PhD Thesis

Carbon-Air Fuel Cells with Molten Tin Anodes

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DECLARATION

I confirm that this report is my own work and where reference is made to other research this is referenced in text.
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Dedicated to my parents, Mónica and Alejandro, and my sister Madeleine, who have encouraged me to make my dreams come true.

“You see, but you do not observe. The distinction is clear.”

Sherlock Holmes, ‘A Scandal in Bohemia’
Abstract

Carbon-air fuel cells are a prospective technology for efficient conversion of the chemical energy of solid carbonaceous fuels directly to electrical energy. Although CO₂ is a product, undiluted by the nitrogen and excess oxygen in typical flue gases, such fuel cells can be considered more environmentally-benign than conventional electrical energy production if carbonaceous wastes are used as fuel. In effect, disposal of this carbonaceous wastes would result in CO₂ emissions e.g. from landfill sites, while oxidation of them into a fuel cell would result in energy and neat CO₂ which is far more amenable to subsequent treatment. In addition, depending on the operating potential difference of the fuel cell, CO₂ emission rates per kWh output can be significantly less than from conventional power stations.

Considering that Ni / yttrium-stabilised zirconia (YSZ) anodes in conventional (H₂ / O₂) solid oxide fuel cells (SOFCs) are irreversibly affected by deposition of carbon and sulphur poisoning, some molten metal anodes offer better alternatives, with high electrical conductivities and stabilities when operating on carbonaceous fuels. Tin (Sn) fulfils these requirements and is non-toxic, has a low melting point and vapour pressure, forms oxide(s) that can be reduced by CO (and H₂), and could be purified of ash, based on its immiscibility with molten metals, and of dissolved metals by electrochemical processes.

The thermodynamics, kinetics and materials stability of a solid oxide fuel cell with a 90 µm thick lanthanum strontium manganite (LSM)-YSZ cathode, a 2 mm thick YSZ electrolyte and a 5 mm thick molten tin anode (Sn₀-SOFC) were studied by electrochemical measurements and X-ray analysis. Platinum wires and mesh were used as current collectors at the cathode, while graphite rods or lanthanum strontium titanate (LST) / lanthanum cerium strontium titanate (LCST) pellets were used at the anode. Sn₀-SOFC performance was tested in the absence of fuel (battery mode) at 900 °C using flow rates of 60 mL min⁻¹ of air at the surface of the cathode and 30 mL min⁻¹ of helium at the surface of the anode. For the Sn₀-SOFC operating in fuel cell mode, helium or hydrogen were fed into a 10 mm thick anode at flow rates of 30 and 20 mL min⁻¹, respectively, and activated carbon particles were sited on the surface of the melt.

Thermodynamic analysis of the open circuit voltages (OCVs) measured in the temperature range between 600 and 900 °C, determined that the global reaction occurring in the Sn₀-SOFC when operating without fuel was oxidation of molten tin at the Sn anode | electrolyte interface. This result was confirmed by current density transients of a Sn₀-SOFC
operating at its maximum power density (constant potential difference) and post-mortem analysis of the fuel cell components. Accumulation of tin dioxide at the Sn anode | electrolyte and Sn anode | graphite current collector surfaces was responsible for the degradation of the Sn_{(l)}-SOFC longer term performance.

The kinetics of the Sn_{(l)}-SOFC operating in absence of fuel were studied using the polarization curves and impedance spectra measured at 900 °C and a mathematical model of the ohmic and polarization losses. The model inputs included kinetic parameters reported in the literature for the electrolyte and cathode, enabling prediction of the anode activation and concentration overpotentials; the model outputs were a charge transfer coefficient of ca. 0.67, an exchange current density of ca. 353 A m\(^{-2}\) and a limiting current density of ca. 3 273 A m\(^{-2}\). These values indicated that the kinetics of the whole Sn_{(l)}-SOFC were limited by the mass transport processes occurring at the anode, since the exchange and limiting current densities associated to the cathode were one order of magnitude higher.

Modelling of the Sn_{(l)}-SOFC with a 200 µm thick electrolyte and negligible ohmic losses at the current collectors resulted in a maximum power density of ca. 1 477 W m\(^{-2}\) at a cell voltage of ca. 0.45 V and a current density of ca. 3 273 A m\(^{-2}\), corresponding to the limiting current density. This maximum power density was approximately 1 000 W m\(^{-2}\) lower than the maximum power density predicted for a conventional SOFC with identical LSM-YSZ cathode and YSZ electrolyte (same dimensions and microstructure), but replacing the molten tin anode by a 100 µm thick Ni-YSZ anode operating on hydrogen. Even though the predicted power density of a Sn_{(l)}-SOFC was lower than that of a conventional SOFC, this result seemed to be promising since the Sn_{(l)}-SOFC kinetics could be enhanced by reducing the molten tin anode thickness and improving its contact with the electrolyte by applying pressure over the melt.

When the Sn_{(l)}-SOFC was operated in fuel cell mode, the kinetics of tin dioxide reduction by carbonaceous fuels was found to be slow and did not have significant effects in the kinetics of the fuel cell, even when a stirred molten tin anode was used. By contrast, even though the rate of tin dioxide formation at the Sn anode | electrolyte interface was higher than the rate of reduction of tin dioxide by hydrogen, the presence of this fuel improved the anode kinetics. This condition was observed in the results reported by CellTech Power Inc. using a quiescent molten tin anode and the results obtained during this research project using a stirred molten tin anode, which suggested that hydrogen oxidation occurred in parallel with tin oxidation at the Sn anode | YSZ electrolyte interface and possibly at the SnO\(_2\) | Sn interface.
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Nomenclature

\( A \) : Cross sectional area / m\(^2\)

\( a_i \) : Activity of species \( i \)

\( C_i \) : Concentration of species \( i \) / mol m\(^3\)

\( C_{p,i} \) : Heat capacity of species \( i \) / J (mol K\(^{-1}\))

\( D_i \) : Diffusion coefficient of species \( i \) / cm\(^2\) s\(^{-1}\)

\( D_{i-j} \) : Molecular diffusion coefficient of the mixture \( i-j \) / cm\(^2\) s\(^{-1}\)

\( D_{k,i} \) : Knudsen diffusion coefficient of species \( i \) / cm\(^2\) s\(^{-1}\)

\( D_{i}^{\text{eff}} \) : Effective diffusion coefficient of species \( i \) / cm\(^2\) s\(^{-1}\)

\( d_i \) : Diameter of component \( i \) / m

\( d_p \) : Electrode average pore size / m

\( E \) : Cell potential / V

\( E_N \) : Nernst potential / V

\( F \) : Faraday constant / 96,485 C mol-eq\(^{-1}\)

\( f \) : Frequency / Hz

\( f_i \) : Fugacity of species \( i \) / Pa

\( I \) : Current / A

\( j \) : Current density / A m\(^{-2}\)

\( j_0 \) : Exchange current density / A m\(^{-2}\)

\( j_l \) : Limiting current density / A m\(^{-2}\)

\( M_i \) : Molar weight of species \( i \) / g mol\(^{-1}\)

\( M_{i-j} \) : Molar weight of the mixture \( i-j \) / g mol\(^{-1}\)
$N_i$ : Molar flux of species $i$ / mol m$^{-2}$ s$^{-1}$

$N_o^s$ : Solubility of oxygen / at%

$n_i$ : Moles of species $i$ / mol

$OCP$ : Open circuit potential / V

$OCV$ : Open circuit voltage / V

$P$ : Total pressure / Pa

$P_{elec}$ : Electrical power density / W m$^{-2}$

$P^0$ : Standard pressure / Pa

$p_i$ : Partial pressure of species $i$ / Pa

$Q$ : Total heat / J mol$^{-1}$

$\dot{Q}$ : Heat flow / W

$Q_e$ : Electric charge / C

$Q_{rev}$ : Reversible heat / J mol$^{-1}$

$R$ : Gas constant / 8.3145 J (mol K)$^{-1}$

$R_i$ : Electrical resistance of component $i$ / $\Omega$

$T$ : Absolute temperature / K

$T_{cp,i}$ : Temperature of change of phase of species $i$ / K

$V_i$ : Fuller et al. diffusion volume of species $i$

$V_{m,i}$ : Molar volume of species $i$ / L mol$^{-1}$

$v$ : Velocity / m s$^{-1}$

$W$ : Total work / J mol$^{-1}$

$W_{elec}$ : Electrical work / J mol$^{-1}$

$W_{rev}$ : Reversible work / J mol$^{-1}$
NOMENCLATURE

\( X_f \) : Fuel utilization

\( x_i \) : Mole fraction of species \( i \)

\( Z \) : Impedance / \( \Omega \)

\( \Delta E_{\text{rev},T} \) : Reversible potential at temperature \( T \) / V

\( \Delta G \) : Total Gibbs free energy / J mol\(^{-1}\)

\( \Delta G_T \) : Total Gibbs free energy at temperature \( T \) / J mol\(^{-1}\)

\( \Delta H \) : Total enthalpy of reaction / J mol\(^{-1}\)

\( \Delta H_T \) : Total enthalpy of reaction at temperature \( T \) / J mol\(^{-1}\)

\( \Delta H_{\text{cp},i} \) : Heat of change of phase of species \( i \) / J mol\(^{-1}\)

\( \Delta H_{i,T} \) : Enthalpy of species \( i \) at temperature \( T \) / J mol\(^{-1}\)

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

\( \Delta S \) : Total entropy of reaction / J (mol K\(^{-1}\))

\( \Delta S_T \) : Total entropy of reaction at temperature \( T \) / J (mol K\(^{-1}\))

\( \Delta S_{i,T} \) : Entropy of species \( i \) at temperature \( T \) / J (mol K\(^{-1}\))

\( S_{i,298.15}^o \) : Standard enthalpy of species \( i \) at 298.15 K / J (mol K\(^{-1}\))

\( \Delta U \) : Total internal energy / J mol\(^{-1}\)

\( \Delta V \) : Variation of molar volume / m\(^3\) mol\(^{-1}\)

\( \Delta \phi_{\text{IR}_{\text{total}}} \) : Total ohmic losses / V

\( \Phi_{\text{SOFC}} \) : Overall efficiency of a solid oxide fuel cell (SOFC)

\( \Phi_{\text{Th}_{\text{elec}}} \) : Thermodynamic (maximum theoretical) efficiency

\( \Phi^V \) : Voltage efficiency

\( \alpha \) : Charge transfer coefficient

\( \delta \) : Electronic path length or diffusion layer thickness / m
NOMENCLATURE

\( \varepsilon \) : Porosity

\( \phi \) : Local potential / V

\( \phi_{f,i} \) : Fugacity coefficient of species \( i \)

\( \eta \) : Overpotential / V

\( \nu_e \) : Reaction electron stoichiometry

\( \nu_i \) : Reaction stoichiometry of species \( i \)

\( \rho_i \) : Electrical resistivity of component \( i \) / \( \Omega \) m

\( \sigma \) : Electrical conductivity / S m\(^{-1}\)

\( \tau \) : Tortuosity

\( \omega \) : Angular frequency / Hz

Subscripts and superscripts

act : Activation

an : Anode

bulk : Electrode bulk

ca : Cathode

conc : Concentration

cp : Change of phase

eff : Effective

exp : Experimental

mdl : Modelled

react : Electrode reaction sites
1. Introduction

Electricity is the most flexible and clean form of energy. It can be converted almost without any losses to useful heat or turned with high efficiency into mechanical energy, is used to produce light and propel public transport (trains and buses), and in the future is expected to power millions of personal vehicles [1]. Nevertheless, electricity is not a primary form of energy. It is generated using a variety of sources and technologies such as oil or carbon-fired electricity stations, hydropower plants, nuclear power plants, photovoltaic or solar power plants, etc.; being more than 60% of the world’s electrical power produced starting from combustion of fossil fuels, as shown in Figure 1.1(a) [2].

