \frac{1}{Z_3} \quad (2.3.10)$$

### 2.3.1.4 Electrochemical Cell Circuit Elements

The elements traditionally used in the modeling of electrochemical cells are defined below.

**Electrolyte Resistance**: Solution resistance is often a significant factor in the impedance of an electrochemical cell. In fuel cells with well designed electrodes (reasonable area specific polarization resistance-ASPR-values), the electrolyte is the most important reason of Ohmic losses in the cell.
CHAPTER 2. FUNDAMENTALS OF ELECTROCHEMISTRY

In a bounded area with area, \( A \), and length, \( l \), carrying a uniform current, the resistance is defined as:

\[
R_{\text{electrolyte}} = \frac{\rho_e l}{A}
\]  
(2.3.11)

where \( \rho_e \) is the resistivity of the electrolyte; the reciprocal value of the resistivity represents the ionic conductivity of the electrolyte, \( \sigma \).

**Charge Transfer Resistance:** The charge transfer resistance is associated with a single, kinetically-controlled electrochemical reaction. The kinetics of this reduction/oxidation reaction can be expressed by the Butler-Volmer equation 2.2.2. When the overpotential, \( \eta \), is very small and the electrochemical system is at equilibrium (stable OCV values), the expression for the charge-transfer resistance can be expressed as:

\[
R_{ct} = \frac{RT}{\nu_e F j_0}
\]  
(2.3.12)

where \( R \) is the gas ideal constant, \( T \) is the temperature, \( \nu_e \) is the number of electrons involved in the electrochemical reactions, \( F \) is the Faraday constant, and \( j_0 \) is the exchange current density, a valuable parameter related to reaction kinetics.

**Diffusion:** Diffusion also can create an impedance called a Warburg impedance. This element depends on the frequency of the potential perturbation. The equation for the “infinite” Warburg impedance is:

\[
Z_W = \sigma_W (\omega)^{-\frac{1}{2}} (1 - i)
\]  
(2.3.13)

On a Nyquist Plot the Warburg impedance appears as a diagonal line with an slope of 45 degrees. On a Bode Plot, the Warburg impedance exhibits a phase shift of 45 degrees.

The \( \sigma_W \) coefficient is defined by equation 2.3.14:

\[
\sigma_W = \frac{RT}{\nu_e^2 F^2 A \sqrt{2}} \left( \frac{1}{C^*_{O\sqrt{D_O}}} + \frac{1}{C^*_{R\sqrt{D_R}}} \right)
\]  
(2.3.14)

where \( C^*_i \) correspond to the concentrations of the oxidant or reducing agent in the bulk of solution of gas flow, and \( D_i \) is the diffusion coefficient of the oxidant or reducing species.

The Warburg impedance in many cases do not represent the impedance data with an adequate fit factor when the electrodes are thin films or porous surface. In this cases it is replaced by the bounded Warburg impedances or porous bounded Warburg impedances.
We can examine the Warburg impedance in terms of concentration gradients near the electrode surface. At high frequencies, the AC potential perturbation changes rapidly, generating minimal changes to the surface concentration of the two forms of the redox couple. As such, there is essentially no dependence of the electrochemical reaction rate on the transport of either species to the electrode surface. This is depicted schematically in Figure 2.3.6a [23].

In contrast, the surface concentrations of the two forms of the redox couple are significantly altered when a sufficiently low frequency AC perturbation is applied as enough time has passed to deplete the reactant proximal to the electrode. In this case, the concentrations of the two forms reach a steady-state at the electrode surface, with the local environment being depleted of the reactant, while the product concentration has built-up. This is depicted in Figure 2.3.6b [23].

**Constant Phase Element (CPE):** Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element. The presence of non ideal capacitances produce depressed semi-circles in the Nyquist plot. The mathematical expression of CPE impedance is shown in equation (2.3.15).

\[ Z_{CPE} = \frac{1}{(i\omega)^{\alpha_{CPE}} Y_0} \]  

(2.3.15)

where \( \alpha_{CPE} \) is a deviation factor of pure capacitor behavior (1 for capacitance) and \( Y_0 \) is a capaci-
The CPE value a parameter of great importance in solid state phenomena studies. This value is altered by adsorption processes and ionic transport which can be used as fingerprint of physical processes [24].

2.3.1.5 Randles Circuit

The simplified Randles cell is one of the most common cell models. It includes an electrolyte resistance, a capacitor and a charge transfer (or polarization) resistance. The capacitance is in parallel with the charge-transfer resistance. In addition to being a useful model in its own right, the simplified Randles cell is the starting point for other more complex models.

The equivalent circuit for a Simplified Randles Cell is shown in Figure 2.3.7.

![Simplified Randles circuit](image)

Figure 2.3.7: Simplified Randles circuit.

The curve obtained from the Randles circuit represented in a Nyquist plot is shown in Figure 2.3.8.

![Nyquist plot of the simplified Randles circuit](image)

Figure 2.3.8: Nyquist plot of the simplified Randles circuit.

The simplified Randles circuit, represent physically an electrochemical cell with kinetic control. If diffusional process are involved in the system, the rate determining step may depend on kinetic and diffusional control. The Randles circuit represent this physical situation introducing a Warburg element (Figure 2.3.9), and the representation of the EIS data in a Nyquist plot are shown in the
The straight line is associated to the influence of the infinite Warburg impedance, which represent the diffusional control.

Figure 2.3.9: Randles circuit with Warburg element.

Figure 2.3.10: Nyquist plot of the Randles circuit, including the effect of the Warburg element.

2.3.2 Complex Non-Linear Least Square (CNLS) Analysis

A first analysis of the Nyquist and Bode graphs can give an initial idea of the possible physical phenomena that might be present in the electrochemical cell under study. From this first graphical analysis, an equivalent circuit, according to the possible physical phenomena found, should be proposed.

An equivalent circuit provides a mathematical expression of the total system impedance, which is dependent on the frequency of the perturbation applied to the system. The mathematical function obtained from the proposed equivalent circuit is fitted to the experimental data by parameter adjustment.

An important mathematical tool is the non-linear least squares fitting method, developed by Marquardt and Levenberg [25], which became the basic engine of several data analysis softwares [25]. The Complex Non-Linear Least Squares (CNLS) method focuses on minimizing the object function $S$ with respect to the parameters $a_k$ of the model function $\hat{Z}(\omega, a_k)$:
\[ S = \sum_{i=1}^{N} w_i \left\{ [Z_{Re,i} - Z_{Re}(\omega_i, a_k)]^2 + [Z_{Im,i} - Z_{Im}(\omega_i, a_k)]^2 \right\} \] (2.3.16)

where \( Z_{Re,i} + iZ_{Im,i} \) represents the measured impedance at frequency \( \omega_i \) and \( w_i \) is the weight factor. An important control tool is the distribution of the residuals versus frequency. Using function weighting the residuals are defined by:

\[ \Delta_{Re,i} = \frac{Z_{Re,i} - Z_{Re}(\omega_i, a_k)}{|Z(\omega_i, a_k)|}, \quad \Delta_{Im,i} = \frac{Z_{Im,i} - Z_{Im}(\omega_i, a_k)}{|Z(\omega_i, a_k)|} \] (2.3.17)

For a good match between data and mathematical model, the residuals should be randomly distributed around the logarithmic frequency axis as shown in Figure [2.3.11]

![Residuals plot](image)

Figure 2.3.11: Residuals plot of a CNLS-fit.

A limitation of the Marquardt and Levenberg algorithm is that the calculation routine requires initial values of the parameters close to the optimal values (deviations less than 50%). Because of this limitation, some researchers have preferred the more robust fit routine based on the Nelder and Mead algorithm (also known as the Simplex routine), which does not put restrictions on the initial parameter values [25].

### 2.3.3 EIS Data Validation: Kramers-Kronig Relations

Sometimes it will be difficult to obtain an acceptable match between experimental measurement and mathematical model (obtained from the equivalent circuit). The reason can be an inadequate model function or data that is corrupted by a systematic deviation. The evaluation of the quality of experimental data obtained in EIS experiments is essential to achieve a good fit of the proposed mathematical model to the experimental impedance data set.

The most common sources of error during the measurement of an electrochemical impedance spectrum of a system are: non-stationary systems, strong non-linearity (too large signal applied) or systematic errors added by the measurement system. It is important to be able to discern between
“bad” data (corrupt data) and an inappropriate model function for the CNLS-method. The Kramers-Kronig (K-K) relations present a very useful tool for data checking. Data that complies with the Kramers-Kronig transformation rules must be:

- Linear: The system obeys Ohm’s law. The value of impedance is independent of the magnitude of the applied perturbation.
- Stable: The system does not change with the time and returns to its original state after the perturbation is removed.
- Causal: The response of the system is due only to the applied perturbation.

It is often the stability condition that is violated: measurements are taken too quickly after, for example, a temperature change, partial pressure or polarization. The K-K relations are very effective in testing data corrupted by non-steady state behavior.

The Kramers-Kronig rules show the relation between the imaginary and real part of a frequency dispersion. Any real value, \( Z_{\text{real}}(\omega) \), can be derived from the imaginary part:

\[
Z_{\text{real}}(\omega) = R_\infty + \frac{2}{\pi} \int_0^\infty \frac{xZ_{\text{im}}(x) - \omega Z_{\text{im}}(\omega)}{x^2 - \omega^2} dx
\] (2.3.18)

where \( R_\infty = Z_{\text{real}}(\omega = \infty) \). Similarly the imaginary part, \( Z_{\text{im}}(\omega) \), is obtained from the real part by:

\[
Z_{\text{im}}(\omega) = \frac{2\omega}{\pi} \int_0^\infty \frac{Z_{\text{real}}(x) - Z_{\text{real}}(\omega)}{x^2 - \omega^2} dx
\] (2.3.19)

The Kramers-Kronig transformation of the experimental data calculates the spectrum of a linear, stable, and causal circuit. No model is assumed. The real part of the experimental data is used to calculate the imaginary part of a linear, stable, and causal circuit. Likewise, the imaginary portion of the experimental data is used to calculate the real part of a linear, stable, and causal circuit. The Kramers-Kronig transformation is shown on the Bode and Nyquist plots. If the Kramers-Kronig transformation and the experimental data do not agree, then the sample may exhibit non-linearity, instability or the influence of unknown variables (non-causal) [26].

To analyze the results of the Kramers-Kronig test it is necessary to observe the Nyquist or Bode diagrams with the Kramer-Kronig transformation curve, and detect those experimental points that are located out of the curve, which are probably corrupt data points. In addition it is necessary to study the residual curves for imaginary and real impedance part. This graphic shows the residual expressed as \( Z_{\text{experimental}} - Z_{\text{calculated}} \big/ |Z| \), also called fractional residual, and present the \( \chi^2 \) value or goodness of fit (GOF). While the GOF value is lower, the experimental data has higher quality and exist major possibilities of a successfully equivalent circuit fit, however, goodness of fit values in the magnitude order of \( 10^{-4} \) are considered acceptable quality data, but not excellent, while a data with a residual unity value over 5% will be considered as corrupt data [25].
2.3.4 Equivalent Circuit Determination

The choice of an electrical circuit requires prior knowledge of the impedance of each element and this is why impedance can be considered difficult to use at first.

Distribution of relaxation times (DRT) is an analysis method which turns impedance data that are function of the frequency into a distribution of the time constants involved in the considered system. DRT can be considered as a tool to help finding an equivalent circuit that should be used to fit impedance data.

In order to explain the basic fundamentals of how DRT analysis elucidates the amount of physical processes involved in the electrochemical system, let’s consider a Voigt circuit (see Figure 2.3.12). The Voigt circuit consists of several units of parallel R(C) circuits, connected in series [27]. The flowing current is equal for all meshes (R(C) subcircuits) and the phenomena modelled by each mesh start instantaneously [28]. Each R(C) subcircuit has its own time constant ($\tau_k$), and therefore each physical process of the system is related to a specific time constant [28]. Voigt model is used basically for description of the impedance of solid state bulk samples, specially in solid oxide fuel cells studies [28]. The structure of the Voigt circuit is frequently modified by the addition of resistances or special elements such as Warburg impedances, however, each of the meshes of the Voigt electrical circuit remains related to a unique time constant value. Hence, the determination of the number of time constants in the system is an indicator of the physical phenomena present in the electrochemical system under study [28].

Considering a Voigt circuit formed by $N$ units of parallel R(C) subcircuits, the mathematical expression of the equivalent impedance for this circuit is expressed by equation 2.3.20.

\[
Z(\omega) = \sum_{k=1}^{N} \frac{R_k}{1 + i\omega\tau_k}
\]  

(2.3.20)

where $\tau_k = R_kC_k$, corresponding to constant time of the parallel R(C) circuit.

In Figure 2.3.12, the red dots correspond to the experimental impedance dataset. The solid line corresponds to the mathematical model proposed, which comes from a Voigt circuit of 11 meshes (11 parallel R(C) subcircuits). When an 11-element Voigt circuit is adjusted to the experimental impedance data by using a CNLS method, 11 different values of resistances, capacitances and consequently 11 different values of time constants are obtained. While the $N$ number of R(C) elements
in the Voigt circuit increase, the fit is better.

By plotting the resistance values $R_k$ as a function of the logarithm of the time constant ($\log(\tau_k)$), a discrete distribution of the time constants is obtained, as shown in Figure 2.3.13b. Note that the resistances values in function of the $\log(\tau)$ follows a Gaussian behavior. The peak in the distribution shown in Figure 2.3.13b, means that at a specific frequency a physical phenomenon controls the experiment and produces the maximum impedance. This result means that although 11 elements were used in the proposed Voigt circuit to adjust the experimental data, only 1 equivalent circuit is sufficient to model the experimental data.

![Figure 2.3.13](image)

Figure 2.3.13: Finite Voigt circuit fitted to experimental data and DRT transformation. a) Finite Voigt fit with $N = 11$ R(C) elements and b) finite distribution of constant times.

Now, consider a Voigt circuit with an infinite number of R(C) elements. It can also be used to fit the impedance data shown in Figure 2.3.13a but instead of discrete values of $R_k$ vs. $\tau_k$, we have a continuous variation of $R(\tau)$, that is to say a distribution function.

The impedance of infinite Voigt circuit [29] is expressed as:

$$Z(\omega) = \int_0^{\infty} \frac{\gamma(\tau)}{1 + i\omega \tau} d\tau$$

(2.3.21)

with $\gamma(\tau)$ the distribution function of the relaxation times $\tau$, which is characteristic of the system under study. If the analytical expression of the impedance of the system $Z(\omega)$ is known, it is possible to use the equation 2.3.21 to express the function $G(\tau)$. For instance, for a R(CPE) parallel circuit (a resistor $R$ connected in parallel with a constant phase element-CPE), the distribution function is expressed by equation 2.3.22 [29].

$$\gamma_{R(CPE)}(\tau) = \frac{R}{2\pi} \frac{\sin((1 - \alpha_{CPE})\pi)}{\cosh(\alpha_{CPE}\ln(\tau/R_{CPE})) - \cos((1 - \alpha_{CPE})\pi))}$$

(2.3.22)

$$\tau_{R(CPE)} = \left(RQ_{CPE}\right)^{\alpha_{CPE}}$$

(2.3.23)
For a given set of parameters $R$, $Q_{CPE}$ and $\alpha_{CPE}$, a $\gamma(\tau)$ plot is obtained. The value of the time constant $\tau$, when the value of $\gamma(\tau)$ is maximum ($\gamma_p$, value of function $\gamma(\tau)$ at peak) corresponds to the value of the time constant of the circuit $\tau_{R(CPE)}$. The value of $\gamma_p$ is expressed by equation \[ (2.3.24) \]

$$
\frac{d\gamma}{d\tau} = 0 \Rightarrow \gamma_p = \frac{R}{2\pi} \tan \left( \frac{\alpha\pi}{2} \right)
$$

The typical representation of the $\gamma(\tau)$ function is a Gaussian distribution as shown Figure 2.3.14.

In the case of experimental data, the mathematical expression of the impedance is not known a priori. This means that equation \[ 2.3.21 \] must be numerically solved using experimental impedance values to extract $\gamma(\tau)$. There are a few methods proposed in the literature to solve this equation: i) Fourier transform \[ 30 \], ii) Maximum entropy \[ 31 \], iii) Bayesian approach \[ 32 \], iv) Ridge and lasso regression methods \[ 33 \] and finally v) Tikhonov regularization \[ 34 \]. Currently the most widely used mathematical method for deconvolution of impedance spectra is Tikhonov regularization. Wan et al. in 2005, developed a MATLAB-based software called DRTtools, extensively used in DRT studies \[ 29 \].

DRT analysis is not only used to determine the amount of physical phenomena present in the electrochemical system under study, but it is also used to determine the effect of specific variables on the physical phenomena studied \[ 35 \].
Chapter 3

Literature Review

Currently, the world needs energy generation solutions that can fulfill the growing demand for electrical energy and in this scenario fuel cells, appear as a promising technology for small and large-scale power generation.

As was stated in the introductory chapter, fuel cell is an electrochemical device that converts the chemical energy of a fuel, commonly hydrogen (can be also hydrocarbons, charcoal, etc.) and an oxidant (air or oxygen) into electricity very efficiently, without combustion and with little or no emission of pollutants \[11, 19, 21\]. Solid oxide fuel cells are considered by many developed countries as an alternative solution for energy generation in the near future. Among the different types of fuel cells described in Section 2.2, the solid oxide fuel cells (SOFCs) stand out from the rest because they are electricity generation systems that operate at high temperature. This feature, favors the kinetics of chemical reactions and reduces other polarization losses described in Section 2.2, consequently, they exhibit a very high efficiency. However, the high operating temperature imposes severe restrictions on materials, which can otherwise be effectively used for construction of the complete device. Degradation of fuel cell performance occurs over a period of time and is related to the deterioration of material properties and interfacial reactions between various fuel cell components \[36\]. This imposes a great challenge for the development of new materials for solid oxide fuel cells, which have the capacity to withstand severe working conditions in the long term, showing good chemical and mechanical stability. Different materials, designs and fabrication technologies have been developed and tested to make it more cost effective and stable \[11\].

In this chapter, a literary review will be presented on the materials used in solid oxide fuel cells and their mechanical and electrical properties, emphasizing the fundamentals and advances in carbon-air solid oxide fuel cells, which represent one of the most promising high-efficiency electric power generation technology.

3.1 Solid Oxide Fuel Cells

The name solid oxide fuel cells comes from the type of material from which the electrodes (cathode and anode) and the electrolyte are made. The components of a SOFC are made of metal oxides (ceramics) or by composites of these, which must be able to withstand the high operating temperatures (800 °C - 1 000 °C).
The basic operation involves systematic oxidation and reduction reactions. These reactions are carried out on the surface of the electrode materials. In SOFCs, the conducting species are the oxide ions (O$_2^-$) which are produced when the gaseous oxygen gets reduced at the cathode by taking electrons. These oxide ions are conducted through a solid electrolyte and carried to the anode surface. In a high temperature range, yttria stabilized zirconia (YSZ) electrolyte is mostly used for conduction of oxide ions. At the anode, oxide ions react with the fuel fed and produce water (if H$_2$ is fed) and carbon dioxide (CO$_2$) (if the fuel is coal, biomass or an hydrocarbon).

The configuration of a SOFC consists of a solid state electrolyte sandwiched between two electrodes (anode and cathode) as shown in Figure 1.2.1. All of these components must work in a concerted manner. The materials must have the capacity to carry out the oxidation and reduction reactions, with adequate catalytic activity; in addition they need to present a high fracture toughness under high temperature conditions and similar thermal expansion coefficients to avoid cracking in the different components of the cell. However, these are not the only challenges that SOFC researchers face, since these materials must be chemically stable to oxidant and reducing environments under high temperature conditions in the long-term operation (40 000 - 50 000 h) [36-38]. Due to these reasons, SOFCs are still a technology in development. Each year new materials are born for their application in SOFCs, with the aim of overcoming the limitations that this technology still has, which represents a great challenge for materials engineering.

As it was stated in the introductory, different criteria are required for the design of each material in SOFCs applications, depending on the operational conditions to which they are subjected and the electric power production capacity expected for these systems. Different materials used in different SOFC components along with their requirements are discussed below.

### 3.1.1 Electrolyte Materials

The electrolyte is the component responsible for the transport of ions between electrodes in a SOFC. There are different solid materials for proton ions and oxide ions conduction, however the carbon-air solid oxide fuel cell system studied in this thesis require an oxide ions electrolyte conductor, thus this review is focused in oxide ion conductive electrolytes.

A material can be a good electrolyte if it meets the following requirements: i) high oxygen conductivity (i.e., > 0.1 S cm$^{-1}$) over a wide range of oxygen partial pressure is needed by electrolyte; ii) the electrolyte must be fully dense with no open porosity in order to avoid any cross diffusion of fuel and oxidant fed to the fuel cell; iii) it must be chemically inert with respect to electrodes and sealing materials as it is in contact with these materials; iv) the electrolyte must also have comparable thermal expansion coefficient (with respect to another components) and withstand high mechanical and thermal stress during operation and fabrication; and v) the electrolyte must be stable both chemically and structurally since it is exposed to extremely oxidizing and reducing environments at electrodes [11,19,39].

The charge transport through the electrolyte occurs by the movement of oxide ions through the crystal lattice. This movement is a result of thermally activated hopping of the oxide ions, moving from one crystal lattice site to its neighbor site. To allow the movement, the crystal must contain
unoccupied sites equivalent to those occupied by the lattice oxide ions, and the energy involved in
the process of migration from one site to the unoccupied equivalent site must be small, certainly less
than about 1 eV. This small barrier to migration would seem, at first glance, difficult to attain since
the oxide ions are the largest components of the lattice, with an ionic radius of 0.14 nm. However,
in certain crystal structures, oxygen defects are predominant, so oxide ions migrate in the electric
field. Examples of these crystal structures with partially occupied oxygen sites are zirconia (ZrO$_2$),
ceria (CeO$_2$) and bismite (Bi$_2$O$_3$) based oxides with fluorite structure, LaGaO$_3$-based perovskites,
derivatives of Bi$_4$V$_2$O$_{11}$ and La$_2$Mo$_2$O$_9$, perovskite- and brownmillerite-like phases (e.g., derived
from Ba$_2$In$_2$O$_5$) and (Gd, Ca)$_2$Ti$_2$O$_{7-\delta}$ [39].

The oxide ion conductivity of several metal oxides is shown in Figure 3.1.1. Among these oxides,
only a few materials have been suitable as SOFC electrolytes due to the already mentioned numer-
ous requirements of these components. These requirements limit the choice of electrolyte materials
to zirconia and ceria fluorites, and LaGaO$_3$-based perovskites. The zirconia electrolyte has been the
most favored electrolyte for SOFCs, especially those operated at temperatures above 800 °C. Sev-
eral books and numerous review articles have been written in recent years on the preparation and
properties of zirconia electrolytes [19,39,40]. The ceria electrolyte is attractive for low-temperature
(400 – 600 °C) SOFCs and as electrolyte interlayers for intermediate temperature (600 – 800 °C)
SOFCs with zirconia electrolytes [39]. In the following subsections, the main characteristics of the
electrolytes based on ceria, zirconia and LaGaO$_3$ will be reviewed.
Zirconia-based Electrolytes

The zirconia-based electrolytes are the most widely used electrolytes for SOFCs operated at high (800 – 1000 °C) and intermediate (600 – 800 °C) temperatures. Most of the SOFC systems currently being developed employ yttria- and scandia-stabilized zirconia electrolytes. This is because of their high ionic conductivity, high mechanical and chemical stability, and compatibility toward other components used in the SOFC. In addition, zirconia is abundant and relatively low in cost. Another important advantage is that zirconia ceramics exhibit a minimum electronic contribution to total conductivity in the oxygen pressure range for practical application of fuel cells: 200 atm - 10^{−30} atm [40].

Zirconia can be found in three different crystalline structures: monoclinic, tetragonal and cubic, as shown in Figure 3.1.2. The monoclinic zirconia, m-ZrO₂, is the stable form at room temperature, the cubic phase, c-ZrO₂, is stable at the high temperature, while the tetragonal phase, t-ZrO₂, is the transition state between m-ZrO₂ and c-ZrO₂. Upon heating, the m→t-ZrO₂ and t→c-ZrO₂ phase transformation occur at 1170 and 2370 °C, respectively [41]. The monoclinic and tetragonal phase transformations are accompanied by a large volume change leading to disintegration of the ceramic body during cooling from high sintering temperatures to subsequent low usage temperatures. Dopants, such as yttria (Y₂O₃), are added to stabilize the high-temperature cubic and tetragonal structures to low temperature by forming solid solutions with ZrO₂ (yttria stabilized zirconia, YSZ).

When Y³⁺ cations are used to substitute Zr⁴⁺ at the corresponding lattice sites, they also create vacancies in the oxygen sublattice (V⁰°) since Y³⁺ cations have a lower valence than Zr⁴⁺. The vacancy production can be shown in Kroger–Vink notation:

\[
Y_2O_3 \xrightarrow{ZrO_2} 2Y'_Zr + V^{°°}_O + 3O^{X}_O
\]  

The formation of oxygen vacancies, increase the oxide ion mobility in the lattice structure of YSZ. The increment in yttria content should produce an increase in ionic conductivity due to the increase of oxygen vacancies (charge carrier), however, the YSZ exhibit its maximum ionic conductivity when the yttria-dopant content is approximately 8 mol% (8-YSZ). This optimal concentration produce an electrostatic equilibrium between the oxygen vacancies, V⁰°, and the substituted dopant cations, Y'_Zr, reducing the activation energy of the hopping oxide ions process [39,40,42,44].
Another zirconia-based material with very interesting properties is the scandia-zirconia solutions (Sc$_2$O$_3$-ZrO$_2$), because of their high ionic conductivity compared with any of the known stabilized zirconia electrolytes \[45\]. Several reports on the ionic conductivity and phase analysis of the scandia-zirconia system indicate that many different phases coexist for a wide range of composition of scandia-zirconia solid solutions. The amount of Sc$_2$O$_3$ required to fully stabilize the cubic structure of zirconia and produce scandia stabilized zirconia (ScSZ) is about 8 to 9 mol\%, while scandia composition below 8 mol\% produce a related fluorite structure that coexist with monoclinic zirconia and composition of scandia above 9 mol\% produce the formation of a rhombohedral β-phase (distortion of the fluorite structure) which is poorly conducting. In addition, the phases present in ScSZ depend on the temperature and the synthesis method. These issues represent a great disadvantage in ScSZ use as SOFC electrolyte in terms of material stability, moreover the equilibrium scandia-zirconia is not fully understood yet.

The higher conductivity of ScSZ is attributed to the smaller mismatch in size between Zr$^{4+}$ and Sc$^{3+}$ ions, as compared with that between Zr$^{4+}$ and Y$^{3+}$ ions, leading to a smaller energy for oxygen migration, and thus higher conductivity. ScSZ with 9 mol\% Sc$_2$O$_3$ has the highest conductivity, 0.343 S cm$^{-1}$ at 1 000 °C \[46\], which is higher than that of 8-YSZ at the same temperature, 0.164 S cm$^{-1}$ \[47\]. However, when the atomic radius of the dopant (Sc$^{3+}$) is closer to that of the cation of the original structure (Zr$^{4+}$) the association energy between oxygen vacancy and dopant cation increases, leading to an increment in activation energy of conduction and consequently reducing the ionic conductivity at lower temperature range. At temperatures below 500 °C the conductivity of ScSZ is similar to, or even lower than, that of YSZ due to the tendency for the activation energy to increase with decreasing temperatures.

### 3.1.1.2 Ceria-based Electrolytes

Pure ceria (stoichiometric ceria, CeO$_2$) is not a good ionic conductor, however its ionic conductivity can be increase by addition of low valance cations as dopant. Consequently, the conductivity in ceria-based electrolytes depends on the characteristics of the dopant elements and their concentration. Figure 3.1.3 shows the ionic conductivity of cation-doped ceria for different cations. It has been noted that the ionic conductivity can be correlated with the ionic radius of the dopant ions, with a maximum in ionic conductivity occurring for those dopants whose radius most closely matches that of Ce$^{4+}$. In this group, gadolinia and samaria doped ceria exhibit the highest ionic conductivities and consequently are widely considered to be the electrolytes for low and intermediate SOFCs.

The addition of Gd$^{3+}$ increase the oxygen vacancies like as shown in reaction 3.1.2 producing a material called gadolinia-doped ceria (GDC).

\[
\text{Gd}_2\text{O}_3 + \text{CeO}_2 \rightarrow 2\text{Gd}^{3+} + \text{V}^{\bullet\bullet}_\text{O} + 3\text{O}_\text{X}^{-}
\]  

The addition of Sm$^{3+}$ produce the same effect explained in reaction 3.1.2 producing a material called samaria-doped ceria (SDC). As expected, an increase in the dopant concentration should promote an increase in the conductivity of the doped ceria-materials, however in GDC and SDC, at low temperatures, defect pairs form due to interaction between the oxide ion vacancies, V$^{\bullet\bullet}_\text{O}$, and aliovalent cations, M$^{\prime}$\text{Ce (M:Gd or Sm):}
Figure 3.1.3: Ionic conductivity of doped ceria at 1 073 K against the radius of dopant cation [48].

\[
\begin{align*}
V_{O}^{**} + M_{Ce}' &= \left( V_{O}^{**}M_{Ce}' \right) \\
V_{O}^{**} + 2M_{Ce}' &= \left( Gd_{Ce}'V_{O}^{**}M_{Ce}' \right)
\end{align*}
\]

(3.1.3) 

(3.1.4)

In the case of the GDC, studies of conductivity of Gd\textsubscript{0.1}Ce\textsubscript{0.9}O\textsubscript{1.95} demonstrate that the defects associations shown in reactions 3.1.3 and 3.1.4 predominate below 400 °C [49]. The value of activation energy of conductivity process at below 400 °C is 0.77 eV and above 400 °C is 0.64 eV, which was related to the dissociation of \( V_{O}^{**}Gd_{Ce}' \) complexes at 400 °C [49].

Ceria-based oxide ion conductors are reported to have purely ionic conductivity at high oxygen partial pressures. At lower oxygen partial pressures, as prevalent on the anode side of a SOFC, these materials become partially reduced. This leads to electronic conductivity in a large volume fraction of the electrolyte extending from the anode side. When a cell is constructed with such an electrolyte with electronic conduction, electronic current flows through the electrolyte even at open circuit, and the terminal voltage is somewhat lower than the theoretical value [19].

Godickemeier and Gauckler [50, 51] analysed the efficiency of cells with Ce\textsubscript{0.8}Sm\textsubscript{0.2}O\textsubscript{1.9} by consideration of the electronic conduction. The maximum efficiency obtained was 50% at 800 °C and 60% at 600 °C. A SOFC with Ce\textsubscript{0.8}Sm\textsubscript{0.2}O\textsubscript{1.9} electrolyte should be operated at temperatures below about 600 °C to avoid such efficiency loss due to electronic leakage. For example, ceria-based electrolytes have been used in SOFCs operating at 550 °C and lower. If higher temperature operation is required, then the electronic conduction can be prevented by protecting the ceria electrolyte with a thin coating of YSZ on the anode side [19]. However, chemical interaction between YSZ and ceria
may occur.

### 3.1.1.3 Perovskite-structured Electrolytes

In addition to fluorite structure electrolytes such as stabilised zirconia and ceria, there are many non-fluorite structure oxides which are potentially attractive for SOFC electrolyte applications. These include perovskites like lanthanum gallate (LaGaO$_3$-based perovskites).

The perovskites based on the general formula ABO$_3$ comprise a rich family of compounds with important applications in solid oxide fuel cells, ferroelectrics, superconducting materials and oxidation catalysts [19, 52]. A schematic of the crystal structure is shown in Figure 3.1.4. The total charge on A and B (A+B = +6) can be achieved by different combinations of oxidation states of A and B (e.g. (1+5), (2+4) and (3+3)), and also in more complex ways as in A$'_{1/2}$A$''_{1/2}$TiO$_3$ where A$'$=Li, Na and A$''$=La, Pr. Due to the high stability of the crystal structure and the variety of cations which can be accommodated within it, perovskites display a wide variety of properties. Many display both ionic and electronic conductivity and so are useful as electrodes in SOFCs [53].

![A$^+$B$^m+$O$_2^-$](image)

Figure 3.1.4: Schematic of a unit cell of the ABO$_3$ perovskite structure [54].

The oxide ion conductivity strongly depends on the particular cation on the A site, and increases in the following order, Pr>La>Nd>Sm. Electrical conductivity of all Ga-based perovskites is almost independent of the oxygen partial pressure, indicating that oxide ion conduction is dominant in these materials. Doping with smaller valence cations the lanthanum gallate (LaGaO$_3$), generally causes oxygen vacancies to form in order to maintain electrical neutrality. Consequently, oxide ion conductivity increases. The ionic conductivity depends strongly on the particular alkaline earth cation doped onto the La site and increases in the order Sr>Ba>Ca. Therefore strontium appears to be the most suitable dopant for LaGaO$_3$. Theoretically, increasing the amount of Sr increases the number of oxygen vacancies and oxide ion conductivity should therefore increase, however the solid solubility of Sr on the La site of LaGaO$_3$ is low and the secondary phases, SrGaO$_3$ or La$_4$SrO$_7$, form when Sr is higher than 10 mol%.

Oxygen vacancies can also be formed by doping an aliovalent cation into the Ga site in addition to the La site. Doping Mg into the Ga site increases conductivity substantially. The oxide ion conductivity attains a maximum at 20 mol% Mg doped on the Ga site. Majewsky et al. [55], demonstrated that the increase in Sr solubility is produced by the enlarged crystal lattice as product of Mg addition. Ishihara et al. [56], found the highest oxide ion conductivity with the compo-
position \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.8}\text{Mg}_{0.2}\text{O}_3 \), this material is called LSGM. Since the initial work in LSGM by Ishihara [56], LaGaO\(_3\) based electrolytes have been studied by various groups and the various cation dopants have been investigated. P. N. Huang et al. [57] reported the highest oxide ion conductivity at the composition \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{0.85}\text{Mg}_{0.15}\text{O}_3 \). On the other hand, K. Huang et al. [58], reported the highest conductivity of 0.17 S cm\(^{-1}\) at \( \text{Sr} = 0.2 \) and \( \text{Mg} = 0.17 \). The composition at the highest ionic conductivity found by the three groups [56–58] was between \( y = 0.15 \) and 0.2 in \( \text{La}_{0.8}\text{Sr}_{0.2}\text{Ga}_{1-y}\text{Mg}_y\text{O}_3 \).