For more than a century, electricity has been generated primarily in thermal power plants, where fossil fuels are burned in a furnace to produce heat that is used to boil water and generate steam. The dynamic pressure generated by expanding steam turns the blades of turbines that rotate generators capable of converting mechanical energy into AC electric energy by creating relative motion between magnetic fields and conductors. This technology can produce electrical power with efficiencies between 30 and 45% depending on the type of fuel being used. Coal has a lower heating value per unit mass than oil and natural gas[1], but it is the most abundant and cheapest fossil fuel. It is predicted that there is coal for about 200 years at the current level of consumption, while oil reserves are expected to run out in approximately 45 years [3]. However, even though combustion of fossil fuels produces a significant amount of energy at accessible cost, it entails a high rate of carbon dioxide (CO₂) emissions, a major contributor to global warming. Figure 1.1(b) presents the carbon dioxide emissions by fuel reported for the International Energy Agency in 2012, showing that combustion of fossil fuels generates more than 30 Gtonne of CO₂ per year [2].

The greatest producer of electricity from coal-fired power plants is China (3 273 TWh), followed by the US (1 994 TWh) and India (653 TWh), whereas Germany (274 TWh) is the largest user in Europe [2]. China generates electricity mainly using this technology, ca. 80% of its total consumption, and for the period 2004 – 2015 has planned to build about eight hundred 1.0 GW coal-fired power plants. Table 1.1 shows the primary energy, electricity consumption and CO₂ emissions of the top 10 world energy consumers.

Combustion of coal can produce not only CO₂ emissions but also additional pollutants due to reaction of oxygen with the inorganic impurities contained in the fuel. These

[1] According to the Center for Transportation Analysis, U.S Department of Energy (http://cta.ornl.gov), natural gas has a higher heating value (HHV) of 52.225 MJ kg⁻¹, while for crude oil this value is 45.543 MJ kg⁻¹. In the case of coal the HHV is only 23.968 MJ kg⁻¹.

---

1
contaminants can be up to 30% of the coal weight and include sulphur, arsenic, cadmium, mercury and radioactive material, all potentially harmful in any waste stream [4]. In addition, nitrogen oxides ($NO_x$) can be generated by reaction of both fuel-bond and atmospheric nitrogen with oxygen at high temperature, resulting in toxic emissions.

Figure 1.1. (a) World total electricity generation by source in 2010. Other includes geothermal, solar, wind, biofuels and waste, and heat. (b) World total $CO_2$ emissions by fuel in 2010. Other includes industrial waste and non-renewable municipal waste [2]

Without considering externalities such as global warming and environmental pollution, the cost of producing electricity by coal combustion is typically lower than that for using any of the emerging technologies to produce renewable energy, such as solar panels and wind farms [4]. For this reason, and because of the abundance of coal reserves in the world, in recent years several international research groups and companies have invested in the development of new technologies to produce energy using coal with lower emission rates of greenhouse gases and higher efficiency than coal-fired power plants.

This chapter will present an overview about some of these technologies, focusing the interest in carbon-air fuel cells and its advantages with respect to conventional combustion methods.
Table 1.1. Population, primary energy, electricity consumption and CO$_2$ emissions from the top 10 world energy consumers

<table>
<thead>
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<tbody>
<tr>
<td></td>
<td>Total / Mtoe</td>
<td>Per capita / toe pers$^{-1}$</td>
<td>Total / TWh</td>
<td>Per capita / kWh pers$^{-1}$</td>
</tr>
<tr>
<td>U.S.</td>
<td>309 045 000</td>
<td>2 269</td>
<td>7.34</td>
<td>4 143</td>
</tr>
<tr>
<td>China</td>
<td>1 330 415 000</td>
<td>2 613</td>
<td>1.96</td>
<td>3 938</td>
</tr>
<tr>
<td>Russia</td>
<td>148 357 000</td>
<td>687</td>
<td>4.63</td>
<td>916</td>
</tr>
<tr>
<td>India</td>
<td>1 172 707 000</td>
<td>559</td>
<td>0.48</td>
<td>755</td>
</tr>
<tr>
<td>Japan</td>
<td>126 810 000</td>
<td>478</td>
<td>3.77</td>
<td>1 070</td>
</tr>
<tr>
<td>Canada</td>
<td>33 760 000</td>
<td>330</td>
<td>9.77</td>
<td>517</td>
</tr>
<tr>
<td>Germany</td>
<td>81 651 000</td>
<td>306</td>
<td>3.75</td>
<td>590</td>
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<tr>
<td>France</td>
<td>64 768 000</td>
<td>243</td>
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<td>503</td>
</tr>
<tr>
<td>South Korea</td>
<td>48 636 000</td>
<td>263</td>
<td>5.41</td>
<td>482</td>
</tr>
<tr>
<td>Brazil</td>
<td>201 029 000</td>
<td>267</td>
<td>1.33</td>
<td>465</td>
</tr>
<tr>
<td>World</td>
<td>6 850 685 000</td>
<td>12 275</td>
<td>1.79</td>
<td>19 738</td>
</tr>
</tbody>
</table>

[$^\dagger$] in 2010, according to US Census Bureau, [http://www.census.gov](http://www.census.gov)
1.1. Clean Coal Technology

Coal is the dirtiest of all fossil fuels. When burned it produces emissions that contribute to global warming and environmental pollution (CO, CO₂ and NOₓ), creating acid rain (SO₂ and NOₓ) and causing respiratory ailments (NOₓ and particulates). However, coal will continue to be the most popular fuel source to produce energy worldwide, since it is inexpensive and abundant.

Clean coal technology is a collection of techniques being developed to mitigate the environmental impact of coal energy generation, removing or reducing pollutant emissions to the atmosphere. Some of the techniques developed to accomplish the reduction of harmful emissions from coal-fired power plants include chemically washing of minerals and impurities from the coal, gasification (such as integrated gasification combined cycle, IGCC), treating the flue gases in a FGD (flue-gas desulphurization) unit to remove sulphur dioxide, carbon capture and storage (CCS) technologies to capture the carbon dioxide from the flue gas, and dewatering lower rank coals (brown coals) to improve the calorific value, and thus the efficiency of the conversion into electricity.

Integrated gasification combined cycle (IGCC) is a technology that combines gasification with gas cleaning, synthesis gas conversion, and turbine power technologies to produce clean and affordable energy. Using a gasifier, a carbon-based feedstock is converted into synthesis gas (syngas), a mixture of carbon monoxide and hydrogen, which is cleaned of particulates, sulphur, and other contaminants and is then combusted in a high-efficiency Brayton-cycle gas turbine/generator. Heat from the turbine exhaust gas is extracted to produce steam in a Rankine-cycle steam turbine/generator [5]. The integration of energy conversion processes provides a more complete use of energy resources, offering efficiencies up to 60% and lower greenhouse gas emissions than conventional coal-fired power plants (ca. 1.20 lb of CO₂ kWh⁻¹ in IGCC power plants compared to ca. 2.25 lb CO₂ kWh⁻¹ in conventional coal-fired power plants) [5, 6].

Additional to the use of cleaner fuels and more efficient coal-based technologies for power generation, the emission of large quantities of CO₂ into the atmosphere can be controlled by capturing and compressing into a liquid the carbon dioxide in the flue gas. Carbon capture and storage (CCS) is the process of capturing waste carbon dioxide from large point sources, such as fossil fuel power plants, transporting and depositing it into a storage site, normally an underground geological formation, where the greenhouse gas is isolated [7]. Even though this practice is considered not to be a final solution for CO₂
reduction in the atmosphere [7], in the near term it provides an achievable alternative while clean technologies to produce energy can be made economically practical.

Control and reduction of sulphur dioxide (SO$_2$) and nitrogen oxides (NO$_x$) contained in the flue gas is another essential aspect related to clean coal technology. Sulphur dioxide can be removed from the gaseous combustion products by reaction with calcium compounds such as limestone and dolomite. This reaction can take place during combustion, as in fluidized bed systems, or by treating the flue gas using wet scrubbers, spray dry scrubbers and sorbent injection processes [8]. Nitrogen oxides emissions can be reduced using low-NO$_x$ burners, where the combustion zone conditions are modified minimizing excess air and reducing the intensity of mixing in the combustion chamber. The objective of these adjustments is reducing oxygen concentrations and maximum flame temperatures to avoid the formation of thermal NO$_x$ (produced by the reaction of oxygen and atmospheric nitrogen). Additionally, coal injected into an initial ‘fuel-rich’ zone promotes conversion of the nitrogenous compounds contained in the fuel to nitrogen (N$_2$) instead of NO$_x$, while the remaining hydrocarbons and carbon monoxide (CO) are fully burned in a secondary oxygen rich zone [9].

Finally, some technologies have been developed to remove particulates contained in the products of coal combustion (such as ash and small amount of unburnt carbon). In pulverized coal combustion boilers, about 80% of the ash is carried out of the furnace chamber entrained in the flue gas, while the other 20% of the ash is removed from the bottom of the furnace chamber. Particulates are removed using electrostatic precipitators or baghouse filters. In electrostatic precipitators, an electric field is used to charge the particles and attract them to the grounded collector plates. Baghouses are typically large enclosures containing numerous porous fabric filter bags, in which ash accumulates as a dry cake on the dirty side of the bag. Both technologies can reduce particulates emissions up to 99.9% and are currently installed in several coal-fired power plants worldwide [10].

The techniques summarized in this section represent an intermediate stage between conventional coal-fired power plants and future technologies aiming to produce clean energy more efficiently. Between these new approaches, carbon-air fuel cells appear as an attractive alternative to convert carbon’s chemical energy to electricity without forming by-products associated with conventional combustion, such as particulates, nitrogen oxides, sulphur oxides and mercury. In addition, because carbon-air fuel cells can be significantly more efficient than coal-fired power plants, CO$_2$ emissions could be reduced significantly for each unit of electricity generated.
1.2. Solid Oxide Fuel Cells and Carbon Conversion

Generation of energy by clean, efficient and environmental-friendly means is nowadays a major challenge for engineers and scientists. Fuel cells convert chemical energy directly into electrical work by the reaction of a fuel and an oxidant on the surface of the electrodes, resulting in a process more efficient and environmentally cleaner than conventional thermo-mechanical methods. In addition, as long as reactants are supplied to the electrodes, the fuel cell operates continuously, without recharging requirements.

Generally, fuel cells are classified by the chemical characteristics of the electrolyte used as the ionic conductor. Table 1.2 summarizes the technical aspects and operating conditions of different fuel cells. The first five types are characterized by their low electrical generation efficiencies (40 – 50% when operated on readily available fuels such as methanol and hydrocarbons, 50% when using pure hydrogen, depending on current densities). The latter three types are characterized by their high temperature of operation (600 – 1 000 °C), their ability to use methane directly in the fuel cell and thus their high inherent efficiency (45 – 60% for common fuels such as natural gas, 90% with heat recovery) [11].

Solid oxide fuel cells (SOFCs) have recently emerged as a promising technology to be used in large, high-power applications such as full scale industrial stations and large scale electricity-generating stations. These systems consist of a ceramic ionically-conducting electrolyte, such as stabilized zirconia or ceria, sandwiched between the electronically-conducting electrodes. Oxygen is fed into the cathode and reduced to oxide ions ($O^{2-}$) which are transported through the solid electrolyte to the anode where hydrogen fuel is oxidized and electrons are released. Equations (1.1), (1.2) and (1.3) present the half reactions at the cathode and anode, and the global reaction, respectively. Hydrogen fuel can be replaced by reforming natural gas, hydrocarbons (such as methane and propane) and carbon monoxide from coal gasification, which eliminates the difficulties associated with steam reforming or water electrolysis processes for $H_2$ production.

Cathode: $\frac{1}{2}O_2 + 2e^- \rightleftharpoons O^{2-}$ \hspace{1cm} (1.1)

Anode: $H_2 + O^{2-} \rightleftharpoons H_2O + 2e^-$ \hspace{1cm} (1.2)

Global: $H_2 + \frac{1}{2}O_2 \rightleftharpoons H_2O$ \hspace{1cm} (1.3)
Table 1.2. Technical characteristics of different fuel cells

<table>
<thead>
<tr>
<th>Type of fuel cell</th>
<th>Electrolyte</th>
<th>Operating T</th>
<th>Fuel</th>
<th>Oxidant</th>
<th>Efficiency[2]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Alkaline (AFC)</td>
<td>Potassium hydroxide (KOH)</td>
<td>50 – 200 °C</td>
<td>pure hydrogen or hydrazine</td>
<td>$O_2$/Air</td>
<td>50 – 55%</td>
</tr>
<tr>
<td>Direct Methanol (DMFC)</td>
<td>Polymer</td>
<td>60 – 200 °C</td>
<td>liquid methanol</td>
<td>$O_2$/Air</td>
<td>40 – 55%</td>
</tr>
<tr>
<td>Phosphoric acid (PAFC)</td>
<td>Phosphoric acid</td>
<td>160 – 210 °C</td>
<td>hydrogen from hydrocarbons and alcohol</td>
<td>$O_2$/Air</td>
<td>40 – 50%</td>
</tr>
<tr>
<td>Sulphuric acid (SAFC)</td>
<td>Sulphuric acid</td>
<td>80 – 90 °C</td>
<td>alcohol or impure hydrogen</td>
<td>$O_2$/Air</td>
<td>40 – 50%</td>
</tr>
<tr>
<td>Proton-exchange membrane (PEMFC)</td>
<td>Polymer, proton exchange membrane</td>
<td>50 – 80 °C</td>
<td>less pure hydrogen from hydrocarbons or methanol</td>
<td>$O_2$/Air</td>
<td>40 – 50%</td>
</tr>
<tr>
<td>Molten carbonate (MCFC)</td>
<td>Molten salt such as nitrate, sulphate, carbonates</td>
<td>630 – 650 °C</td>
<td>hydrogen, carbon monoxide, natural gas, propane, marine diesel</td>
<td>$CO_2$/O$_2$/Air</td>
<td>50 – 60%</td>
</tr>
<tr>
<td>Solid oxide (SOFC)</td>
<td>Ceramic as stabilized zirconia and doped perovskite</td>
<td>600 – 1 000 °C</td>
<td>hydrogen, natural gas or propane</td>
<td>$O_2$/Air</td>
<td>45 – 60%</td>
</tr>
<tr>
<td>Protonic ceramic (PCFC)</td>
<td>Thin membrane of barium cerium oxide</td>
<td>600 – 700 °C</td>
<td>hydrogen or hydrocarbons</td>
<td>$O_2$/Air</td>
<td>45 – 60%</td>
</tr>
</tbody>
</table>

[2] A detailed definition of the electrical generation efficiency of a fuel cell (overall fuel cell efficiency) and the derivation of its mathematical expression are presented in Chapter 2.
Since the electrochemical process occurs at extremely high temperatures (between 600 and 1,000 °C), internal reforming, rapid electrocatalysis with non-precious metals, and production of high quality by-product heat for co-generation are promoted. All these advantages result in efficiencies up to 60% for this type of fuel cells, with an additional 30% when heat is recovered.

Instead of operating on a gaseous fuel, there is a family of fuel cells to which solid carbon can be fed directly into the anode compartment to produce \( \text{CO}_2 \) and electrical power at high temperature. They are known as carbon-air fuel cells and the overall reaction in this case is given by equation:

\[
\text{C} + \text{O}_2 \rightleftharpoons \text{CO}_2
\]  

(1.4)

The reactant carbon and the product carbon dioxide exist as pure substances in separate phases, their concentrations being fixed and independent of extent of fuel conversion or position within the cell. Consequently, the fuel utilization efficiency could reach 100%, giving a practical typical coal to electricity efficiency of ca. 80% (direct electrical generation alone without co-generation) \([12]\) depending on the current density. In addition, carbon-air fuel cells may cut carbon emissions from coal by 50% and reduce off-gas volume by ten times compared to conventional coal-burning power plants \([13]\). This is because, in contrast to combustion in a boiler, oxidation of carbon in carbon-air fuel cells occurs electrochemically at the anode compartment without direct mixing with air, resulting in no release of particulates and pure \( \text{CO}_2 \) generation, which facilitates its sequestration and storage.

Figure 1.2 presents an idealized schematic of a carbon-air fuel cell and the hypothetical half-reactions occurring at each electrode. The solid fuel is housed inside the anode compartment where ‘combustion’ is achieved by the oxidant ions supplied from the cathode through the electrolyte. Depending on the electrolyte used, carbon-air fuel cells are based in three types of fuel cell technologies:

- Solid oxide fuel cells (SOFCs), in which the atmospheric oxygen oxidant is delivered to the solid fuel in the form of oxide ions (\( O^2- \)) transported through an ionically conductive ceramic (for example, yttrium stabilized zirconia).

- Molten hydroxides fuel cells (MHFCs), in which the oxidant is delivered to the solid fuel in the form of hydroxide ions (\( OH^- \)) contained in the electrolyte (for example, sodium hydroxide).
Molten carbonate fuel cells (MCFCs), in which the oxidant is delivered to the solid fuel in the form of carbonate ions ($CO_3^{2-}$) contained in the electrolyte (for example, sodium carbonate).

These technologies can be combined to produce hybrid technologies such as solid oxide/molten carbonate fuel cells, in which a SOFC element (cathode and solid oxide electrolyte) is coupled in series with a molten carbonate electrolyte containing densely dispersed carbon particles acting as an anode. Alternatively, a molten metal can be used as the anode producing metal oxides that can be reduced continuously with the carbonaceous fuel in order to maintain the conductivity of the electrochemical cell [14].

![Figure 1.2. Schematic of an idealized carbon-air fuel cell](image)

Since carbon-air fuel cells are still at an early stage of technological readiness, substantial effort is needed to address the challenges related to their fundamental and technical aspects. For example, many inexpensive and readily available carbon fuels, such as coal, coke, biomass and organic waste contain impurities such as sulphur, nitrogen, mercury and minerals [4, 15]. The influence of these impurities on the carbon electro-oxidation rate and the stability of the electrolyte, anode and other fuel cells component materials should be examined. Similarly, the mechanism of electrochemical oxidation of carbon in various molten salt electrolytes or molten metal anodes and the dynamic behaviour at the carbon | electrolyte interface should be studied further to better understand the anodic process at the molecular level.
1.3. Project Aims

Energy and environment are undoubtedly the main concerns of the 21st century, being intrinsically related to the way we manage and use our fuel resources. In recent decades, fuel cells have become a promising technology for energy conversion as they represent a clean approach for using carbonaceous fuels.

The project presented in this thesis aimed to fabricate, characterize and optimize the performance of a novel prototype high temperature fuel cell for carbon oxidation which has higher efficiencies and lower greenhouse emissions than conventional coal-fired power plants.
2. Thermodynamics and Kinetic Principles of SOFCs

Direct conversion of the chemical energy of a fuel and an oxidant gas into electricity without irreversible oxidation, can be treated thermodynamically in terms of the Gibbs energy of reaction. This treatment allows the calculation of the reversible work generated and the heat transferred to the surrounding environment as a product of the electrochemical reaction occurring within a solid oxide or a carbon air fuel cell [16, 17].

In principle, conversion of the chemical energy of a fuel into electricity is possible without any losses (100% efficiency). However, during operation of high temperature fuel cells two effects intervene to reduce the total electrical power available: (1) ohmic resistances, which generate heat losses and, (2) irreversible mixing of gases, which causes the voltage to fall as progressively more fuel is used in the reaction. Essentially, it means that a solid oxide or a carbon air fuel cell cannot realistically use all the fuel fed into it, which results typically in about $10-20\%$ of the reactant left unreacted in the exit gas stream [18, 19]. In a real engineering application, the heat output of a high temperature fuel cell can be used to drive a heat engine such as a piston engine or a gas turbine (combined SOFC/heat engine cycles) [20]. Alternatively, it can be exchanged in several ways including fuel processing, air preheating and flue gas cooling, in order to increase the energy efficiency of the process [21, 22]. In addition, other methods such as excess of air and conversion of hydrocarbons into hydrogen and carbon monoxide are usually applied to prevent overheating of the system [23].

To avoid undesired fuel losses in the exit gas stream, it can be reacted with oxygen from the external environment as soon as it leaves the electrochemical cell. This generates additional heat that can be used to keep the fuel cell at the required temperature or can be incorporated to an engine cycle as described before.