The oxide ion conductivity of Sr and Mg doped LaGaO\(_3\) is higher than that of typical YSZ or ceria based materials, consequently the doubly doped LaGaO\(_3\) formulations are very promising electrolytes for SOFCs in terms of ionic conductivity.

### 3.1.2 Cathode Materials

As was stated previously, the reduction of the oxygen takes place at cathode. The cathode must have high electronic and ionic (oxide ion) conductivity, matching thermal expansion coefficient with electrolyte, chemical stability at operating temperatures, sufficient porosity and good catalytic activity for reduction reaction. The oxygen reduction can be described by the following equation:

\[
\frac{1}{2} \text{O}_2(\text{gas}) + 2\text{e}^- \rightarrow \text{O}_2^-(\text{electrolyte})
\]

(3.1.5)

In the earliest stages of SOFC development, platinum was used as cathode since other appropriate materials were not available. However, platinum is expensive and its use in cost-effective commercial SOFCs for power generation is not possible. In addition, the use of platinum as cathode material exhibited high voltage losses by activation polarization, which suggested that the cathode should not only be a good electrical conductor with good electrocatalytic properties [19].

It is generally considered that electrochemical reaction takes place only at the triple phase boundaries (TPBs). TPBs are defined as the group of sites where electronic conductor, oxide ion conductor and gas are in contact as shown in Figure 3.1.5. The way in which the ionic and electronic conductor are connected is studied in the field of cathodic materials, due to the importance of TPBs in the oxygen reduction reaction (ORR) and its implication in the voltage losses by activation over-potential.

![Figure 3.1.5: Schematic of the triple phase boundary in the cathode.](image-url)
Perovskites, which are less expensive than platinum, possess the required properties and consequently attracted much interest [19]. In 1969, LaCoO$_3$ was tested by Tedmon et al. [59] and its initial performance in cells was good. However, severe degradation occurred with increasing time of operation due to reactions with yttria-stabilized zirconia (YSZ) electrolyte. Investigations on cathodes then moved to lanthanum manganite (LaMnO$_3$)-based materials. Although degradation of lanthanum manganite cathodes was not as severe, some potential reactions with YSZ, particularly at higher cell fabrication temperatures, were recognized [60].

The reactivity of lanthanum manganites with YSZ was investigated using thermodynamic considerations [61], and to avoid La$_2$Zr$_2$O$_7$ formation, A-site (La)-deficient LaMnO$_3$ was proposed for the cathode. The material used conventionally as dopant of LaMnO$_3$ in SOFC cathodes is strontium (La$_{1-x}$Sr$_x$MnO$_3$, LSM). It is associated to a manganite family of perovskites in which lanthanum is partially replaced with strontium. Perovskite structures give a great deal of variation in compositional and oxygen stoichiometry that helps in optimizing catalytic and electrical properties. This cathode material exhibits better performance at high temperatures because this efficiency is significantly good at a temperature above 800 °C. LSM has negligible oxide ion conductivity at 900 °C with high electronic conductivity. Hence, the region of reaction is limited only to electrode|electrolyte interface. This leads towards the necessity that cathodes must be porous enough to diffuse oxygen at interface of electrode|electrolyte so that reduction of oxygen can take place. A composite layer or graded structure of LSM/YSZ is in practice to increase triple phase boundaries (TPBs) [39, 62-64].

A number of cathode materials having better electronic/ionic conductivity and increased oxygen exchange rate have been investigated. It would permit the oxygen reduction action to prolong inside the cathode structure which will consequently increase the reaction rate [39, 65-67]. For this purpose, other perovskite materials like a La$_{1-x}$Sr$_x$Fe$_{1-y}$Co$_y$O$_3$ (LSCF) are being explored.

The LSM cathodes as well as their LSM/YSZ composites have been widely used as cathode materials of high and intermediate temperature fuel cells, while the LSCF cathodes exhibit interesting properties such as mixed ionic and electronic conductivity (MIEC); consequently the most important aspects of both materials will be reviewed below.

### 3.1.2.1 Lanthanum Strontium Manganite Cathodes

Oxygen nonstoichiometry and oxygen defects have a great effect on the ionic and electronic transport properties of cathode materials. LaMnO$_3$-based oxides have either oxygen-excess or oxygen deficient nonstoichiometry. This is generally formulated by La$_{1-x}$A$_x$MnO$_{3+\delta}$ (A is a divalent cation, such as Sr$^{2+}$ or Ca$^{2+}$; “+” denotes oxygen excess, and “-” denotes oxygen deficiency).

For lanthanum manganite, the most commonly used dopant is strontium because its size matches with lanthanum. The Sr dopant in La$_{1-x}$Sr$_x$MnO$_{3+\delta}$ ($x \leq 0.5$) does not increase the oxygen vacancy concentration, a common phenomenon in most of the other perovskite cathode materials studied but rather oxidizes the manganese ion according to equation 3.1.6 [66, 68]:

$$\text{Mn}^x_{\text{Mn}} + \text{SrO} \xrightleftharpoons{\text{LaMnO}_3} \text{Sr}^{2+}_{\text{i}} + \text{Mn}^{2+}_{\text{o}} + \text{O}^x_{\text{o}} \quad (3.1.6)$$
This reaction effectively increases the electron-hole concentration and improves the electrical conductivity. The electronic conductivity of LSM increases approximately linearly with increasing Sr concentration up to a maximum around 50 mol% \[66\]. At high temperature, LaMnO\(_3\) undergoes a solid-phase reaction with YSZ to form La\(_2\)Zr\(_2\)O\(_7\) (LZ) at the electrode|electrolyte interface \[60\,72\]. A little amount of Sr substitution decreases the reactivity of LSM compound with YSZ. However, SrZrO\(_3\) (SZ) forms when Sr concentration is above about 30 mol% \[72, 73\]. Therefore, an Sr content of 30 mol% is considered as optimal against the formation of unwanted electronically insulating phases.

The relative amounts of LZ and SZ depend on the La/Sr ratio in the LSM \[74, 75\] and increase with increasing reaction time and sintering temperature \[74, 76\]. The great problem of the formation of these zirconates is that their conductivities is two to three orders of magnitude lower than that of YSZ, which must be prevented to avoid high ohmic losses.

Generally, the electrical properties of manganite-based perovskite compounds are not sufficient for operation at temperatures below 800 \(^\circ\)C. The absence of oxygen vacancies in LSM restricts the reduction of oxygen to the three-phase boundary regions. This limitation is the primary reason why LSM does not have acceptable performance at lower temperatures. Usually, two approaches have been taken to improve the performance of LSM cathodes so that they may be used at lower temperatures \[68\]. The first is to add a second ioniically conducting phase to LSM, like YSZ. As mentioned above, this extends the surface area over which the oxygen reduction can occur. The second approach has been to replace La with other rare earth elements (such as Pr, Nd, Sm, Gd, Yb, or Y) or dope LSM with a cation (such as, Co, Fe, or Ni) that promotes the formation of oxygen vacancies when strontium is doped on the A-site.

\[3.1.2.2\] **Lanthanum Cobaltite and Ferrite Cathodes**

The lanthanum strontium cobaltite ferrite (LSCF) is a promising material for applications in solid oxide fuel cells. Several research studies on the properties of cobaltites (LaCoO\(_3\)) and ferrites (LaFeO\(_3\)) of lanthanum-based materials as cathodes preceded the synthesis of LSCF due to their interesting electrical and catalytic properties \[77\,79\].

LaCoO\(_3\) exhibits high electronic conductivity and marked catalytic properties, due to their density of states and the electron occupation of d orbitals. Petrov et al. \[78\] proposed a defect model associated with the defect structure of La\(_{1-x}\)Sr\(_x\)CoO\(_{3-\delta}\) in which strontium ions are assumed to occupy the regular La lattice sites, Sr\(_{La}\). This model proposes that the addition of Sr to the crystalline structure of LaCoO\(_3\) produces the appearance of electron holes and oxygen vacancies to reach the electroneutrality of the crystal lattice, consequently enhancing the electronic and ionic conductivities.

Usually, cobalt-based materials display higher ionic and electronic conductivities than other cathode materials. Therefore, the use of cobalt-containing cathode materials should result in a decreased cathode polarization resistance. La\(_{1-x}\)Sr\(_x\)CoO\(_{3-\delta}\) has a marked electrode activity due to high oxygen diffusivity and high dissociation ability of oxygen molecules \[80\]. However, a large amount of cobalt results in an increased thermal expansion coefficient, which may result in a delamination at the cathode|electrolyte interface or cracking of the electrolyte \[13\].
On the other hand, lanthanum ferrite (LaFeO$_3$) exhibits interesting electrical properties because of Fe$^{3+}$ ions confer a stable electronic configuration 3d$^5$. The addition of Sr to LaFeO$_3$ creates Sr$^{4+}$ thus causing a charge unbalance. The charge neutrality is then maintained by the formation of Fe$^{4+}$ ions or oxygen vacancies. Sr-doped LaFeO$_3$ (LSF) cathodes have shown promising performance with respect to power density generated and stability at 750 °C [79, 81, 82]. In iron-based cathodes, reactivity with YSZ electrolyte is significantly reduced. In addition, TECs of the ferrite perovskites are relatively close to those of the YSZ and GDC electrolyte.

The ferro-cobaltite La$_{1-x}$Sr$_x$Fe$_{1-y}$Co$_y$O$_3$ also called LSCF, shows good electrical conductivity, a high oxygen surface exchange coefficient, and a good oxygen self-diffusion coefficient between 600 and 800 °C. The oxygen self-diffusion coefficient of LSCF is 2.6·10$^{-9}$ cm$^2$ s$^{-1}$ at 500 °C, which is superior in performance to that of La$_{0.8}$Sr$_{0.2}$MnO$_3$ which has a oxygen self-diffusion coefficient of 10$^{-12}$ cm$^2$ s$^{-1}$ at 1 000 °C [83, 84]. In addition, LSCF does not react with ceria-based electrolytes [49, 66]. For La$_{0.6}$Sr$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ the TEC value is 13.8·10$^{-6}$ K$^{-1}$ which matches commonly used electrolytes [85].

At lower operation temperatures, LSCF-based cathodes are superior to LSM-type cathodes due to a lower area-specific resistance. However, LSCF-type perovskites are generally incompatible with YSZ electrolytes due to undesirable interface reactions. Therefore, a CGO diffusion barrier layer is used to prevent the formation of low conductive compounds without negatively affecting the electrochemical performance [86, 87]. Another cause of higher degradation rates for cells with LSCF cathodes lies in the diffusion of strontium out of LSCF, which leads to a strontium depletion in the cathode and significantly lower performances. It has been observed that the cells with slightly less Sr in the cathode (La$_{0.58}$Sr$_{0.38}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$) showed lower performance than that of the La$_{0.58}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ [88, 89]. It has been found that partial decomposition of the perovskite usually has greater influence on the cell degradation than interface reactions during the operation [90, 91].

### 3.1.3 Anode Materials and Fuels

The primary function of the anode for a solid oxide fuel cell (SOFC) is to promote the electrochemical oxidation of fuels. When a hydrocarbon fuel such as methane is used as the fuel, additional functions of the anode may include internal reforming or partial oxidation of the fuel. The chemical and electrochemical processes often take place preferentially at certain surface and interfacial sites or triple-phase boundaries (TPBs) [39].

The general requirements for an SOFC anode material include good chemical and thermal stability during fuel cell fabrication and operation, high electronic conductivity under fuel cell operating conditions, excellent catalytic activity toward the oxidation of fuels, manageable mismatch in coefficient of thermal expansion (CTE) with adjacent cell components, sufficient mechanical strength and flexibility, ease of fabrication into desired microstructures (e.g., sufficient porosity and surface area), and low cost [39, 92, 93]. Further, ionic conductivity would be beneficial to the extension of active reaction sites for fuel oxidation from the TPBs to anode surfaces. Some other desirable, but not yet readily achieved, properties include tolerance to carbon deposition, sulfur poisoning, and reoxidation, which are vital to achieving direct utilization of readily available fuels or renewable fuels in SOFCs.
Anode materials studied in the early stage of SOFC development include graphite, platinum, iron, cobalt, and nickel. Ni was chosen as an anode material because of its low cost, good chemical stability, and excellent catalytic activity toward hydrogen oxidation and reforming of hydrocarbon fuels. The most widely used anode in SOFC is the Ni-YSZ composite. This material has been tested early in SOFCs fueled with hydrogen. However, some drawbacks appear with carbonaceous fuels such as sulfur poisoning and deactivation by carbon deposition. In the following subsections a brief description of the Ni-YSZ material and the possible alternative materials to be used in SOFC fueled with carbonaceous fuels will be provided.

### 3.1.3.1 Ni-YSZ Composite Anodes

Pure nickel has a melting point of 1 453 °C, a thermal expansion coefficient of $13.3 \cdot 10^{-6} \text{ K}^{-1}$ and electronic conductivities of $138 \cdot 10^4 \text{ S cm}^{-1}$ and ca. $2 \cdot 10^4 \text{ S cm}^{-1}$ at 25 °C and 1 000 °C, respectively. Its relatively low melting temperature results in the tendency of lower sintering temperature (1 000 °C) and the thermal expansion coefficient of Ni is higher than that of YSZ electrolyte (the thermal expansion coefficient of YSZ is in the range of ca. $10.5 \cdot 10^{-6} \text{ K}^{-1}$). Addition of YSZ electrolyte phase into Ni significantly reduces the thermal expansion of the composite material in order to be thermally compatible with the electrolyte [94, 95]. The anode in the fuel cell is exposed to both a reducing (fuel) and an oxidizing (oxide ions) environment, causing the anode to undergo consecutive reduction and oxidation cycles. The large volume change involved in the oxidation and reduction cycle of Ni/NiO (theoretical density is 8.9 g cm$^{-3}$ for Ni and 6.96 g cm$^{-3}$ for NiO) could cause the instability of the Ni/YSZ cermet microstructure.

It is generally accepted that the electrochemical activity of Ni anodes for H$_2$ oxidation reaction depends strongly on the triple phase boundary zones (TPB where fuel gas, Ni and YSZ phases meet) [96, 98]. De Boer et al. [99] observed the significant reduction of electrode polarization resistance of porous Ni electrode modified by deposition of fine YSZ particles as compared to pure Ni electrode. This indicates that the YSZ phase in the cermet plays an important electrocatalytic role in the creation of additional reaction sites by extending the two-dimensional reaction zone into three-dimensional reaction zone, as shown in Figure [3.1.6] significantly enhancing the reaction kinetics in addition to the inhibition of the coarsening and grain growth of the Ni phase [100–102]. Therefore, the system of composite anode usually consisting of metal-oxide or ceramic-metal (cermet) structure has been widely accepted. Today, the Ni/Y$_2$O$_3$-ZrO$_2$ (Ni/YSZ) cermet materials are still the most common anodes for SOFCs.

Fuel cells that directly use hydrocarbon fuels such as natural gas, without first reforming those hydrocarbons to hydrogen, will have enormous advantages over conventional hydrogen-based fuel cells [103]. Removing the need either to supply hydrogen to the fuel cell or to include a hydrocarbon-reforming system greatly decreases the complexity, size and cost of the fuel cell system. Natural gas is regarded as a relatively cheap and clean fuel. The advantage of SOFCs over other fuel cells is that the natural gas can be directly used without the need to external fuel reformer and water-gas shift reactor. The main component of natural gas is methane and following reforming reactions can take place directly inside a Ni/YSZ cermet anode:

\[
\text{CH}_4 + \text{H}_2\text{O} \rightleftharpoons \text{H}_2 + \text{CO} \quad (3.1.7)
\]
CHAPTER 3. LITERATURE REVIEW

Figure 3.1.6: Schematic of anode cermet structure, showing interpenetrating network of pores and conductors (nickel for electrons, yttria-stabilized zirconia for oxide ions). The reactive sites are located at the TPB, which are accessible to fuel through the porosity [19].

\[ CO + H_2O \rightleftharpoons CO_2 + H_2 \quad (3.1.8) \]

Internal reforming of hydrocarbon fuels is often accompanied by carbon deposition in the catalyst. Carbon deposition covers the active sites of the anodes, resulting in the loss of cell performance [104][105]. High steam/carbon (S/C) ratios (e.g., up to 3) are typically used in conventional steam reformers to suppress the carbon formation. However, high S/C ratio is unattractive for fuel cells as it lowers the electrical efficiency of the fuel cell by steam dilution of the fuel. The endothermic nature of steam reforming reactions (Equations 3.1.7 and 3.1.8) can cause local cooling and extreme differences in thermal gradients potentially capable of mechanically damaging the cell stack [106]. Nevertheless, the impact of the endothermicity of methane steam reforming process on the cell stability can be reduced by the combination of both external and internal reforming activity [107].

Despite the excellent electrocatalytic properties of Ni/YSZ cermet materials for operation in H\textsubscript{2} fuel, Ni/YSZ based anode suffers a number of drawbacks in systems where natural gas is used as the fuel, notably sulfur poisoning and carbon deposition caused by cracking of methane. Under a high carbon activity environment, iron, nickel, cobalt and alloys based on these metals could corrode by a process known as metal dusting. Metal dusting involves the disintegration of bulk metals and alloys into metal particles at high and intermediate temperatures (300 – 850 °C) in environment that are supersaturated with carbon. Ni corrosion process strongly depends on the temperature and the gas composition and in general Ni corrosion rate increases with temperature [108]. The form of carbon deposited on Ni in wet methane was found to be graphite as observed by in situ Raman spectroscopy and the deposited carbon cannot be burned by electrochemically permeated oxygen [109].

The performance of conventional Ni/YSZ cermet anodes is also not satisfactory at temperatures between 500 and 600 °C due to the low ionic conductivity of the YSZ phase in the cermet. Thus, the driving force for the development of alternative anodes is mainly due to the need to replace Ni/YSZ cermet anodes for the direct oxidation of carbonaceous fuels such as methane or carbon [110][111].

In recent years, there have been numerous studies on alternate anode materials. The areas of interest
include carbon-tolerant anode materials, sulfur-tolerant anode materials, and redox-stable anode materials.

3.1.3.2 Carbon-tolerant Anodes

Conventional Ni/YSZ cermet materials with catalyst modification have been extensively studied for the internal reforming of methane (equation 3.1.7). The internal reforming activity of the anodes is important as it converts methane into more electrochemically active species such as H\textsubscript{2} and CO.

Finnerty \textit{et al.} \cite{112} found that the quantity of carbon deposited on the anode during methane reforming is strongly affected by the operating temperature and the methane/steam ratio, while the addition of small quantities of molybdenum (1\% of MoO\textsubscript{3} and 99\% of Ni-YSZ) leads to a significant reduction in the amount of carbon deposited.

Takeguchi \textit{et al.} \cite{113} studied the carbon deposition and steam reforming of methane on Ni/YSZ anodes modified with metal oxides addition of MgO, CaO, SrO and CeO\textsubscript{2}. CaO, SrO and CeO\textsubscript{2} addition suppressed the carbon deposition while MgO addition promoted the carbon deposition rate and decreased the steam reforming activity of the anodes. High content (ca. 2 wt.\%) of SrO and CeO\textsubscript{2} in the Ni/YSZ cerments also reduced the steam reforming activity significantly. Further studies \cite{114, 115} show that Ru and Pt addition promotes the reforming activity and suppress the carbon deposition.

The steam reforming reaction and carbon deposition are also reported by Onuma \textit{et al.} \cite{116} on Pt electrodes and Horita \textit{et al.} \cite{117} on Ni/YSZ and Fe/YSZ anodes. Sato \textit{et al.} \cite{118} studied Ni-Co alloy/YSZ cermet anodes for the oxidation of H\textsubscript{2} and CH\textsubscript{4}. Ni-Co alloy was prepared by co-precipitation, followed by sintering at 1 100 °C for 24 h. Co content in Ni-Co/YSZ anodes has little effect on the cell performance with H\textsubscript{2} fed but increases the cell performance with CH\textsubscript{4} fed. The best composition was found to be Ni\textsubscript{0.5}Co\textsubscript{0.5}/YSZ. The increased activity of Ni-Co/YSZ cermet anodes for CH\textsubscript{4} oxidation was explained by the preferential crystal orientation along (111) plane at the alloy surface, which was not observed for pure Ni powder. The exposure of the most densely packed plane in the face-centered cubic structure could contribute to the formation of surface active sites for the electrochemical oxidation of methane. Ni-Co/YSZ cermet anodes achieved lowest electrode polarization resistance as compared to that of Ni-Cu/YSZ and Ni-Fe/YSZ cermet anodes for H\textsubscript{2} oxidation reaction in wet H\textsubscript{2} \cite{119}.

The addition of copper in composite anodes has been found to prevent the formation of carbon deposits during the oxidation of carbonaceous fuels. Kim \textit{et al.} \cite{120} studied the carbon deposition and CH\textsubscript{4} oxidation on Ni-Cu alloy/YSZ cermet anode prepared by impregnation of porous YSZ layer with copper and nickel precursors. After oxidation of CH\textsubscript{4}, carbon deposits were found on the surface of the Ni-Cu alloy, presenting a lower amount of carbon deposits, those anodes with lower Ni content, such as Ni\textsubscript{0.2}Cu\textsubscript{0.8}/YSZ. Sin \textit{et al.} studied the oxidation of dry CH\textsubscript{4} on Ni\textsubscript{0.8}Mg\textsubscript{0.2}/YSZ cermet anodes (replacing the Cu by Mg), presenting appreciable amounts of carbon deposits and relating this carbon deposits to absence of copper content \cite{121}.
3.1.3.3 Sulfur-tolerant Anodes

Although sulfur poisoning for SOFCs has been known for some time, it is interesting to note that most earlier studies on sulfur-tolerant anodes were directed toward the utilization of fuels containing significant amount of $\text{H}_2\text{S}$ (usually on the percentage level). Only recently did studies on low concentration sulfur-containing fuels start to show up in the literature. Table 3.1.1 provides a brief summary of both types of studies (studies that use exclusively platinum as the anode material for SOFC are excluded since they do not have practical significance).

Table 3.1.1: Summary of previous studies on potential sulfur-tolerant anode materials for solid oxide fuel cells [39].

<table>
<thead>
<tr>
<th>Materials</th>
<th>Year First Reported</th>
<th>Major Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>CuCo$_2$S$_4$, CuFe$_2$S$_4$, CuNi$_2$S$_4$, NiFe$_2$S$_4$, NiCo$_2$S$_4$, WS$_2$ [122][123]</td>
<td>1987</td>
<td>$P_{\text{max}}$ of up to 10 mW cm$^{-2}$ at 900 $^\circ$C in 100% $\text{H}_2\text{S}$ for NiFe$_2$S$_4$. Anode exchange current density decreases in the sequence of: NiFe$_2$S$_4$ &gt; WS$_2$ &gt; CuCo$_2$S$_4$ &gt; CuFe$_2$S$_4$ &gt; NiCo$_2$S$_4$ &gt; CuNi$_2$S$_4$.</td>
</tr>
<tr>
<td>CoS$_{1.035}$, WS$_2$, Li$<em>2$S/CoS$</em>{1.035}$ [124]</td>
<td>1999</td>
<td>$P_{\text{max}}$ of up to ca. 400 mW cm$^{-2}$ (after IR correction) at 770 $^\circ$C in 15% $\text{H}_2\text{S}$. Pt mesh current collector.</td>
</tr>
<tr>
<td>Co-Mo-S, Fe-Mo-S, Ni-Mo-S, and MoS$_2$ with or without Ag and YSZ [125][126]</td>
<td>2003</td>
<td>$P_{\text{max}}$ of up to ca. 220 mW cm$^{-2}$ (after IR correction) at 850 $^\circ$C in 100% $\text{H}_2\text{S}$. Pt current collector layer.</td>
</tr>
<tr>
<td>La$<em>{0.35}$Sr$</em>{0.65}$TiO$<em>3$(LST)–Ce$</em>{1-x}$La$<em>x$O$</em>{2-x}$ composite [127][128]</td>
<td>2003</td>
<td>$P_{\text{max}}$ of ca. 400 mW cm$^{-2}$ at 850 $^\circ$C in $\text{H}_2$ poisoned by 26 - 1000 ppm $\text{H}_2\text{S}$. Pt or Au current collector layer.</td>
</tr>
<tr>
<td>La$<em>{0.4}$Sr$</em>{0.6}$TiO$_3$ (LST) [129]</td>
<td>2004</td>
<td>$P_{\text{max}}$ of ca. 200 mW cm$^{-2}$ at 1000 $^\circ$C in $\text{H}_2$. Performance not influenced by up to 1000 ppm $\text{H}_2\text{S}$ and enhanced by 5000 ppm $\text{H}_2\text{S}$.</td>
</tr>
</tbody>
</table>

Clearly, for any of the candidate materials, the number of studies is quite small—often by only one group. For materials that have been studied by multiple groups, the results could be totally conflicting. Take the example of strontium-doped lanthanum titanate (LST), while some researchers reported sulfur poisoning by $\text{H}_2\text{S}$ in the range of 26 to 1000 ppm [127][128], some others reported no poisoning effect in 1000 ppm $\text{H}_2\text{S}$ and an enhanced effect in 5000 ppm $\text{H}_2\text{S}$. 

Due to the problems mentioned above, only limited evaluation of the real potential for any of these
Table 3.1.2: Summary of previous studies on potential sulfur-tolerant anode materials for solid oxide fuel cells [39] (continued).

<table>
<thead>
<tr>
<th>Materials</th>
<th>Year First Reported</th>
<th>Major Observations</th>
</tr>
</thead>
<tbody>
<tr>
<td>La_{0.7}Sr_{0.3}VO_3 (LSV) [130-133]</td>
<td>2004</td>
<td>( P_{\text{max}} ) of ca. 280 mW cm(^{-2}) at 950 °C in 5% H(_2)S/95%CH(_4). Better performance in fuels with 5% H(_2)S than in pure H(_2). Pt current collector layer.</td>
</tr>
<tr>
<td>Cu-CeO(_2) cermet [134]</td>
<td>2005</td>
<td>( P_{\text{max}} ) of ca. 320 mW cm(^{-2}) at 800 °C, in H(_2)/H(<em>2)O. Sulfur resistance up to 450 ppm. Au current collector layer ( P</em>{\text{max}} ) of ca. 350 mW cm(^{-2}) at 950 °C in H(_2).</td>
</tr>
<tr>
<td>La(<em>{0.75})Sr(</em>{0.25})Cr(<em>{0.5})Mn(</em>{0.5})O(_3) (LSCM) [135]</td>
<td>2005</td>
<td>Cell poisoned in the presence of 10% H(_2)S. Pt current collector layer.</td>
</tr>
<tr>
<td>Gd(<em>2)Ti(</em>{1.4})Mo(_{0.6})O(_7) (GTMO) [136]</td>
<td>2005</td>
<td>( P_{\text{max}} ) of ca. 340 mW cm(^{-2}) at 950 °C in 10%H(_2)S/90% H(_2). Better performance in fuels with 10% H(_2)S than in pure H(<em>2). Pt current collector layer. ( P</em>{\text{max}} ) of ca. 300 mW cm(^{-2}) at 750 °C in H(_2).</td>
</tr>
<tr>
<td>Ni-YSZ cermet infiltrated by Mo or W precursors [137]</td>
<td>2005</td>
<td>Still poisoned by sulfur (C(_4)H(<em>4)S) but to a lesser extent and showed gradual recovery. No Pt current collector layer. ( P</em>{\text{max}} ) of ca. 300 mW cm(^{-2}) at 750 °C in H(_2).</td>
</tr>
<tr>
<td>Sr(_2)MgMoO(<em>6)(</em>{−δ}) and Sr(_2)MnMoO(<em>6)(</em>{−δ}) [138, 139]</td>
<td>2006</td>
<td>( P_{\text{max}} ) of ca. 800 mW cm(^{-2}) at 800 °C in H(_2). Still slightly poisoned by 5–50 ppm H(_2)S. Pt current collector layer.</td>
</tr>
<tr>
<td>Ni-YSZ infiltrated with ceria [140]</td>
<td>2007</td>
<td>( P_{\text{max}} ) of ca. 300 mW cm(^{-2}) at 700 °C in H(_2). Still poisoned by 40 ppm H(_2)S but to a lesser extent</td>
</tr>
<tr>
<td>Ni-YSZ sputtered with Nb(_2)O(_5) [141]</td>
<td>2008</td>
<td>( P_{\text{max}} ) of 50 mW cm(^{-2}) at 700 °C in H(_2). Not poisoned by 50 ppm H(_2)S</td>
</tr>
</tbody>
</table>

Materials is possible. For example, as shown in the table, metal sulfides are functional as anodes in fuels with very high concentrations (up to 100\%) of H\(_2\)S [122–126]. However, these sulfide materials have limited potential because they tend to decompose back into the metal phase in a typical reformed fuel containing only ppm-level of sulfur based on thermodynamic considerations [142]. In addition, for materials such as La\(_{0.7}\)Sr\(_{0.3}\)VO\(_3\) (LSV) and Gd\(_2\)Ti\(_{1.4}\)Mo\(_{0.6}\)O\(_7\) (GTMO),
even though they demonstrate sulfur tolerance (or even sulfur enhancement effect), consideration from many other aspects would greatly limit, if not eliminate, their practical applications. For the example of LSV material shows that: (a) its electrical conductivity is only 1/10 to 1/200 of that for pure nickel; (b) it is made from $V_2O_5$, which is highly poisonous; (c) it can be oxidized into $La_{0.7}Sr_{0.3}VO_4$ and lose its properties and expand significantly; and (d) it is difficult to integrate into current SOFC fabrication procedure. Nevertheless, studies into new materials are still of scientific importance since they may shed some light into future directions for anode studies for SOFCs. For example, Choi et al. [141] recently demonstrated that the enhanced sulfur tolerance (in 100 ppm $H_2S$) for a dense Ni-YSZ anode sputtered with niobium oxide was due to the transformation of the metal surface from NbO$_2$ to niobium sulfides. Although the cell performance is still low, the study together with the studies by Smith and McEvoy [137] and Kurokawa et al. [140] may help to set the path for modifying the Ni-YSZ cermet anodes to achieve enhanced sulfur tolerance.

### 3.1.3.4 Molybdenum-doped Ceria (CMO)

Cerium dioxide or ceria ($CeO_2$) has shown an excellent electrocatalytic activity for oxidation of carbonaceous fuels, due to the $CeO_2$-$Ce_2O_3$ transition taking place during this process [143]; besides it does not suffer from carbon deposition [144] and presents both electronic and ionic conductivity at high temperatures (above ca. 700 °C) and under low oxygen partial pressures [145,146]. Similarly, molybdenum oxides (MoO$_2$ and MoO$_3$) present catalytic activity for the oxidation of carbonaceous fuels without deactivation by coke deposition. MoO$_2$ exhibits a selective lattice oxygen donation from metal oxide to fuels [147], and shows high electronic conductivity due to its relatively high density of states in the valence band energy region [148,149]. In addition, MoO$_3$ has been investigated early due to its catalytic activity in the oxidation process of methanol [150] and the oxidative dehydrogenation of methane [151]; besides its electrical properties have been widely studied showing semiconductor properties and good electrical conductivity following varied mechanisms at different temperatures [152–154].

As was stated in Section 3.1.1.2, the oxygen vacancies can be increased in ceria based systems by doping with lower valence cations, however the electronic conductivity of ceria can be increase by addition of cations dopants with higher valence. In this respect, Mo-doped ceria ($Ce_{1-x}Mo_xO_{2+δ}$) presents a higher electronic conductivity than pure ceria and is stable under hydrogen and methane atmospheres [146,155]. The substitution of $Ce^{4+}$ ions with $Mo^{6+}$ ions into the fluorite-type structure of ceria can be expressed as follows 3.1.9 using the Kröger-Vink notation:

$$MoO_3 \xrightarrow{CeO_2} Mo^{••} \text{ce} + O_1^i + 2O_O^X$$

(3.1.9)

where $Mo^{••}$$\text{ce}$, $O_1^i$ and $O_O^X$ represent an hexavalent molybdenum ion ($Mo^{6+}$) at a $Ce^{4+}$ ion site, an oxide ion at an interstitial site and an oxide ion at a regular oxide ion site, respectively [155]. The increase in the electronic conductivity produced by the doping is related to interstitial oxide ions in the Fm-3m fluorite-type structure [146].

The synthesis of Mo-doped ceria for solid oxide fuel cell applications has been reported mainly through the conventional solid-state reaction [146,155]. The material obtained corresponds to $Ce_{1-x}Mo_xO_{2+δ}$ ($x = 0.05, 0.07$ and $0.1$ weight fraction) with trace impurities and a total electrical conductivity that increases with increasing molybdenum content. The highest conductivity reported
is 5.08·10⁻² S cm⁻¹ for Ce₁₋ₓMoₓO₂₊δ at 550 °C in wet hydrogen, which could be improved by eliminating the impurities remaining from the solid-state reaction.

3.1.4 Mechanical Properties of Anode Materials

The mechanical properties of solid oxide fuel cell (SOFC) materials play an important role in manufacturability, durability and lifetime of the devices. Operational conditions can affect the mechanical properties of materials [156]. The mechanical failure of one cell is sufficient to lead to the end of service of a solid oxide fuel cell (SOFC) stack [1]. Therefore, there is growing interest in gaining knowledge on the mechanical properties of the cell materials for stress analysis [157].