Independently of the type of fuel used and the materials chosen to fabricate its components, high temperature fuel cells operate under the same thermodynamics and kinetic principles. Considering this, a general revision of the thermodynamic and kinetic theory for solid oxide fuel cells (SOFCs) will be presented in this chapter in order to understand better the concepts to be discussed during the literature review (Chapter 3). In addition, the basic equations required in Chapter 5 for model development are introduced. In this context, expressions for the power and heat produced by a high temperature fuel cell will be presented which allows the derivation of an expression for the overall efficiency as a function of the operating conditions.
2.1. Thermodynamic Aspects: Energy Generation and Efficiency

In a SOFC the electrochemical reaction between fuel and oxidant, which enter the cell as non-mixed flows of different components, takes place at a reaction temperature, \( T \), and pressure, \( P \), maintained constant by reversible removal or addition of heat. If the isothermal boundary around the considered thermodynamic system is maintained at this constant temperature \( T \), then the SOFC will deliver heat, expressed as \( Q_{\text{rev}} \), reversibly to the environment.

The fuel and oxidant enter the system at temperature \( T \) with a total enthalpy
\[
\left( \sum_{i} \nu_i \Delta H_{i,T} \right)_{\text{reactants}},
\]
where \( \nu_i \) and \( \Delta H_{i,T} \) are the stoichiometric coefficient and enthalpy of reactant \( i \), respectively. Similarly, a total enthalpy
\[
\left( \sum_{j} \nu_j \Delta H_{j,T} \right)_{\text{products}}
\]
leaves the cell with the reaction products. The difference between these two amounts is defined as the enthalpy of reaction of the system, \( \Delta H_T \), which corresponds to the total energy produced by the fuel cell (electrical work generated plus heat transferred). A schematic of the thermodynamic system described is shown in Figure 2.1, where the reversible electrical work is expressed as \( W_{\text{elec}} \).

![Figure 2.1. Energy balance for a reversible SOFC system](image)

From the first law of thermodynamics the change of internal energy \( \Delta U \) can be calculated as follows:
\[ \Delta U = Q + W = Q + W_{\text{elec}} - P\Delta V \]  

(2.1)

where \( Q \) and \( W \) are the total heat and work produced or applied to the system, respectively, and \( P\Delta V \) is the expansion/compression work. The relationship between the changes of Gibbs free energy, \( \Delta G \), enthalpy, \( \Delta H \), and entropy, \( \Delta S \), of reaction at constant temperature \( T \) and pressure \( P \) is given by:

\[ \Delta G = \Delta H - T\Delta S = (\Delta U + P\Delta V) - T\Delta S \]  

(2.2)

Therefore, from equation (2.1) the Gibbs free energy can be expressed as a function of the heat, electrical work and reversible entropy as:

\[ \Delta G = Q + W_{\text{elec}} - T\Delta S \]  

(2.3)

For reversible conditions:

\[ Q = Q_{\text{rev}} = T\Delta S \]  

(2.4)

thus,

\[ \Delta G = W_{\text{elec,rev}} \]  

(2.5)

This is the maximum external work that can be done in passing reversibly a mole of charge, \( \nu_{\text{e}}F \), through an external circuit connected to a galvanic cell between two points differing in electrical potential by \( E_{\text{rev}} \). Considering that the thermodynamic system is at a constant temperature \( T \), the reversible potential \( E_{\text{rev}} \) can be defined in terms of Gibbs free energy as follows\(^{[3]}\):

\[ \Delta E_{\text{rev},T} = -\frac{\Delta G_{\text{r}}}{\nu_{\text{e}}F} \]  

(2.6)

The negative sign in equation (2.6) follows the convention that states that any work done by the system is negative, which is the case of a SOFC converting chemical to electrical

\(^{[3]}\) From now on it will be considered that the pressure of the system, \( P \), is maintained constant at least a different condition is indicated.
energy. In the case of an electrolytic cell work is done on the system, therefore $W_{\text{elec, rev}}$ is positive and $E_{\text{rev}}$ results negative.

In the SOFC studied in this thesis there is no contribution from expansion work, i.e. $\Delta V = 0$, thus the total chemical energy change $\Delta U$ occurring during the electrochemical reduction-oxidation process can be expressed in terms of the enthalpy of reaction (from equation (2.2): $\Delta U = \Delta H$). Therefore, the thermodynamic or maximum theoretical efficiency of the fuel cell system, defined as the ratio of electrical work output to chemical energy input, can be expressed as:

$$\Phi^{\text{Th}}_{\text{elec}} = -\frac{W_{\text{elec, rev}}}{\Delta H_T} = -\frac{\Delta G_T}{\Delta H_T}$$  \hspace{1cm} (2.7)

In the following subsections is presented an overview of the mathematical equations used in the calculation of the thermodynamic functions of interest in the study of SOFCs performance.

### 2.1.1. Enthalpy of Reaction: Total Energy Generation

As it was stated before, the enthalpy of reaction $\Delta H_T$ represents the total energy produced by the fuel cell system. This thermodynamic function depends on the enthalphy of each species $i$ involved in the electrochemical process, which can be calculated in accordance with equation:

$$\Delta H_{i,T} = \Delta H_{i,298.15}^{\circ} + \int_{298.15}^{T} C_{p,i}(T) dT$$  \hspace{1cm} (2.8)

where $\Delta H_{i,298.15}^{\circ}$ and $C_{p,i}$ are the standard enthalpy and heat capacity of species $i$, respectively. If there is a change of phase of species $i$, equation (2.8) becomes to the expression:

$$\Delta H_{i,T} = \Delta H_{i,298.15}^{\circ} + \int_{298.15}^{T_{p,i}} C_{p,i}(T) dT + \Delta H_{q,p,i} + \int_{T_{p,i}}^{T} C_{p,i}(T) dT$$  \hspace{1cm} (2.9)

where $T_{p,i}$ and $\Delta H_{q,p,i}$ are the temperature and heat of change of phase of species $i$, respectively.
2.1.2. Entropy of Reaction: Thermal Energy Generation

According to equation (2.4), the entropy of reaction $\Delta S_T$ is the thermodynamic property that represents the thermal energy produced by the fuel cell. This thermodynamic function, similarly to the enthalpy of reaction, depends on the entropy of each species $i$ involved in the electrochemical process, which can be calculated in accordance with equation:

$$\Delta S_{i,T} = S^\circ_{i,298.15} + \int_{298.15}^{T} \frac{C_{p,i}(T)}{T} dT$$

(2.10)

where $S^\circ_{i,298.15}$ is the standard entropy of the species $i$. If there is a change of phase of species $i$, equation (2.10) becomes to the expression:

$$\Delta S_{i,T} = S^\circ_{i,298.15} + \int_{298.15}^{T} \frac{C_{p,i}(T)}{T} dT + \frac{\Delta H_{cp,i}}{T_{cp,i}} + \int_{T_{cp,i}}^{T} \frac{C_{p,i}}{T} dT$$

(2.11)

2.1.3. Gibbs Free Energy: Electrical Energy Generation

According to equation (2.5), the Gibbs free energy $\Delta G_T$ represents the electrical energy produced by the fuel cell. This thermodynamic property can be defined, based on equation (2.2), as a function of enthalpy and entropy at temperature $T$ in accordance with the expression:

$$\Delta G_T = \Delta H_T - T \Delta S_T$$

(2.12)

Using equations (2.8) to (2.11) the enthalpy and entropy of each species $i$ involved in the global reaction of a fuel cell can be determined. Hence, the enthalpy and entropy of reaction necessary to determine $\Delta G_T$ in equation (2.12) can be calculated using the equations:

$$\Delta H_T = \left( \sum_{j} v_{j} \Delta H_{j,T} \right)_{products} - \left( \sum_{i} v_{i} \Delta H_{i,T} \right)_{reactants}$$

(2.13)

$$\Delta S_T = \left( \sum_{j} v_{j} \Delta S_{j,T} \right)_{products} - \left( \sum_{i} v_{i} \Delta S_{i,T} \right)_{reactants}$$

(2.14)
where the subscripts $i$ and $j$ refer to reactants and products, respectively.

### 2.1.4. Open Circuit or Nernst Potential

The reversible potential presented in equation (2.6) represents the potential of the SOFC at the standard state in terms of the reactants and products activities ($a_i = 1.0$ for all species $i$). Operating temperature dependence is intrinsic as the change of Gibbs free energy is temperature dependent (see equation (2.12)).

When the reactant and/or product activities (often simplified to partial pressures in these high temperature systems) deviate from the standard state, a correction for the theoretical reversible potential is required. This potential, which has been corrected to reflect the local activities of the reactant and product species, is often referred to as the open circuit voltage (OCV) or Nernst potential.

The Nernst potential can be calculated using the activities of the reactant and product species, reaction stoichiometry ($v_i$) and reaction electron stoichiometry ($v_e$) at equilibrium. Considering the oxidation of hydrogen presented in equation (1.3) the reaction stoichiometry is $1, 0.5$ and $1$ for hydrogen, oxygen and water, respectively, and the reaction electron stoichiometry is $2$. The Nernst potential is calculated for the case of no-current flow through the external circuit and therefore does not take into account reaction kinetics or the irreversible losses that occur during cell operation under load. Thus, the Nernst potential is calculated using the equation:

$$E_N = \Delta E_{\text{rev},r} + \frac{RT}{2F} \ln \left( \frac{a_{H_2} a_{H^2O}^{1/2}}{a_{H_2O}} \right)$$

(2.15)

Assuming that the activity of the species $i$, which can be expressed using the fugacity ($f_i$), total pressure ($P$), standard pressure ($P^0$), the fugacity coefficient ($\phi_j$) and the mole fraction ($x_i$), can be approximated by the partial pressure ($p_i$) in accordance with the equation [24]:

$$a_i = \frac{f_i}{P^0} = \phi_j x_i \frac{P}{P^0} \approx p_i$$

(2.16)

Therefore, the Nernst potential (2.15) can be expressed in terms of the partial pressure as follows:
\[ E_N = \Delta E_{\text{rev}, T} + \frac{RT}{2F} \ln \left( \frac{P_{H_2} P_{O_2}^{1/2}}{P_{H_2O}} \right) \] (2.17)

The equilibrium cell potential \( E_N \) will depend on axial position if significant compositional and temperature changes occur, due to consumption and production processes.

2.2. Kinetic Principles: Fuel Cell Polarization and Ohmic Losses

When a potential \( E \) is applied to a fuel cell a flux of electrons is transferred from the anode to the cathode producing an electrical current density \( j \). This phenomenon, referred to as polarization, depends on the equilibrium potential \( E_N \) and polarization losses associated with the kinetics of the electrical and chemical processes occurring when the fuel cell is operational. Considering this, the applied potential \( E \) can be defined using the equation:

\[ E = E_N - \eta_{i}^{\text{act}} - |\eta_{i}^{\text{act}}| - \eta_{i}^{\text{conc}} - |\eta_{i}^{\text{conc}}| - \Delta \phi_{\text{total}}^{IR} \] (2.18)

where \( \eta_{i}^{\text{act}} \) and \( \eta_{i}^{\text{conc}} \) correspond to the anodic or cathodic (\( i = \text{an}, \text{ca} \)) activation and concentration polarization, respectively, and \( \Delta \phi_{\text{total}}^{IR} \) are the total ohmic losses which include the electrolyte, electrodes and current collectors resistances.

In the following subsections the mathematical expressions used to calculate the polarization losses contained in equation (2.18) are deduced. In addition, equations to determine the fuel consumption, electrical power and heat generated by the fuel cell are presented as a function of the thermodynamic and kinetic parameters introduced.

2.2.1. Activation Overpotential

The activation overpotential is a measure of the electrodes activity, which represents the additional potential required to overcome the activation energy barriers associated to the charge transfer reactions occurring at the electrode | electrolyte interfaces. In a SOFC, at the cathode charge transfer converts oxygen molecules (\( O_2 \)) into oxide ions (\( O^2- \)) in accordance with the half-reaction (1.1), while at the anode gaseous hydrogen (\( H_2 \)) reacts with these oxide ions to form the product water steam (\( H_2O \)) following half-reaction (1.2). These electrode processes depend not only on charge transfer reactions but also in the mass transport between the electrode | electrolyte interface and the bulk of the gases.
For rapid mass transfer, the relationship between the electrode activation overpotential $\eta_i^{act}$ ($i = an, ca$) and the current density $j$ can be expressed by the Butler–Volmer equation:

$$j = j_{0,i} \left[ \exp \left( \frac{\alpha_i \nu_e F \eta_i^{act}}{RT} \right) - \exp \left( - \frac{(1-\alpha_i) \nu_e F \eta_i^{act}}{RT} \right) \right]$$

(2.19)

where $j_{0,i}$ is the exchange current density, $\alpha_i$ is the charge transfer coefficient, $\nu_e$ is the reaction electron stoichiometry, $F$ is the Faraday constant, $R$ is the gas constant, and $T$ is the operating temperature.

The exchange current density $j_{0,i}$ is a measure of the electrocatalytic activity at the triple phase boundaries (TPBs) reactant-electrode-electrolyte for a given electrochemical reaction and depends on the operating conditions and material properties [17]. At the cathode of a SOFC the electrochemical reaction steps include adsorption of oxygen at the TPBs, electrons transfer and oxide ions inclusion into the electrolyte. At the anode the key steps are adsorption of hydrogen at the TPBs, charge transfer and desorption of steam molecules.

Large values of $j_{0,i}$ mean that the electrode reactions are fast and large current densities can be obtained with small activation overpotentials. This situation is desirable since it means that more current, and thus electrical power, can be obtained at a lower voltage penalty. Therefore, most of the research in the SOFC domain is focused on optimizing the materials used for its fabrication and their microstructure to increase the kinetics of the charge transfer reactions at the electrodes. A detailed review of the different fuel cell components studied and their performance improvements will be presented in Chapter 3.

The dependence of the activation overpotential on the local reactant and product activities is often accounted by the expressions that relate the exchange current density to the local species activities. However, when using the kinetic form of the Butler–Volmer equation (2.19) the additional potential drop due to concentration gradients in the electrodes is not explicitly included. In order to resolve this deficiency, the potential drop due to concentrations gradients, referred to as the concentration overpotential $\eta^{conc}$, can be calculated as an additional voltage loss added to the total potential loss as shown in equation (2.18).
2.2.2. Concentration Overpotential

The concentration overpotential is caused by the resistance to transport of reactant species approaching to the reaction sites and the transport of product species leaving them. In a SOFC the reacting gaseous species $O_2$ and $H_2$ must be transported from their respective flow streams through the porous electrodes (cathode and anode, respectively) to the electrode | electrolyte interfaces where the reactions occur. Similarly, the anode product $H_2O$ must be transported away from the interface to the bulk exit stream.

In the steady state the following equation must be obeyed [17]:

$$|N_{H_2}| = |N_{H_2O}| = 2|N_{O_2}| = \frac{j}{v_i F} \quad (2.20)$$

where $N_{H_2}$, $N_{O_2}$ are the molar fluxes of $H_2$ and $O_2$ through the porous anode and cathode respectively, and $N_{H_2O}$ is the flux of water steam away from the anode reaction sites.

The reactions at the anode and cathode reaction sites result in the consumption of hydrogen and oxygen, respectively, which means that the partial pressures of these reacting species at these points decrease and the partial pressure of the product water vapour increases. This situation creates a concentration gradient of the different reacting species between the bulk stream and the electrode | electrolyte interface which results in an electrical potential difference $\eta^{conc}$. In the case of a conventional solid oxide fuel cell it is often reported as [25]:

$$|\eta_{total}^{conc}| = OCV^{react} - OCV^{bulk} \quad (2.21)$$

where $react$ represents the reaction zones which will be distributed in the electrodes. Consequently, the concentration overpotential $\eta_{i}^{conc}$ at each electrode ($i = an, ca$) can be estimated from the local partial pressures at the reaction sites and bulk as follows:

Cathode:

$$|\eta_{ca}^{conc}| = \frac{RT}{2F} \ln \left( \frac{P_{O_2}^{bulk}}{P_{O_2}^{react}} \right)^{1/2} \quad (2.22)$$

Anode:

$$\eta_{an}^{conc} = \frac{RT}{2F} \ln \left( \frac{P_{H_2}^{bulk} P_{H_2O}^{react}}{P_{H_2}^{react} P_{H_2O}^{bulk}} \right) \quad (2.23)$$
Estimation of the concentration overpotentials from equations (2.22) and (2.23) is not a simple task since measurements of the local reactant partial pressures at the electrode active sites is difficult to quantify in practice. For this reason, alternative formulations exist to estimate the concentration overpotential as a function of the limiting current densities, which corresponds to the current density at which the partial pressure of the reacting species at the reaction sites tends to zero \[17\]. The mathematical derivation of these alternative equations will be discussed in Chapter 5, where modelling of a conventional solid oxide fuel cell is presented.

2.2.3. Ohmic Potential Losses

Ohmic losses arise due to the resistance offered by the various fuel cell components (cathode, anode, electrolyte and interconnects) to the flow current. According to Ohm’s law, the ohmic potential drop \( \Delta \phi_{\text{total}}^{\text{IR}} \) due to a current flowing through an electrochemical cell of total resistance \( R_{\text{cell}} \) can be calculated as:

\[
\Delta \phi_{\text{total}}^{\text{IR}} = j R_{\text{cell}}
\]  

(2.24)

The linear behaviour between potential drop and operating current can be described in terms of the conductivity of the cell components and the path length for the flow of the charged species. Thus, equation (2.24) can be re-written as follows:

\[
\Delta \phi_{\text{total}}^{\text{IR}} = j \sum_i \frac{\delta_i}{A_i \sigma_i}
\]  

(2.25)

where \( \delta_i \) is the corresponding path length of the fuel cell component \( i \), \( A_i \) is the cross-sectional area of this component, and \( \sigma_i \) is its conductivity. From this equation is immediately clear that minimization of the ohmic losses requires increasing the materials conductivities or cross-sectional areas or decreasing the path length.

Contact resistance losses represent an additional potential loss due to the interfacial resistance to flow of the charged species at, for example, current collector | electrode interface. Typically, these losses are neglected as being insignificant. However, in carbon-air fuel cells where molten electrolytes or anodes are used it can be difficult to achieve high quality electrical contacts considering the instability or low wettability of the materials used (see Chapter 3 and Chapter 6 for more details).
2.2.4. Fuel Cell Power Density and Heat Generation

The operating cell voltage $E$ of a SOFC at any current density $j$ can be estimated by subtracting all the potential losses presented in Sections 2.2.1 to Section 2.2.3 from the OCV as shown in equation (2.18). Figure 2.2 shows the total losses and cell potential as a function of the operating current density. In addition, the mass transfer limited current density at high voltages is also shown.

![Figure 2.2. Schematic of a typical SOFC current-voltage or polarization curve showing the operating cell voltage and potential losses](image)

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

$$P_{elec} = j \times E$$  \hspace{2cm} (2.26)

The active area used to compute the current density $j$ is usually the area of the fuel or working electrode. In a planar SOFC where the anode (fuel electrode) of radius $r_{an}$ is commonly supported on one of the faces of a disc electrolyte, the cell area $A_{cell}$ is given by:

$$A_{cell} = \frac{\pi r_{an}^2}{4}$$  \hspace{2cm} (2.27)
The current density can be then computed from the measured current $I$ using the following equation:

$$ j = \frac{I}{A_{\text{cell}}} $$  \hspace{1cm} (2.28)

The voltage efficiency, which gives account of the kinetic and transport shortcomings of the chemical to electrical transformation, can be represented as the ratio of the cell voltage to the Nernst potential:

$$ \Phi^v = \frac{E}{E_N} $$  \hspace{1cm} (2.29)

As more current is drawn from the SOFC, the irreversible losses increase and the voltage efficiency decreases. These irreversible losses can be expressed as heat and added to the entropic losses associated to the oxidation reactions. Therefore, the total rate of heat flow $\dot{Q}$ produced by a fuel cell using hydrogen, as a representative example, can be calculated as follows:

$$ \dot{Q} = (E_N - E) I + \frac{I}{2F} T \Delta S_{H_2O,T} $$  \hspace{1cm} (2.30)

where $\Delta S_{H_2O,T}$ corresponds to the entropy of reaction (1.3) at temperature $T$.

### 2.2.5. Fuel Utilization and SOFC efficiency

The fuel utilization of a SOFC is a measure of the fuel conversion within the electrochemical reactor. This can be expressed as the ratio of the amount of fuel consumed in the electrochemical reaction to the amount of fuel supplied to the SOFC. Therefore, in the steady state the fuel utilization can be defined in terms of the mole fraction of the fuel at the exit and inlet. Using hydrogen as a representative example, the fuel utilization $X_f$ can be defined as:

$$ X_f = \frac{x_{H_2}^{\text{out}}}{x_{H_2}^{\text{in}}} $$  \hspace{1cm} (2.31)

In the absence of recycle of fuel streams, the chemical energy of un-reacted fuel leaving the reactor represents an efficiency loss. Consequently, the overall efficiency of a SOFC,
\( \Phi_{SOFC} \), can be defined in terms of the thermodynamic efficiency \( \Phi_{Th} \), the voltage efficiency \( \Phi^V \) and the fuel utilization \( X_f \), as follows:

\[
\Phi_{SOFC} = \Phi_{Th}^{\text{elec}} \times \Phi^V \times X_f
\]  

(2.32)
3. Literature Review: High Temperature Fuel Cells

As stated in Chapter 1, fuel cells are electrochemical devices that convert the chemical energy of a fuel directly into electricity and heat. They operate like a battery, but do not need to be recharged since power can be produced continuously while a fuel and an oxidant are supplied. Hydrogen is the fuel most commonly used for this technology, but additionally hydrocarbons such as natural gas, alcohols like methanol, coal and carbonaceous wastes can be used depending on the type of fuel cell considered.