Structural reliability of SOFCs is a prominent issue, which currently impedes their large-scale commercialization. The in-series assembly of the single repeating units (SRU) to build a stack and the use of brittle ceramic materials for the manufacturing of the cells are striking weaknesses [157]. The mechanical failure of one cell component usually induces a succession of detrimental effects that act in a coupled manner. For instance, delamination or cracking of the electrode layers breaks the ionic and/or electronic conduction paths to the reaction sites. The subsequent local loss of performance induces a harmful redistribution of the current density [158, 159]. Once cracked, the electrolyte does not any longer ensure the separation of the fuel and air compartments to the fullest extent. The local and unsteady combustion draw a local increase of the temperature, as well as diverse chemical alterations of the cell layers, such as the reduction and reoxidation (redox) of the nickel in the composite anode (e.g. Ni-YSZ) and the reduction of the cathode material [160]. All these undesirable chemical and electrochemical phenomena promote in turn additional stresses, which reach critical values in an accelerated manner.

Ceramic materials are widely used as components in SOFCs and also as oxygen transport membranes, due to their favorable transport properties and chemical stability [161]. The basic problems such as reliability and robustness [162] are always issues for brittle ceramic materials, which emphasizes the need to understand and characterize necessary mechanical parameters. Following, a brief description of the mechanical properties of these ceramic materials and the techniques used for their determination are introduced.

3.1.4.1 Elastic Behavior

The elastic modulus, $E_Y$, defines the elastic behavior of a material. The elastic modulus $E_Y$ describes the resistance to elastic deformation of an isotropic material when it is loaded uniaxially. It is defined by Hooke’s law as the ratio of stress to strain during elastic loading:

$$E_Y = \frac{\sigma_u}{\epsilon}$$  \hspace{1cm} (3.1.10)

where $\sigma_u$ is the stress and $\epsilon$ is the strain.

---

1Set of single fuel cells units, electrically connected, that work simultaneously to generate large amounts of electrical power.
Elastic modulus can be determined using different methods. For brittle ceramic materials, indentation as non-destructive method as well as bending test and impulse excitation technique are commonly used [163].

**Micro-indentation test:**
In indentation testing, the elastic modulus can be determined from the load-depth curve [164]. Indentation with a Vickers tip is the most common test; other indenter tips like Berkovich, Rockwell, Knoop or Shore are also widely used [165]. The elastic modulus is calculated from the unloading curve, which represents elastic response of the material (See Figure 3.1.7) [166, 167]. The general advantage of the indentation test is that it is a fast serial test and only a small specimen volume is required, so it can be considered as a macroscopically non-destructive test. The disadvantage is that the properties are representative only for the location where the test is carried out. Especially for highly porous materials the scatter can be very large.

![Load-depth curve](image)

**Figure 3.1.7:** Load-depth curve obtained from micro-indentation test for Young’s modulus determination [166, 167].

**Bending test:**
The bending test is a widespread method for analyzing materials’ behavior especially for ceramics where tensile testing is not an option [168]. The alignment is easily achieved and specimens with simple geometric shapes can be used. The elastic modulus is usually determined from the load-displacement curve obtained in either a three- or four-point bending test for bar-type specimens (Figure 3.1.8 a and b)) or for plates via ring-on-ring, ball-on-ring or ball-on-three balls test (Figure 3.1.8 c, d and e)) [169]. The testing of plates has become very common since advanced materials processing often relies on tape casting techniques [170], yielding plate type specimens in either dense or porous state. The latter are representative for the porous substrate and used in SOFCs or membrane designs [171]. For tubular geometries, which are still occasionally used as SOFC, testing methods such as O-ring, C-ring (Figure 3.1.8 g and h) [172] or four-point bending of semi-cylindrical specimens [173] can be applied (Figure 3.1.8 f)). The initial part of the load-displacement curve can be affected by contact problems related to roughness or biased by surface waviness. Hence, sometimes a grinding or polishing process is advantageous for plates or bars to
yield materials representative curves which lead to a more precise determination of elastic modulus [174].

Figure 3.1.8: Different methods to test elastic modulus in bending: a) four-point bending, b) three-point bending, c) ring-on-ring, d) ball-on-ring, e) ball-on-three balls, f) four-point bending of semi-cylindrical specimens, g) O-ring, and h) C-ring [163].

**Impulse excitation test:**
An advanced method to determine the elastic modulus for certain specimen geometries is the impulse excitation method, where the specimens resonance induced by a mechanical impulse is detected acoustically [163]. Figure 3.1.9 is a simple schematic of the impulse excitation technique, where a slight impact is induced at a side of the solid specimen. For circular geometry the calculus of Young’s modulus can be determined using the equation [3.1.11] [175]:

\[
f_{20} = \frac{0.2458 \cdot h}{r^2} \left( \frac{E_Y}{\rho \cdot (1 - \nu^2)} \right)^{0.5} \tag{3.1.11}
\]

where \(f_{20}\) is the resonance frequency of the circular sample obtained, when this is excited by a mechanical impulse in the border of the sample, \(r\) is the radius of the circular sample, \(\rho\) is the experimental density, \(h\) is the thickness and \(\nu\) is the Poisson’s ratio.
3.1.4.2 Fracture Toughness

Ceramic and ceramic composites can have a rather high strength but also a quite low crack resistance at the same time [177]. The crack resistance, which is proportional to the fracture toughness, is critical for ceramic components as used as cell in SOFCs operating under extreme mechanical and thermal loads. Hence, fracture toughness is an important property of advance ceramics and is one measure of brittleness and crack resistance [178].

Different testing methods have been developed and optimized to determine fracture toughness of ceramics [163]. Indentation testing is one of the methods that might be used to determine fracture toughness. In this test fracture toughness can be determined from the length of cracks, which might propagate from the vertices of the indents and the microhardness of the material. Crack initiation depends on the applied load and the material’s fracture toughness [179].

The microhardness is a measure of the resistant to localized plastic deformation induced by either mechanical indentation or abrasion. The microhardness can be determined by Vickers indentation test. The sample is indented with different loads and different Vickers impressions are obtained (see Figure 3.1.10). Measuring the diagonal shown in Figure 3.1.10 the Vickers microhardness, $H_V$, is obtained using the equation 3.1.12:

$$H_V = \frac{1.854 \cdot P_V}{d_V^2}$$  \hspace{1cm} (3.1.12)

where $P_V$ is the applied load and $d_V$ is the diagonal average length in indented area.

![Diamond indenter and Vickers indentation mark.](image)

Fracture toughness is calculated using the Niihara and Anstis equations, considering the length of the fracture caused by indentation on the surface of a sintered pellet and the microhardness previously calculated [179][180]. Niihara and Anstis formulas are presented in equations 3.1.13 and 3.1.14 correspondingly:

$$K_{IC} = 0.0089 \cdot \left( \frac{E_Y}{0.927 \cdot H_V} \right)^{0.5} \cdot \frac{P_V}{A \cdot \sqrt{l_c}}$$  \hspace{1cm} (3.1.13)
\[ K_{IC} = 0.016 \cdot \left( \frac{E_Y}{H_V} \right)^{0.5} \cdot \frac{P_V}{(A_V + l_c)^{1.5}} \] (3.1.14)

where \( K_{IC} \) is the fracture toughness, \( A_V \) is the half average length of the diagonal of the Vickers marks, and \( l_c \) is the average length of the cracks.

The advantages of this test are that only a small specimen size is required and the easy experimental routine, requiring only a measurement of the crack length after the test. This technique found widespread use for the analysis of ceramics used in SOFC anodes, ceramic membrane materials and sealants [181–185]. However, this testing method reveals an apparent disadvantage: the crack path could be terminated and blurred by pores in the materials. Hence, it can be very difficult to determine the crack length precisely.

Bending tests as an alternative method are also widely used to investigate the fracture toughness [163]. They avoid the shortage of indentation on porous materials and also obtain a more representative property for the materials [163]. For plate-shaped specimens like SOFC cell layers, the double torsion (DT) test is as an effective means, which requires the edge of a notched plate specimen to be loaded in a bending mode. The fracture toughness can be determined from a controlled crack propagation load as exemplified for SOFC materials in [186]. Similarly, a double cantilever beam (DCB) test is another testing method which is suitable for testing of notched plate-shaped specimens or thin solid films. The sample is also loaded via pure bending moments [187]. The methods can be used for elevated temperature testing. Schematics of both methods are shown in Figure 3.1.11.

![Schematics of bending tests](image)

Figure 3.1.11: Types of bending tests for fracture toughness determination: a) Double torsion test and b) Double cantilever beam test [163].

### 3.1.4.3 Elasticity Modulus and Fracture Toughness of Anode Materials

The elastic modulus of cell layers are also considered as important parameters for analysis and simulations of stress states. Literature data for elastic moduli of typical cell layer materials are summarized in Table 3.1.3.

Impulse excitation has been used in most of the studies to investigate elastic modulus, since the value obtained from indentation test might be significantly influenced by the indentation region,
Table 3.1.3: Elastic modulus of typical SOFC materials measured by different techniques. *RT: measurement at room temperature.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Material</th>
<th>Porosity / (%)</th>
<th>Test Method</th>
<th>Elastic Modulus / GPa</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Electrolye</td>
<td>8YSZ</td>
<td>0</td>
<td>Impulse excitation</td>
<td>190</td>
<td></td>
</tr>
<tr>
<td></td>
<td>8YSZ</td>
<td>2</td>
<td></td>
<td>205 113 157</td>
<td>[189]</td>
</tr>
<tr>
<td></td>
<td>3YSZ</td>
<td>0</td>
<td></td>
<td>190</td>
<td>[190]</td>
</tr>
<tr>
<td></td>
<td>Ceria</td>
<td>2.6</td>
<td></td>
<td>236.7</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>EDC</td>
<td>2.3</td>
<td>Impulse excitation</td>
<td>224.2</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>YDC</td>
<td>5.8</td>
<td></td>
<td>215.4</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>GDC</td>
<td>0.1</td>
<td></td>
<td>200.2</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>SDC</td>
<td>0.9</td>
<td></td>
<td>207.4</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>NDC</td>
<td>3.3</td>
<td></td>
<td>226.8</td>
<td>[176]</td>
</tr>
<tr>
<td></td>
<td>YSZ</td>
<td>0</td>
<td>Nano-indentation</td>
<td>224</td>
<td>[191]</td>
</tr>
<tr>
<td>Anode support</td>
<td>NiO-3YSZ</td>
<td>11</td>
<td>Impulse excitation</td>
<td>155</td>
<td>[192]</td>
</tr>
<tr>
<td></td>
<td>NiO-3YSZ</td>
<td>30</td>
<td>Slender cantilever beam</td>
<td>136</td>
<td>[193]</td>
</tr>
<tr>
<td></td>
<td>Ni-8YSZ</td>
<td>45</td>
<td>Impulse excitation</td>
<td>45 24</td>
<td>[194]</td>
</tr>
<tr>
<td></td>
<td>Ni-8YSZ</td>
<td>40</td>
<td>Slender cantilever beam</td>
<td>55</td>
<td>[195]</td>
</tr>
<tr>
<td></td>
<td>NiO-8YSZ</td>
<td>27</td>
<td>Impulse excitation</td>
<td>74 68</td>
<td>[194]</td>
</tr>
<tr>
<td></td>
<td>NiO-8YSZ</td>
<td>-</td>
<td>Nano-indentation</td>
<td>219</td>
<td>[196]</td>
</tr>
<tr>
<td>Cathode</td>
<td>LSM</td>
<td>30</td>
<td>Impulse excitation</td>
<td>41 98</td>
<td>[189]</td>
</tr>
<tr>
<td></td>
<td>LSCF</td>
<td>25</td>
<td>Nano-indentation</td>
<td>91</td>
<td>[197]</td>
</tr>
<tr>
<td>Buffer layer</td>
<td>CGO</td>
<td>3</td>
<td>Impulse excitation</td>
<td>201</td>
<td>[198]</td>
</tr>
</tbody>
</table>

due to porous structure and substrate effects [192, 199].

Selçuk and Atkinson [198] reported the effect of porosity on the elastic modulus of NiO-8YSZ anode materials at room temperature, see Figure 3.1.12. The elastic modulus decreased with increasing porosity. Radovic and Lara-Curzio [195] also studied the changes in elastic modulus of YSZ-containing Ni-based anode materials as a function of the amount of reduced NiO. It was found that elastic modulus decreased significantly with increasing fraction of reduced NiO amount.

Fracture toughness of the anode material and other SOFC components plays an important role for designing SOFC stack as it has to withstand high stresses, arising from a mismatch in thermal...
expansion coefficients of the different ceramic layers as well as metallic components and thermal gradients during the operation. As already mentioned in previous chapters, porous NiO/YSZ and its reduced state cermet are usually being used as anode material for SOFC applications. Data concerning fracture toughness of the anode materials are still limited. Some fracture toughness values of SOFC components tested using different methods are given in Table 3.1.4.

Table 3.1.4: Fracture toughness values of typical SOFC materials. *RT: measurement at room temperature.

<table>
<thead>
<tr>
<th>Material</th>
<th>Testing method</th>
<th>Porosity / %</th>
<th>Temperature</th>
<th>$K_{IC}$ / MPa m$^{1/2}$</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiO-8YSZ</td>
<td>Double torsion</td>
<td>14</td>
<td>RT</td>
<td>2.1 ± 0.2</td>
<td>[186]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>22</td>
<td></td>
<td>1.6 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Ni-8YSZ</td>
<td>Double torsion</td>
<td>27</td>
<td>RT</td>
<td>3.4 ± 0.2</td>
<td>[186]</td>
</tr>
<tr>
<td></td>
<td></td>
<td>40</td>
<td></td>
<td>2.3 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>NiO-3YSZ</td>
<td>Double cantilever beam</td>
<td>16</td>
<td>RT</td>
<td>2.0 ± 0.1</td>
<td>[187]</td>
</tr>
<tr>
<td>YSZ</td>
<td>Double torsion</td>
<td>0</td>
<td>RT</td>
<td>1.6 ± 0.1</td>
<td>[200]</td>
</tr>
<tr>
<td></td>
<td>Indentation</td>
<td>0</td>
<td>RT</td>
<td>1.8 ± 0.2</td>
<td></td>
</tr>
<tr>
<td>Ceria</td>
<td></td>
<td>2.6</td>
<td></td>
<td>2.7 ± 0.6</td>
<td></td>
</tr>
<tr>
<td>GDC</td>
<td></td>
<td>0.1</td>
<td></td>
<td>2.8 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>SDC</td>
<td></td>
<td>0.9</td>
<td></td>
<td>2.5 ± 0.5</td>
<td></td>
</tr>
<tr>
<td>YDC</td>
<td>Indentation</td>
<td>5.8</td>
<td>RT</td>
<td>2.1 ± 0.3</td>
<td>[176]</td>
</tr>
<tr>
<td>EDC</td>
<td></td>
<td>2.3</td>
<td></td>
<td>2.0 ± 0.4</td>
<td></td>
</tr>
<tr>
<td>NDC</td>
<td></td>
<td>3.3</td>
<td></td>
<td>1.9 ± 0.2</td>
<td></td>
</tr>
</tbody>
</table>

On the other hand, pure and doped ceria($\text{CeO}_2$) have a wide range of applications in SOFCs components such as electrolyte, anode, cathode and barrier layers [201, 202]. Several authors have
studied the mechanical properties of rare earth-doped ceria. Sameshima et al. [203] and Morales et al. [204] reported the Young’s modulus values for rare earth-doped ceria, using samarium, lanthanum and gadolinium as dopant. Their results indicate that the Young’s modulus decreases when the concentration of trivalent ions in ceria increases, which is in good agreement with the results obtained by Wachtel and Lubomirsky [205], who indicated that an increment of oxygen vacancies produce a decrease of the elastic modulus since it makes the bonds “softer” (the strength of chemical bonds decreases).

Sato et al. [206] studied the effect of different rare earth cation-dopants on the Vickers microhardness and the fracture toughness of pure ceria. This study concludes that an increase of dopant content increases the Vickers microhardness value and decrease the fracture toughness value; in addition, this work reports that the value of Young’s modulus and fracture toughness of doped ceria are lower than those of pure ceria.

### 3.2 Carbon-Air Solid Oxide Fuel Cells

During power generation, coal is typically combusted in air or gasified by steam where irreversible mixing of the reactants and products is followed by a series of individual process steps to eventually generate electricity although at low efficiency. Thermoelectric power plants operate between pressure and temperature limits which determine their efficiency (i.e. Carnot’s efficiency). Unlike them, electrochemical oxidation of carbon inside a carbon-air solid oxide fuel cell (CA-SOFC) occurs isothermally and isobarically, where the reactant and product streams are kept separate. This further eliminates entropic losses due to mixing, and increases efficiency.

![Figure 3.2.1: Schematic of a carbon-air solid oxide fuel cell (CA-SOFC)](image)

An idealized CA-SOFC, schematically depicted in Figure 3.2.1, consists of an ionically conducting but electronically insulating solid, liquid or molten electrolyte (or, membrane). The solid fuel is housed inside the anode compartment where electrochemical oxidation is achieved by reaction of carbon with the oxide ions supplied through the electrolyte. The idealized net anode and cathode
reactions for CA-SOFC are, respectively:

\[ \text{CO}_2(g) + 4e^-_{(electrode)} \rightleftharpoons C(s) + 2O^{2-}_{(electrolyte)} \]  \hspace{1cm} (3.2.1)

\[ O_2(g) + 4e^-_{(electrode)} \rightarrow 2O^{2-}_{(electrolyte)} \]  \hspace{1cm} (3.2.2)

The overall net reaction is:

\[ C(s) + O_2(g) \rightarrow \text{CO}_2(g) \]  \hspace{1cm} (3.2.3)

The values of Gibbs free energy change for full oxidation of carbon (equation 3.2.3) are -394.4 kJ mol\(^{-1}\) at 300 K and -396.1 kJ mol\(^{-1}\) at 1 200 K. The corresponding values for the entropy change within the practical fuel cell operating temperatures remain quite small (e.g., 2.88 J K\(^{-1}\) at 300 K and 0.58 J K\(^{-1}\) at 1 200 K). Considering the equation 2.1.4 and the values of Gibbs free energy and entropy, the value of theoretical efficiency \( \Phi_{Th}^{\text{elec}} \) and reversible potential \( E_{rev,T} \) are both independent of temperature for all practical purposes. Most importantly, the small value for the entropy change results in comparable values of Gibbs free energy and enthalpy changes in equation 2.1.10 yielding a conversion efficiency of unity (i.e., 100\%) \[9\]. This high ceiling value of 100\% for efficiency theoretically available at useful operating temperatures provides a major advantage for electrochemical conversion of carbon over chemical processes, although it is usually difficult to achieve direct conversion. Naturally during actual fuel cell operation, values for operating cell voltages and conversion efficiencies are expected to be lower than theoretical predictions. Practical systems invariably exhibit irreversible losses due to finite rates for electrochemical reactions, heat and mass transport, current collection and distribution in the cells and stacks, and other system losses. Consequently the overall SOFC efficiency \( \Phi^{\text{SOFC}} \) is given by equation 2.2.17 (review Section 2.1).

The definitions of efficiency and cell voltage require modification due to the presence of the solid carbon fuel in the CA-SOFC, where solid carbon fuel activity correspond to unity during the oxidation reaction irrespective of the extent of conversion. In contrast, the activity (or, the concentration) of gaseous fuels, in conventional fuel cells, changes with extent of conversion. Accordingly, a general definition \[207\] of electrical cell efficiency, for CA-SOFC (\( \Phi^{\text{CA-SOFC}} \)) is given by:

\[ \Phi^{\text{CA-SOFC}} = \frac{W_{\text{CA-SOFC}}^{\text{out}}}{m_{\text{coal}} \cdot \text{HHV}_{\text{coal}}} \]  \hspace{1cm} (3.2.4)

where \( W_{\text{CA-SOFC}}^{\text{out}} \) is the power output of the cell, \( m_{\text{coal}} \) is the mass consumption rate of coal, and \( \text{HHV}_{\text{coal}} \) is its higher heating value. However, the experimental difficulties do not permit accurate determination of the amount of carbon consumed. This is especially true for CA-SOFC that employ a molten medium either in the form of a molten metal anode or a molten electrolyte, which makes it difficult to separate out the solid fuel and determine weight loss in a reliable manner. Moreover, full oxidation of carbon to the desired product \( \text{CO}_2 \) may not always be realized. Not only partial oxidation of carbon to CO (see equation 3.2.5) but also the Boudouard (see equation 3.2.6) reaction
may independently occur in the cell. Hence, the anode product gases generally contain not only CO\(_2\) but also CO depending on the type of CA-SOFC arrangement and its operating conditions. Naturally, for high cell efficiency the anode product gas is desired to be primarily CO\(_2\).

\[
\text{C(s)} + \frac{1}{2}\text{O}_2(\text{g}) \rightarrow \text{CO}(\text{g})
\]

(3.2.5)

\[
\text{C(s)} + \text{CO}_2(\text{g}) \rightleftharpoons 2\text{CO}(\text{g})
\]

(3.2.6)

Alexander et al. [208] proposed a generalized expression for cell electrical efficiency that takes into account the product distribution in the anode exhaust. The mass consumption rate of coal is expressed in experimentally accessible and measurable quantities of electrical current, \(I\), through the cell, and the respective molar fractions of anode product gases as follow:

\[
\left( \frac{x_{\text{C,coal}} \cdot m_{\text{coal}}}{M_C} \right) \cdot \left[ \frac{2 \left( x_{\text{CO}} + 2x_{\text{CO}_2} \right)}{4 \left( x_{\text{CO}} + x_{\text{CO}_2} \right)} \right] = \frac{I}{2F}
\]

(3.2.7)

This equation allows the determination of the coal consumption rate. Here, \(x_{\text{C,coal}}\) denotes the fraction of carbon in the coal, \(M_C\) is the molecular weight of carbon, \(x_{\text{CO}}\) and \(x_{\text{CO}_2}\) denote the molar fractions of CO and CO\(_2\) in the anode product gases respectively, and \(F\) is the Faraday constant.

Ideally, high conversion efficiency is desired at practically useful cell performance values. Although high conversion efficiency of 80\% was previously estimated [209], practically high values for cell performance obtained at such high efficiencies have not been experimentally demonstrated yet. Recent modeling work has in fact indicated a trade off between performance and efficiency as expected [208].

In electrochemical systems, electrochemical reaction sites (ERSs) are necessarily restricted to the electrode|electrolyte interface, and this constraint presents major challenges for solid carbon conversion. Generally, ERSs are not readily and widely accessible to either the carbon particles or oxygen. Accordingly, all carbon fuel cells configurations aim to overcome the physical barriers to electrochemical oxidation by providing effective delivery mechanisms to bring either the oxygen or carbon together at ERSs in a transformed chemical vehicle [17, 210].

In the following subsections, the different delivery modes of oxygen and carbon in convenient chemical carriers and the types of fuel cells based on these delivery mechanisms will be described.

### 3.2.1 Molten Electrolytes

The use of molten electrolytes in electrochemical oxidation of carbon in carbon-air fuel cells has the aim to ensure intimate contact between the carbon and oxygen. Oxygen from air is reduced at the cathode into a suitable oxygen donor such as a carbonate (CO\(_3^{2-}\)) or a hydroxyl (OH\(^-\)) ion that is compatible with the type of molten electrolyte used, or as an oxide (O\(^{2-}\)) ion in the form of a metal oxide. The oxygen donor ion supplied to the ERSs residing at the carbon|molten medium interface reacts with the carbon, provided that electrical connectivity is properly maintained at all
times. This is schematically illustrated in Figure 3.2.2 where the interfacial sites accessible to elec-
trons, carbon particles, and the electrolyte simultaneously through proper connectivity and wetting
serve as active ERSs, where electro-oxidation can be accomplished.

Figure 3.2.2: Schematic of the delivery of oxygen to electrochemical reaction sites (ERSs) in
molten hydroxide or carbonate electrolyte with dispersed carbon fuel [17].

3.2.1.1 Molten Hydroxide-based Carbon Fuel Cells

The molten hydroxide electrolyte approach for carbon conversion offers several advantages. In
general, hydroxide eutectics melt at much lower temperatures than their molten carbonate coun-
terparts, expanding the carbon-air fuel cells operation regime to lower temperatures. For example,
the NaOH-KOH eutectic melts at about 170 °C, while the individual hydroxides themselves melt at
much higher temperatures, 318 °C and 360 °C, respectively. Oxygen is highly soluble in molten
hydroxides in the form of peroxide (i.e., \( O_2^{2-} \)) and oxide (i.e., \( O^{2-} \)) ions, which are expected to
participate in the carbon oxidation reaction. Also, the high ionic conductivity (ca. 300 S m\(^{-1}\)) [9]
of hydroxide melts allows such cells to operate at intermediate temperatures in the range of 500 -
650 °C, where full oxidation to CO\(_2\) is thermodynamically favorable as opposed to the partial
oxidation product CO.

A schematic of a molten hydroxide carbon fuel cell is shown in Figure 3.2.3.

The net anodic half reaction for electro-oxidation of carbon is:

\[
CO_2(g) + 2H_2O(g) + 4e_{(electrode)} \leftrightarrow C(s) + 4OH^-_{(electrolyte)} \tag{3.2.8}
\]

At the cathode, oxygen is reduced to hydroxide ions according with the following reaction 3.2.9:

\[
O_2(g) + 2H_2O(g) + 4e_{(electrode)} \rightarrow 4OH^-_{(electrolyte)} \tag{3.2.9}
\]
Zecevic et al. [211] adopted the molten hydroxide approach and reported successful conversion of cylindrical graphite rods used as consumable anodes immersed in reagent grade NaOH melt. Open circuit voltages ranged between 0.7 and 0.85 V, significantly lower than 1.02 V expected for the full oxidation of carbon. Cell performance at 630 °C with Ni foam cathode showed a maximum current density of 2500 A m$^{-2}$ at about 0.15 V (or 370 W m$^{-2}$), while with mild steel doped cathode with 2 wt.% Ti (Fe$_2$Ti) conversion efficiency was 60% at 500 A m$^{-2}$. Cathodic losses were high due to mass transport limitations as well as ohmic losses that increased with increasing bubbling in the melt. While stirring reduced cathode polarization, gas bubbling increased ohmic resistance of the electrolyte, indicating a trade-off between the two.

In this cell configuration, however, one of the major concerns is the stability of the hydroxide melt against carbonation given by the reaction (3.2.10):

$$2\text{CO}_2(g) + 4\text{OH}^-(\text{electrolyte}) \rightleftharpoons 2\text{CO}_3^{2-}(\text{electrolyte}) + 2\text{H}_2\text{O}(g) \quad (3.2.10)$$

As the solubility limit of the CO$_3^{2-}$ ion in the hydroxide melt is exceeded, it precipitates out as alkali metal carbonate inside the melt. Naturally, this parasitic reaction (3.2.10) is undesirable and consumes the OH$^-$ ions in the molten electrolyte. The solid precipitate may also obstruct the cell and its components. As a result, the performance of this carbon fuel cell configuration is expected to degrade rapidly over time. Hackett et al. [212] demonstrated improved cell performance over those reported by Zecevic et al. [211] by employing prehumidified air at 70 °C supplied to the cathode compartment of the molten NaOH electrolyte cell operating at 600 - 700 °C. Open circuit voltage values for graphite ranged between 0.705 and 0.788 V, which were lower than expected, while the maximum power density was 840 W m$^{-2}$.

Clearly, for the practical application of molten hydroxide carbon fuel cells there is need to greatly
improve and optimize the cell performance, as well as address the stability issues due to the highly reactive nature of the molten hydroxide melt.

### 3.2.1.2 Molten Carbonate-based Carbon Fuel Cells

The replace of molten hydroxide for molten carbonate avoids the formation of carbonate in the hydroxide electrolyte. The molten carbonate used in a molten carbonate carbon fuel cell is typically a binary or ternary eutectic mixture of \( \text{Li}_2\text{CO}_3 - \text{Na}_2\text{CO}_3 - \text{K}_2\text{CO}_3 \), a porous NiO cathode and a Ni-Cr anode. However, NiO is not stable [213] in the molten carbonate environment due to the dissolution of the NiO into \( \text{Ni}^{2+} \), particularly in \( \text{K}_2\text{CO}_3 \); thus, Li-Na carbonate melts are preferable when compared to \( \text{Li}_2\text{CO}_3 - \text{K}_2\text{CO}_3 \) melts.

A simplified depiction of a molten carbonate carbon fuel cell is shown in Figure 3.2.4.

![Figure 3.2.4: Schematic of a molten carbonate carbon fuel cell for electro-oxidation of the carbon fuel particles dispersed in the molten carbonate electrolyte [17].](image)

In the molten carbonate fuel cell, multiple species are involved in the electrochemical process in both ionic (e.g., \( \text{CO}_3^{2-} \) and \( \text{O}_2^- \)) and dissolved form (\( \text{CO}_2 \), \( \text{O}_2 \) and \( \text{CO} \)), consequently, the mechanistically elementary details of the electrochemical reaction are not fully established or understood yet. However, the desired anode reaction is:

\[
3\text{CO}_2(\text{g}) + 4\text{e}^-_{(\text{electrode})} \leftrightarrow \text{C(s)} + 2\text{CO}_3^{2-}_{(\text{electrolyte})} \quad (3.2.11)
\]

Other reactions also need to be considered for the anode compartment. Peelen et al. [214] suggested the reactions:

\[
\text{CO}_3^{2-}_{(\text{electrolyte})} \rightleftharpoons \text{CO}_2(\text{g}) + \text{O}_2^-_{(\text{electrolyte})} \quad (3.2.12)
\]
The anodic reactions involve the carbonate ion participation, which delivers the oxygen required to oxidize the carbon fuel electrochemically. The carbonate ions are formed by the oxygen reduction in the cathode according with equation 3.2.13:

$$O_2(g) + 2CO_2(g) + 4e^-_{(electrode)} \leftrightarrow 2CO_3^{2-}_{(electrolyte)}$$  \hspace{1cm} (3.2.13)

Utilization and conversion of carbon in a molten carbonate electrolyte has several inherent advantages. Unlike molten hydroxide electrolyte, carbon is stable in the carbonate environment. By selecting from a wide range of binary or ternary alkali carbonates, one can adjust the desired eutectic temperature of the molten electrolyte and thus carbon fuel cell operating temperature. Upon wetting, molten carbonate electrolyte provides an extended solid|liquid interface and consequently, a high population of electrochemical reaction sites. Alkali metal ions in the carbonate melt also help to promote gasification of carbon [215]. However, molten carbonate carbon fuel cells require a complex CO$_2$ management system and cathode materials that are not tolerant to carbonate attack, which is a challenging problem at these elevated temperatures.

Inspired by early work on oxidation of carbon in aqueous [216, 217] and molten carbonate [218] cells, Vutekakis et al. [219] studied electrochemical oxidation of various carbonaceous solid fuels dispersed in a 32.1 wt.% Li$_2$CO$_3$ - 34.5 wt.% K$_2$CO$_3$ - 33.4 wt.% Na$_2$CO$_3$ ternary molten carbonate fuel cell arrangement at temperatures between 500 and 800 °C. At 700 °C, they reported about 13% carbon efficiency indicating that 87% is chemically converted to CO by the Boudouard reaction (equation 3.2.6).

Using various forms of pyrolytic carbon, Cooper and co-workers [209, 220-224] reported cell power densities between 400 and 840 W m$^{-2}$ at 0.8 V and 800 °C, where biochar-derived carbons with high degree of lattice disorder demonstrated relatively higher power densities than others.

Cooper [209] calculated an electrical conversion efficiency of 78-80% for rates up to 1 000 A m$^{-2}$ at 800 °C based on estimates of cell losses. This exceptionally high efficiency value was in good agreement with 78% efficiency estimated theoretically by Hemmes et al. [225] for the same system at 800 °C. Contrary to such high estimates, experimental measurements [226] indicate the difficulty in achieving high conversion efficiencies due to the significant role played by the Boudouard reaction in molten carbonate carbon fuel cells, in agreement with similar reports [219]. Naturally, such chemical losses due to Boudouard consumption dramatically affect carbon conversion efficiency in molten carbonate based carbon fuel cell arrangements.

### 3.2.2 Carbon-air Fuel Cells Based on Carbon Gasification

In the context of SOFCs, the electrochemical reaction sites (ERSs) and triple phase boundaries (TPBs) are synonymous and denote the same sites where charge transfer reactions take place. Even for ultrafine carbon particles less than 1 µm in size, accessibility to ERSs is inevitably limited. So this strategy involves conversion of carbon particles into a convenient chemical delivery vehicle in the form of a gaseous fuel that can readily be supplied to the ERSs by diffusion as is illustrated in Figure 3.2.5. The advantage of this approach, which is commonly employed in the context of
solid oxide electrolytes, is to circumvent the slow kinetics for the electro-oxidation of solid carbon, to gain ready access to the ERSs (i.e., TPBs), and to avoid the constrained electronic pathway between the TPBs at anode|electrolyte interface and the solid fuel particle. This approach is the most common strategy employed for CA-SOFC arrangements, where solid-to-solid contact at the TPBs is inevitably poor. It is accomplished typically by steam gasification of the solid fuel to produce syngas (i.e., a mixture of H$_2$ and CO), which can be cleaned up to remove contaminants if necessary. The syngas generally undergoes a catalytic water-gas shift reaction in case H$_2$ is the desired fuel to supply to the fuel cell.

![Schematic illustration depicting delivery of the fuel to ERS (TPB) on solid oxide based fuel cell via gasification of carbon by either steam or carbon dioxide](image)

Gür and co-workers [16,227–229] have proposed dry gasification for this purpose and successfully employed CO$_2$ to gasify carbon [17,210,230–232], coal [16,230] and biomass [207,230,233] to produce CO, which is then supplied to the TPBs at the fuel cell anode for electrochemical oxidation. Steam gasification is employed to generate H$_2$ and CO, or syngas, via the reaction\[3.2.14\]:

$$C(s) + H_2O(g) \rightarrow H_2(g) + CO(g) \quad (3.2.14)$$

Contaminants such as sulfur can be removed from the syngas produced, so cleaned syngas readily diffuses into the anode microstructure and undergoes electrochemical oxidation at the TPBs to CO$_2$ and H$_2$O. Alternatively, clean syngas can be water-shifted to produce additional hydrogen, which can then be electrochemically oxidized at the anode. The water-gas shift is an endothermic reaction with an overall enthalpy change of +102 kJ mol$^{-1}$ at 1 100 K. Steam gasification reaction \[3.2.14\] of carbon is an endothermic process with an enthalpy of +136 kJ mol$^{-1}$ at 1 100 K [9]. So usually, oxygen (or air) is injected into the gasifier along with steam to sacrificially burn part of the carbon in coal in order to supply the heat necessary to drive the endothermic gasification reaction. Catalytic shifting of syngas is accomplished by further addition of steam to produce more H$_2$ for the fuel cell:
The net overall reaction for steam gasification after steps 3.2.14 and 3.2.15 is given by:

\[ C(s) + 2\text{H}_2\text{O}(g) \rightarrow 2\text{H}_2(g) + \text{CO}_2(g) \] (3.2.16)

Alternatively, gasification of solid carbon can be achieved without the use of steam, *i.e.*, via dry gasification [234] using the Boudouard reaction:

\[ C(s) + \text{CO}_2(g) \rightleftharpoons 2\text{CO}(g) \] (3.2.17)

The enthalpy change in Boudouard reaction (equation 3.2.17) is slightly more endothermic than in the overall steam gasification reaction (equation 3.2.16), with a value of +169 kJ mol\(^{-1}\) at 1 100 K. Moreover, Gibbs free energy change indicates that Boudouard reaction is thermodynamically favored above 1 000 K. Consequently, there is clear thermodynamic incentive to perform dry gasification at elevated temperatures in order to achieve fast equilibration and maximum conversion of carbon to CO for subsequent utilization at the fuel cell anode.

The two fuels (H\(_2\) and CO), regardless of the type of gasification, are oxidized at the anode TPBs of the SOFC according with the reactions:

\[ 2\text{H}_2\text{O}(g) + 4e^-_{(electrode)} \leftarrow 2\text{H}_2(g) + 2\text{O}_2^-(_{(electrolyte)}) \] (3.2.18)

\[ 2\text{CO}_2(g) + 4e^-_{(electrode)} \leftarrow 2\text{CO}(g) + 2\text{O}_2^-(_{(electrolyte)}) \] (3.2.19)

Thermodynamics of H\(_2\) and CO oxidation reactions 3.2.18 and 3.2.19 indicate that the enthalpy change for the CO oxidation reaction is significantly more exothermic than for the oxidation of H\(_2\) (*i.e.*, -562 kJ mol\(^{-1}\) of O\(_2\) versus -495 kJ mol\(^{-1}\) of O\(_2\), respectively). Considering the enthalpy changes for reactions 3.2.16, 3.2.17, 3.2.18 and 3.2.19 it is possible infers that there is no significant energetic difference between steam and dry gasification.

Moreover, reactions 3.2.18 and 3.2.19 exhibit similar values for the standard Gibbs energy (*i.e.*, -185 kJ mol\(^{-1}\) of O\(_2\) versus -186 kJ mol\(^{-1}\) of O\(_2\), respectively at 850 °C), indicating that almost identical work potentials are offered by the oxidation of either fuel. Although energetically similar, however, steam gasification process requires large quantities of water, making dry gasification an attractive option for locations where water resources are scarce.
3.2.3 Gür’s Carbon-Air Solid Oxide Fuel Cell

The possibility of converting solid carbonaceous fuels to electricity in a fluidized bed solid oxide fuel cell arrangement was first proposed by Gür and Huggins [227, 235] two decades ago. More recently, the fluidized bed carbon-air solid oxide fuel cell (FB+CA-SOFC) [228] approach was investigated further by Gür and co-workers using different coke, coal and biomass. FB+CA-SOFC employs a SOFC element that is physically and thermally integrated with a dry gasifier [228]. The anode reaction product CO$_2$ is recirculated through the carbon bed minimally fluidizing the carbon particles while producing CO via the Boudouard reaction (equation 3.2.17). As the CO rise through the carbon bed, its interaction with solid carbon is minimal and can be ignored. In fact, in thermogravimetric experiments carried out between 250 and 1 100 °C, no significant interaction between CO and Spherocarb was observed [236].

![Schematic of a conceptual fluidized bed carbon air solid oxide fuel cell (FB+CA-SOFC) using CO$_2$ as fluidization gas for produce dry gasification and accomplish the electro oxidation of CO [17].](image)

Figure 3.2.6: Schematic of a conceptual fluidized bed carbon air solid oxide fuel cell (FB+CA-SOFC) using CO$_2$ as fluidization gas for produce dry gasification and accomplish the electro oxidation of CO [17].

The fuel cell element is made of YSZ electrolyte with a catalytic cermet anode such as Ni/YSZ and a mixed conducting cathode such as LSM/YSZ. Oxygen from air is reduced to oxide ions at the cathode, transported through the YSZ lattice, and electrochemically reacts with the CO at the anode TPBs. The FB+CA-SOFC process is schematically depicted in Figure 3.2.6, which illustrates the individual reaction steps. The reactor chamber that houses the fuel cell and the Boudouard gasifier typically operates between 800 and 900 °C. Lee et al. tested a FB+CA-SOFC with active cathode area of 5 cm$^2$. A maximum power density of 2 200 W m$^{-2}$ at 0.68 V was achieved [232], with activated carbon at 905 °C as shown in Figure 3.2.7.

A similar FB+CA-SOFC arrangement with 24 cm$^2$ active cathode area, was studied by Gür et al. in 2010 [16]; the results demonstrated an attractive power density of 4 500 W m$^{-2}$ for a single cell power of 11 W at a practical cell operating voltage of 0.64 V at 850 °C using untreated Alaska (Waterfall Seam Kenai-Cook Inlet County, AK) coal powder as the solid fuel in the Boudouard gasifier. Electrical conversion efficiencies measured experimentally were around 50% [16], slightly lower than potentially offered by molten hydroxide or carbonate based carbon-air fuel cells. The tubular fuel cell is located above the Boudouard gasifier, as can be seen in the schematic of the arrangement illustrated in Figure 3.2.8. An interesting result of this experiment is that over a period of
around 30 h, the cell voltage dropped gradually from 0.8 V to ca. 0.71 V. The initial degradation rate was about 1.3 mV h\(^{-1}\). Towards the end of the test, the rate of degradation was greater and the voltage also fluctuated significantly (see Figure 3.2.9). This decrease in performance and the fluctuations was primarily related to loss of fuel. This assumption was supported by estimates of coal bed contents. During the 36 h test run, approximately 45% of the carbon in the batch gasifier was consumed. In addition, the sulfur poisoning should occur at initial hours of the test. Moreover, after the performance tests, the SOFC anodes were visually examined and no obvious signs of carbon deposition, or coking, were observed. However, carbon deposition was observe under open circuit potential conditions.
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Figure 3.2.9: Performance stability of the SOFC operating at 850 °C directly on gasified Alaska coal char. The current density was maintained at 0.33 A cm\(^{-2}\) [16].

3.3 Hypothesis

Anodes based on cerium and molybdenum oxides are suitable to be use in carbon-air solid oxide fuel cells, having characteristics such as: adequate mechanical properties, electrocatalytic activity for oxidation of fuels, electrical and ionic conductivity comparable to that of other materials reported in the literature, and good thermal stability.

3.4 Thesis Objectives

The aim of this thesis was to fabricate, characterize and test a new anodic material for CA-SOFCs, resistant to sulfur poisoning and carbon deposition and with electrical and mechanical properties comparable to that of conventional SOFCs anode materials. To achieve this aim, the specific objectives were:

- To synthesize and characterize molybdenum-doped ceria nanoparticles with 5 wt.%, 7 wt.% and 10 wt.% of molybdenum contents for the fabrication of the fuel cell anodes and dense pellets for mechanical testing and conductivity measurements.
- To determine the Young’s modulus, microhardness and fracture toughness of the materials synthesized to characterize its mechanical properties.
- To determine the electronic-ionic conductivity of molybdenum-doped ceria (between 400 - 800 °C) to compare with other anodic materials and to evaluate whether these conductivity values are suitable for use in solid oxide fuel cell anodes.
- To determine the CMO area specific polarization resistance (ASPR) values and diffusion coefficients of oxygen, hydrogen and water (gas) using EIS measurements in symmetric cells under air and wet hydrogen atmospheres. This information allows to characterize the physicochemical phenomena involved in the system and its incidence in the electrical resistance of the cell.
• To determine the maximum electrical power density of a CMO/CMO-YSZ/YSZ/LSM-YSZ/LSM SOFC, where the CMO-YSZ composite is the anode of the cell. This information allows to check if the material presents electrocatalytic activity for fuel oxidation and compare with power density values reported in the literature.
Chapter 4

Experimental

In this chapter, a brief description of the experimental techniques and equipment used during this research work will be presented, as well as the protocol of fabrication of the dense ceramic discs, symmetric-cells and fuel cells.

4.1 Synthesis of CMO Nanopowders

CMO nanopowders were synthesized by the nitrate-fuel combustion method using citric acid (C_6H_8O_7, Sigma-Aldrich, 99.5% purity) as organic fuel and chelating agent. Cerium nitrate (Ce(NO_3)_3·6H_2O, Sigma-Aldrich, 99% purity) and ammonium molybdate ((NH_4)_6Mo_7O_24·4H_2O, Merck, 99% purity) were used as precursors.

The CMO nanoparticles were synthesized with three different compositions: 5 wt.%, 7 wt.% and 10 wt.% of molybdenum content. The stoichiometric proportion of precursors and citric acid were dissolved in deionized water; solution concentrations and volumes are summarized in Table 4.1.1.

<table>
<thead>
<tr>
<th>CMO (Mo content)</th>
<th>Cerium nitrate Ce(NO_3)_3·6H_2O</th>
<th>Citric acid C_6H_8O_7</th>
<th>Ammonium molybdate (NH_4)_6Mo_7O_24·4H_2O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Concentration / M</td>
<td>Volume / ml</td>
<td>Concentration / M</td>
</tr>
<tr>
<td>10 wt.%</td>
<td>0.889</td>
<td>30</td>
<td>0.704</td>
</tr>
<tr>
<td>7 wt.%</td>
<td>0.956</td>
<td>30</td>
<td>0.881</td>
</tr>
<tr>
<td>5 wt.%</td>
<td>1.000</td>
<td>30</td>
<td>1.000</td>
</tr>
</tbody>
</table>

The cerium nitrate and citric acid solutions were mixed and stirred for 20 minutes (at room temperature). After that, the ammonium molybdate solution was slowly added to the previous mixture and stirred for 1 h. The solution obtained was inserted inside a preheated furnace at 500 °C (in air) for 10 minutes (in a Brasimet K-400 furnace) and a porous foam was formed. This porous foam was grinded in a mortar and the as-prepared powder was obtained. Two samples of each as-prepared CMO powder were saved for thermogravimetric analysis (TGA) and X-ray diffraction.
analysis (XRD), for determination of the adequate calcination temperature and crystallinity of the material, correspondingly. Finally, the as-prepared powder was calcined at the determined temperature for 2 hours and the CMO fully-crystalline nanopowder was obtained, which was once again grinded in a mortar.

### 4.2 Fabrication of CMO and CeO$_2$ Dense Pellets

CMO dense pellets of ca. 20 mm of diameter and ca. 1 mm of thickness were produced for mechanical properties characterizations. Additionally, dense pellets of ca. 10 mm of diameter and ca. 1 mm of thickness were produced for measuring the electrical conductivity of the material by the four-probe method. The dense CMO pellets were produced by uni-axial compression (pressure applied of ca. 105 MPa) of the CMO nanopowders synthesized after calcination. The green pellets obtained were sintered in air at 1 200 °C for 4 hours in a tubular furnace (Nabertherm 120/150/16), using a heating rate and cooling rate of 1 °C min$^{-1}$. The sintered pellets were polished with sandpaper and exposed to a thermal etching process at 1 100 °C for 2 hours, using a heating rate of 5 °C min$^{-1}$ and a cooling rate of 2 °C min$^{-1}$ to reduce residual stress in the final product.

Figure 4.2.1: CMO discs with different molybdenum content. Right: three green pellets (before sintering process); left: three sintered discs of ca. 10 mm.

The photographs of the green discs (no sintered) and sintered discs are shown in Figure 4.2.1. It is worth to note the reduction of the discs size after the sinterization process due to the densification of the material.

Besides, CeO$_2$ dense pellets of ca. 10 mm of diameter and ca. 1 mm thickness were fabricated as a reference for electrical conductivity measurements. The CeO$_2$ nanopowders were synthesized using the same combustion method mentioned in Section 4.1. The dense CeO$_2$ pellets were produced by uni-axial compression (pressure applied of ca. 105 MPa) of the CeO$_2$ nanopowders synthesized after calcination. The green pellets obtained were sintered at 1 300 °C for 5 hours in a tubular furnace, using a heating rate and cooling rate of 1 °C min$^{-1}$. The sintered pellets were polished with sandpaper and exposed to a thermal etching process at 1 250 °C for 3 hours, using a heating rate of 5 °C min$^{-1}$ and a cooling rate of 2 °C min$^{-1}$ to reduce residual stress in the final product.
4.3 Crystalline Structure and Chemical Composition of CMO

The crystalline structure of the as-prepared CMO nanoparticles, calcined CMO nanoparticles and sintered CMO discs was studied by XRD analysis using a Bruker D8 Advance diffractometer. The analysis of the surface morphology of the dense CMO discs and the determination of the elemental composition of the CMO nanoparticles were studied by scanning electron microscopy and energy dispersive spectroscopy (SEM-EDS) using a Zeis EVO MA10 – Oxford Instruments X-act EDX. The oxidation states of the elements present in the CMO nanoparticles were determined by x-ray photoelectron spectroscopy (XPS) using a Physical Electronics 1257 XPS system. The study of shape, size and crystallinity of the CMO nanoparticles was done by transmission electron microscopy (TEM) coupled with selected area electron diffraction (SAED) using a Hitachi Model HT7700 operated at 120 kV. Finally, the thermal stability analysis of the material and the selection of its adequate calcination temperature were accomplished by thermogravimetric analysis (TGA) in nitrogen and oxygen atmospheres using a NETZSCH TG 209 F1 Libra analyser.

4.4 Specific Surface Area and Catalytic Activity of CMO

The specific surface area of CMO nanoparticles and commercial pure ceria (CeO$_2$, Sigma Aldrich, 99% purity) was calculated fitting BET isotherms to the nitrogen physisorption data obtained using a Quantachrome NOV Ae gas sorption analyser.

The catalytic effect of CMO and pure ceria in the wet carbon gasification was tested in a fluidized bed reactor. Inside of a quartz tube, 1.5 g of activated charcoal (Sigma Aldrich), 33 – 43 µm of particle size, and 1.5 g of CMO nanoparticles with 10 wt.% Mo or pure ceria were fed. A stream of 1.0 l min$^{-1}$ of extra pure nitrogen gas with 5 wt.% H$_2$O was continuously supplied inside the quartz tube reactor. The charged fluidized bed reactor was placed inside a vertical tubular furnace and heated up to 850 °C using a ramp rate of 5 °C min$^{-1}$. The gas product outlet was analysed using a Perkin Elmer Clarus 500 chromatograph. A gasification experiment without catalyst was carried out for comparative purposes.

The equipment used in the catalytic activity tests is composed by a tubular furnace with temperature controller, gas controller systems, an humidification system, and a differential manometer to reach the fluidized bed condition. The experimental setup is depicted in Figure 4.4.1.

4.5 Mechanical Strength Tests

4.5.1 Determination of the Young’s Modulus

A sintered pellet (20 mm of diameter) is suspended with soft springs and excited with an impact hammer. Its vibration is captured with a microphone and the sound signal is converted and stored by a data acquisition software. This information is processed in a computer and the resonance frequencies of the material are determined when the pellet is impacted at various positions by the hammer. As result of this analysis, the Young’s modulus ($E_Y$) can be determined using the value obtained for the resonance frequency of the sintered pellet when impacted in the border ($f_{20}$) using
Figure 4.4.1: Experimental setup used in catalytic activity tests.

The equation 3.1.11 introduced in the Section 3.1.4.1.

The schematic of the experimental setup used in this essay is the same presented in Figure 3.1.9 of the Section 3.1.4.1.

### 4.5.2 Determination of the Vickers Microhardness and Fracture Toughness

The microhardness was measured using a Struers microhardness tester under ambient conditions with a Vickers indenter. A sintered pellet of 10 mm is indented with different loads, ten times for each load. The loads used in these tests were 4.903 N and 9.807 N (default load values in the equipment), these loads were set to produce a crack in the sample. The Vickers microhardness ($H_V$) is calculated using equation 3.1.12 introduced in Section 3.1.4.2.

Fracture toughness ($K_{IC}$) is calculated using the Niihara and Anstis equations, considering the length of the fracture caused by indentation on the surface of a sintered pellet and the microhardness previously calculated. Niihara and Anstis formulas are presented in equations 3.1.13 and 3.1.14 correspondingly.

### 4.6 Electrical Conductivity Measurements

Electrical conductivity measurements were performed on CMO sintered discs (ca. 1.0 mm of thickness and ca. 10 mm of diameter; 5 wt.%, 7 wt.% and 10 wt.% of Mo) and pure CeO$_2$ sintered discs, under ultra-pure air atmosphere (100 ml min$^{-1}$ flow rate) and under 10 % H$_2$ / 90 % Ar atmosphere (100 ml min$^{-1}$ flow rate) using a four-probe arrangement. Connections were made with 4 spots of...
silver paste (Fuel Cells Materials) and silver wires (99.99% metal basis and 0.5 mm of diameter), connecting the silver wires with the surface of the sintered disc. Silver paste was dried at 100 °C for 1 hour and then cured at 800 °C for 1 hour using a heating rate and cooling rate of 1 °C min⁻¹. A picture of the electrical connections are shown in Figure 4.6.1.

The sintered discs were heated to the desired temperature in the range of 400 °C – 800 °C using a Nabertherm tubular furnace (model P330). A potentiostat/galvanostat/ZRA Gamry Reference 3000 was used to determine the electrical conductivity of the material through cyclic voltammetry measurements for each temperature. The data obtained was fitted using the van der Pauw equation and the conductivity values were obtained for each temperature [237]. A photograph of the experimental setup is shown in Figure 4.6.2.
An special device was designed during this thesis for measurements at high temperature in hydrogen atmosphere. This device consist in a quartz tube sealed by flanges and high temperature silicone. The hydrogen is fed in both sides of the ceramic CMO disc and the hydrogen is purged from an exit quartz tube. This device is presented in Figure 4.6.3.

![Device](image1)

**Figure 4.6.3:** Device used during the four probe test in hydrogen.

The schematic of the electrical connections to the potentiostat/galvanostat is depicted in Figure 4.6.4.

![Schematic](image2)

**Figure 4.6.4:** Schematic of the electrical setup used during four probe tests.

The crystalline structure of CMO sintered discs was analysed by XRD diffraction after conductivity tests. These results were compared with the diffractograms obtained before conductivity measurements.

Further understanding of the behaviour of CMO sintered pellets under H$_2$ atmosphere was achieved by a temperature programmed reduction (TPR) essay using a sample of 0.1 g of CMO calcined nanopowders with 10 wt.% Mo. The essay was run between 25 - 800 °C (heating rate of 10 °C min$^{-1}$) under a flowrate of 20 ml min$^{-1}$ of 10% H$_2$ / 90% Ar gas. The TPR allows to determine the temperature at which the reduction process occurs (if so) and detects changes in the oxidation states of the metal oxides. For comparative purposes, commercial MoO$_3$ (Sigma-Aldrich, 99% purity) and CeO$_2$ (Sigma Aldrich, 99% purity) powders were also analysed.
4.7 Fabrication of Symmetric-Cells and Fuel Cells

4.7.1 Fabrication of Symmetric-Cells

For the fabrication of symmetric test cells commercial 8-YSZ electrolyte discs of 20 mm of diameter and thickness 0.25-0.30 mm (Fuel Cell Materials) were used as support. These electrolyte discs were painted in both sides of the disc with nanoparticles-ink prepared with a commercial terpineol-based organic carrier (Fuel Cell Materials).

The proportion of solids (nanoparticles) to organic carrier, used in the preparation of the nanoparticles-inks, was maintained at: 70 wt.% solids / 30 wt.% organic carrier. A summary of the amounts of solids (nanoparticles) and organic carrier used in the preparation of the nanoparticles-inks is presented in Table 4.7.1. For the nanoparticles-inks preparation, the powders (solids) were mixed with the organic carrier and the mixture was stirred by hand until an homogeneous paste was obtained. Then, these inks were heated with continuous stir for 10 min at 50 °C. Finally, wait for the inks to cool down to 25 °C is needed.

Table 4.7.1: Description of the solid and organic carrier content present in the nanoparticles-inks used in the fabrication of symmetric-cells.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Function</th>
<th>Solids / g</th>
<th>Organic carrier / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO</td>
<td>Anode current collector</td>
<td>2 g CMO</td>
<td>0.8571</td>
</tr>
<tr>
<td>CMO-YSZ</td>
<td>Anode composite</td>
<td>1 g CMO 1 g YSZ</td>
<td>0.8571</td>
</tr>
</tbody>
</table>

Once the inks have been prepared, a first layer of CMO-YSZ ink was paintbrushed on both sides of the YSZ commercial disc. The painted surface corresponds to a circular section of 1.54 cm² in the centre of the disc (14 mm diameter). The ink was then dried on a hot plate for 1 hour at 50 °C.

When the first layer of CMO-YSZ was dried, a second layer of CMO ink was paintbrushed on the CMO-YSZ surface on both sides of the cell. The painted CMO ink was then dried on a hot plate for 1 hour at 50 °C.

After the ink was dried, the cell was sintered in a Nabertherm 120/150/16 tubular furnace at 1 100 °C for 3 h with a heating and cooling rate of 3 °C min⁻¹. An schematic of the cell dimensions and the layers coated on YSZ surface (cross-sectional schematic) are shown in Figures 4.7.1a and 4.7.1b, respectively.

A diagram with the fabrication stages and the experimental conditions is shown in Figure 4.7.2.

A photograph of a fabricated symmetrical cell is shown in 4.7.3.
4.7.2 Fabrication of Fuel Cells

For the fabrication of fuel cells, commercial 8-YSZ electrolyte discs of 20 mm of diameter (Fuel Cell Materials) were used as support. These electrolyte discs were paintbrushed in both sides of the disc with nanoparticles-ink (cathode ink and anode ink) prepared with a commercial terpineol-based organic carrier (Fuel Cell Materials).

The proportion of solids (nanoparticles) to organic carrier, used in the preparation of the nanoparticles-inks, was maintained at: 70 wt.% solids / 30 wt.% organic carrier. A summary of the amounts of solids (nanoparticles) and organic carrier used in the preparation of the nanoparticles-inks is pre-
Table 4.7.2: Description of the solid and organic carrier content present in the nanoparticles-inks used in the fabrication of fuel cells.

<table>
<thead>
<tr>
<th>Ink</th>
<th>Function</th>
<th>Solids / g</th>
<th>Organic carrier / g</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO</td>
<td>Anode current collector</td>
<td>2 g CMO</td>
<td>0.8571</td>
</tr>
<tr>
<td>CMO-YSZ</td>
<td>Anode composite</td>
<td>1 g CMO</td>
<td>0.8571</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 g YSZ</td>
<td></td>
</tr>
<tr>
<td>LSM</td>
<td>Cathode current collector</td>
<td>2 g CMO</td>
<td>0.8571</td>
</tr>
<tr>
<td>LSM-YSZ</td>
<td>Cathode composite</td>
<td>1 g CMO</td>
<td>0.8571</td>
</tr>
<tr>
<td></td>
<td></td>
<td>1 g YSZ</td>
<td></td>
</tr>
</tbody>
</table>

For the nanoparticles-inks preparation, the powders (solids) were mixed with the organic carrier and the mixture was stirred by hand until an homogeneous paste was obtained. Then, these inks were heated with continuous stir for 10 min at 50 °C. Finally, wait for the inks to cool down to 25 °C is needed. For the manufacture of fuel cells, four inks had to be prepared, which are detailed in Table 4.7.2.

Once the inks have been prepared, a first layer of LSM-YSZ ink (cathode matherial) was paintbrushed on one side of the YSZ commercial disc. The painted surface corresponds to a circular section of 1.54 cm² in the centre of the disc (14 mm diameter). The ink was then dried on a hot plate for 1 hour at 50 °C.

When the first layer of LSM-YSZ was dried, a second layer of LSM ink was paintbrushed on the LSM-YSZ surface of the cell. The painted LSM ink was then dried on a hot plate for 1 hour at 50 °C.

After the cathode inks were both dried, the semi-cell (LSM/LSM-YSZ/YSZ) was sintered in a Nabertherm 120/150/16 tubular furnace at 1150 °C for 3 h with a heating and cooling rate of 3 °C min⁻¹.

Once the cathode side was prepared, a first layer of CMO-YSZ ink (anode material) was paintbrushed on the other face of the YSZ commercial disc (opposite to the cathode side). The painted surface corresponds to the same circular section of the cathode (1.54 cm²), in the centre of the disc (14 mm diameter). The ink was then dried on a hot plate for 1 hour at 50 °C. When the first layer of CMO-YSZ was dried, a second layer of CMO ink was paintbrushed on the CMO-YSZ surface of the cell. The painted CMO ink was then dried on a hot plate for 1 hour at 50 °C.

After the anode inks were both dried, the complete fuel cell (LSM/LSM-YSZ/YSZ/CMO-YSZ/CMO) was sintered in a Nabertherm 120/150/16 tubular furnace at 1100 °C for 3 h with a heating and cooling rate of 3 °C min⁻¹.

An schematic of the fuel cell dimensions and the layers coated on YSZ surface (cross-sectional schematic) are shown in Figures 4.7.4.a-b and 4.7.4.c, respectively.

A diagram with the fabrication stages and the experimental conditions is shown in Figure 4.7.5.
Figure 4.7.4: Schematic of the fabricated fuel cell: a) dimensions of the anode side, b) dimensions of the cathode side and c) cross sectional schematic of the fuel cell.

Figure 4.7.5: Experimental procedure for the fabrication of the fuel cells.

Figure 4.7.6 shows a photograph of the fabricated fuel cell, where Figure 4.7.6a shows the LSM/LSM-YSZ electrode, corresponding to the cathode and Figure 4.7.6b shows the CMO/CMO-YSZ electrode corresponding to the anode.
4.8 **EIS and Current Density/Power Density-Potential Measurements**

### 4.8.1 EIS Measurements

The EIS measurements were performed on symmetric-cell CMO-YSZ/YSZ/CMO-YSZ (CMO 10 wt.% of Mo) under air and wet hydrogen atmosphere.

The first step consists of making the electrical connections to each electrode of the symmetric-cell. First, two circular sections of silver mesh (0.1 mm of diameter, 99.9% metal basis) of 16 mm of diameter and four silver wires (0.5 mm of diameter, 99.9% metal basis) of 25 cm in length each one were cut. Then, two wires were fixed with silver paste (fuel cells materials) on the borders of the mesh as shown in Figure 4.8.1. This procedure was performed for the two cut meshes. The silver paste was dried at 100 °C for 1 hour in a hot plate.

Once the connection between the silver mesh and the silver wires was ready, the mesh was joined to the electrodes of the symmetric-cell. A thin layer of silver paste was painted over the electrode and the silver mesh. Then, both surfaces are put in contact. To dry the silver paste, the cell attached to the mesh was placed on a hot plate at 100 °C for 1 hour. This procedure was performed for both electrodes of the symmetric-cell. Once the silver paste was dried, the cell attached to the two silver meshes and its four silver wires were placed into a Nabertherm 120/150/16 tubular furnace for sintering at 800 °C for 1 hour, using a heating rate and cooling rate of 1 °C min⁻¹. The symmetric-cell with its electrical connections is shown in Figure 4.8.2.

The EIS tests in air were carried out under ultra-pure air atmosphere (100 ml min⁻¹ flow rate). The temperatures selected in each measurement were in the range between 400 °C - 800 °C, changing...
CHAPTER 4. EXPERIMENTAL

Figure 4.8.2: Electrical connections in the cell.

Figure 4.8.3: Electrical connections to galvanostat/potentiostat.

The EIS tests were performed in a potentiostat/galvanostat/ZRA Gamry Reference 3000. An schematic of the electrical connections to the Gamry Reference 3000 is shown in Figure 4.8.3.

The EIS tests in wet hydrogen were performed under H$_2$/Ar atmosphere (60 ml min$^{-1}$ of total flow rate). The wet H$_2$/Ar mixture was fed on each side of the symmetric-cell. The electrical connections in the symmetric-cell are made with the same procedure indicated for EIS measurements in air (Figure 4.8.1 and Figure 4.8.2).

The EIS measurements were carried out varying the temperature and varying the hydrogen composition (vol.%). These tests were completed in the Centro Atómico Constituyentes (Buenos Aires, Argentina). A summary of the operational conditions set during the EIS measurements is shown in Tables 4.8.1 and 4.8.2.
Table 4.8.1: Temperatures selected for EIS measurements with a constant flow rate of 60 ml min\(^{-1}\) of 10\%H\(_2\)/Ar, 3\% H\(_2\)O mixture.

<table>
<thead>
<tr>
<th>Measurement</th>
<th>Temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>650</td>
</tr>
<tr>
<td>2</td>
<td>700</td>
</tr>
<tr>
<td>3</td>
<td>750</td>
</tr>
<tr>
<td>4</td>
<td>800</td>
</tr>
</tbody>
</table>

Table 4.8.2: Different hydrogen compositions used in EIS tests at constant temperature of 800 °C (The water content in the dry gas is 3 wt.%).

<table>
<thead>
<tr>
<th>Measurement</th>
<th>(\text{H}_2) flow rate / ml min(^{-1})</th>
<th>(\text{Ar}) flow rate / ml min(^{-1})</th>
<th>vol.% (\text{H}_2)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>60</td>
<td>0</td>
<td>10</td>
</tr>
<tr>
<td>2</td>
<td>30</td>
<td>30</td>
<td>5</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>45</td>
<td>2.5</td>
</tr>
<tr>
<td>4</td>
<td>7.5</td>
<td>52.5</td>
<td>1.25</td>
</tr>
</tbody>
</table>

The equipment used during the EIS hydrogen tests consisted of a closed quartz tube where the symmetric-cell is placed inside. A photograph of the equipment used in EIS hydrogen tests is shown in Figure 4.8.4.

4.8.2 Current Density/Power Density-Potential (\(j/P-E\)) Curves

The \(j/P-E\) curves associated to the cell were obtained on a ProboStat Fuel Cell system for SOFC tests in the CITEDEF (Instituto de Investigaciones Científicas y Técnicas para la Defensa, Buenos Aires, Argentina) facilities. The experimental setup used during the fuel cell tests is shown in Figure 4.8.5.
The fuel cell was pasted to one end of the alumina tube with refractory cement at 700 °C. The temperature was held at 700 °C for SOFC conditioning. The air was purged from the cell with nitrogen during 15 minutes. Then, the hydrogen was fed to the anode, increasing the concentration slowly. The initial flow fed into the anode was 40 ml min\(^{-1}\) with 3.5 vol.% \(\text{H}_2 / \text{N}_2\). When 30 min were elapsed, the hydrogen concentration is increased, keeping the same total flow rate (40 ml min\(^{-1}\)), to 5 vol.% \(\text{H}_2 / \text{N}_2\). Finally, once 30 min were elapsed, the flow rate was changed to 7 vol.% \(\text{H}_2 / \text{N}_2\).

Once the cell was conditioned, the furnace temperature was increased until reach the temperature of measurements, 800 °C. When the temperature was reached, the cathode was fed with 200 ml min\(^{-1}\) of ultra-pure air, and the flow of hydrogen is wetted in a humidifier. The water content in the inlet stream was \(\text{ca. } 3 \text{ wt.}\% \text{ of H}_2\text{O}\).

Once the fuel and air are fed to the fuel cell and the process temperature (800 °C) is stable, it is necessary to wait for the system to reach the steady state. This time can vary from 1 to 2 hours or even more. The system is ready to start measurements when the OCV value is stable and in the range of 1-1.1 V (typical value for \(\text{H}_2\) (fuel) / \(\text{O}_2\) (oxidant) system).

The electrochemical measurements were carried out in a Autolab PGSTAT302N 30 V / 2000 mA potentiostat/galvanostat.
Chapter 5

Molybdenum-doped Ceria: Material Characterization, Mechanical and Electrical Properties

The selection of CMO as anodic material in this research work is based on its interesting properties for carbon-air solid oxide fuel cell applications, reviewed in Section 3.1.3.4. CMO nanoparticles were synthesized by the combustion synthesis method detailed in Section 4. This method is proposed as an alternative of the conventional solid state reaction, used by Li and Thangadurai (2009) [155], due to its higher synthesis rates and lower contamination traces in the products obtained.

This chapter presents the results of the characterization of the synthesized nanoparticles of Mo-doped ceria (CMO), including the analysis of its crystalline structure, composition and thermal behavior, which were studied to determine the best conditions to fabricate the dense discs used in mechanical and electrical tests. In addition, the results of mechanical and electrical tests are also presented, emphasizing the influence of the molybdenum concentration on them.