Attempts to develop fuel cells as power sources started many years ago with the objective of using them for space and defence applications [26]. Nevertheless, the growing menace of depletion of fossil fuels reserves and the dramatic environmental effects of greenhouse emissions focussed the efforts on developing more efficient and less polluting electricity generation technologies. Consequently, considering that they can produce energy with efficiencies not limited by the Carnot cycle of a heat engine and their pollutant outputs are magnitudes lower than from conventional technologies, fuel cells have the potential to revolutionize the power generation industry with a shift from central power stations and long transmission lines to dispersed power generation at user sites.

Since fuel cells can operate in a wide range of temperatures (between 50 and 1 000 °C), they can be classified in three groups:

- Low temperature fuel cells (50 – 300 °C), such as the proton exchange membrane fuel cells (PEMFCs) and the alkaline fuel cells (AFCs), which are used mainly for transport applications.

- Intermediate temperature fuel cells (300 – 600 °C), such as some of the direct ammonia fuel cell technologies, to be used for stationary power generation.

- High temperature fuel cells (600 – 1 000 °C), such as molten carbonate fuel cells (MCFCs) and solid oxide fuel cells (SOFCs), which are expected to be the most efficient and versatile power generation systems of the future.

In this chapter, the principles of design, manufacture and operation of high temperature fuel cells are comprehensively outlined, with special emphasis on the characteristics of carbon–air fuel cells and their advantages with respect to the use of conventional SOFCs.
3.1. Solid Oxide Fuel Cells (SOFCs)

Solid oxide fuel cells (SOFCs) differ from other fuel cell technologies because of two main reasons: they operate at temperatures as high as 1000 °C and their components are all solid state materials. These two characteristics made them advantageous in comparison with low/intermediate temperature fuel cells, since their kinetics are enhanced at these elevated operating temperatures and there is no fundamental restriction on the cell configuration considering the solid state of its components (they can be planar or tubular structures).

As it was stated in Section 1.2, a solid oxide fuel cell consists of three key components: a dense ionic conducting electrolyte and two porous electrodes. At the cathode, oxygen gas ($O_2$) is fed and diffuse through the porous structure of the electrode to the reaction sites (cathode | electrolyte interface) to be reduced to oxide ions ($O^{2-}$). These oxide ions are transported through the dense electrolyte to the anode | electrolyte interface, where reaction with hydrogen gas ($H_2$) occurs to produce water steam molecules ($H_2O$), which diffuse to the anode surface to be collected or exhausted to the air. Alternatively to oxide ions, protons ($H^+$) can be transported through the electrolyte in order to produce water steam molecules at the oxygen electrode. Schematics of the operation of a SOFC with oxide and proton conductive electrolytes are presented in Figure 3.1(a) and Figure 3.1(b), respectively.

![Figure 3.1](image)

Figure 3.1. Schematic of a SOFC with (a) an oxide conductive electrolyte, (b) a proton conductive electrolyte

To have an efficient and cost-effective energy production, SOFC components must meet some special requirements. In the case of the electrolyte, it must have high ionic and low electronic conductivity because the presence of electronic conductivity reduces its ionic...
counterpart, resulting in poor current efficiencies. Additionally, the electrolyte needs to be: (1) gastight, to prevent any possibility of hydrogen and oxygen mixing during the electrochemical process; (2) as thin as possible, to minimize the electrolyte ohmic losses (energy consumption); and (3) chemically stable, to avoid cell performance decays (degradation of the components). Both electrodes should have suitable porosity and pore size in order to support gas transport between the electrode surfaces and the electrode | electrolyte interfaces, and provide sufficient electrolyte-electrode-gas triple phase boundaries (reaction sites). In addition, the thermal expansion coefficients of both electrodes should be close to that of the electrolyte to prevent material failure of the electrolyte due to exceedingly high mechanical stress induced by thermal expansion mismatch.

This section presents a review of the materials used to manufacture the components of SOFCs, describing their properties, the reaction mechanism and the operating conditions used to optimize the energy generation of these systems.

3.1.1. SOFC Electrolytes

Stabilized zirconias based on oxide ions (O\(^{2-}\)) transport have been the solid non-porous electrolytes most commonly used to date, being yttrium stabilized zirconia (Y\(_2\)O\(_3\) stabilized ZrO\(_2\) or YSZ) the most widely held because of its high conductivity and good mechanical strength. Alternatively, CaO, MgO, Sc\(_2\)O\(_3\) and certain rare earth oxides such as Nd\(_2\)O\(_3\), Sm\(_2\)O\(_3\), Yb\(_2\)O\(_3\), can be used as stabilizing dopants for zirconia, while ceria (CeO\(_2\)) doped with samarium, gadolinium or yttrium (SDC, GDC, YDC), and lanthanum strontium gallium magnesium oxide (LSGM) represent interesting alternative electrolytes for SOFCs operating at temperatures lower than 800 °C [27, 28].

In the case of proton conductive ceramics, barium and strontium cerate (BCN, SYC) can be used as electrolytes in SOFCs operating in the range of 600 – 800 °C. Gadolinium, calcium, samarium, yttrium and neodymium have been used as dopants of these ceramics to enhance their ionic conductivities [29].

The operation of the carbon-air fuel cell fabricated and studied during this research project was based on the transport of oxide ions (O\(^{2-}\)) through a solid oxide membrane (pellet), which allowed maintaining the charge transfer between the electrodes. For this reason, this subsection presents an overview of the main structural characteristics and physical-chemical properties of the most commonly used oxide ions conductive electrolyte materials.
3.1.1.1. Stabilized Zirconias

Zirconia or zirconium dioxide (ZrO$_2$) is a white crystalline oxide which occurs naturally in the form of a monoclinic structure. It has a high melting point of around 2 700 °C, but suffers from phase transformation from the monoclinic to the tetragonal form at around 1 100 °C, and to cubic fluorite form at around 2 370 °C [30]. Schematics of the crystalline structures presented by zirconium dioxide at these temperatures are shown in Figure 3.2. The continuous phase transformation of zirconia can lead to a large and disruptive volume change that needs to be prevented to avoid mechanical fracture of the fuel cell components. The addition of some alkaline or rare earths to the zirconia lattice sites (doping), stabilize the cubic and tetragonal structures and increase the concentration of oxygen vacancies, enhancing the oxide conductivity. Some experimental data on the ionic conductivity of doped zirconia dioxide are summarized in Table 3.1.

![Figure 3.2. Crystalline structures presented by zirconium dioxide (ZrO$_2$) at different temperatures [31]](image)

It can be seen from Table 3.1 that the electrolyte presents high conductivities when it is doped with Y$_2$O$_3$ and Sc$_2$O$_3$, while doping with MgO, La$_2$O$_3$, and CaO results in relatively low conductivities. The Sc$_2$O$_3$ doped ZrO$_2$ (ScSZ) exhibits the highest ionic conductivity because the ionic radius of Sc$^{3+}$ is close to the radius of Zr$^{4+}$ (see Figure 3.3), which yields to lower association energies between the dopant and the oxygen vacancies, and consequently lower activation energies of the conduction process, according to Kilner and Brooks’s research [32]. However, despite its high ionic conductivity, ScSZ is not widely used as an electrolyte for high temperature operation mainly because of its high cost. Therefore, YSZ is the material choice for SOFCs electrolyte since it is much more economical and offers the best combination of ionic conductivity and stability.
### Table 3.1. Reported ionic conductivity of different doped zirconia materials [28]

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity / S m(^{-1})</th>
<th>Temperature / °C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>8YSZ</td>
<td>13</td>
<td>1 000</td>
<td>Prepared by spray drying of nitrate precursor solution</td>
</tr>
<tr>
<td>10.5YSZ</td>
<td>3.4</td>
<td>800</td>
<td>Prepared by aerosol-assisted metal-organic chemical</td>
</tr>
<tr>
<td>10 YSZ</td>
<td>4.52 x 10(^{-4})</td>
<td>400</td>
<td>Prepared by atomic laser deposition</td>
</tr>
<tr>
<td>9.5YSZ</td>
<td>5.7</td>
<td>900</td>
<td>Prepared by magnetic pulse compaction of tape-casted nanopowders</td>
</tr>
<tr>
<td>8YSZ</td>
<td>8.3</td>
<td>900</td>
<td>Spark Plasma Sintering</td>
</tr>
<tr>
<td>CaO-ZrO(_2) with 12.5 mol% CaO</td>
<td>5.5</td>
<td>1 000</td>
<td>---</td>
</tr>
<tr>
<td>La(_2)O(_3)-ZrO(_2) with 5 mol% La(_2)O(_3)</td>
<td>0.44</td>
<td>1 000</td>
<td>---</td>
</tr>
<tr>
<td>MgO-ZrO(_2) with 13.7 mol% MgO</td>
<td>9.8</td>
<td>1 000</td>
<td>Prepared by conventional ceramic processing</td>
</tr>
<tr>
<td>Sc(_2)O(_3)-ZrO(_2) with 9 – 11 mol% Sc(_2)O(_3)</td>
<td>28 – 34</td>
<td>1 000</td>
<td>Prepared by sintering of coprecipitated powders</td>
</tr>
<tr>
<td>Sc(_2)O(_3)-ZrO(_2) with 6 mol% Sc(_2)O(_3)</td>
<td>18</td>
<td>1 000</td>
<td>The sintered film was treated by hot isostatic pressing (HIP)</td>
</tr>
</tbody>
</table>

![Figure 3.3. Relationship between ionic conductivity and dopant radius [28]](image)

Figure 3.3. Relationship between ionic conductivity and dopant radius [28]
The concentration of the dopant is another property that determines the ionic conductivity of the electrolyte. Figure 3.4 shows the dependence of ionic conductivity on dopant concentration for zirconia stabilized with $\text{Sc}_2\text{O}_3$, $\text{Y}_2\text{O}_3$, $\text{Yb}_2\text{O}_3$ and $\text{Gd}_2\text{O}_3$ at 1 000 °C. It can be seen that YSZ presents its maximum ionic conductivity when the molar fraction of dopant ($\text{Y}_2\text{O}_3$) is between 7 and 8 mol%. Nevertheless, Irvine et al. [33] have observed that this electrolyte suffers from degradation during longer term operation. In fact, if the concentration of $\text{Y}_2\text{O}_3$ is ca. 7.7 mol% the ionic conductivity of YSZ decreases from 16.0 to ca. 13.7 S m$^{-1}$ after 5 000 min. Therefore, a slight increase in the doping concentration (9 or 10 mol% of $\text{Y}_2\text{O}_3$) is recommended to prevent degradation of the electrolyte performance. Compared with YSZ, ScSZ suffers from more serious degradation in ionic conduction because of phase transformation. The ageing effect of ScSZ can be reduced by increasing the content of $\text{Sc}_2\text{O}_3$, or by co-doping with $\text{Al}_2\text{O}_3$ or $\text{TiO}_2$, which can suppress the phase transformation of ScSZ [34]. However, the oxide ion conductivity decreases with increasing content of $\text{Al}_2\text{O}_3$ or $\text{TiO}_2$.

![Figure 3.4. Dependence of electrolyte ionic conductivity on dopant concentration at 1 273 K][35]

A study conducted by Kosacki et al. [36] reveals that the electrolyte thickness also influences the oxygen ion conductivity. The conductivity of YSZ electrolyte decreased when the film thickness decreased from 2 µm to 60 nm, but increased for the thicknesses less than 60 nm, phenomena that indicate the transition from lattice (grain boundaries) to interface (electrode | electrolyte) controlled diffusivity. Therefore, grain boundaries of the doped ZrO$_2$ are also important in determining its oxygen ion conduction [37]. For both YSZ and ScSZ, the grain boundary resistance is insignificant at temperatures higher than 800 °C.
but at lower temperatures the grain boundary resistance becomes important and governs the oxygen ion conduction in the electrolyte. This finding indicates that the ionic conductivity of ScSZ at an intermediate temperature (600 – 800 °C) can be increased by reducing the grain boundary resistance.

Temperature is another factor that affects the conductivity of solid oxide electrolytes. It can be seen from Figure 3.5 that the oxygen ion conductivity decreases with temperature in the following order: ScSZ > YbSZ > YSZ. At low temperatures the difference of conductivity between ScSZ and YSZ is of about one order of magnitude, which indicates that ScSZ can be used as electrolyte between 600 and 800 °C. On the other hand, at higher temperatures (800 – 1 000 °C) the difference among them is less obvious and YSZ seems to be the best option because of its lower cost.

![Figure 3.5. Temperature effect on oxygen ionic conductivity of the electrolytes 9YSZ, 9YbSZ and 9ScSZ [30]](image)

Finally, the effect of co-doping with additional oxides has been examined in recent years. Density of YSZ ceramics can be considerably improved and its ionic conductivity can be increased by doping small amount of zinc oxide (ZnO). With a doping of 0.5 wt% ZnO, the conductivity of 8YSZ increases from 1.31 to 2.89 S m⁻¹ at 800 °C [38]. Similarly, doping of alumina (Al₂O₃) into YSZ leads to the creation of space charge regions which in turn can enhance ionic conductivity. Nevertheless, the presence of Al₂O₃ also leads to a blocking effect that suppress conductivity, resulting in a minimal combined effect of Al₂O₃ doping on YSZ conductivity [39].
All the studies mentioned in this subsection indicate the existence of several effective methods for improving the mechanical strength and the ionic conductivity of zirconia based electrolytes operating at different temperatures. Consequently, research works are expected to be continued in order to produce materials suitable to manufacture SOFCs that could be competitive with conventional coal-fired power plants and operate in a wide range of conditions.

3.1.1.2. Doped LaGaO$_3$

The doped LaGaO$_3$ materials were found to have good ionic conductivity operating at temperatures between 400 and 800 °C. Early works on LaGaO$_3$-based electrolytes were conducted by Ishihara et al. [40] who found that doping strontium for the lanthanum sites could increase the conductivity of LaGaO$_3$, while the conductivity could be further enhanced by doping magnesium for the gallium sites. Some of the conductivity data from literature is summarized in Table 3.2. La$_{0.9}$Sr$_{0.1}$Ga$_{0.8}$Mg$_{0.2}$O$_3$ (LSGM) was found to have a conductivity higher than YSZ and ScSZ: it is about 17.0 S m$^{-1}$ at 800 °C compared to conventional YSZ which conductivity is about 2.6 S m$^{-1}$ [41]. The difference is more pronounced at a lower temperature, being 3.0 S m$^{-1}$ for LSGM and 0.173 S m$^{-1}$ for YSZ at 600 °C. This data indicates that LSGM could be a promising electrolyte for intermediate temperature SOFCs.

Similarly to YSZ, the conductivity of LSGM depends on the concentration of dopants. Zheng et al. [42] investigated the secondary phases formed in terms of doping content, and it was found that when the doping contents of Sr and Mg were less than 20 mol% no secondary phases would be formed. However, when the doping contents exceeded 20 mol% the secondary phase of SrLaGaO$_4$ was formed, decreasing the conductivity of LSGM electrolyte. In another study conducted by Liu et al. [43] the secondary phase LaSrGa$_3$O$_7$ was formed with doping content of Sr and Mg of 15 mol%, which caused relatively lower conductivity. In conclusion, the optimal Sr and Mg doping content in LaGaO$_3$ are around 15 and 20 mol%.

The main problem of LSGM is its reactivity with the nickel-cermet anodes to form lanthanum nickelates. Zhang et al. [44] investigated the reaction between the LSGM electrolyte with pure nickel oxide (NiO) and Sm-doped ceria (SDC). It was found that a LaNiO$_3$-based compound was formed in the powder mixture of NiO and LSGM after firing it at 1 150 °C, leading to a significant loss in the conductivity of the material. However, the reaction between NiO and SDC was not significant, and therefore the reaction of LSGM with Ni could be prevented by using a thin interlayer of Ce$_{0.8}$Sm$_{0.2}$O$_{1.9}$ at the electrode | electrolyte interface.
Table 3.2. Reported ionic conductivity of different \( \text{LaGaO}_3 \)-based materials [28]

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity / S m(^{-1})</th>
<th>Temperature / °C</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{La}<em>{0.8} \text{Sr}</em>{0.2} \text{Ga}<em>{0.8} \text{Mg}</em>{0.2} \text{O}_3 )</td>
<td>45</td>
<td>1 000</td>
<td>Prepared by a combustion synthesis technique</td>
</tr>
<tr>
<td></td>
<td>17</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.5</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.8} \text{Sr}</em>{0.2} \text{Ga}<em>{0.83} \text{Mg}</em>{0.17} \text{O}_{2.815} )</td>
<td>17</td>
<td>800</td>
<td>Stable over a weeklong test</td>
</tr>
<tr>
<td></td>
<td>8.0</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>3.0</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.9} \text{Sr}</em>{0.1} \text{Ga}<em>{0.8} \text{Mg}</em>{0.2} \text{O}_{3.3} )</td>
<td>19.7</td>
<td>900</td>
<td>Prepared by solid-state reactions of sintering, ball milling and calcination</td>
</tr>
<tr>
<td></td>
<td>11.93</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td></td>
<td>5.32</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.8} \text{Sr}</em>{0.2} \text{Ga}<em>{0.85} \text{Mg}</em>{0.15} \text{O}_{2.8} )</td>
<td>7.82</td>
<td>900</td>
<td>Synthesized using glycine-nitrate combustion method</td>
</tr>
<tr>
<td></td>
<td>6.06</td>
<td>800</td>
<td></td>
</tr>
<tr>
<td></td>
<td>2.63</td>
<td>700</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.809</td>
<td>600</td>
<td></td>
</tr>
<tr>
<td>( \text{La}<em>{0.8} \text{Sr}</em>{0.2} \text{Ga}<em>{0.83} \text{Mg}</em>{0.17} \text{O}_{2.815} )</td>
<td>1.96</td>
<td>627</td>
<td>Prepared by microwave assisted processing in a very short time of 10 minutes</td>
</tr>
<tr>
<td>( \text{La}<em>{0.9} \text{Sr}</em>{0.1} \text{Ga}<em>{0.8} \text{Mg}</em>{0.2} \text{O}_{2.8} )</td>
<td>5.10</td>
<td>800</td>
<td>Prepared by citrate sol-gel method and by subsequent calcination at 1 673 K</td>
</tr>
<tr>
<td>( \text{La}<em>{0.85} \text{Sr}</em>{0.15} \text{Ga}<em>{0.85} \text{Mg}</em>{0.15} \text{O}_{2.85} )</td>
<td>5.10</td>
<td>700</td>
<td>Prepared by a novel method based on acrylamide polymerization technique</td>
</tr>
<tr>
<td></td>
<td>1.50</td>
<td>600</td>
<td></td>
</tr>
</tbody>
</table>

3.1.1.3. Ceria-based Oxides

Similar to \( \text{LSGM} \), doped ceria is considered as a promising intermediate temperature electrolyte because of its high ionic conductivity at temperatures between 600 and 800 °C. As stated before, the maximum conductivity of an electrolyte oxide, in this case ceria, is obtained when the radius mismatch between the dopant cation and the replaced ion, in this case \( \text{Ce}^{4+} \), is minimized. Considering that, \( \text{Gd}^{3+} \) doped and \( \text{Sm}^{3+} \) doped \( \text{CeO}_2 \) electrolytes (\( \text{GDC} \) and \( \text{SDC} \)) exhibit high ionic conductivity and thus they have been investigated extensively. Table 3.3 presents the conductivities of different ceria-based materials, demonstrating that \( \text{GDC} \) and \( \text{SDC} \) show high conductivity at intermediate temperatures. For example, \( 25\text{GDC} \) can go up to 1.01 S m\(^{-1}\) at 600 °C, while the conductivity of the
conventional YSZ is about $1.0 \times 10^{-2}$ S m$^{-1}$ at this temperature, two orders of magnitude lower. In addition, comparable to YSZ and LSGM, the conductivity of ceria-based electrolytes also depends on the dopant concentration. Generally, the conductivity increases with increasing dopant concentration and after reaching the maximum, the conductivity decreases with further increase in dopant concentration. In literature, the optimal dopant concentration is in the range of 15 – 25 mol% doping of Gd$^{3+}$ or Sm$^{3+}$ [45].