5.1 Determination of the Calcination Temperature of CMO as-Prepared Powders

The calcination temperature of the as-prepared CMO nanopowders is a crucial parameter to obtain nanoparticles with high crystallinity and without the presence of residual precursors. Firstly, the thermal behaviour of the as-prepared CMO nanopowders and the selection of the appropriate calcination temperature was studied based on TGA analysis of the material in nitrogen atmosphere. The results obtained are shown in Figure 5.1.1a, from which it can be observed that the mass of the as-prepared CMO nanopowders samples (with 10 wt.% of Mo) decreases up to 400 °C, presumably due to the decomposition of residual precursors. For temperatures between 400 and 950 °C the sample begins to gain mass, probably due to the adsorption of nitrogen gas on the porous surface of the CMO nanopowders (this porosity is associated with the high surface area of the CMO nanopowders -see Table 5.4.1-, which was estimated by nitrogen physisorption analysis). From the analysis of these results, a calcination temperature of 700 °C was initially selected. Secondly, the thermal behaviour of CMO nanopowders (with 10 wt.% of Mo) pre-calcined at 700 °C was studied
under nitrogen and air atmospheres (see Figure 5.1.1 a for comparison with as-prepared nanopowders under nitrogen atmosphere, and Figure 5.1.1 b for comparison of pre-calcined nanopowders under nitrogen and air atmospheres). The mass of the pre-calcined nanopowders decreases slightly up to 600 °C under nitrogen atmosphere, and then increases from this temperature up to 950 °C. The initial mass decrease indicates that 700 °C is not an adequate calcination temperature to eliminate the residual precursors.

The TGA analysis in air atmosphere of CMO nanopowders (with 10 wt. % of molybdenum, pre-calcination temperature: 700 °C) shows a rapid mass decrease at low temperatures, related to calcination of residual precursors, and a mass gain of almost double the mass gain under nitrogen atmosphere. The latter results suggest that air is adsorbed on the surface of the nanopowders and that oxygen is incorporated to the lattice structure of CMO promoting this mass gain.

Figure 5.1.1: TGA of as-prepared and pre-calcined CMO nanopowders under nitrogen and air atmospheres: a) TGA in nitrogen atmosphere of as-prepared and pre-calcined CMO nanopowders (with 10 wt. % of molybdenum, pre-calcination temperature: 700 °C), b) TGA in nitrogen and air atmospheres of CMO nanopowders (with 10 wt. % of molybdenum) pre-calcined at 700 °C.

To support the discussion above, a DTA analysis of the pre-calcined CMO nanopowders (10 wt. % of Mo) was performed under air atmosphere. The DTA plot in Figure 5.1.2 a shows a first sharp peak at around 120 °C related to the endothermic process of water evaporation; the second peak at around 250 °C is an exothermic process associated with the chemical decomposition of residual precursors; finally, at ca. 700 °C the broader peak can be related to a crystal growth process. These results confirm the hypothesis raised in the previous paragraph and thus a new calcination temperature of 850 °C was selected.

The influence of the calcination temperature in the morphology of sintered CMO nanoparticles was studied by SEM analysis of two dense CMO discs (sintered at 1 200 °C) prepared using nanopowders calcined at 700 °C and 850 °C, respectively. The dense sintered discs were pricked in the surface with a fine stainless-steel needle and sonicated for removing the detached material; the punched surface was analysed by SEM. Figure 5.1.2 b and Figure 5.1.2 c show the pricked surface of sintered discs fabricated using nanopowders calcined at 700 °C and 850 °C, correspondingly. Comparing the two images, it is possible to observe that for nanoparticles calcined at 700 °C the
Figure 5.1.2: DTA in air atmosphere of CMO nanopowders and SEM micrographs of the surface of CMO sintered discs prepared using these nanopowders: a) DTA in air atmosphere of CMO nanopowders (with 10 wt.% of molybdenum) pre-calcined at 700 °C; SEM micrographs of the surface of CMO sintered discs prepared using nanopowders pre-calcined at: b) 700 °C and c) 850 °C.

The sintered disc present amorphous like-flower structures that can be associated with residual precursors which did not reach complete conversion at this temperature, while for nanoparticles calcined at 850 °C fully-crystalline CMO sintered nanoparticles are observed. These results agree with TGA and DTA results and indicate that 850 °C is an appropriate calcination temperature to obtain fully crystalline CMO nanoparticles and dense sintered discs.

Based on this result, the selected calcination temperature was 850 °C and the dense discs were prepared using calcined nanoparticles at this temperature.
5.2 Characterization of the CMO Crystallinity and Microstructure

The XRD patterns of as-prepared and calcined CMO nanopowders (for 10 wt.% of Mo content) are shown in Figure 5.2.1. These results indicate that CMO crystallize as a fluorite-type structure, likewise its CeO$_2$ parent, and that the calcined nanopowders exhibits more crystallinity than the as-prepared nanopowders. The CMO nanoparticles were synthesized with four different molybdenum content: 5, 7, 10 and 12 wt.%. Figure 5.2.1b shows the diffractogram for CMO calcined nanopowders with 5, 7 and 10 wt.%, where no presence of the free-MoO$_3$ crystalline phase is observed; for CMO with 12 wt.% of molybdenum, MoO$_3$ was found as a secondary phase (see Figure 5.2.2). Probably a composition over 10 wt.% exceeds the solubility limit of MoO$_3$ in the CeO$_2$ crystalline structure, and consequently the remaining molybdenum ions produce MoO$_3$ as a separate phase during the calcination process. For this reason, the maximum content of molybdenum suggested for the synthesis of CMO is 10 wt.%. Figure 5.2.3 compares the XRD patterns of sintered CMO discs and calcined nanopowders with 10 wt.% of molybdenum, which confirms the absence of secondary phases in the product.

An XRD analysis was carried out for dense sintered discs with 5 and 7 wt.% of molybdenum, showing no significant differences with the previously described CMO disc with 10 wt.% of molybdenum. The thermal stability of CMO at sintering conditions is confirmed by the unaffected crystalline pattern shown by the sintered discs.

The different XRD patterns obtained were fitted by Rietveld refinement using the FullProf Suite v.3.0 freeware (https://www.ill.eu/sites/fullprof/php/downloads.html) to determine the lattice parameter ($a$) and density ($\rho$) of the material. The structural parameters used in Rietveld refinement were these reported by Ramezanipour et al. in a previous work [146]. Crystallite size was calculate using Scherrer’s formula [238].

Figure 5.2.1: XRD analysis of as-prepared and calcined CMO nanopowders: a) comparison of the XRD patterns of as-prepared and calcined CMO nanopowders with 10 wt.% of molybdenum and b) XRD patterns of calcined CMO nanopowders with 5, 7 and 10 wt.% of molybdenum.
Figure 5.2.2: XRD patterns of calcined CMO nanopowder with 12 wt.% of molybdenum.

Figure 5.2.3: Comparison between XRD patterns of calcined CMO nanopowders and sintered CMO discs with 10 wt.% of molybdenum.

\[ D = \frac{0.9 \cdot \lambda}{\left( \beta_{\text{sample}}^2 - \beta_{\text{ref}}^2 \right)^{0.5} \cdot \cos(\theta)} \]  

(5.2.1)

where \( D \) is the crystallite diameter size, \( \lambda \) is the wavelength of radiation source (1.54 Å for K\(_{\alpha}\) Cu), \( \theta \) is the Bragg angle, \( \beta_{\text{sample}} \) is the full width at half maximum (FWHM, expressed in rad) of (1 1 1) reflection from diffractograms, and \( \beta_{\text{ref}} \) corresponds to the instrumental FWHM (0.02 for this diffractometer). The lattice strain was calculated with an approximate relationship from Bragg’s law, relating the inhomogeneous strain to the peak broadening it produces [239]:
Table 5.2.1: Crystalline structure parameters of pure ceria and CMO nanoparticles.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a) / nm</th>
<th>(\rho) / g cm(^{-3})</th>
<th>(%R_{\text{exp}})</th>
<th>(%R_{\text{wp}})</th>
<th>(%R_p)</th>
<th>GOF</th>
<th>(D) / nm</th>
<th>(%L_S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>As-prepared 10 wt.% Mo</td>
<td>5.431</td>
<td>7.144</td>
<td>12.24</td>
<td>15.2</td>
<td>19.6</td>
<td>1.1</td>
<td>14.3</td>
<td>0.950</td>
</tr>
<tr>
<td>Calcined 10 wt.% Mo</td>
<td>5.421</td>
<td>7.463</td>
<td>10.12</td>
<td>16.6</td>
<td>23.4</td>
<td>1.3</td>
<td>20.0</td>
<td>0.670</td>
</tr>
<tr>
<td>Calcined 7 wt.% Mo</td>
<td>5.427</td>
<td>7.365</td>
<td>8.48</td>
<td>14.4</td>
<td>19.2</td>
<td>1.5</td>
<td>23.6</td>
<td>0.596</td>
</tr>
<tr>
<td>Calcined 5 wt.% Mo</td>
<td>5.422</td>
<td>7.299</td>
<td>8.81</td>
<td>12.3</td>
<td>16.7</td>
<td>1.4</td>
<td>29.2</td>
<td>0.447</td>
</tr>
<tr>
<td>Pure ceria*</td>
<td>5.411</td>
<td>7.220</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
<td>—</td>
</tr>
</tbody>
</table>

\(\%R_{\text{exp}}\): expected R-weighted pattern; \(\%R_{\text{wp}}\): R-weighted pattern; \(\%R_p\): R-pattern; GOF: goodness of fit.


\[ L_S = \frac{\left(\beta_{\text{sample}}^2 - \beta_{\text{ref}}^2\right)^{0.5}}{4 \cdot \tan(\theta)} \]  

(5.2.2)

where \(L_S\) is the lattice strain.

The values obtained for lattice parameter, density, crystallite diameter size and lattice strain of the synthesized CMO nanoparticles and the sintered CMO dense pellets are reported in Table 5.2.1 and Table 5.2.2 respectively.

Table 5.2.2: Crystalline structure parameters of CMO sintered dense discs.

<table>
<thead>
<tr>
<th>Sample</th>
<th>(a) / nm</th>
<th>(\rho) / g cm(^{-3})</th>
<th>(%R_{\text{exp}})</th>
<th>(%R_{\text{wp}})</th>
<th>(%R_p)</th>
<th>GOF</th>
<th>(D) / nm</th>
<th>(%L_S)</th>
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<tbody>
<tr>
<td>10 wt.% Mo</td>
<td>5.4107</td>
<td>7.2403</td>
<td>9.63</td>
<td>19.7</td>
<td>25.4</td>
<td>1.6</td>
<td>100</td>
<td>0.171</td>
</tr>
<tr>
<td>7 wt.% Mo</td>
<td>5.4107</td>
<td>7.2301</td>
<td>12.03</td>
<td>19.8</td>
<td>26.2</td>
<td>1.4</td>
<td>93.2</td>
<td>0.182</td>
</tr>
<tr>
<td>5 wt.% Mo</td>
<td>5.4098</td>
<td>7.2214</td>
<td>11.12</td>
<td>19.5</td>
<td>24.3</td>
<td>1.3</td>
<td>93.2</td>
<td>0.182</td>
</tr>
</tbody>
</table>

The change in the lattice parameter compared to the value reported in literature for pure ceria (shown in Table 5.2.1) confirms the substitutional doping process. The ionic radius of \(\text{Mo}^{6+}\) (0.55 Å) is less than that of \(\text{Ce}^{4+}\) (1.11 Å), and consequently the substitutional process should produce compressive tensile in the crystal structure and a decrease of the lattice parameter is expected; however, the electroneutrality in this compound is reached through interstitial oxygen anions (see reaction 3.1.9) which produce a slight increment in the lattice parameter and density when compared to pure ceria. Additionally, a \(\text{Mo}^{6+}\) increment in the CMO composition involves a higher amount of interstitial oxygen anions in the lattice structure; accordingly, a density increment is expected as the \(\text{Mo}^{6+}\) content in CMO increases, which is confirmed by the results presented in Table 5.2.1 and Table 5.2.2. It is worth to note that the increase in the lattice parameter and density values is small (maximum 3\%), which explains that no monotonous increase in the lattice parameter of CMO can be noticed when the Mo content rises from 5 to 10 wt.\%.
The calcination and sintering processes promote a decrease of the lattice parameter and lattice strain, and an increase of the crystallite diameter size (see Table 5.2.1 and Table 5.2.2), since the thermal treatment release stress in the material and promote the crystal growth. The values for the lattice parameters reported in this work are in good agreement with those reported by Li and Thangadurai for sintered CMO nanopowders synthesized by the solid-state reaction method [155].

Figures 5.2.4 a-c show the TEM micrographs and SAED patterns of calcined CMO nanoparticles with 5, 7 and 10 wt.% of molybdenum. TEM micrographs shows nanoparticles with irregular spherical morphology. In addition, it is observed the presence of well defined straight sides in the boundary of nanoparticles, which is typical for cubic crystalline systems. The SAED patterns show a well-defined polycrystalline fluorite-type structure without presence of secondary phases.

![TEM micrographs and SAED patterns of CMO nanoparticles](image)

Figure 5.2.4: TEM micrographs and SAED patterns of CMO nanoparticles calcined at 850 °C with: a) 5 wt.%, b) 7 wt.% and c) 10 wt.% of molybdenum; d) indexation of SAED pattern of CMO nanoparticles with 10 wt.%; e) HRTEM of CMO nanoparticles with 10 wt.% of molybdenum.

The particle sizes were estimated according to ASTM standards [240] and the results obtained are presented in Figure 5.2.5. The particle sizes obtained by this approach are close to the values of crystallite diameter sizes presented in Table 5.2.1. The diminution of crystallite sizes with the increasing content of dopant is related to the increase of strain in lattice structure; however, it does not exist a direct relationship between particle size and dopant content because it depends on different factors, such as synthesis route and agglomeration. The same dependence between crystallite size and dopant content was reported in previous works for Mn-doped ZnO [241] and Eu-doped TiO$_2$ [242]. Huang et al. observed the same behaviour when synthesizing Mo-doped TiO$_2$ with different Mo content using the sol-gel route [243]; since Mo$^{6+}$ has an ionic radii slightly lower than Ti$^{4+}$ but a higher oxidation state, an increment in Mo content increase the lattice distortion and inhibit the crystallite growth.
Figure 5.2.5: Average size of CMO nanoparticles with different molybdenum content expressed as wt. %.

As can be seen from the HRTEM micrograph in Figure 5.2.4(e), only one kind of periodicity of the lattice fringes can be observed for CMO nanoparticles, which matches with the distance expected between the (1 1 1) and (2 0 0) reticular planes of the samples. This result indicates that the most exposed crystallographic planes of the samples should be the (1 1 1) and (2 0 0) planes.

5.3 Chemical Characterization of CMO

The chemical composition of CMO nanopowders was studied by EDS analysis. The results indicate a homogeneous distribution of molybdenum in CMO, which can be observed in the elemental mapping in Figure 5.3.1(a-c). In addition, the content of molybdenum in CMO determined by EDS analysis is in good agreement with the stoichiometric amount calculated for the preparation (combustion method) of CMO nanopowders with different molybdenum contents (see Figure 5.3.1(d)). The slight differences between EDS results and stoichiometric amounts are attributed to experimental errors.

Although the results obtained by EDS are as expected, it is necessary to clarify that this technique corresponds to a semi-quantitative analysis and these results should be corroborated by specific measurements (such as inductive coupled plasma-ICP).

The precursor agent used, ammonium heptamolybdate, produces molybdenum trioxide (MoO$_3$) when calcined under oxygen atmosphere [244]. For this reason, probably the oxidation state of molybdenum in CMO correspond to +6, when the molybdenum ion replaces the cerium ion in the lattice structure. Bo et al. [245] prepared a Mo and Y co-doped CeO$_2$ with a nominal composition of Ce$_{6−x}$Y$_x$MoO$_{15−δ}$ ($x = 0.1–1.4$), for this compound an XPS analysis revealed an oxidation state of +6 for Mo ion. Li et al. [155] did not present an XPS analysis for CMO, but stated the possibility of the molybdenum ion oxidation state should be +6 based on Bo et al. study.
Figure 5.3.1: EDS analysis of CMO nanopowders with: a) 5 wt.%., b) 7 wt.% and c) 10 wt.% of molybdenum; d) comparison of theoretical (stoichiometric) and EDS measured concentrations of molybdenum in CMO.

The core level spectra of Mo$_{3d}$ and O$_{1s}$ for CMO nanopowders with 10 wt.% of molybdenum, synthesized in this work, are presented in Figure 5.3.2.

Figure 5.3.2: XPS patterns of (a) Mo$_{3d}$ and (b) O$_{1s}$ for CMO nanopowders with 10 wt.% of molybdenum.

The Mo$_{3d}$ signals consist of a photoelectron peak at 235.5 eV and 232 eV which is a typical Mo$^{6+}$ doublet signal that is consistent with the literature [246, 247]. No other signals of different oxidation states of molybdenum are presented in the spectra. The O$_{1s}$ spectra was decomposed in two components, one photoelectron peak at 530 eV corresponding to oxidized species (oxygen from
metal oxides) and a second signal at 533.2 eV which corresponds to adventitious oxygen gas probably adsorbed on the porous surface of the nanomaterial.

5.4 Specific Surface Area and Catalytic Activity of CMO.

A nitrogen physisorption analysis allowed to determine the specific surface area of the calcined CMO nanoparticles and commercial pure ceria powders used for gasification tests; the results are summarized in Table 5.4.1. The values of surface area presented in this work for CMO are lower compared to values reported in other works for metal-doped ceria systems, synthesized by sol-gel methods [248, 249]. However, in this work the calcination temperature used to produce nanoparticles was higher than that reported and probably produce the coarsening of nanoparticles, reducing their surface area. On the other hand, the surface area of the CMO nanoparticles is nearly twice the surface area of the commercial pure ceria nanoparticles, which impacts positively in the catalytic activity of the first.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Specific surface / m² g⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>10 wt. % Mo</td>
<td>15.075</td>
</tr>
<tr>
<td>7 wt. % Mo</td>
<td>14.296</td>
</tr>
<tr>
<td>5 wt. % Mo</td>
<td>14.657</td>
</tr>
<tr>
<td>Ceria (commercial)</td>
<td>7.621</td>
</tr>
</tbody>
</table>

The results of syngas production adding commercial pure ceria or CMO with 10 wt.% Mo nanoparticles as catalyst in a fluidized-bed reactor are shown in Figure 5.4.1. Comparing the cumulative production of syngas (H₂ + CO + CO₂) after 2 hours of reaction at 800 °C, it is possible to observe that commercial pure ceria and CMO with 10 wt.% Mo present catalytic activity for the wet gasification of carbon. The addition of molybdenum to ceria enhances the catalytic activity of the material, increasing the final carbon conversion after 2 hours of reaction in ca. 20%. This effect must be due to the known catalytic activity of MoO₃ for the oxidation of carbonaceous fuels [150, 151] and the higher specific surface area of the synthesized CMO nanoparticles compared to commercial pure ceria. However, a more profound study of this catalytic process is needed to determine the scale at which each of these properties influences the reaction mechanism.

5.5 Mechanical Properties of the CMO

The mechanical properties of rare earth-doped ceria have been extensively studied because of the applications of these materials as electrolyte and electrode in SOFCs. Sameshima et al. [203] and Morales et al. [204] studied the Young’s modulus values for samarium-, lanthanum- and gadolinium- doped ceria. The results obtained from this experiments indicate that the Young’s
modulus decreases when the concentration of trivalent ions (Sm$^{3+}$, La$^{3+}$ and Gd$^{3+}$ in ceria increases. Wachtel and Lubomirsky [205] explained this behavior, noting that the trivalent ions doping, produces the formation of additional oxygen vacancies and consequently, the increment of oxygen vacancies produce a decrease of the elastic modulus since it makes the bonds “softer” (the strength of chemical bonds decreases). The effects of Mo$^{6+}$ ions on the mechanical properties of ceria has not been investigated, as well as the effect of doping ceria with metallic ions with higher oxidation state than Ce$^{4+}$, thus the results presented in this section represent a first approach to this.

Figure 5.4.1: Production of synthesis gas and carbon conversion in a wet gasification process using a fluidized bed reactor with pure ceria or CMO with 10 wt.% Mo particles as catalysts.

Figure 5.5.1: Impulse essay results: a) Resonance frequencies (obtained by the impulse method) and b) Young's modulus values calculated for pure ceria* and CMO sintered discs with 5, 7 and 10 wt.% of molybdenum. (*data for ceria obtained from [176])
CHAPTER 5. MOLYBDENUM-DOPED CERIA: MATERIAL CHARACTERIZATION, MECHANICAL AND ELECTRICAL PROPERTIES

Figure 5.5.1a shows the resonant frequencies plots associated to the impact essays on CMO dense discs with 5, 7 and 10 wt.% of molybdenum. Using these results and equation 3.1.11, the Young’s modulus for each sample was calculated and the results obtained are summarized in Figure 5.5.1b, including that for pure ceria (reported by Akbari-Fakhrabadi *et al.* [176]). The results presented in 5.5.1b were corrected considering the porosity effect, using an empirical relationship employed by Selcuk and Atkinson [198]:

\[
E_o = \frac{E_Y}{\exp(-4.5\varepsilon_p)} \tag{5.5.1}
\]

where \(E_o\) is the elastic modulus at zero porosity (\(\varepsilon_p = 0\)) and \(E_Y\) is the elastic modulus. The porosity values and the values of \(E_Y\) and \(E_o\) can be found in Appendix A.

An increment of Young’s modulus is observed when the molybdenum content increases. This behaviour can be related to the mechanism whereby CMO gets electroneutrality. Trivalent ions like Sm\(^{3+}\), Ga\(^{3+}\) and La\(^{3+}\) produce oxygen vacancies when doping in a substitutional form the ceria structure; on the contrary, Mo\(^{6+}\) has an oxidation state higher than that of Ce\(^{4+}\), thus the electroneutrality is achieved through vacancies disappearance and interstitial oxygen formation as shown in equation 3.1.9, which would suggest an increase of the Young’s modulus of the material. The lower Young’s modulus shown by CMO with 5 wt.% and 7 wt.% of molybdenum with respect to pure ceria can be explained by the different optimal sintering temperature applied for each material (1 300 °C / 5 h for pure ceria and 1 200 °C / 4 h for CMO); however, the increasing tendency of the Young’s modulus of CMO samples and the higher Young’s modulus of CMO with 10 wt.% of Mo with respect to pure ceria, indicate that the results obtained are in good agreement with that previously stated.

Figure 5.5.2: Vickers microhardness values of sintered CMO discs and SEM micrograph of indented disc surface: a) Vickers microhardness values determined for CMO sintered discs with 5, 7 and 10 wt.% of molybdenum and b) SEM micrograph of Vickers indenter impression on CMO 10 wt.% of molybdenum sintered disc. (*data for ceria obtained from [176])

The Vickers microhardness values determined for CMO samples with 5, 7 and 10 wt.% of molyb-
denum are summarized in Figure 5.5.2a, which shows a behaviour totally opposite to that reported for trivalent cation-doped ceria by Sato et al. [206]. For CMO, the Vickers microhardness decreases when molybdenum content increases. Analysing the diagonal lengths of Vickers impressions during microhardness essays (as that shown in Figure 5.5.2b), its size increases while molybdenum content increases, which means that most of the indentation energy is transformed to plastic deformation and the residual energy is converted into cracks. The microhardness depends on the interatomic distances and nature of the atoms; Kishan Rao and Sirdeshmukh [250] demonstrated for several fluorite crystals that Vickers microhardness increase while the interatomic distances decrease, following Powarjonnych’s formula [251]. The formation of interstitial oxygen in CMO and disappearance of oxygen vacancies produce an increment of interatomic distances with respect to pure ceria and doped-ceria with high vacancies content, therefore a decrease of the microhardness values is observed. In the same way, the values of fracture toughness obtained by Palmqvist’s crack method [180] are related with Vickers microhardness values. Vickers indenter impressions with bigger sizes indicate that less energy is converted into cracks, thus a decrease on microhardness is related to an increase of the fracture toughness of the material. Figure 5.5.3 shows that increment as a function of the increasing dopant content, which indicates that the mechanical properties of the material are improved by an augmentation of the elasticity of the material, particularly for the case of CMO with 10 wt.% of Mo with respect to pure ceria.

![Figure 5.5.3: Fracture toughness values determined for CMO sintered discs with 5, 7 and 10 wt.% of molybdenum. (*data for ceria obtained from [176])](image)

The mechanical properties of ceramic materials are closely related to the granular structure of the material. Figure 5.5.4 shows the comparison between the different surfaces of sintered pellets, clearly exhibiting the granular structure of the material. At first glance it is possible to observe that pure ceria has a larger grain size than doped ceria. This same effect was reported by Sato et al. [206] for rare earth-doped ceria compounds. Table 5.5.1 shows a summary of the grain size estimate for each of the materials studied. From these results it is possible to appreciate that although there is a decrease in grain size in the doped ceria with respect to the pure ceria, the difference between grain sizes at different concentrations of molybdenum is not appreciable. The standard deviation values show a great variability between the grain sizes present in the material, which could adversely affect the mechanical properties of the material.
5.6 Electrical Conductivity of CMO

Plots for total electrical conductivity of pure ceria and CMO with 5, 7 and 10 wt.% of molybdenum under air atmosphere are shown in Figure 5.6.1(a). The experimental data exhibits an Arrhenius-like behaviour with good determination coefficients ($R^2$ between 0.995 and 1).

The values of conductivity for pure ceria at 400 °C and 450 °C are equal to zero considering that the equipment used did not detect electrical conductivity at these temperatures for this material. The higher total electrical conductivity of pure ceria determined corresponds to $5.92 \times 10^{-4}$ S cm$^{-1}$ at 800 °C and the activation energy associated corresponds to 0.92 eV. Lavik and Chiang [252] performed measurements to determine the conductivity and activation energy for pure ceria with different thermal treatments. The values reported for annealed-CeO$_2$, as-densified-CeO$_2$ and coarsened-CeO$_2$ corresponded to $6.91 \times 10^{-6}$ S cm$^{-1}$, $3.02 \times 10^{-5}$ S cm$^{-1}$ and $1.44 \times 10^{-5}$ S cm$^{-1}$, correspondingly at 500 °C, which is in accordance with the experimental values obtained for sintered pure ceria discs in this work ($1.73 \times 10^{-5}$ S cm$^{-1}$). The activation energies reported by Lavik and Chiang [252] for annealed, as-densified and coarsened CeO$_2$, correspond to 1.4 eV, 1.16 eV and 0.38 eV, correspondingly, which exhibit a large difference depending on thermal treatment of the samples. Subsequently, Tschöpe, Sommer and Birringer [253] related the conductivity and activation energy values with the grain and boundary grain size. The difference in thermal treatment...
Conductivity measurements of pure ceria and CMO with 5, 7 and 10 wt.% of molybdenum; b) linear fit of conductivity measurements for CMO with 5, 7 and 10 wt.% of molybdenum.

Figure 5.6.1: Electrical conductivity of CMO in air atmosphere: a) Conductivity measurements of pure ceria and CMO with 5, 7 and 10 wt.% of molybdenum; b) linear fit of conductivity measurements for CMO with 5, 7 and 10 wt.% of molybdenum.

Figure 5.6.1a shows that CMO with different molybdenum contents present higher electrical conductivities than pure ceria and that the electrical conductivity of CMO increases as the molybdenum concentration increases. This behaviour is in good agreement with the experimental results reported for this material in a previous work [155]. The highest conductivities values were obtained at 800 °C, being $1.01 \times 10^{-3}$ S cm$^{-1}$, $1.12 \times 10^{-3}$ S cm$^{-1}$ and $1.87 \times 10^{-3}$ S cm$^{-1}$ for CMO with 5, 7 and 10
wt.% of molybdenum, correspondingly. The values of conductivity at high temperature (800 °C) are quite similar, showing conductivities slightly higher when the molybdenum content increase. A notorious difference of about one order of magnitude is found when comparing the CMO conductivities obtained with that of pure ceria. Comparing with electrical conductivity values previously reported for CMO \[155\] (0.59 \times 10^{-3} \text{ S cm}^{-1}, 0.93 \times 10^{-3} \text{ S cm}^{-1} and 1.66 \times 10^{-3} \text{ S cm}^{-1} for CMO with 5, 7 and 10 wt.%, respectively), the material synthesize in this work exhibit a slightly higher electrical conductivity in air atmosphere. The values of activation energy obtained are summarized in Table 5.6.1. Two different activation energies were obtained depending on the temperature range for CMO with 7 wt.% and 10 wt.% of molybdenum (see Figure 5.6.1b). This behaviour can be related to the change in the charge transport mechanism in cation-doped CeO$_2$ taking place between 550 - 600 °C \[254\]. Comparing the activation energies of the doped materials and the un-doped ceria clearly the addition of molybdenum to the cerium oxide structure promotes a decrease of the energy activation barrier, which is in good agreement with the better electrical properties of MoO$_3$.

Table 5.6.1: Activation energies (of electrical conductivity) obtained for pure ceria and CMO from Arrhenius plot under air atmosphere.

<table>
<thead>
<tr>
<th>Sintered disc sample</th>
<th>Activation energy / eV</th>
<th>Range of temperature / °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO 10 wt.% of Mo</td>
<td>0.76</td>
<td>800 - 650</td>
</tr>
<tr>
<td></td>
<td>0.87</td>
<td>650 - 400</td>
</tr>
<tr>
<td>CMO 7 wt.% of Mo</td>
<td>0.84</td>
<td>800 - 600</td>
</tr>
<tr>
<td></td>
<td>0.87</td>
<td>600 - 400</td>
</tr>
<tr>
<td>CMO 5 wt.% of Mo</td>
<td>0.86</td>
<td>800 - 400</td>
</tr>
<tr>
<td>Pure ceria</td>
<td>0.92</td>
<td>800 - 500</td>
</tr>
</tbody>
</table>

To corroborate the thermal stability of the sintered CMO discs with different molybdenum contents, an XRD characterization of the samples before and after the high-temperature four-probe tests was performed. The results obtained are presented in Figure 5.6.2 which show the stability of the material under air atmosphere.

Figure 5.6.3 shows the total electrical conductivity at different temperatures (400 – 800 °C) under hydrogen atmosphere (10 % H$_2$ / 90 % Ar). As shown in this figure, the electrical conductivity values present an Arrhenius behaviour between 400 – 550 °C which is typical for ceramics materials. From 550 °C to 800 °C the conductivity results show a deviation from the Arrhenius behaviour.

Analysing the cyclic voltammograms shown in Figure 5.6.4a it is possible to observe that at a temperature of 600 °C the slope of the curves (cycles) increases with the time, indicating a change in the value of the electrical conductivity throughout the time of experimentation. This increase in the conductivity value above 550 °C is probably due to the reduction of metal oxides that form part of the CMO. For determining the temperature of reduction of CMO under hydrogen atmosphere a TPR analysis was carried out for CMO with 10 wt.% of Mo, CeO$_2$ and MoO$_3$. Figure 5.6.4b shows that MoO$_3$ presents a first reduction peak at ca. 450 °C, which correspond to reduction of Mo$^{6+}$ to Mo$^{4+}$. This peak could explain the higher electrical conductivity values of CMO in hydrogen atmosphere compared with CMO in air atmosphere showed in Figure 5.6.5 (in the range of temperature between 400 – 550 °C). A second higher peak at ca. 600 °C corresponds to the reduction
of Mo$^{4+}$ to metallic Mo, which confers a metallic behaviour to CMO. Besides, the CeO$_2$ presents a reduction peak around 600 °C which corresponds to reduction from Ce$^{4+}$ to Ce$^{3+}$. A similar peak is observed for CMO with 10 wt.% of molybdenum. These reduction processes, and particularly the formation of metallic Mo, favour the rise in the electrical conductivity of CMO under H$_2$ atmosphere compared with air atmosphere (almost two orders of magnitude higher), observed in Figure 5.6.5 for temperatures higher than 550 °C (deviation of Arrhenius behaviour for total electrical conductivities in ceramic materials shown in Figure 5.6.3.a and Figure 5.6.3.b). However, the electrical conductivity of metals (Mo) is disfavoured at high temperatures [255, 256], which is in good agreement with the results shown in Figure 5.6.3.a above ca. 700 °C where the electrical conductivity tends to reach a plateau.

An XRD analysis of the dense CMO discs samples after conductivity tests under hydrogen atmosphere corroborate the previous discussion about the phases formed. Figure 5.6.6 shows a comparison of crystalline structure of CMO with 5, 7 and 10 wt.% of molybdenum before and after hydrogen-conductivity tests. The diffraction patterns obtained show the presence of Ce$_2$O$_3$ (JCPDS 00-049-1458) and metallic Mo (JCPDS 00-004-0809) after conductivity test for each sample, which agrees with the TPR results discussed. These phases are present in minor concentrations compared to the fluorite structure of CMO, however long-term tests in fuel cell mode are required to determine the stability of this material under operating conditions in a reducing atmosphere.

The electrical conductivity of CMO with 10 wt.% Mo measured at 550 °C under a 10%H$_2$/90%Ar atmosphere is 4.66$\cdot$10$^{-3}$ S cm$^{-1}$, while the total electrical conductivity reported for this material under a H$_2$/H$_2$O(g) atmosphere (using EIS measurements) is equal to 5.08$\cdot$10$^{-2}$ S cm$^{-1}$ [155]. However, this property experiments a sudden increment at 600 °C (see Figure 5.6.3.a), reaching the highest electrical conductivity values measured at 800 °C: 3.87$\cdot$10$^{-1}$ S cm$^{-1}$, 5.82$\cdot$10$^{-1}$ S cm$^{-1}$ and 9.37$\cdot$10$^{-1}$ S cm$^{-1}$ for CMO with 5 wt.%, 7 wt.% and 10 wt.% Mo, respectively. The activation
energy reported for CMO with 10 wt.% Mo (between 250 – 550 °C) correspond to 0.29 eV in a H₂/H₂O(g) atmosphere [155], while in this work the value estimated (between 400 – 550 °C) correspond to 1.36 eV under a 10 % H₂ / 90 % Ar atmosphere (see Figure 5.6.3 b), which explains the lower electrical conductivities measured below 600 °C.
Figure 5.6.4: Cyclic voltammograms for CMO with 10 wt.% of molybdenum and Temperature programmed reduction (TPR) analysis in hydrogen for MoO$_3$, CeO$_2$ and CMO with 10 wt.% of molybdenum: a) Cyclic voltammograms at 500, 600 and 650 °C and b) TPR in 10 % H$_2$ / 90 % Ar atmosphere for MoO$_3$, CeO$_2$ and CMO with 10 wt.% of molybdenum.
Figure 5.6.5: Comparison of total electrical conductivities obtained under air and H\textsubscript{2} / Ar atmospheres for CMO and ceria: a) CMO 10 wt.% of Mo, b) CMO 7 wt.% of Mo, c) CMO 5 wt.% of Mo and d) ceria.
Figure 5.6.6: XRD patterns of CMO sintered discs with 5, 7 and 10 wt.% of molybdenum before and after conductivity tests in H₂ / Ar atmosphere.
Chapter 6

CMO-based Anodes: Symmetric-Cell Tests

Based on the previous results of catalytic activity, mechanical properties and electrical conductivity, CMO 10 wt.% Mo was chosen as the best option for the fabrication of symmetric-cells and solid oxide fuel cells (SOFCs).

The chapter presents the results of electrochemical impedance spectroscopy (EIS) measurements on symmetric-cells. The EIS measurements were performed in two atmospheres: air and hydrogen-water gas, under open circuit voltage (OCV) conditions. These measurements allowed to determine area specific polarization resistance (ASPR) values and diffusion coefficients of oxygen and hydrogen-water gas at different operating conditions: temperature variation in air and temperature and concentration variation in hydrogen-water gas. The characterization of the cells by SEM, EDS and XRD before and after the EIS measurements was also performed aiming to find changes at the microstructural level that could affect the EIS measurements and the performance of the material.

6.1 Symmetric-Cells Characterization

6.1.1 Thickness and Microstructure of Cell Components

Electrochemical symmetric-cells with CMO electrodes (10 wt.% Mo) coated on both sides of commercial YSZ discs (electrolyte) were fabricated for EIS measurements (active area of electrodes: 1.54 cm$^2$). For more details about the methods of preparation, see Section 4.7. These symmetric-cells were characterized by SEM-EDS analysis to determine the most relevant aspects about their microstructure and chemical composition.

Figure 6.1.1 corresponds to an SEM micrograph of a symmetric-cell cross-section. The electrodes of the symmetric-cell were labeled as side A and B for use as a reference for different analyses. Figure 6.1.2 shows different micrographs of the symmetric-cell cross-section at different magnifications (120x, 600x, 1500x). CMO-YSZ and CMO layers on both sides of the symmetric-cells were produced by paintbrush. It is difficult to distinguish these two different layers. The adhesion of the electrode particles seem adequate and no presence of cracks was found in the cross-section of the symmetric-cell. The electrode thickness is variable, consequently thicker and thinner areas were found. The electrode thickness was estimated as the average of many measurements using the software ImageJ version 1.51j8. The result of average thickness of electrodes is shown in Table...
6.1.1

Figure 6.1.1: SEM micrographs of a symmetric-cell (CMO/CMO-YSZ/YSZ/CMO-YSZ/CMO, CMO 10 wt.% Mo) cross-section, indicating sides A and B used as reference for different analyses.

Figure 6.1.2: SEM micrographs of a symmetric-cell (CMO/CMO-YSZ/YSZ/CMO-YSZ/CMO, CMO 10 wt.% Mo) cross-section at different magnifications: a) 120x, b) 600x and c) 1500x.

The difference of thicknesses between the two CMO/CMO-YSZ coated electrodes and the high value of the standard deviations associated to their measurements, suggest a non-reproducible fabrication process (paintbrushing). In addition, an important factor that affects the coating quality is the particle size of the powders. The CMO-YSZ composite anode was prepared with CMO nanoparticles with 10 wt.% Mo of ca. 16.6 nm of particles size, while the YSZ corresponds to submicron particles of ca. 700 nm. Figure 6.1.2 obtained by backscattered electrons technique, shows clearly that the YSZ and CMO phases present differences in particle sizes. These considerable differences in particles size could produce stress during the sintering process of the coating.
and a non-homogeneous composite.

The chemical composition of the cross-section of the symmetric-cell was studied by EDS analysis to determine the distribution of the different oxides. In addition, EDS analysis was performed as a complimentary analysis to SEM to determine rigorously the thicknesses of each electrode layer.

Figure 6.1.3 shows an EDS analysis in the cross-section of a symmetric-cell (selected area on side B), at which it is possible to observe the separation between coated electrodes and electrolyte through the elemental mapping. The dashed lines on Figure 6.1.3 represent the boundary of the different layers of the electrode and the boundary between the coating and the electrolyte. The boundary between the different layers was determined by analyzing the presence of the characteristic elements of each layer, that means for example that Y and Zr will be found in those phases where YSZ is present, consequently these elements can be found in both the YSZ dense electrolyte and in the CMO-YSZ composite, but not in the coating of CMO. On the other hand, the presence of Ce will be found in those layers containing CMO (i.e. CMO and CMO-YSZ), but it should not be present in the YSZ dense electrolyte. These analysis were carried out for both sides (A and B) and in different areas of the cross-section of the sample, allowing to estimate the average thickness of both layers that form the electrodes. The results obtained are summarized in Table 6.1.2.

Table 6.1.2: Estimation of the thickness of the symmetric-cell layers.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness / µm</th>
<th>Standard deviation / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO coating side A</td>
<td>26</td>
<td>5</td>
</tr>
<tr>
<td>CMO-YSZ coating side A</td>
<td>24</td>
<td>4</td>
</tr>
<tr>
<td>CMO-YSZ coating side B</td>
<td>36</td>
<td>4</td>
</tr>
<tr>
<td>CMO coating side B</td>
<td>41</td>
<td>7</td>
</tr>
</tbody>
</table>

An SEM analysis of the coating surface of a symmetric-cell reveals the presence of cracks in several sectors of the CMO/CMO-YSZ coating (Figure 6.1.4a). The average of cracks length estimated was ca. 50.8 ± 16.3 µm. It is important to mention that many of these cracks seem to come from the addition of several pores as shown in Figure 6.1.4b. The average values of pore diameter and porosity (estimated from SEM micrographs) correspond to ca. 0.174 ± 0.190 µm and ca. 35.9%, respectively. In Figure 6.1.4a it can be observed that bigger cracks are located in the proximity of irregularities on surface. These cracks or “surface reliefs” are probably formed by big YSZ particles in composite which are appreciable in Figure 6.1.2.
Figure 6.1.3: EDS analysis of the side B (selected area) cross-section of a symmetric-cell CMO/CMO-YSZ/YSZ/CMO-YSZ/CMO (CMO with 10 wt.% Mo): a) SEM micrograph of the selected area analysed by EDS for b) zirconium, c) cerium, d) yttrium, e) oxygen and f) molybdenum; g) quantification of the elemental composition in the selected area.

6.1.2 Chemical Stability of Cell Components

Analysing the EDS elemental mapping micrographs in Figure 6.1.3, it is possible to detect the presence of molybdenum in the dense electrolyte phase, and little quantities of cerium which suggest the chemical interaction between the YSZ solid electrolyte and the CMO/CMO-YSZ electrode. An XRD analysis of the coatings was performed to corroborate this hypothesis. The results of the XRD analysis are shown in Figure 6.1.3a and 6.1.3b, and corroborate the formation of secondary phases: $Y_2MoO_6$ (JCPDS 00-052-0650), $Zr(MoO_4)_2$ (JCPDS 00-038-1465) and $Zr_{0.4}Ce_{0.6}O_2$ (JCPDS 00-038-1439). Probably these secondary phases were produce at high temperature during the sintering process. The formation of secondary phases can adversely affect the performance of a fuel cell due to increased polarization losses [39, 257]. The diffusion of metallic species from the electrodes of the cell to the dense electrolyte could change the electrical properties of the cell; this could produce a current flow through the electrolyte (short circuit) and decrease the electrical conductivity of the electrodes [39]. To avoid the chemical reaction between the components of the cell, it is suggested to decrease the sintering temperature of the coated electrodes or to include the use of interlayers (buffer layers) [39, 257].
6.2 EIS Data Validation: Kramers-Kronig Test

Figure 6.2.1 shows the results of the Kramers-Kronig test (Section 2.3.3) fulfilled with the EIS data of a symmetric-cell CMO/CMO-YSZ/YSZ/CMO-YSZ/CMO under air atmosphere at 400 °C (a.1 and a.2) and 600 °C (b.1 and b.2). In the case of the impedance data at 400 °C it can be observed the presence of probably corrupt data at intermediate and high frequencies. Analyzing the residual graphic, from 100 kHz the fractional residual percentage exceeds 20% and the GOF value of the Kramers-Kronig transformation is $2.93 \times 10^{-3}$, which demonstrates the low reliability of these measurements. However the impedance data at 600 °C are clearly Kramers-Kronig transformable, consequently, there are no presence of corrupt data. Small deviations are observed over 100 kHz, at which the residual error percentage is not higher than 5%. In agreement with the Bode and residual graphics, the GOF at 600 °C present an acceptable value of $1.102 \times 10^{-4}$ which is an indicator that almost all values of spectra are Kramers-Kronig transformable [22]. Analyzing the residual plot of the EIS measurement at 400 °C and 600 °C (Figure 6.2.1[a.2 and b.2]), the percentage of residual error begins to increase from 100 kHz of frequency. This deviation is due to the fact that the system behaves like an inductor from 100 kHz (see Section 2.3.1) and the Kramers-Kronig method does not show good results in this domain ($-Z_{im} < 0$) [26]. If the inductance data ($-Z_{im} < 0$) are not considered in the Kramers-Kronig test, the GOF index is improved to $7.33 \times 10^{-9}$, presenting only 0.32% of maximum residual error.
Figure 6.1.5: XRD patterns of the coated anode surface of a symmetric-cell before EIS measurements: a) and b) correspond to the A and B sides of the coated anode on YSZ disc, correspondingly.

The Kramers-Kronig test was carried out for each EIS experimental data. The experimental data that presented a bad GOF index, and consequently a high error percentage in the residual graphic with corrupted data, were excluded as valid measurements. Thus, the results of the validation analysis of the impedance experiments are shown in Table 6.2.1 for air measurement and Tables 6.2.2 and 6.2.3 for hydrogen measurements.

Table 6.2.1: Goodness of fit parameter and maximum residual error of Kramers-Kronig test of EIS measurements under air atmosphere at different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>GOF</th>
<th>Maximum residual error / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>400</td>
<td>2.93·10⁻³</td>
<td>30 %</td>
</tr>
<tr>
<td>450</td>
<td>1.08·10⁻⁴</td>
<td>5.40 %</td>
</tr>
<tr>
<td>500</td>
<td>4.77·10⁻⁶</td>
<td>0.48 %</td>
</tr>
<tr>
<td>550</td>
<td>1.61·10⁻⁶</td>
<td>0.40 %</td>
</tr>
<tr>
<td>600</td>
<td>7.33·10⁻⁹</td>
<td>0.32 %</td>
</tr>
<tr>
<td>650</td>
<td>8.28·10⁻⁷</td>
<td>0.34 %</td>
</tr>
<tr>
<td>700</td>
<td>1.22·10⁻⁶</td>
<td>0.33 %</td>
</tr>
<tr>
<td>750</td>
<td>1.11·10⁻⁶</td>
<td>0.41 %</td>
</tr>
<tr>
<td>800</td>
<td>1.15·10⁻⁶</td>
<td>0.50 %</td>
</tr>
</tbody>
</table>
The Kramers-Kronig analysis indicates an important quantity of corrupted data in EIS measurements in air atmosphere at 400 °C; consequently, these experimental measurements were not considered in the further analysis. The other experimental measurements under air atmosphere, present a good value of GOF (maximum ca. $10^{-4}$) with a low residual error (maximum ca. 5%). With respect to the EIS measurements under hydrogen atmosphere, the values of GOF and maximum residual error shown in Tables 6.2.2 and 6.2.3 are low enough to consider all these measurements Kramers-Kronig transformable.

Once the valid experimental results were identified, it was possible finding an electrical circuit that represent the phenomenology and fit the experimental data as good as possible.
Table 6.2.2: Goodness of fit parameter and maximum residual error of Kramers-Kronig test of EIS measurements under 10% H\textsubscript{2}/Ar at different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>GOF</th>
<th>Maximum residual error / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>650</td>
<td>2.19·10\textsuperscript{-6}</td>
<td>0.36%</td>
</tr>
<tr>
<td>700</td>
<td>1.64·10\textsuperscript{-6}</td>
<td>0.25%</td>
</tr>
<tr>
<td>750</td>
<td>1.18·10\textsuperscript{-5}</td>
<td>1.03%</td>
</tr>
<tr>
<td>800</td>
<td>1.35·10\textsuperscript{-5}</td>
<td>1.20%</td>
</tr>
</tbody>
</table>

Table 6.2.3: Goodness of fit parameter and maximum residual error of Kramers-Kronig test of EIS measurements at 800 °C under different H\textsubscript{2} concentrations.

<table>
<thead>
<tr>
<th>Concentration / vol.%</th>
<th>GOF</th>
<th>Maximum residual error / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>10%H\textsubscript{2}/Ar</td>
<td>1.35·10\textsuperscript{-5}</td>
<td>1.20%</td>
</tr>
<tr>
<td>5%H\textsubscript{2}/Ar</td>
<td>3.08·10\textsuperscript{-6}</td>
<td>0.32%</td>
</tr>
<tr>
<td>2.5%H\textsubscript{2}/Ar</td>
<td>1.41·10\textsuperscript{-5}</td>
<td>2.19%</td>
</tr>
<tr>
<td>1.25%H\textsubscript{2}/Ar</td>
<td>2.14·10\textsuperscript{-5}</td>
<td>0.58%</td>
</tr>
</tbody>
</table>

6.3 EIS Analysis in Air Atmosphere

6.3.1 EIS Data Analysis

6.3.1.1 Nyquist Plots

The results of EIS measurements in symmetric-cells under air atmosphere at different temperatures (450 °C - 800 °C) are presented in Figure 6.3.1.a and Figure 6.3.1.b in the form of Nyquist plots. The effect of the increment of the temperature is clear: a decrease of the total ohmic resistance (intercept with Z\textsubscript{Re} axis at high frequencies) is observed, which is related to the displacement of the impedance curves toward the left of the Z\textsubscript{Re} axis. In addition, the increment of temperature produce a decrease of the charge transfer resistance (related to the size of the semicircles and the intercept of the curve with the Z\textsubscript{Re} axis at low frequencies). The change in the charge transfer resistance is better observed in Figure 6.3.2, where the curves were manipulated, subtracting the total ohmic resistance value for comparatives purposes.

Observing the form of the impedance curves in Nyquist plot, the curves present apparently three semicircles at 450 °C and 500 °C and two semicircles since 550 °C, which suggests that probably with the temperature one impedance element becomes negligible compared to others. The shape of these semicircles looks like depressed, this is observed in the difference between the radius of the semicircles. For example, the curve at 650 °C in Figure 6.3.1.b present a value of the radius in the real part of the highest semicircle (r\textsubscript{Re}) of ca. 60 Ω cm\textsuperscript{2} while the value of the radius in the imaginary part (r\textsubscript{Im}) is ca. 18 Ω cm\textsuperscript{2}. This indicate a non-ideal behavior, so consequently the use of constant phase elements (CPEs) is required when the electrical circuit model is proposed \[22\].
Figure 6.3.1: Nyquist plot of the impedance measurements on symmetric-cells tested in air at different temperatures (450 °C - 800 °C): a) EIS measurements between 450 - 550 °C and b) EIS measurements between 600 - 800 °C.

Figure 6.3.2: Nyquist plot of the impedance measurements of the symmetric-cell tested in air at different temperatures (600 °C - 800 °C), with ohmic correction.

### 6.3.1.2 Distribution of Relaxation Times (DRT)

The DRT calculations were carried out using an open MATLAB GUI code, called DRTools developed by Wan et al. in 2015 [29]. The computation of the DRT code is based on Tikhonov regularization with continuous function discretization [29].

The results of the distribution of relaxation times (DRT) analyses are presented in Figure 6.3.3. From these plots the variation in the number of peaks with the temperature can be clearly observed, which confirms that some physical phenomena have a negligible influence when the temperature is increased.

Analyzing the Figure 6.3.3a, the results at 450 °C and 500 °C show at high frequencies (ca. 200 kHz - 10 kHz) two peaks, PA and PB which decrease in intensity while the temperature increase.
This peaks disappear since 550 °C. Probably, these two processes correspond to grain boundaries and bulk resistances. Electric and ionic conduction in electroceramics materials with granular structure occurs through the crystalline grain (intra grain-bulk conduction); this electric charge conduction is affected when it is transported from one grain to another through the grain boundaries (intergrain conduction) as shown in Figure 6.3.3.a. The grain boundary resistance \( R_{gb} \) and grain bulk resistance \( R_b \) exhibit an appreciable effect in the impedance spectrum at low temperatures, however this effect is almost negligible at higher temperatures (above 600 °C) [155]. The grain boundary and grain bulk resistances appear at high frequencies in Nyquist plots [258]. A valid method to determine if the processes correspond to bulk or grain boundary conduction is to study the capacitance value of the R(CPE) circuit fitted to that process. Irvine et al. have classified the capacitances values (obtained from R(CPE) circuits by EIS studies) associated with different processes studied in semiconductor physics; the capacitance values for grain bulk conduction should be in the order of magnitude of \( 10^{-12} \) F, while the grain boundary capacitances values should be in the range of \( 10^{-11} - 10^{-8} \) F [258]. In Section 6.3.2 it will be demonstrated whether or not these
processes correspond to bulk grain and boundary grain resistances, by analyzing the capacitance values obtained from the mathematical fit of the proposed equivalent circuit. The phenomena related to the PA and PB processes will be modeled as two R(CPE) circuits in series, representing intergrain and grain bulk conduction, as represented in Figure 6.3.4.b.

Figure 6.3.4: Intra grain bulk and intergrain conduction: a) Charge conduction in a granular structure; b) equivalent circuit representing the intergrain and grain bulk conduction in a granular structure.

The DRT results for all the temperatures show the presence of three peaks related to three physical phenomena (frequencies between 30 Hz - 10 mHz for 450 °C and 500 °C; and 800 Hz - 10 mHz for 550 °C - 800 °C). Two of these peaks (P1 and P2) are presented at intermediate frequencies (frequencies between 30 Hz - 1 Hz for 450 °C and 500 °C; and 800 Hz - 10 Hz for 550 °C - 800 °C) and their intensity decrease with the temperature, which suggests that these physical phenomena correspond to charge transfer processes related to electrochemical reactions. The two impedances related to processes P1 and P2 will be modeled as two R(CPE) circuits in series. The electrical resistor of the circuit (R_{ct}) represents the charge transfer resistance, while the constant phase element (CPE) represents the ionic conduction of the material and the gas adsorption phenomena on the surface of the material. Figure 6.3.5 shows the electrical circuit associated with processes P1 and P2 and a schematic of the physical phenomena represented.

A predominant peak present at low frequency (between 10 and 100 mHz) is observed in all DRT plots in Figure 6.3.3, this should be related to diffusional transport at the interface gas|electrode-electrolyte (see Figure 6.3.6.a). Diffusion can be associated to a Warburg impedance (see Section 2.3), which depends on the frequency of the potential perturbation. At high frequencies Warburg impedance is small and can be neglected, but at low frequencies presents a high value, consequently the diffusion is the controlling stage [259]. Figure 6.3.6.b presents the equivalent circuit associated to these phenomena.

A small peak is observed between 450 - 650 °C at frequencies in the range of 800 Hz - 4 kHz. This small peak, tagged as P3*, corresponds to an additional diffusional process. Ivers-Tiffée and Weber demonstrated mathematically that diffusive phenomena related to Warburg elements produce more than one peak at a specific frequency in the DRT spectrum, and that these peaks occur approximately three or four decades of frequency (three or four orders of magnitude of frequency) greater from the frequency at which the main peak appears [260]. Consequently the peak P3* does not correspond to a process but is part of the same P3 process.
6.3.2 Equivalent Electrical Circuit

Considering the previous DRT analysis, the equivalent electrical circuit for the symmetric-cell under air atmosphere should be composed by four main physicochemical processes (between 550 - 800 °C): ohmic resistance (the ohmic electrolyte resistance is the most important ohmic resistance, however even this term, resistances in electrodes and current collectors are also included), charge transfer resistance in CMO coating, charge transfer resistance in CMO-YSZ electrode and diffusional transport of reagents and products. The different physical processes and the equivalent circuit proposed are schematized in Figure 6.3.7.

In the model proposed in this work, two charge transfer processes were considered: electronic-ionic charge transfer in CMO current collector and electronic-ionic charge transfer in CMO-YSZ composites. The initial model proposed included a bounded finite Warburg impedance (\(-W\)) as impedance \(Z_4\) (see Figure 6.3.7.b) in series with impedances \(Z_1, Z_2\) and \(Z_3\). The \(R_{diff}\) resistance was defined as the fraction of the charge transfer resistance which is affected by the diffusional...
Figure 6.3.7: Equivalent circuit proposed for EIS data in air: a) physical model of different impedances in the system; b) equivalent circuit proposed.

phenomena. It is important to note that, this resistance term is not the same charge transfer term in CMO-YSZ due to electrochemical reaction (processes highly activated with temperature). The addition of the CPE in series with the bounded Warburg impedance explains the solid state incorporation of the oxygen species to TPB which is affected by diffusional processes (see Figure 6.3.6).

Modifications where applied to equivalent circuit of Figure 6.3.7 depending on the temperature of experimental measurements. For 450 °C and 500 °C the two impedances related to bulk grain and boundary grain resistances were added to the electrical circuit model (see Figure 6.3.8). A deep analysis on these impedances was not carried out, because it is out of the scope of this research work; however, from the mathematical fit the capacitance values were obtained to corroborate the hypothesis that relates these physical processes with bulk and intergrain resistances (see Section 6.3.2.1).

An example of the results obtained by fitting the model in Figure 6.3.7 is shown in Figure 6.3.9. The impedance spectra correspond to measurements at 700 °C (a) and 750 °C (c), with their residual plots (b) and (d). An important observation is that since 550 °C and higher temperatures an inductance component appeared in the Nyquist plot ($-Z_{Im} < 0$) as shown in Figure 6.3.1 b. This inductance impedance is produced probably by inadequate connections setup, as stated by Klotz et al. in [261]. The inductance component was not considered in the equivalent circuit models and consequently was subtracted from the Nyquist plot. A fitting of an equivalent circuit including an inductor element showed that the inductance values were between $10^{-8} - 10^{-9}$ H cm$^2$. Using
equation of the impedance of an inductor presented in Table 2.3.1 in Section 2.3.1.3, it is possible to obtain the impedance of this inductor, which is within the order of magnitude of $10^{-3}$ Ω cm$^2$ so not considering the inductance data, almost does not affect the values of the other parameters (less than 2% of variation with respect to the model with inductor), and improves the value of GOF and also saves time of iterative calculations.

The values of the GOF for the experimental data fitted at different temperatures can be found in Table B.1.1 of the appendix B. The GOF values are in the range of $10^{-5} - 10^{-6}$, which indicates that the equivalent circuit model is well-fitted for EIS measurements between 500 - 800 °C.
iteration routine for results at 450 °C was interrupted since it was impossible to obtain the fitting parameters. This was expected considering the high GOF value obtained for the Kramers-Kronig test of this data, compared to that obtained at higher temperatures. Therefore, this temperature was excluded from the analysis of EIS spectra. The low electrical activity of CMO 10 wt.% Mo at 400 °C and 450 °C could be a cause of the data obtained at these temperatures.

6.3.2.1 CPE of the Grain Bulk and Boundary Grain Impedances

The equivalent circuit in Figure 6.3.8 was used to fit the experimental impedance data, two capacitance values were obtained for these elements: 1.82·10⁻⁹ F and 4.44·10⁻¹² F for the grain boundary and bulk grain, respectively. Irvine et al. stated that capacitance values provide a fingerprint for certain physicochemical processes that occur in electrochemical systems [258]. Bulk grain conduction processes should have a capacitance value of ca. 10⁻¹² F, while grain boundary conduction processes should have a value between 10⁻¹¹ - 10⁻⁸ F. This suggests that the R(CPE) elements here adjusted would represent indeed bulk grain and grain boundary conduction processes, so the initial hypothesis is correct and the circuit in Figure 6.3.8 is valid for the fitting of the data at 500°C.

6.3.2.2 Area Specific Polarization Resistance (ASPR)

The area specific polarization resistance (ASPR) is typically obtained from the difference between the low frequency intercept and the high frequency intercept in the Nyquist plot [155, 262]. The ASPR value matches with the sum of the charge transfer resistances (R_{ct}) and the resistances produced by mass transport (R_{diff}) present in the equivalent circuits (Figures 6.3.7 and 6.3.8):

\[
\text{ASPR} = \frac{R_{ct}^{\text{CMO}} + R_{ct}^{\text{CMO-YSZ}} + R_{\text{interface}}}{2}
\] (6.3.1)

To obtain the ASPR graphically from the Nyquist plot, a Visual Basic script provided by Gamry Echem Analyst v.7.06 was used to simulate the curve (using the fitting parameters obtained from models proposed in Figure 6.3.7 and Figure 6.3.8). This simulation was performed in the frequency range 1 MHz - 10 µHz, which allows to visualize the intercept of the impedance curve in the Nyquist plot at very low frequencies. The value of ASPR calculated using equation [6.3.1] with the fitted parameters is in agreement with the difference between the high frequency intercept and the low frequency extrapolated intercept in the Nyquist plot for all experimental EIS data between 500 - 800 °C. An example is shown in Figure 6.3.10.

The ASPR values estimated are summarized in Table B.1.3 in appendix B. These ASPR values correspond to half of the value obtained from the simulation, since it is a symmetrical cell and the resistances obtained correspond to the contribution of both electrodes [155, 263]. The ASPR values are presented in the form of an Arrhenius plot in Figure 6.3.11 by means of a linear adjustment, an
activation energy of 0.91 eV was obtained. This value is better than the activation energy obtained by Li et al. of 1.12 eV for the same material, tested between 550 - 800 °C [155].

The value of ASPR is very sensitive to the microstructure of the studied material [263]: the particles size and the distribution of the particles have a big influence on the TPBs distribution and consequently in the value of the charge resistance [263]. A high ASPR value is related to an inadequate fabrication process, thus it is possible to reduce this value by improving the fabrication methods of the cell. The different particle sizes used in the preparation of composite materials (CMO and YSZ) have an important influence on the microstructure of the material (see Section 6.1), consequently this could have an adverse effect on the ASPR value, so it is proposed to improve the fabrication method to decrease the ASPR of the cell, replacing manual paintbrushing with some technique that allows to obtain more reproducible cells, such as the spin-coating technique.
The EIS tests in air were carried out with the aim to study the ionic transport properties in the composite material YSZ-CMO and in the CMO. Some authors prefer to study the properties of the anodic materials in symmetric-cells fed with wet hydrogen [35,264], however some drawbacks are present as reduction \(^1\) of the electrode materials occurs, since chemical instability and unstable EIS measurements are promoted. This thesis presents results of EIS measurements on symmetric-cells under air and hydrogen atmospheres, for comparative purposes.

6.3.2.3 Oxygen Gas Diffusion Coefficient

The DRT plots in Figure [6.3.3] show the presence of processes at low frequencies, which are highly dependent on the temperature. These processes are also visible in Nyquist plots as depressed semi-circles at low frequencies, which decrease its size with the increase of temperature (see Figure [6.3.2]). Boukamp related this low frequency processes to diffusional control [25] and the kinetics of the electrochemical reactions [265]. As it was stated previously, the oxygen gas diffusion was modelled with a bounded Warburg impedance, which represent a diffusional process taking place in a layer of finite thickness [266].

The mathematical expression of the bounded Warburg impedance is:

\[
W = \frac{1}{Y_0 \sqrt{i\omega} \coth \left( B \sqrt{i\omega} \right)} \tag{6.3.2}
\]

where \(Y_0\) and \(B\) are the adjustable parameters. The mathematical expression for \(B\) is the following:

\[
B = \frac{\delta}{\left( D_{O_2}^{eff} \right)^{1/2}} \tag{6.3.3}
\]

where \(\delta\) is the diffusion layer thickness in cm, which can be approximated by the thickness of the coated electrode and \(D_{O_2}^{eff}\) is the effective diffusion coefficient of oxygen gas in cm\(^2\) s\(^{-1}\). The \(D_{O_2}^{eff}\) values obtained at different temperatures are summarized in Table [6.3.1].

The one-dimensional diffusion of gas molecules in porous media involves molecular interactions between gas molecules as well as collisions between gas molecules and the porous media [267–269]. As gas fuel molecules travel through the porous media, one of three mechanisms can occur, depending on the characteristic of the diffusing gas species and the intrinsic microstructure of the porous media: molecular diffusion, viscous diffusion, and Knudsen diffusion. To distinguish

---

\(^1\)Reducing the anode is not a problem, even in the Ni-YSZ anode the reduction of NiO is desired to produce the reduced anodic material (Ni-YSZ); however, the reduction changes the properties of the material. If the ionic conductivity of the CMO in H\(_2\) atmosphere is studied, it is not ensured to measure the ionic and electrical conductivity of the oxidized CMO, since metallic phases can appear.
Table 6.3.1: B parameter, effective diffusion coefficient of oxygen gas and mean free path estimation of the oxygen gas molecules at different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>B / s^{0.5}</th>
<th>D_{O_2}^{eff} / cm^2 s^{-1}</th>
<th>Λ / µm</th>
<th>K_n</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>3.896</td>
<td>2.87·10^{-6}</td>
<td>0.387</td>
<td>2.2</td>
</tr>
<tr>
<td>550</td>
<td>0.6235</td>
<td>1.12·10^{-4}</td>
<td>0.412</td>
<td>2.4</td>
</tr>
<tr>
<td>600</td>
<td>0.4357</td>
<td>2.29·10^{-4}</td>
<td>0.437</td>
<td>2.5</td>
</tr>
<tr>
<td>650</td>
<td>0.3174</td>
<td>4.32·10^{-4}</td>
<td>0.462</td>
<td>2.7</td>
</tr>
<tr>
<td>700</td>
<td>0.2735</td>
<td>5.83·10^{-4}</td>
<td>0.487</td>
<td>2.8</td>
</tr>
<tr>
<td>750</td>
<td>0.8367</td>
<td>6.22·10^{-5}</td>
<td>0.512</td>
<td>2.9</td>
</tr>
<tr>
<td>800</td>
<td>0.4822</td>
<td>1.87·10^{-4}</td>
<td>0.537</td>
<td>3.1</td>
</tr>
</tbody>
</table>

among the three mechanisms, the Knudsen number ($K_n$), which is the ratio of the gas mean free path ($Λ$) to the pore size ($d_{pore}$) of the electrode, is calculated [270]:

$$K_n = \frac{Λ}{d_p} \quad (6.3.4)$$

The gas mean free path can be calculated by equation 6.3.5:

$$Λ = \frac{RT}{\sqrt{2}P_{O_2}N_Aπd_{O_2}^2} \quad (6.3.5)$$

where $P_{O_2}$ is the oxygen gas partial pressure and $d_{O_2} ≈ 0.292$ nm. The mean free path and Knudsen number values estimated are summarized in Table 6.3.1.

The pore size ($d_{pore}$: pore diameter) estimated in this work for the CMO/CMO-YSZ coatings is ca. 0.174 µm, which is in the same order of magnitude than the mean free path estimated for the oxygen molecule at different temperatures. If $K_n$ is much greater than 10, collisions between gas molecules and the porous electrode are more dominant than the collisions between gas molecules, resulting in negligible molecular diffusion and viscous diffusion. If $K_n$ is much smaller than 0.1, collisions and interactions between gas molecules become dominant, and Knudsen diffusion becomes negligible compared with molecular diffusion and viscous diffusion. As $K_n$ of a system ranges between 0.1 and 10, all three mechanisms govern gas transport. The values of Knudsen number in this work are in the range $2.2 ≤ K_n ≤ 3.1$ (see Table 6.3.1) which indicates that the three diffusion mechanisms are present in the diffusion process. On the other hand, Flura et al. indicate that the Knudsen diffusion governs the diffusional process when the pore size is of the same order of magnitude than the mean free path [271], which is consistent with experimental data of pore size (see Section 6.1.1), and probably the mass transport mechanism is of the Knudsen-type.

The equation for estimation of diffusion coefficient in Knudsen regimen is 6.3.6. In this equation it is possible to observe that the Knudsen diffusion coefficient is proportional to $T^{1/2}$, consequently if the diffusion regime is Knudsen type, the experimental diffusion coefficients reported in Table 6.3.1 should be proportional to $T^{1/2}$. This proportionality is maintained only if there are no changes
in porosity and tortuosity in the electrode, as shown in equation\(^{(6.3.7)}\).

\[
D_{O_2}^{Knudsen} = \frac{1}{3} d_{pore} \left(\frac{8RT}{\pi M_{O_2}}\right)^{1/2}
\]

\[
D_{O_2}^{eff,Knudsen} = \frac{\varepsilon_p \tau_p}{\tau_p} D_{O_2}^{Knudsen}
\]  

(6.3.7)

where \(M_{O_2}\) is the molar mass of the \(O_2\), \(\varepsilon_p\) is the porosity of the material and \(\tau_p\) is the tortuosity.

Figure 6.3.12 shows the experimental value of the diffusion coefficient estimated from EIS results (see Table 6.3.1) against \(T^{0.5}\). This plot follows a Knudsen behavior between 500 - 700 °C. The value of diffusion coefficient experiment an abrupt decrease above 700 °C (see Figure 6.3.12). The value of the effective Knudsen diffusion coefficient depends on the porosity and the tortuosity of the material which is expressed in equation\(^{(6.3.7)}\). High temperatures promote the coarsening of the coating particles [19], consequently this effect should produce a decrease in the porosity of the material, making the diffusion more difficult. Probably the reduction of the pore size, produce a decrease of the diffusion coefficient since 700 °C. However, to corroborate this hypothesis it is necessary to analyze the samples after impedance tests to determine changes in the microstructure. The analysis discussed in Section 6.5 corroborate a change in the microstructure, exhibiting a decrease of the porosity.

Figure 6.3.12: Diffusion coefficient of oxygen gas estimated from EIS measurements at different temperatures.
6.3.2.4 Oxygen Ionic and Electronic Conductivity

The electrode of the symmetric-cell has two different layers (see Figure 4.7.1b), the adjacent-dense electrolyte layer correspond to a composite of CMO nanoparticles and YSZ submicron particles. The addition of YSZ particles to CMO aims to increase the TPBs of the material, which means to expands the active sites into the volume of the electrode in the same way that the Ni-YSZ composite does [35]. The DRT calculations demonstrated that all physical processes in the EIS in air are affected by temperature (see Figure 6.3.3) which mean that all processes are thermally activated. Once the equivalent circuit has been proposed and the parameters have been fitted, it is necessary to determine which physical phenomenon corresponds to each of the parameters obtained. The difficulty of this process was to determine which impedance corresponded to the CMO layer and which one to the CMO-YSZ composite. Many authors corroborate that addition of YSZ to the electrodes facilitates the charge transfer process [18, 19, 21]; under this supposition the CMO-YSZ layer was associated to the impedance with lower $R_{ct}$ value.

To study the electrical properties in composite materials, Paasch et al. proposed to model the electrode through the transmission line approach [272, 273]. In the case of CMO-YSZ electrodes, the model proposed based in Paasch et al. approach is shown in Figure 6.3.13.

The impedance corresponding to the charge transfer processes in the CMO-YSZ phase was replaced by the transmission line model (unified element, included in the software Gamry Echem Analyst v.7.06), maintaining constant all the other parameters obtained from the circuit adjustment proposed in Section 6.3.2 ($R_{ohm}$, $R_{ct}$, $R_{diff}$ and $Q_{CPE}$). In Figure 6.3.13, the resistance $r_1$ represents the electronic resistance of CMO, $r_2$ is the ionic resistance of YSZ, and the impedance $Z_3$ represents the TPBs present in the CMO-YSZ composite (electrochemical reaction sites, where $r_{ct}$ is the charge transfer resistance).

The transmission line model considers that one phase is exclusively an electronic conductor and the other phase is an ionic conductor; in the case of this work, it is known that CMO increases its...
electronic conductivity by the incorporation of molybdenum as dopant (equation 3.1.9), decreasing its oxygen vacancies by incorporation of interstitial oxygen into the lattice structure (decrease of ion conductivity), consequently the application of the transmission line model is adequate for CMO-YSZ phase. It is important to mention that CMO also exhibits ionic conductivity which is observed mainly under 600 °C (Figure 5.6.1b).

The values of $r_1$, $r_2$ and $r_{ct}$ obtained from the fitting of the unified element (transmission line) and their respective error, can be consulted in Table B.1.4 of the appendix B. The Arrhenius plot of the $r_1$ and $r_2$ expressed as conductivities are shown in Figure 6.3.14. The values obtained of activation energy and conductivities allows to make a link between the material and its electrical properties.

Based on the results presented in the Figure 6.3.14, the conductivity $\sigma_2$ (obtained from $r_2$) is linked to YSZ phase, since the value of activation energy of 0.91 eV (this work) is in agreement with the activation energy found in ionic conductivity measurements of YSZ reported in different works (0.90 eV) \[35\]. Therefore, the conductivity $\sigma_1$ (obtained from $r_1$) was related to the CMO phase. It is important to explain that the $\sigma_1$ value is a combination of electrical and ionic conductivity, however for ceria-based systems, the electrical conductivity prevails over ionic conductivity between 600 - 650 °C, and the change in the slope of curve in Figure 6.3.14 can be attributed to a change in the charge transport mechanism \[19, 48, 51\]. The activation energy obtained between 550 °C and 650 °C for CMO phase is 1.06 eV, which is higher than the 0.86 eV value obtained through the four probe measurements under air atmosphere reported in Table 5.6.1. The activation energy values are expected to have high values below 650 °C because the ionic conductivity in the symmetrical cell depends on the electrical behaviour of the dense YSZ electrolyte, and the electrical activity of the YSZ is low at these temperatures. The values of $\sigma_1$ are comparable with the conductivity values obtained by four probe method and corroborate that this resistance impedance component is related to CMO phase.

![Figure 6.3.14: Arrhenius plot of ionic ($\sigma_2$) and ionic-electronic ($\sigma_1$) conductivities obtained from transmission line model.](image_url)
6.4 EIS Analysis in Hydrogen Atmosphere

EIS measurements in hydrogen were carried out in two different ways: a) varying the temperature in the range between 650 - 800 °C\(^2\) at constant concentration of hydrogen (10% H\(_2\)/Ar - 3 wt.% H\(_2\)O); and b) varying the hydrogen concentration at constant temperature (800 °C).

6.4.1 EIS Data Analysis

6.4.1.1 Nyquist Plots

Figure 6.4.1.a, shows the results of EIS spectra under wet hydrogen atmosphere at different temperatures and a constant hydrogen flow composition. It can be observed that the total ohmic resistance (intercept of the curve at high frequency) decreases with the increment of the temperature. This effect is the same observed in the impedance measurements in air, which is in agreement with the behavior of the conductivity of the YSZ solid electrolyte with the temperature (cell component with highest ohmic resistance). Also at high frequencies, an inductive behavior of the curves (\(-Z_{im} < 0\)) can be observed. This inductive physical process was also found in air measurements and is more appreciable at high temperature. Similarly to the case of EIS measurements in air, this data was deleted of impedance analysis considering that it is related to electrical connections problems. While the frequency decreases, a little semicircle is observed for all temperatures which is followed for a depressed big semicircle which is not closed. Finally, an apparent straight line at low frequencies can be observed, which is probably related to diffusional controlled process [19].

Figure 6.4.1.b shows the EIS results when hydrogen composition in the flow rate is varied. At high and intermediate frequencies the semi-circles decrease their size while the concentration of hydrogen increases, which indicates that the impedance decreases. The low frequency behavior in the spectra is difficult to analyze, because some curves overlay and it is not clear the behaviour with the change of the hydrogen concentration. The decrease in the ohmic resistance while the hydrogen concentration increase, is an indicator that the cell components, including the electrolyte, are less resistive at high hydrogen concentrations. This can be an indicator of changes in the materials under reducing atmospheres. SEM and XRD analyses were carried out in order to study the changes undergone in the materials after the EIS tests under reducing atmosphere, from which it was possible to determine the reduction of some metallic oxides that compose the electrodes of the cell. On the other hand, the initial characterization of the symmetrical cell before the EIS tests (see Section 6.1) demonstrated by EDS the presence of molybdenum in the dense YSZ electrolyte, so that a reducing atmosphere could decrease the electrical resistance of the electrolyte. A more detailed analysis of the chemical composition of the cell and of the crystalline phases present in the cell after hydrogen EIS tests can be found in Section 6.5.2.

\[^2\]Unlike the EIS measurements in air, the hydrogen atmosphere produces the partial reduction of CMO, which was studied extensively in Section 5.6. Therefore, EIS measurements below 650 °C could produce not valid results due to the instability of the material. Then, to avoid an incorrect analysis, the spectra were analyzed at different temperatures in the range of 800 °C - 650 °C.
6.4.1.2 Distribution of Relaxation Times (DRT)

The determination of the number of physicochemical processes involved in the EIS measurements in hydrogen atmosphere was studied through the analyses of the distribution of relaxation times. Figure 6.4.2a show the DRT analysis at different temperatures holding the hydrogen concentration. This figure shows the presence of six peaks, related to four different physical process. This four different processes (P1, P2, P3 and P4) are sensitive to temperature changes in the system. In addition, the results shown in Figure 6.4.2b demonstrate that the processes P3 and P4 are affected by changes in the hydrogen concentration. These results allow to conclude that P1 and P2 correspond to charge transfer resistances processes due to electrochemical reactions, which is in accordance with the high frequency of the processes. Processes P1 and P2 are represented by $R(CPE)$ circuit and are related to the electrochemical reaction in the CMO and CMO-YSZ phases as shown in Figure 6.4.3.

The processes P3 and P4 are processes affected by diffusional phenomena, and occur at low frequency, which is in accordance with the theory [259]. Peaks $P3^*$ and $P4^*$, located at 100 Hz and 1 Hz of frequency, respectively, are part of the diffusional processes P3 and P4. Ivers-Tiffée and Weber demonstrated mathematically that diffusive phenomena related to Warburg elements produce more than one peak at a specific frequency in the DRT spectrum, and that these peaks occur approximately three or four decades of frequency (three or four orders of magnitude of frequency) greater from the frequency at which the main peak appears [260]. Processes P3 and P4 are represented by $R(CPE-W)$ circuit and are related to diffusional transport of the species, adsorption processes and electrochemical reaction in the CMO and CMO-YSZ phases as shown in Figure 6.4.4.

In accordance with the number of the processes determined by DRT analysis and the physical phenomenology of the process determined by DRT comparison analysis an equivalent electrical circuit was proposed for the EIS results in symmetric-cells tested in hydrogen.
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Figure 6.4.2: Comparison of DRT analyses for different operational conditions: a) DRT analysis obtained from EIS in hydrogen atmosphere (10 vol.% H_2/Ar - 3 wt.% H_2O) at different temperatures, b) DRT analysis obtained at 800 °C with different H_2 concentrations.

Figure 6.4.3: Impedances related to charge transfer processes in H_2: a) physicochemical model of the hydrogen oxidation on the CMO surface and b) equivalent circuit modelling the phenomena; c) physicochemical model of the hydrogen oxidation on the CMO-YSZ surface and b) equivalent circuit modelling the phenomena.

6.4.2 Equivalent Electrical Circuit

The equivalent electrical circuit (Figure 6.4.5) was constructed in accordance with the information provided by the DRT analysis. On the contrary with the DRT results obtained from EIS in air, these impedance results in wet hydrogen do not present a variation of the number of physicochemical processes with the change of the temperature.

The total ohmic resistances in the system are represented by $R_{ohm}$ term. As was stated in Section 6.4.1.2, the processes P1, and P2, were represented as R(CPE) parallel circuits while the processes
Figure 6.4.4: Impedances related to mass transport processes in \( \text{H}_2 \): a) physicochemical model of the hydrogen transport and oxidation on the CMO-YSZ surface and b) equivalent circuit modelling the phenomena; c) physicochemical model of the hydrogen transport and oxidation on the CMO surface and b) equivalent circuit modelling the phenomena.

P3 and P4 were represented as \( R(CPE-W) \). These bounded Warburg elements (\( W \)) represent the diffusional phenomena in both phases: CMO coating layer and CMO-YSZ composite coating layer. The \( R_{\text{diff}} \) resistance was defined as the fraction of the charge transfer resistance which is affected by the diffusional phenomena, while \( R_{\text{ct}} \) was defined as the pure charge transfer resistance produced exclusively by the electrochemical reaction on the TPBs.

Figure 6.4.5: Equivalent circuit proposed for EIS data in \( \text{H}_2/\text{Ar} - 3\% \text{H}_2\text{O} \).

Figure 6.4.6 shows the Nyquist plot of the EIS experimental data at 650 °C and 700 °C and their corresponding residual plots with the GOF value. These results indicate that the experimental data is adequately fitted by the electrical circuit model, presenting a good GOF value with residual values below 1%. GOF values are in the range \( 10^{-5} - 10^{-6} \) for all fits of the equivalent circuits to experimental data, while the maximum residual error of the fitting is below 2% for all fitting. A summary of the values of GOF obtained from EIS experimental data fitted can be consulted in Table C.1.1 of the appendix C. This table corroborate the validity of the model proposed.
6.4.2.1 Area Specific Polarization Resistance (ASPR)

The determination of the area specific polarization resistance (ASPR) was estimated by the sum of the different resistances of the equivalent electrical circuit shown in Figure 6.4.5. The ASPR estimation is obtained from equations 6.4.1 and 6.4.2:

\[
ASPR = \frac{\sum R_i}{2} \quad (6.4.1)
\]

\[
\sum R_i = R_{Ct}^{CMO} + R_{Ct}^{CMO-YSZ} + R_{diff}^{CMO} + R_{diff}^{CMO-YSZ} \quad (6.4.2)
\]

Equation 6.4.1 is divided by 2, because as it was stated in the previous calculation of the ASPR in air atmosphere, the EIS fitted model calculate the value of the physical processes of the complete symmetric-cell, and this approximation is useful to obtain the ASPR value of the coating of the one side of the symmetric-cell. The resistance values obtained from the equivalent electrical circuit...
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model and their respective error values can be found in appendix C, Table C.1.2.

\[ \frac{\ln(1/\text{ASPR})}{\Omega^{-1} \text{cm}^{-2}} = 1000 \cdot T^{-1} / K^{-1} \]

\[ R^2 = 0.985 \]

\[ E_A = 0.97 \text{ eV} \]

Figure 6.4.7: Arrhenius plot for ASPR measurements under H\(_2\) atmosphere.

Figure 6.4.7 shows the Arrhenius plot of the ASPR obtained for symmetric-cells tested under hydrogen atmosphere. The correlation coefficient confirms that the experimental data follow an Arrhenius behavior. Li and Thangadurai [155] reported an ASPR value of 8.58 \( \Omega \) cm\(^2\) at 800 \( ^\circ \)C for the same system. The value obtained of ASPR in this work at 800 \( ^\circ \)C is almost 34\% lower than Li and Thangadurai reported value, reaching a value of 5.68 \( \Omega \) cm\(^2\). While the activation energy value reported by Li and Thangadurai for the same system is 1.44 eV, the one obtained for this work is 0.97 eV. In addition, the activation energy reported in this work is lower than the activation energy obtained for different anode materials tested in hydrogen in symmetric-cells: La\(_4\)Sr\(_5\)Ti\(_{11}\)Mn\(_{0.5}\)Ga\(_{0.5}\)O\(_{37.5-\delta}\)-YSZ-Cu (1.09-1.48 eV) [274], La\(_{0.75}\)Sr\(_{0.25}\)Cr\(_{0.5}\)Mn\(_{0.5}\)O\(_{3-\delta}\)-YSZ-Cu (1.05-1.14 eV) [274], Ni–YSZ [275, 276], Ce\(_{0.8}\)Fe\(_{0.2}\)O\(_{2-\delta}\) (1.18 eV) [277] and La\(_{0.2}\)Sr\(_{0.8}\)TiO\(_3\)-Gd\(_{0.2}\)Ce\(_{0.8}\)O\(_{2-\delta}\)-Ni (1.22 eV) [278]. These results show that CMO-YSZ is a good candidate as an anodic material due to its low specific resistance to polarization and its low energy barrier related to charge transport processes compared to other materials tested in hydrogen.

6.4.2.2 Hydrogen/Water Diffusion Coefficient

The values of the diffusion coefficient, \( D_{\text{H}_2,\text{H}_2\text{O}} \), estimated from EIS measurements at different temperatures and at different hydrogen concentrations are represented in Figures 6.4.8 and 6.4.9, respectively. Calculations were made using equation 6.3.3 and the \( B \) parameter obtained from the EIS measurements. The numerical values of the \( B \) parameter, diffusion coefficients and the fit error of the equivalent electrical circuit can be consulted in Tables C.1.4 and C.1.5 of the appendix C.

The most used models to predict the gradient of concentration in fuel cells are the Stefan-Maxwell model and the Dusty Gas model [279]. In both models, the binary diffusion coefficient \( D_{i,j} \) is calculated using the Chapman-Enskog equation [280], which in the case of \( \text{H}_2, \text{H}_2\text{O} \) can be expressed
as follows:

\[
D_{H_2,H_2O} = \frac{1.86 \cdot 10^{-3} \cdot T^{3/2} \cdot \left( \frac{1}{M_{H_2}} + \frac{1}{M_{H_2O}} \right)^{1/2}}{P \cdot \Omega_c \cdot \sigma^2_{H_2,H_2O}}
\]  

(6.4.3)

where \( T \) is the temperature in K, \( P \) is the pressure in Pa, \( \Omega_c \) is the collision integral, \( \sigma_{i,j} \) is the collision diameter and \( M_i \) is the molecular weight of the species \( i \) \[281\].

The diffusion coefficients obtained from EIS measurements, using the equivalent circuit model, for the case of variable temperature were plotted as a function of \( T^{1.5} \) to analyze the deviation of the Chapman-Enskog model. Figure [6.4.8] shows that the experimental diffusion coefficients do not follow the Chapman-Enskog model (correlation coefficients \( R^2 < 0.98 \)). The estimation of the diffusion coefficient through the Chapman-Enskog model do not consider the Knudsen diffusion in a porous media. In contrast with the results of diffusion coefficients obtained for measurements in air, the diffusion coefficients obtained for measurements in hydrogen are not fitted by Knudsen model too. This indicates that probably the transport mechanism is a Knudsen-molecular combined-type mechanism, and a more complex model is required. The binary Chapman-Enskog diffusion coefficient should be composed by \( H_2O \) and \( H_2 \) components, where water produce problems with the diffusion of the species to electrochemical cell which can be producing instability in the measurements. Water accumulation in the pores of the electrodes is in the most of cases the responsible of the increase in ASPR value \[19\]. An inadequate water feed produce diffusional limitations which have finally an effect in the charge transfer resistances process \[19\] \[261\]. Because of this, one way to decrease the ASPR of the anode of a symmetric cell (or of a fuel cell) is to design a system that adequately controls the water content in the hydrogen stream and prevents water condensation in the feed pipelines; in addition to conducting a study to determine the optimal water content in the hydrogen stream that decreases the ASPR value.

In a similar way with the diffusion coefficients obtained in air, the diffusion coefficients estimated in hydrogen measurements present a high diffusivity value at 650 °C which suddenly decrease almost two orders of magnitude at 700 °C for the both phases, CMO and CMO-YSZ. Following the same analysis in the air measurements, this sudden decrease in the diffusivity is related to changes in the porosity and tortuosity of the porous coating (studied in Section 6.5.2), besides the hydrogen atmosphere has an reducing effect over the metal oxides, probably producing changes in the microstructure.

The CPE value and its behavior with the temperature provides valious information about the diffusional phenomena in the system. The values of pseudo-capacitances (\( Q_{CPE} \)) and their respective mathematical fitting error can be found in Table C.1.6 of appendix C. The values of capacitances of the CPE elements were calculated with equation 6.4.4 for the different phases: CMO and CMO-YSZ.

\[
C = \frac{(Q \cdot R)^{1/a}}{R}
\]

(6.4.4)
where \( Q \) is the value of the pseudo-capacitance, \( a \) is a parameter that indicate a deviation of the capacitor ideal behavior (see Table C.1.6), and \( R \) is the resistor in parallel (see Table C.1.2) with CPE element in the circuit model (see Figure 6.4.3.b and 6.4.3.d).

Holtappels et al. indicates that the variation of the capacitance with the temperature and with the gas environment, particularly the partial pressure of hydrogen and steam, indicate dependence on adsorption process in the TPB region [282]. Boukamp and Holtappels define that the capacitance order of magnitude is a fingerprint of the physicochemical process which take place in the complete cell or symmetric-cell [283]. Analyzing Figure 6.4.8 it can be seen that the capacitance value related to CMO-YSZ phase increases with the increment of temperature, which indicate the presence of an adsorption process. In addition, the values of the capacitances for the CMO-YSZ phase presented in Table C.1.6 are in the order of magnitude of \( ca. 10 - 50 \text{ mF cm}^{-2} \) which are classified by Boukamp as capacitances related to adsorbed species [283]. Analyzing the CMO phase, the capacitance value is almost constant with the temperature, which means that the predominant diffusional process is not related with the adsorption of the species. The higher values of capacitances classified their fingerprint as diffusional process in closed pores [283].

The results of the diffusion coefficients presented in Table C.1.5 show that the values of the diffusion coefficients decrease with the increase of the hydrogen concentration at constant temperature. Mogensen proposed that the water has an important catalytic role in electro-oxidation of fuels in the anode surface providing the oxygen necessary in the anode involved in alternative catalytic ways for hydrogen electro-oxidation [284]. To study the influence of the local concentration of the oxygen at different hydrogen concentrations, the correlation proposed by Hatung and Möbius for the water dissociation equilibrium in a water electrolyzer cell was used [285]:

\[
P_{O_2} = \left( \frac{P_{H_2O}}{P_{H_2} \cdot 10^{-(2.958 - 13022/T)}} \right)^2
\]  

(6.4.5)

The effect of the local oxygen partial pressure \( P_{O_2} \) in the values of the binary diffusion coefficients, \( D_{H_2,H_2O} \), at constant temperature (800 °C) is shown in Figure 6.4.9. There is an evident linear dependence between the diffusion coefficients and the local oxygen partial pressure for both CMO and CMO-YSZ phases. These results indicate a clear dependence between the diffusion coefficients with the local oxygen partial pressures. Probably the transport properties are affected by the kinetics of the adsorption of oxygen species, however other tests are needed to corroborate this hypothesis. The values of diffusion coefficient for CMO-YSZ phases are higher than those for CMO phases, because the adsorption process of water is favored in the YSZ surface, which follows a hydroxylated adsorption group mechanism [286, 287].

### 6.5 Symmetric-Cells Analysis After EIS Tests

#### 6.5.1 Cells Tested in Air Atmosphere

SEM micrographs of the symmetrical cells after EIS tests show a slight decrease in pore diameter, reaching an average value of 0.148 ± 0.574 µm compared to the initial average value of 0.174
± 0.190 µm (see Section 6.1). In the same way, the porosity decreased after the measurements exhibiting a value of ca. 26.7% compared with an initial porosity value of ca. 35.9%. It is possible that the change in porosity begins to be considerable when measurements exceed 700 °C, this...
Figure 6.4.9: H$_2$-H$_2$O diffusion coefficients obtained from fit of equivalent circuit model (symmetric-cells tested in H$_2$-H$_2$O atmosphere) at different hydrogen concentrations, expressed as oxygen partial pressures: a) for CMO layer and b) for CMO-YSZ layer.

would explain the abrupt change in the diffusion coefficient $D_{O_2}$ from this temperature, however porosity measurements are required at different temperatures to corroborate this hypothesis.

An analysis of the surface of the anode is shown in Figure 6.5.1 which presents delamination and deep cracks across the anode surface. The estimated mean crack length after EIS tests correspond to 52.7 ± 27.1 μm, a value which is similar to crack length measured before EIS tests (see Figure 6.1.4). The delamination and cracks could be produced for the differences in thermal expansion coefficients of CMO and YSZ. The thermal expansion coefficient of CMO was not measured, thus it is recommendable to measure it in a future a work.

The changes that might have taken place in the phases and chemical stability of the materials were investigated by XRD analysis of the anode surface.

In the diffractograms of figures 6.5.2a and 6.5.2b, the presence of two secondary phases is observed: Y$_2$MoO$_6$ (JCPDS 00-052-0650) and Zr(MoO$_4$)$_2$ (JCPDS 00-038-1465). These two secondary phases are the same found in the diffractograms of the symmetric cell before the EIS tests (see Figure 6.1.5), so their presence is not a thermal instability effect. The results of the diffractograms indicate that CMO and CMO-YSZ phases were stable at experimental temperatures (400 °C - 800 °C) because new phases were not found.
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Figure 6.5.1: Surface of the coated anode in the symmetric-cell after EIS measurements.

Figure 6.5.2: XRD pattern of the coated anode in the symmetric-cell after EIS measurements: a) and b) correspond to the A and B sides of the symmetric-cell, respectively.

6.5.2 Cells Tested in Hydrogen Atmosphere

The Figures 6.5.3a and 6.5.3b show the aspect of the symmetric-cell after EIS tests under air and hydrogen atmospheres, correspondingly. As it can be seen, the symmetric-cell tested in air does not present significant visible differences with the symmetric-cell before EIS tests (see Figure 4.7.3), however the symmetric-cell tested in wet hydrogen exhibited color change and delamination. On the contrary with air EIS tests, the coating after hydrogen tests presented weak adherence and it was possible to remove manually from the YSZ dense electrolyte. The color change in symmetric-cell after EIS measurements under hydrogen atmosphere is related to the formation of metallic molybdenum (JCPDS 00-047-1081), which was determined by XRD analysis (see Figure 6.5.5).

The SEM analysis of the anode coated surface of the symmetric-cell after EIS measurements in
hydrogen atmosphere is presented in Figure 6.5.4. This micrograph confirms the presence of delamination in the CMO coating surface. The pore size estimated in this micrograph is ca. $0.244 \pm 1.9$ µm, which indicate that the pore size is slightly increased in hydrogen atmosphere, compared with the initial value of $0.174 \pm 0.190$ µm (see Section 6.1). However, the SEM micrograph exhibit the presence of coarsened particles which is in accordance with the decrease of the estimated porosity (ca. 21%). The estimation of the crack lengths was difficult to obtain because the cracks are difficult to differentiate from porosity grooves in the coating surface.

The determination of the chemical phases after EIS hydrogen tests were determined by XRD diffraction. Figures 6.5.5.a and 6.5.5.b show the diffractograms of the coated material on both sides of the YSZ surface. The signals of silver (JCPDS 00-004-0783) phase belongs to the electrical connections in the symmetric-cells. It is very interesting to discuss the presence of metallic molybdenum phase (JCPDS 00-004-0809), which is in agreement with the diffractograms presented in Figure 5.6.6 for pure CMO discs, and confirms that CMO in hydrogen atmosphere present the reduction of a fraction of the total molybdenum content. The presence of MoO$_3$ phase (JCPDS 00-047-1081) suggests that molybdenum comes out of the fluorite structure, indicating low stability under hydrogen atmosphere.

Figure 6.5.3.b shows that the YSZ disc has a blackish coloration after EIS measurements under...
Figure 6.5.5: XRD pattern of anode surface after EIS test under hydrogen atmosphere.

hydrogen atmosphere. This coloration is probably due to the reduced molybdenum coming out of
the CMO structure and diffusing into the dense YSZ electrolyte. To prove this hypothesis an EDS
analysis was performed on the cross-section of the symmetrical cell after EIS measurements under
hydrogen atmosphere. These results presented in Figure 6.5.6 show the presence of molybdenum
and cerium within the structure of the dense YSZ electrolyte, which confirms that the contamina-
tion in the YSZ disk is due to the presence of these elements.

Figure 6.5.6: SEM-EDS analysis of the cross-section of the symmetric-cell after EIS measurements
in H₂-H₂O atmosphere: a) SEM micrograph of the selected area analysed by EDS for b) zirconium,
c) oxygen, d) yttrium, e) molybdenum and f) cerium.
Chapter 7

CA-SOFC Preliminary Tests

In this chapter, the polarization curve and electrical power density curve of a SOFC with CMO-YSZ anode tested at 800 °C under a H₂ atmosphere is presented. The fabricated SOFC consisted of a CMO-YSZ anode, a YSZ dense electrolyte and a LSM-YSZ cathode, and was characterized by SEM, EDS and XRD before and after polarization measurements, to determine changes in the cell and find possible reasons for the results obtained.

7.1 SOFC Pre-Tests Characterization

Figure 7.1.1 shows an SEM micrograph of the cross-section of a complete fuel cell before being tested in fuel cell mode (with hydrogen in the anode and air in the cathode). The fabrication methodology followed to fabricate these SOFCs is detailed in Figure 4.7.5 (see Section 4.7.2). Each side of the dense electrolyte was coated with a first layer of LSM-YSZ or CMO-YSZ in the case of cathode or anode, correspondingly, and a second layer of LSM or CMO as current collector. The cathode side shows less thickness than the anode side and looks more dense. The estimation of the thickness of the different SOFC components are summarized in Table 7.1.1.

<table>
<thead>
<tr>
<th>Layer</th>
<th>Thickness / µm</th>
</tr>
</thead>
<tbody>
<tr>
<td>CMO/CMO-YSZ (current collector/anode)</td>
<td>66 ± 9</td>
</tr>
<tr>
<td>YSZ dense (electrolyte)</td>
<td>244 ± 2</td>
</tr>
<tr>
<td>LSM/LSM-YSZ (current collector/cathode)</td>
<td>23 ± 3</td>
</tr>
</tbody>
</table>

Table 7.1.1: Thickness of different SOFC components of CMO/CMO-YSZ/YSZ/LSM-YSZ/LSM determined through SEM analysis.

SEM micrographs of the coated surface are presented in Figure 7.1.2. The pore size of CMO anodes is approximately 0.352 ± 2 µm while the porosity value is ca. 29.7 %. In the case of LSM cathodes, the pore size is approximately 0.550 ± 1.7 µm, while the porosity is ca. 17.3 %. Clearly from Figure 7.1.2 it can be seen that the LSM particles have a particle size higher than that of CMO particles, which produce pores bigger than that in the anode phase; however, the porosity is less...
than that at the anode. A detailed analysis of Figure 7.1.2 allows to distinguish the start of the sintering process of LSM particles (coarse LSM particles), which is in accordance with the decrease of the cathode thickness shown in the cross-sectional micrograph (Figure 7.1.1). A possible reason for these results is the temperature set for the sintering of the cathode (1 150 °C). This temperature was reported by Jorgensen et al. for fabrication of porous cathodes [288], however, some authors suggest the use of 1 100 °C as sintering temperature of LSM porous cathodes [289–291]. The selection of 1 150 °C as sintering temperature could lead to densification of the porous cathode; consequently, the porosity of the cathode phase is expected to decrease, which could have repercussions on access to TPB sites and on the increase in diffusion limitations.

An EDS analysis was performed to determine the distribution of the chemical elements in the different SOFC components (current collectors, dense electrolyte, cathode and anode) and to determine the possible chemical interaction of the different SOFC components during the fabrication process. In Section 6.1, the EDS analysis was also applied in the determination of the thickness of each layer that formed part of the electrodes of the symmetric-cells (current collector and anode: CMO-CMO/YSZ), however, this analysis could not be carried out, for the SOFCs fabricated, because the boundary of each of the layers in Figure 7.1.1 is not clear.

Figure 7.1.3 shows the presence of strontium and lanthanum in the electrolyte phase, while the electrolyte and cathode phases exhibit the presence of molybdenum. The reaction between LSM and YSZ produces the formation of strontium and lanthanum zirconates. Chen et al. investigated the in-
Figure 7.1.2: SEM micrograph of anode and cathode surface before SOFC tests: anode surface at a) 65x and b) 3000x of magnification; cathode surface at c) 65x and d) 3000x of magnification.

fluence of oxygen partial pressure on the formation of two electrically insulating phases $\text{La}_2\text{Zr}_2\text{O}_7$ and $\text{SrZrO}_3$, concluding that high oxygen partial pressures (greater than 0.21 atm) would prevent the formation of zirconates during the sintering process [292]. The chemical reaction would be produced by the destabilization of the YSZ in oxygen-poor atmospheres, which would produce the diffusion of the reacting species in the YSZ matrix, as can be seen in Figure 7.1.3. On the other hand, Li [293] states that above 1000°C, if the sintering temperature is higher, there is a higher probability of a chemical reaction between YSZ and LSM and consequently the appearance of secondary phases. In the case of the presence of molybdenum in the electrolyte and cathode of the cell, the chemical reaction between the CMO and YSZ has been reported, producing $\text{Zr}_{0.4}\text{Ce}_{0.6}\text{O}_2$ at elevated temperatures (above 1000 °C) [155]. The reaction between CMO and YSZ produces the destabilization of the structure and the release of molybdenum, which can diffuse into the YSZ phase [155], which is associated with the presence of molybdenum in the electrolyte shown in Figure 7.1.3.

The chemical reactions of the different SOFC components could be avoid through the use of buffer layers [19, 39]. This contamination decrease the SOFC performance and in addition could produce short circuit by the addition of the electric conductors to the YSZ phase. For future works the use of a buffer layer will be considered to obtain better fuel cell performances.

For the identification of the secondary phases formed by chemical interaction of the different SOFC components, both sides of the SOFCs were analyzed by XRD. Figure 7.1.4.a corresponds to the analysis of the anode layer, which does not present secondary phases. Figure 7.1.4.b corresponds
to the cathode side and shows the presence of two additional phases: $\text{Mn}_3\text{O}_4$ (JCPDS 00-024-0734) and $\text{La}_2\text{O}_3$ (JCPDS 00-040-1281). Both phases, due to their composition, belong to the LSM phase. These phases can be related to residual undoped oxides from LSM commercial powder and additional analysis of the commercial LSM are required. The presence of some molybdenum phase in the cathode (see Figure 7.1.3.h) could not be confirmed through XRD, which is an indicator that its presence is very low in this phase.

Figure 7.1.4: XRD analysis of a) anode and b) cathode surface before SOFC tests.
CHAPTER 7. CA-SOFC PRELIMINARY TESTS

7.2 SOFC Polarization and Power Density Curves

The polarization and power density curves were obtained using a ProboStat Fuel Cell system. The SOFC tested consists of a dense YSZ disc with a diameter of 20 mm with electrodes coated on each of its faces. The fuel electrode consists of a first layer of a CMO-YSZ composite material and a second layer of the current collector or CMO. The air electrode consists of a first layer of a LSM-YSZ composite material and a second layer of the current collector or LSM (more details about the fabrication and characteristics of the tested cell can be found in Section 4.7.2). The SOFC was placed inside the ProboStat and it was electrically connected by platinum wires and gold ink. Once the cell is inside of the system, the ProboStat is closed and the cell undergoes a conditioning process, in which the temperature was raised very slowly and the gases were fed to the cathode and anode gradually (see Section 4.8.2 for more details on the SOFC conditioning process).

The measurement temperature was 800 °C; the cathode was fed with a flowrate of 200 ml min⁻¹ of ultra-pure air and the anode was fed by a flowrate of 40 ml min⁻¹ of 7 vol.% H₂/N₂ with a water content of 3 wt.%.

The open circuit voltage (OCV) value provided by the system corresponds to 1.1 V. The OCV values reported for SOFCs fed with wet hydrogen (3 wt.% of water) as fuel and air as oxidant, are in the range of 1.0 - 1.1 V [11,19,39,294,295], which is in accordance with the result reported in this work.

Figure 7.2.1 shows the polarization (j-E: current density-potential) and power density (P-E: power density-potential) curves for the operating SOFC system. The maximum electrical power density obtained in the SOFC tested was 48.9 mW cm⁻² at 105.7 mA cm⁻² of current density. This value of maximum power electric density is very low compared with the broadly studied Ni-YSZ/YSZ/LSM fuel cell. Ding et al. performed measurements on a Ni-YSZ/YSZ/LSM-YSZ SOFC fed with wet hydrogen (3% H₂O), obtaining a maximum power density of 990 mW cm⁻² at 800 °C [296]. Tietz et al. succeeded in increasing the maximum electrical power density obtained by Ding et al. by replacing the LSM-YSZ cathode with LSCF (La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ) and adding a GDC (Ce₀.₉Gd₀.₁O₂₋δ) buffer layer (in the cathode side) to the YSZ electrolyte; achieving a maximum power density value of 1 230 mW cm⁻² at 800 °C [297]. Similar maximum power density values were obtained by Liu et al. testing a SOFC of NiO-GDC anode (NiO-Ce₀.₉Gd₀.₁O₁.₉₅), GDC electrolyte (Ce₀.₉Gd₀.₁O₁.₉₅) and an LSCF-GDC cathode (La₀.₆Sr₀.₄Co₀.₂Fe₀.₈O₃₋δ - Ce₀.₉Gd₀.₁O₁.₉₅), fed with hydrogen with 3 wt.% of water; the maximum power density obtained was 35 mW cm⁻² at 550 °C and 60 mW cm⁻² at 600 °C. However, this low power density is related to the intermediate operating temperature.

The study of EIS in symmetric cells in wet hydrogen showed that the CMO is a good candidate for use as an anode in SOFCs due to its low specific polarization resistance (low ASPR value; see Section 6.4.2.1); on the other hand the LSM-YSZ cathode was not studied by EIS measurements, so its ASPR value is unknown for the system studied. The signs of coarsening of the particles in the cathode shown in Section 7.1 (Figure 7.1.1) and the abrupt reduction of the porosity shown after the SOFC tests in Section 7.3 (Figure 7.3.2c) indicate that probably the low value of maximum electrical power density obtained is due to problems in the cathode, however further analysis and a complete study of EIS at the cathode are required to determine properly the origin of the low performance.
7.3 SOFC Post-Tests Characterization

As can be seen in Figures 7.3.1 a-b, the anode surface did not suffer microstructural changes during the SOFC test: the estimated porosity is ca. 28.3% and the pore size is ca. 0.295 ± 0.84 µm. The XRD analysis of the SOFC anode surface presented in Figure 7.3.1 c shows do not change compared to the fuel cell before test (see Figure 7.1.4 a). This situation is very different compared to the results discussed for symmetric-cells in wet hydrogen (see Section 6.5.2 and Figure 6.5.5). The hydrogen atmosphere in symmetric-cells produced the reduction of many chemical species, such as the formation of metallic molybdenum, while in SOFC tests the simultaneous oxidation-reduction cycles avoid the extreme occurrence of these reduction processes. The flow of $O^{2-}$ ions from the cathode to the anode avoids the complete reduction of the anode because the anode is subjected to redox cycles.

The cathode surface after SOFC tests shows clear signs of sinterization (see Figures 7.3.2 a-b), which is evidenced by a critical reduction of its porosity. This result can be the most important reason because of the low maximum power electric density obtained in the fuel cell measurements compared to other results obtained in SOFCs fed with hydrogen as fuel and air as oxidant (see Section 7.2). The sinterization of the cathode restricts the access of oxygen to TPB sites decreasing the performance of the SOFC.

The cathode phases determined by XRD analysis are presented in Figure 7.3.2 c. The diffractogram present the same phases determined before the SOFC test, however there is an additional phase: MnO$_2$ (JCPDS 00-042-1316). The gold signals (JCPDS 00-004-0784) presented in the diffractograms after SOFC measurements belongs to the electrical connections used in the SOFC tests.

From the results discussed in this section, it can be inferred that it is necessary to improve the SOFC fabrication process in order to avoid some drawbacks, such as the formation of secondary...
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Figure 7.3.1: SEM micrograph and XRD of anode surface after SOFC tests: CMO surface at a) 70x and b) 3 000x of magnification; c) Diffractogram of the anode surface.

Figure 7.3.2: SEM micrograph and XRD of cathode surface after SOFC tests: LSM surface at a) 65x and b) 1 500x of magnification; c) Diffractogram of the cathode surface.

phases by the chemical reaction between the SOFC components or the compaction and sintering of the LSM-YSZ porous cathode. Another important aspect to consider is the quality of the reagents used in the elaboration of the cathode (LSM, Sigma-Aldrich), due to the fact that this product did not show good stability at high temperature (1 150 °C, cathode fabrication temperature); it is recommended to use the paste of LSM-YSZ and LSM of Fuel Cells Materials, which are designed for the elaboration of SOFC cathodes. The use of buffer layers in the electrodes, the decrease of the sintering temperature and the control of the oxygen partial pressures during the sintering in SOFC fabrication are aspects that must be taken into account for the improvement in the SOFC fabrication in future works.
Chapter 8

General Discussion

As it was stated in the Literature Review (Chapter 3), solid oxide fuel cells (SOFCs) have become one of the most attractive alternatives for large-scale power generation due to their high conversion efficiencies and high generation capacities. SOFCs are formed by a dense solid electrolyte, formed by complex metal oxides (commonly YSZ), which acts as an ionic conductor and as a barrier impermeable to gases. This electrolyte is sandwiched by two electrodes: cathode and anode, both formed by complex metal oxides. These electrodes must meet various requirements. In the case of the cathode, it must have sufficient electrocatalytic activity to produce the reduction of gaseous oxygen by converting it into oxide ions ($O^{2-}$), in addition it must be porous to allow the diffusion of oxygen within the electrode as well as having a high electrical and ionic conductivity. On the other hand, the anode must be porous to allow the diffusion of the fuel inside the electrode, it must have a sufficient electrocatalytic activity to produce the oxidation of the fuel and it must also have a high electrical and ionic conductivity. A subclass of SOFCs are the carbon-air solid oxide fuel cells (CA-SOFCs), which can use coal or biomass as fuel. This SOFCs are attractive due to the thermodynamics of the system at high temperatures (850 - 900 °C): its theoretical efficiency (chemical to electrical energy conversion) is close to 100 %. However, using carbonaceous fuels to feed a CA-SOFC poses new challenges to the materials: resistance to deactivation by coke deposition and tolerance to sulfur poisoning.

Molybdenum-doped ceria (CMO) was proposed in this thesis as a material for CA-SOFCs anodes, due to the excellent properties of resistance to coke formation, sulfur poisoning, catalytic oxidation activity of carbonaceous fuels and interesting electrical properties of ceria ($CeO_2$) and molybdenum oxides ($MoO_2$ and $MoO_3$). The synthesis of the material was carried out through the combustion method, obtaining nanoparticles of ca. 16 nm in diameter. The determined crystalline structure was of the fluorite-type and the absence of secondary phases confirms that molybdenum dope the ceria in a substitutional way. The maximum concentration of molybdenum used in the synthesis was 10 wt.%, due to the fact that higher concentrations promoted the formation of secondary phases. CMO nanoparticles were used to manufacture dense discs for use in mechanical and electrical tests. An interesting result was that the calcination temperature of the nanoparticles had an effect on the quality of the sintered discs. Experiments with TGA and DSC determined that the proper calcination temperature of the nanoparticles is 850 °C; the use of lower temperatures promoted the formation of amorphous structures in the sintered disc (determined by SEM micrographs), which had an influence on sintered disc quality.

Experiments carried out in a fluidized bed reactor showed that these nanoparticles present catalytic...
activity for the reaction of wet gasification of carbon. This result shows that it is possible to develop a catalytic fluidized-bed system coupled to a CA-SOFC. However, long-term catalytic tests and characterization of nanoparticles after the chemical reaction are needed to determine whether they are affected by coke formation or sulfur.

In addition to the general characteristics that SOFC components must possess (mentioned above), these components are subjected to demanding operational conditions, so they must have an acceptable mechanical resistance. The mechanical properties of the compounds (M\(^{3+}\))-doped ceria (M: Sm, La, Gd) have been extensively investigated due to their uses as electrolytes; however, there is no information in the literature on mechanical properties of CMO. The Young’s modulus measured in this work showed an increase as the concentration of Mo increases, which was related to the decrease of oxygen vacancies and the formation of interstitial oxygen in the material. An interesting result is that the Vickers microhardness decreased as the molybdenum content increases, which directly influences the fracture toughness value. Vickers indenter impressions generated much larger diameter marks than radial cracks, which is probably due to most of the indenter energy is transformed into deformation rather than cracks; consequently, the CMO showed higher fracture toughness than pure ceria. A very important property to be studied and that was not characterized in this thesis work, is the coefficient of thermal expansion. The difference in thermal expansion coefficients produces stress between the materials and the possibility of fracture. Due to its importance it is suggested to measured it in future research works.

The highest electrical conductivities measured in air, using the four-probe method, were obtained at 800 °C with 1.01·10\(^{-3}\) S cm\(^{-1}\), 1.12·10\(^{-3}\) S cm\(^{-1}\) and 1.87·10\(^{-3}\) S cm\(^{-1}\) for CMO with 5 wt.%, 7 wt.% and 10 wt.% molybdenum, respectively, which shows that an increase in molybdenum concentration improves the electrical conductivity of the CMO. The electrical conductivity values reported in this work were slightly higher than the conductivity values reported in the literature for CMO. An XRD analysis of CMO sintered discs after air conductivity tests showed that the material is stable at high temperatures in air atmosphere, because no secondary phases were found in the diffractogram. Hydrogen conductivity tests showed electrical conductivity results almost two orders of magnitude higher than in air tests, with maximum values obtained at 800 °C: 3.87·10\(^{-1}\) S cm\(^{-1}\), 5.82·10\(^{-1}\) S cm\(^{-1}\) and 9.37·10\(^{-1}\) S cm\(^{-1}\) for CMO with 5 wt.%, 7 wt% and 10 wt.% molybdenum, respectively. The conductivity values follow an Arrhenius behaviour up to 600 °C, temperature at which they suffer a sudden increase. Using temperature programmed reduction tests (TPR), cyclic voltammetries and XRD analysis after the measurements, it was possible to determine that the partial reduction of the material and the formation of secondary metallic phases are responsible for this increase in conductivity from 600 °C onwards.

The four-probe method provides information on the total electrical conductivity of the material reliably, but its use is limited to a dense, pure sample of the material and with a specific geometry (CMO sintered disc). When it is necessary to know information about the electrical behavior of the material as an electrode of an SOFC, it is recommended to carry out an electrochemical impedance spectroscopy (EIS) study of the cell. The EIS is a powerful technique that allows to study physicochemical phenomena that occur in the SOFC and determine valuable parameters such as cell polarization resistance, diffusion coefficients and in some cases reaction kinetics parameters.

EIS measurements were performed in symmetric-cells, fabricated with CMO 10 wt.% molybdenum electrodes, because it was the material that exhibited the highest electrical conductivities in
air and hydrogen. The symmetric-cells were fabricated using the protocol detailed in Chapter 4, Section 4.7. The coating process of the electrodes was carried out with paintbrush, which is the main reason why the SEM analyses showed irregularities in the thickness of the electrodes. The irregularity of thickness could affect the results obtained from the EIS. Therefore, the use of a different technique for the fabrication of symmetric-cells, such as spin coating, is recommended to ensure the reproducibility of the fabricated cells. In addition, EDS and XRD analyses showed the formation of three secondary phases formed by the interaction of molybdenum and ceria with YSZ. In order to avoid the formation of these secondary phases, the use of a buffer layer such as GDC is also recommended.

The EIS analyses were performed in two atmospheres: air and wet hydrogen (3 wt. % water). Measurements in air were performed by varying the temperature in a range of 400 - 800 °C, while measurements in hydrogen were first performed by varying the temperature in a range of 650 - 800 °C with a constant flow of 10 vol. % H₂ / Ar - 3 wt. % H₂O, and then varying the hydrogen compositions between 10 - 1.25 vol. % H₂ / Ar - 3 wt. % H₂O at a constant temperature of 800 °C. All measurements obtained were validated using the Kramers-Kronig test. In the case of air, two measurements were discarded: 400 and 450 °C, due to the bad value of GOF. In the case of hydrogen measurements, all GOF values were acceptable.

For EIS measurements in air and H₂, a DRT (distribution of relaxation times) analysis was performed, which made it possible to determine the number of physicochemical processes involved in the system and to propose the equivalent circuit for both cases. The fitting of the experimental data with the equivalent circuit in both cases was successful, presenting good GOF values and low residual error values. In the case of air, the fitting of the equivalent circuit allowed the determination of ASPR (area specific polarization resistance) values, oxygen diffusion coefficients and ionic-electronic conductivity by means of the transmission line model. Hydrogen EIS measurements allowed to obtain ASPR values, H₂ / H₂O diffusion coefficients, and the capacitance behaviour at different temperatures.

The ASPR value in air reported in the literature at 550 °C for the same symmetrical cell is ca. 10⁴ Ω cm² [155], while the value obtained in this work corresponds to 126 Ω cm², so this material has less resistance to polarization. The estimated activation energy is ca. 0.91 eV which is lower than the 1.12 eV reported for the same system [155], this means that the energy barrier of the electrochemical reactions is lower. The oxygen diffusion coefficients obtained fit the Knudsen model, which is probably the mass transport mechanism that governs the process. Above 700 °C, the diffusion values suffer a sudden drop. This is related to a decrease in porosity from that temperature, which would make it difficult to transport the reagents to the reaction zones. An SEM analysis after the EIS test confirmed the reduction of the material porosity, however additional porosity measurement tests at different temperatures are required. The transmission line method succeeded in verifying the electrical conductivity values obtained through the four-probe method.

In the case of hydrogen measurements, the ASPR value obtained in this work is 5.68 Ω cm², almost 34 % lower than the value reported in the literature (8.58 Ω cm²). The activation energy value obtained is 0.97 eV, lower than the value of 1.44 eV reported for this same system and material. The values of the diffusion coefficients obtained could not be fitted to either the Knudsen model or the Chapman-Enskog model, which is why the hydrogen-water diffusion coefficient probably comes from a mixed transport mechanism (molecular diffusion and Knudsen). The constant phase element
(CPE) provides valuable information on solid-state phenomena, such as adsorption of species on the surface. The increase of the capacitance value with the temperature increase in the CMO-YSZ phase indicates that a species is adsorbed preferably in the CMO-YSZ phase and not in the CMO phase, which did not show variation of its capacitance value with temperature. The increase of the diffusion coefficient value with the increase of partial pressure of equivalent oxygen, shows an improvement in the transport of species; probably the transport properties are affected by adsorption of oxygen species on the surface of CMO-YSZ.

The SEM-EDS and XRD analyses showed the stability of the CMO after the EIS measurements in air, however after the EIS measurements in H₂ - H₂O, the material presented the formation of new phases and the delamination of the electrodes, so the material is not stable in a strictly reducing atmosphere.

To demonstrate that the material possesses the proper characteristics to operate as anode, a complete SOFC was fabricated, using a CMO-YSZ composite as anode, a dense YSZ disc as electrolyte and a LSM-YSZ composite as cathode. SEM-EDS and XRD analyses demonstrated the formation of strontium zirconates, a phenomenon widely reported in the literature when a protective buffer layer is not used (see Section 7.1). In addition, the presence of molybdenum in the electrolyte was found. This interaction between the SOFC components makes it necessary to modify the fabrication methods of the fuel cell, in a future research work. The cell was fed with hydrogen as fuel, because it is the most reported fuel in the literature to make comparisons of electric power generation, however this anodic material (CMO) was designed to be used in a CA-SOFC (carbon-air solid oxide fuel cells). Future tests are required using coal as fuel, directly, or previously gasified as proposed by Gür et al. [16]. The maximum electrical power density obtained by this cell is ca. 48.9 mW cm⁻² at 800 °C, a very low value compared to the one reported for the same system using Ni-YSZ as anode (990 mW cm⁻²), YSZ as electrolyte and LSM-YSZ as cathode [296]. Impedance results in both air and H₂ - H₂O showed that the CMO-YSZ has a low ASPR value even compared to several anodic materials based on perovskites (see sections 6.3.2.2 and 6.4.2.1), which means that the polarization resistance problem is probably located in the LSM-YSZ cathode. SEM analysis revealed that the sintering temperature (1 150 °C) produced the densification of the cathodic material, obtaining a low porosity value (17.3 %) which could produce problems in the access to the TPBs and in the transport of species towards the TPB. In addition, the formation of zirconates that have been reported as insulating phases, would also promote the low density of electrical power obtained.

SEM and XRD analyses post-power density measurements demonstrated the stability of the CMO anode. There was no delamination or formation of secondary phases at the anode. This was directly related to the fact that when operating as a complete fuel cell (SOFC mode), continuous oxide-reduction cycles are produced that prevent material reduction (unlike EIS measurements, in which the symmetric cell was in a stricter reducing environment).
Chapter 9

Conclusions

Molybdenum-doped ceria (CMO) nanoparticles were synthesized by the combustion method and its mechanical and electrical properties were studied. The obtained material presents a good thermal stability up to ca. 1200 °C, while the addition of molybdenum to the structure of the ceria, enhances its mechanical properties. The electrical conductivities measured resulted to be slightly higher than those previously reported under air atmosphere for CMO synthesized by the solid diffusion method, while under hydrogen atmosphere the conductivities are improved by nearly two orders of magnitude with respect to measurements under air. The catalytic tests performed demonstrated the catalytic activity of CMO for the wet gasification of carbon, which indicates that this material could be used as a gasification-catalyst and an oxidation-electrocatalyst in a combined fluidized bed-solid oxide fuel cell.

Symmetric-cells were fabricated successfully for electrochemical impedance spectroscopy (EIS) tests. The experimental data obtained under air and hydrogen atmosphere was validated by the Kramers-Kronig transformation and only the data with good GOF value was selected. The DRT analysis allowed to determine an adequate equivalent electrical circuit model for both experimental cases (air or hydrogen atmosphere). The ASPR values estimated through EIS tests under air and hydrogen atmospheres were better than those reported in literature; in addition, better values of activation energy of the charge transfer processes can be observed in this work, which indicates that the material is less resistant to polarization, presenting a lower energy barrier for the evolution of electrochemical reactions. The diffusion coefficients estimated by EIS tests clearly show a Knudsen-type diffusion mechanism in the case of the air atmosphere, whereas in the case of the hydrogen atmosphere, it probably corresponds to a mixed mechanism between molecular and Knudsen-type diffusion.

A complete CMO-YSZ/YSZ/LSM-YSZ fuel cell was fed with wet hydrogen as fuel and air as oxidant. It was successfully tested and it was possible to measure the maximum power electrical density. The obtained value is very low compared to the values reported in the literature, which was mainly attributed to problems in the SOFC cathode, related to inadequate SOFC fabrication protocols. It is suggested to improve the fabrication methods using spin coating method or some method that allows the fabrication of SOFC in a more reproducible way, as well as to incorporate the use of buffer layers to avoid the formation of secondary insulating phases and the chemical reaction between the different SOFC components.
Chapter 10

Future Work

It is suggested for a future work that:

1. The CMO anode is designed to be tested on a carbon-air solid oxide fuel cell (CA-SOFC). Because of this, the SOFC anode must be fueled with a carbonaceous fuel to test its electrocatalytic activity and resistance to carbon deposition and sulfur poisoning. It is suggested to repeat SOFC and symmetric cell tests by feeding a carbonaceous fuel (Coal, methane, synthesis gas, etc).

2. Continuing with the previous point, CMO resistance to coke deposition and tolerance to sulfur poisoning must be tested. For this purpose, it is suggested to make tests of electrical power density in the long-term. This should be accompanied by characterization of the SOFC materials after long-term tests to determine coke formation and sulfur presence in the materials.

3. The method of fabrication of symmetric-cells and SOFCs must be improved to obtain more reproducible results. It is suggested to manufacture symmetric-cells and SOFCs using the spin coating technique. In this context it is also suggested the study of the incorporation of buffer layers to the electrodes of the cell.

4. Finally, an issue not addressed in this work but of great importance, is the improvement of the electrical connections in the measurements of EIS and SOFCs. It is suggested to shorten the length of the silver cables connected to the cells, to use twisted wires to avoid inductance contributions, and to calibrate the potentiostat/galvanostat each time EIS and polarization curve measurements are made, considering the cable extensions, to determine the inductance values of the cables and that these are compensated by the system.
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Appendix A

Mechanical Properties

A.1 Elastic Modulus

Table A.1.1: Values of elastic modulus with correction by porosity.

<table>
<thead>
<tr>
<th>CMO</th>
<th>Density / g cm$^{-3}$</th>
<th>Porosity</th>
<th>$E_Y$ / GPa</th>
<th>$E_o$ / GPa</th>
</tr>
</thead>
<tbody>
<tr>
<td>5 wt.%</td>
<td>7.0121</td>
<td>0.029</td>
<td>101.4</td>
<td>115.5</td>
</tr>
<tr>
<td>7 wt.%</td>
<td>7.0214</td>
<td>0.029</td>
<td>152.4</td>
<td>173.6</td>
</tr>
<tr>
<td>10 wt.%</td>
<td>6.9820</td>
<td>0.036</td>
<td>289.4</td>
<td>340.3</td>
</tr>
</tbody>
</table>
Appendix B

EIS Analysis in Air Atmosphere

B.1 Results Obtained from Equivalent Electrical Circuit Fit under Air Atmosphere

Table B.1.1: Goodness of fit value for fitted EIS experimental values at different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>450</td>
<td>—</td>
</tr>
<tr>
<td>500</td>
<td>8.89·10^-6</td>
</tr>
<tr>
<td>550</td>
<td>2.47·10^-5</td>
</tr>
<tr>
<td>600</td>
<td>1.49·10^-5</td>
</tr>
<tr>
<td>650</td>
<td>2.03·10^-5</td>
</tr>
<tr>
<td>700</td>
<td>3.10·10^-6</td>
</tr>
<tr>
<td>750</td>
<td>2.90·10^-6</td>
</tr>
<tr>
<td>800</td>
<td>2.72·10^-6</td>
</tr>
</tbody>
</table>

Table B.1.2: Bulk and grain boundary impedances obtained of the equivalent circuit fit.

<table>
<thead>
<tr>
<th>Impedance</th>
<th>$R$ / Ω</th>
<th>% error</th>
<th>$Q_{CPE}$ / S s^a</th>
<th>% error</th>
<th>$a$</th>
<th>% error</th>
<th>$C$ / F</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bulk</td>
<td>1.471</td>
<td>0.23</td>
<td>5.835·10^-11</td>
<td>2.32</td>
<td>0.90</td>
<td>1.14</td>
<td>4.44·10^-12</td>
</tr>
<tr>
<td>Grain boundary</td>
<td>1.383</td>
<td>1.25</td>
<td>4.013·10^-9</td>
<td>1.24</td>
<td>0.96</td>
<td>2.21</td>
<td>1.82·10^-9</td>
</tr>
</tbody>
</table>
### Table B.1.3: ASPR values obtained from Nyquist plot spectra at different temperatures.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>ASPR / Ω cm²</th>
</tr>
</thead>
<tbody>
<tr>
<td>500</td>
<td>335.75</td>
</tr>
<tr>
<td>550</td>
<td>126.00</td>
</tr>
<tr>
<td>600</td>
<td>63.45</td>
</tr>
<tr>
<td>650</td>
<td>32.39</td>
</tr>
<tr>
<td>700</td>
<td>19.03</td>
</tr>
<tr>
<td>750</td>
<td>11.28</td>
</tr>
<tr>
<td>800</td>
<td>6.79</td>
</tr>
</tbody>
</table>

### Table B.1.4: Ionic and electronic conductivities obtained from resistances $r_1$ and $r_2$ estimated from transmission line model.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$r_1$ / Ω m</th>
<th>Error / %</th>
<th>$r_2$ / Ω m</th>
<th>Error / %</th>
<th>$r_{ct}$ / Ω m</th>
<th>Error / %</th>
<th>$\sigma_1$ / S cm⁻¹</th>
<th>$\sigma_2$ / S cm⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>1.849</td>
<td>1.21</td>
<td>1.543</td>
<td>0.15</td>
<td>3.188</td>
<td>2.03%</td>
<td>5.41·10⁻³</td>
<td>6.49·10⁻³</td>
</tr>
<tr>
<td>750</td>
<td>3.697</td>
<td>1.02</td>
<td>3.126</td>
<td>0.30</td>
<td>14.56</td>
<td>2.05%</td>
<td>2.70·10⁻³</td>
<td>3.20·10⁻³</td>
</tr>
<tr>
<td>700</td>
<td>5.503</td>
<td>0.15</td>
<td>4.462</td>
<td>1.25</td>
<td>29.53</td>
<td>1.12%</td>
<td>1.82·10⁻³</td>
<td>2.24·10⁻³</td>
</tr>
<tr>
<td>650</td>
<td>10.89</td>
<td>0.23</td>
<td>8.996</td>
<td>1.51</td>
<td>43.72</td>
<td>1.18%</td>
<td>9.18·10⁻⁴</td>
<td>1.11·10⁻³</td>
</tr>
<tr>
<td>600</td>
<td>21.29</td>
<td>3.12</td>
<td>16.38</td>
<td>1.32</td>
<td>61.65</td>
<td>3.05%</td>
<td>4.70·10⁻⁴</td>
<td>6.11·10⁻⁴</td>
</tr>
<tr>
<td>550</td>
<td>56.58</td>
<td>2.21</td>
<td>35.05</td>
<td>1.54</td>
<td>180.3</td>
<td>4.28%</td>
<td>1.77·10⁻⁴</td>
<td>2.85·10⁻⁴</td>
</tr>
</tbody>
</table>
Appendix C

EIS Analysis in Hydrogen/Water Atmosphere

C.1 Results Obtained from Equivalent Electrical Circuit Fit under H₂-H₂O Atmosphere

Table C.1.1: Goodness of fit value for the experimental EIS data measured in hydrogen atmosphere, fitted with the equivalent electrical circuit in Figure 6.4.5.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>% H₂</th>
<th>GOF</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>10</td>
<td>2.1⋅10⁻⁶</td>
</tr>
<tr>
<td>750</td>
<td>10</td>
<td>1.3⋅10⁻⁵</td>
</tr>
<tr>
<td>700</td>
<td>10</td>
<td>5.1⋅10⁻⁶</td>
</tr>
<tr>
<td>650</td>
<td>10</td>
<td>4.7⋅10⁻⁶</td>
</tr>
<tr>
<td>800</td>
<td>5</td>
<td>8.6⋅10⁻⁶</td>
</tr>
<tr>
<td>800</td>
<td>2.5</td>
<td>6.7⋅10⁻⁵</td>
</tr>
<tr>
<td>800</td>
<td>1.25</td>
<td>6.1⋅10⁻⁶</td>
</tr>
</tbody>
</table>

Table C.1.2: Charge transfer resistances obtained from EIS equivalent electrical circuit model for measurements in H₂ atmosphere at different temperatures and ASPR estimation.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>R_CM0 / Ω cm²</th>
<th>Error / %</th>
<th>R_CM0-YSZ / Ω cm²</th>
<th>Error / %</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>4.4630</td>
<td>2.13</td>
<td>0.7873</td>
<td>1.33</td>
</tr>
<tr>
<td>750</td>
<td>20.4900</td>
<td>1.24</td>
<td>1.0722</td>
<td>1.43</td>
</tr>
<tr>
<td>700</td>
<td>57.1713</td>
<td>2.34</td>
<td>1.4340</td>
<td>0.23</td>
</tr>
<tr>
<td>650</td>
<td>75.3709</td>
<td>0.23</td>
<td>1.7114</td>
<td>2.24</td>
</tr>
</tbody>
</table>
Table C.1.3: Charge transfer resistances obtained from EIS equivalent electrical circuit model for measurements in H$_2$ atmosphere at different temperatures and ASPR estimation (continuation).

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$R_{diff}^{CMO}$ / Ω cm$^2$</th>
<th>Error / %</th>
<th>$R_{diff}^{CMO-YSZ}$ / Ω cm$^2$</th>
<th>Error / %</th>
<th>ASPR / Ω cm$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>5.7870</td>
<td>0.33</td>
<td>0.3222</td>
<td>1.13</td>
<td>5.6798</td>
</tr>
<tr>
<td>750</td>
<td>8.8970</td>
<td>0.45</td>
<td>1.1402</td>
<td>2.40</td>
<td>15.7997</td>
</tr>
<tr>
<td>700</td>
<td>10.3286</td>
<td>0.22</td>
<td>1.2429</td>
<td>2.43</td>
<td>35.0883</td>
</tr>
<tr>
<td>650</td>
<td>19.6512</td>
<td>0.43</td>
<td>1.6750</td>
<td>1.88</td>
<td>49.2043</td>
</tr>
</tbody>
</table>

Table C.1.4: $B$ parameter and diffusion coefficients estimation for CMO and CMO-YSZ phases at different temperatures, measured at 10% H$_2$/Ar, 3% H$_2$O.

<table>
<thead>
<tr>
<th>Temperature / °C</th>
<th>$B^{CMO}$ / s$^{0.5}$</th>
<th>Error / %</th>
<th>$D_{eff}^{CMO}$ / H$_2$ / cm$^2$ s$^{-1}$</th>
<th>$B^{CMO-YSZ}$ / s$^{0.5}$</th>
<th>Error / %</th>
<th>$D_{eff}^{CMO-YSZ}$ / H$_2$ / cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>6.6560</td>
<td>1.32</td>
<td>9.8324·10$^{-7}$</td>
<td>0.1370</td>
<td>3.02</td>
<td>2.3208·10$^{-3}$</td>
</tr>
<tr>
<td>750</td>
<td>54.7800</td>
<td>3.45</td>
<td>1.4516·10$^{-8}$</td>
<td>1.0590</td>
<td>2.01</td>
<td>3.8841·10$^{-5}$</td>
</tr>
<tr>
<td>700</td>
<td>60.9900</td>
<td>2.43</td>
<td>1.1710·10$^{-8}$</td>
<td>17.7700</td>
<td>1.01</td>
<td>1.3795·10$^{-7}$</td>
</tr>
<tr>
<td>650</td>
<td>5.5760</td>
<td>1.76</td>
<td>1.4010·10$^{-6}$</td>
<td>0.0098</td>
<td>2.04</td>
<td>4.5729·10$^{-1}$</td>
</tr>
</tbody>
</table>

Table C.1.5: $B$ parameter and diffusion coefficients estimation for CMO and CMO-YSZ phases at different hydrogen composition, measured at 800 °C.

<table>
<thead>
<tr>
<th>% H$_2$</th>
<th>$B^{CMO}$ / s$^{0.5}$</th>
<th>Error / %</th>
<th>$D_{eff}^{CMO}$ / H$_2$O / cm$^2$ s$^{-1}$</th>
<th>$B^{CMO-YSZ}$ / s$^{0.5}$</th>
<th>Error / %</th>
<th>$D_{eff}^{CMO-YSZ}$ / H$_2$O / cm$^2$ s$^{-1}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>10</td>
<td>54.7800</td>
<td>0.36</td>
<td>1.5416·10$^{-7}$</td>
<td>0.1370</td>
<td>1.07</td>
<td>2.3208·10$^{-3}$</td>
</tr>
<tr>
<td>5</td>
<td>14.9800</td>
<td>1.02</td>
<td>1.9412·10$^{-7}$</td>
<td>0.1106</td>
<td>1.02</td>
<td>3.5610·10$^{-3}$</td>
</tr>
<tr>
<td>2.5</td>
<td>10.9540</td>
<td>0.85</td>
<td>3.6237·10$^{-7}$</td>
<td>0.0697</td>
<td>2.01</td>
<td>8.9665·10$^{-3}$</td>
</tr>
<tr>
<td>1.25</td>
<td>5.3630</td>
<td>0.88</td>
<td>1.5145·10$^{-6}$</td>
<td>0.0342</td>
<td>0.51</td>
<td>3.7242·10$^{-2}$</td>
</tr>
</tbody>
</table>

Table C.1.6: CPE parameters and capacitances related to the diffusional process for the CMO and CMO-YSZ phases at different temperatures.

<table>
<thead>
<tr>
<th>T / °C</th>
<th>$Q_{CPE}^{CMO-YSZ}$ / S s$^3$ cm$^{-2}$</th>
<th>Error / %</th>
<th>$a$</th>
<th>$C_{CPE}^{CMO-YSZ}$ / F cm$^{-2}$</th>
<th>Error / %</th>
<th>$Q_{CPE}^{CMO}$ / S s$^3$ cm$^{-2}$</th>
<th>Error / %</th>
<th>$a$</th>
<th>$C_{CPE}^{CMO}$ / F cm$^{-2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>800</td>
<td>0.0630</td>
<td>1.03</td>
<td>0.96</td>
<td>5.135·10$^{-2}$</td>
<td>0.3260</td>
<td>0.22</td>
<td>0.96</td>
<td>0.55</td>
<td>4.980·10$^{-1}$</td>
</tr>
<tr>
<td>750</td>
<td>0.0416</td>
<td>2.30</td>
<td>0.99</td>
<td>3.966·10$^{-2}$</td>
<td>0.3081</td>
<td>0.15</td>
<td>0.96</td>
<td>0.25</td>
<td>4.910·10$^{-1}$</td>
</tr>
<tr>
<td>700</td>
<td>0.0339</td>
<td>0.21</td>
<td>0.95</td>
<td>2.622·10$^{-2}$</td>
<td>0.3322</td>
<td>0.12</td>
<td>0.96</td>
<td>0.41</td>
<td>5.339·10$^{-1}$</td>
</tr>
<tr>
<td>650</td>
<td>0.0153</td>
<td>0.10</td>
<td>0.99</td>
<td>1.526·10$^{-2}$</td>
<td>0.2817</td>
<td>0.50</td>
<td>0.93</td>
<td>1.12</td>
<td>4.923·10$^{-1}$</td>
</tr>
</tbody>
</table>