Table 3.3. Reported ionic conductivity of different ceria-based materials at typical temperatures [28]

<table>
<thead>
<tr>
<th>Material</th>
<th>Conductivity / S m$^{-1}$</th>
<th>Temperature / K</th>
<th>Remarks</th>
</tr>
</thead>
<tbody>
<tr>
<td>15GDC ($Ce_{0.85}Gd_{0.15}O_{2-x}$)</td>
<td>4.07</td>
<td>973</td>
<td>High purity $CeO_2$ and $Gd_2O_3$ powders were used as the starting materials</td>
</tr>
<tr>
<td>25GDC ($Ce_{0.75}Gd_{0.25}O_{1.875}$)</td>
<td>1.01</td>
<td>873</td>
<td>Prepared by the flame spray pyrolysis method</td>
</tr>
<tr>
<td>25GDC ($Ce_{0.75}Gd_{0.25}O_{1.875}$)</td>
<td>0.75</td>
<td>873</td>
<td>Prepared by hydrothermal method</td>
</tr>
<tr>
<td>20GDC</td>
<td>9.0</td>
<td>1 073</td>
<td>Prepared by oxalate coprecipitation method</td>
</tr>
<tr>
<td></td>
<td>4.2</td>
<td>973</td>
<td></td>
</tr>
<tr>
<td>20SDC</td>
<td>8.8</td>
<td>1 073</td>
<td>Prepared by oxalate coprecipitation method</td>
</tr>
<tr>
<td></td>
<td>4.1</td>
<td>973</td>
<td></td>
</tr>
<tr>
<td>20YDC</td>
<td>7.7</td>
<td>1 073</td>
<td>Prepared by oxalate coprecipitation method</td>
</tr>
<tr>
<td></td>
<td>3.5</td>
<td>973</td>
<td></td>
</tr>
<tr>
<td>17SDC ($Ce_{0.85}Gd_{0.15}O_{1.93}$)</td>
<td>0.57</td>
<td>873</td>
<td>Prepared by hydrothermal method</td>
</tr>
<tr>
<td>20YDC ($Ce_{0.8}Gd_{0.2}O_{1.9}$)</td>
<td>3.4</td>
<td>973</td>
<td>Prepared by citric acid nitrate low temperature combustion process</td>
</tr>
</tbody>
</table>

The main problem of ceria-based electrolyte is that $Ce^{4+}$ can be partially reduced to $Ce^{3+}$ under a reducing environment. This is detrimental since electronic conduction causes a partial internal electronic short-circuit in the electrolyte, reducing the current efficiency and resulting in lattice expansion which may lead to mechanical failure. The partial reduction of ceria electrolyte can be partially solved by combining the ceria electrolyte with other electrolyte, such as YSZ or LSGM, to block the reducing environment from the ceria electrolyte. It has been demonstrated that 1 – 2 µm thick YSZ is sufficient to block electron
conduction, and the thermal expansion mismatch between the two layers could be acceptable if the cell is operated at an intermediate temperature (below 800 °C) [46].

Apart from zirconia, LaGaO$_3$ and ceria based electrolytes, other oxygen ion conducting ceramics have been studied, being bismuth one of the most well-known alternatives to these oxides. The oxygen ion conductivity of bismuth at an intermediate temperature is about 1 – 2 orders of magnitude higher than conventional YSZ. Therefore, bismuth has been investigated as possible electrolyte material despite it decomposes at low oxygen partial pressure, limiting its practical applications [47, 48]. This problem can be solved to some extent by combining bismuth with other electrolyte materials such as Y$_2$O$_3$ and CeO$_2$ [49]. Proton conducting ceramics are alternative materials for use as intermediate temperature electrolyte. Doped BaCeO$_3$ shows good conductivity and can be applied in SOFCs [50-52].

The selection of the suitable electrolyte material depends on the working temperature, cost, and the compatibility with other fuel cells components, such as electrode materials and current collectors or interconnects.

3.1.2. SOFC Cathodes

As stated before, in SOFCs the cathode functions as the site for the electrochemical reduction of oxygen. Therefore, it has to be stable under high oxidizing environments and consequently only two classes of materials are feasible: (1) noble metals such as platinum and gold, and (2) electronically conducting mixed oxides. Taking into account their high cost and shortage, the use of noble metals is not considered a feasible alternative for SOFCs fabrication, turning electronically conducting oxides into the best choice to manufacture cathodes for these high temperature devices.

On the surface of the cathode, the oxygen reduction can be described by the following equation:

$$\frac{1}{2}O_2(gas) + 2e^- (cathode) \rightleftharpoons O^{2-} (electrolyte) \quad (3.1)$$

This electrochemical reaction can only occur at the triple-phase boundaries (TPBs), which are defined as the confluence of sites where the oxide ion conductor, electronic conductor, and the gas phase come in contact. A schematic illustration of the region between the electrolyte and the cathode where the TPB exists is shown in Figure 3.6. If there is a breakdown in connectivity in any one of the three phases or the access for any of the
reactive species (ions, gases or electrons) to the active site is interrupted, the reaction cannot occur [53].

![Schematic diagram of the cathode triple-phase boundaries (TPBs)](image)

**Figure 3.6**: Schematic diagram of the cathode triple-phase boundaries (TPBs)

Microstructure and composition clearly affect the size and distribution of the TPBs. One compositional design option employed is to provide a single-phase electrode with mixed conductivities permitting both oxide ion and electron mobility within the cathode material, such as $La_{1-x}Sr_xCo_{1-y}Fe_yO_{3-δ}$ (LSCF). Thus, electrochemical oxygen reduction can occur at the electrode surface as well as within the bulk electrode (pore sites) and most of the TPBs are replaced by the two phase gas-electrode boundaries. Another strategy is to use a porous composite consisting of an electronic conducting cathode material and an appropriate amount of ionic conducting electrolyte material, such as Sr-doped $LaMnO_3$ (LSM) mixed with YSZ. By using these strategies, the electrochemically active reaction sites can be orders of magnitude greater than that of a porous cathode exhibiting only electronic conductivity. Obviously, the degree of this extension depends critically on the rate of defect transport through the solid electrode, the gas transport through the pores of the electrode to promote surface coverage, and the catalytic activity at the interfaces.

### 3.1.2.1. Kinetics and Reaction Mechanisms of SOFC Cathodes

Although the molecular species involved in the overall electrochemical reactions at the cathode is a single diatomic species ($O_2$), it must first be converted to some electroactive intermediate form via one or more processes. The electrochemical processes going on in the cathode involve different bulk and surface steps [53, 54]. The elementary reactions in the overall electrode reaction are usually considered as follows [55, 56]: (1) reduction of $O_2$ molecules involving adsorption, dissociation, reduction, and incorporation of the oxygen anion into the lattice of the cathode materials; (2) ionic transport through the porous cathode towards the electrolyte; and (3) the ion jumping into the electrolyte lattice. Among all three elementary reaction steps, several steps could be rate-limiting for the oxygen reduction
process. Nonetheless, the oxygen reduction step is the biggest contributor to total cell resistance, and improvements in the catalytic activity of the cathode have a strong impact on the final performance [57, 58].

For electron-conducting perovskite-type materials, Fleig [59] summarized three possible paths for the cathodic reaction (3.1): the electrode surface path, the bulk path, and the electrolyte surface path, as shown in Figure 3.7. These three paths are in sequence more suitable for the cases of an electronic conductor (e.g. pure $LSM$), a mixed ionic-electronic conductor (e.g. $LSCF$), and a composite (e.g. $LSM$-$YSZ$), respectively.

![Figure 3.7. Schematics of the three reaction paths of oxygen reduction](image)

The cathodic reaction can simultaneously occur via all three paths, and for each path, one or more elementary steps determine the corresponding reaction rate. Which elementary reaction will be the rate-limiting step is not always predictable and may depend on local conditions like temperature and oxygen partial pressure or on microstructural conditions. In addition, there may be parallel reaction pathways and a crossover of these various reaction pathways may cause interference. For example, the incorporation rate into the cathode (bulk path) depends on the surface concentration of adsorbed oxygen and thus can be influenced by the surface diffusion occurring via the electrode surface path mechanism. Despite the complicated nature of the reaction mechanism, oxygen reduction mechanistic studies provide very insightful understanding information, especially on well-defined systems [59]. The use of dense thin films [60, 61] and microelectrodes [62, 63] with well-defined geometry has provided insights into the kinetics of the oxygen reduction reaction (ORR) by quantitative correlation of cathode geometry with ORR impedance.

The electrode polarization losses (resistance) are usually associated with the generation and transport of oxide ions within the porous cathode structure [64]. In order to obtain a good performance of the SOFC, the composition and structure of the electrodes can be optimized using the Adler or ALS model [65]. In effect, providing that values for the oxygen self-diffusion coefficient ($D^*$, cm$^2$ s$^{-1}$), oxygen surface exchange coefficient ($k$, cm s$^{-1}$), and
appropriate microstructural parameters are available, the heterogeneous chemical reaction contribution ($R_{chem}$) can be calculated as follows:

$$R_{chem} = \frac{RT}{2F^2} \sqrt{\frac{\tau}{(1 - \varepsilon) \alpha C_0 D^* k}}$$  \hspace{1cm} (3.2)$$

where $\tau$ is the tortuosity, $\varepsilon$ is the fractional porosity, $\alpha$ is the internal surface area/unit volume, and $C_0$ is the surface concentration of oxygen. Isotopic exchange is an important technique to determine the oxygen diffusion in mixed ionic-electronic conducting materials. For example, Kilner et al. [66] measured the oxygen surface exchange and oxygen self-diffusion coefficients of $La_{0.8}Sr_{0.2}MnO_3$ using the $^{18}O/^{16}O$ isotope exchange depth profile method, obtaining $k = 1.0 \times 10^{-8}$ cm s$^{-1}$ and $D^* = 3.2 \times 10^{-13}$ cm$^2$ s$^{-1}$ at 900 °C.

Following the idea of reducing the polarization losses at the cathode, pure experimental analysis can be added to theoretical studies of kinetics to determine the optimized composition and structure of the electrodes. In this respect, Endo et al. [67] studied the electrochemical properties of three microstructural types (dense, porous and porous/dense double layer) of cathode materials based on $La_{1-x}Sr_xCoO_3$ (LSC) and $La_{1-x}Sr_xMnO_3$ (LSM). Their results revealed that surface area is an important factor for reaction rate on the electrode and high performance electrodes can be obtained by using a mixed ionic and electronic conducting (MIEC) electrode or a composite (cermet) electrode with a large surface area. For the cathodes, the role of surface area in improving their performance lies in the fact that a higher surface area leads to more active sites for the oxygen reduction reaction, which in the case of composite electrodes can only occur at the TPBs.

An alternative method to enhance cathode activity is using cathodic biasing (application of high cathodic polarizations/high current densities) [68-70], which has been shown to significantly reduce the overpotential of the oxygen reduction reaction on the porous LSM and LSM-YSZ composite cathodes. This phenomenon is called the activation effect or hysteretic behaviour of cathodes, and not only influences the surface microstructural and compositional changes of the cathode but also causes a morphological change at the interface between the cathode and the electrolyte under the polarization/biasing treatment. The ORR activity is enhanced via formation of oxygen vacancies associated with surface and compositional changes adjacent to the TPBs [69] or by promoting direct incorporation of oxygen from the gas into the electrolyte due to partially reduction of the manganese oxide [68].
In recent years, new in situ experimental technologies and computational tools are leading to new insight into the cathode reaction mechanism. Conventional electrochemical techniques such as impedance spectroscopy and voltammetry can provide detailed information about the rates of processes occurring in situ, but are not informative for assigning which molecular species participate in the electrochemical reactions or the interactions between oxygen molecules and the electrode surfaces. In contrast, optical spectroscopy [71, 72] and quantum chemical calculations [73] are capable of identifying the molecular structures present on the SOFC electrode surfaces and the reaction barriers of oxygen reduction processes.

3.1.2.2. Materials for SOFC Cathodes

Perovskite materials have been widely used as cathode materials in SOFCs [74]. A perovskite-type oxide has the general formula $\text{ABO}_3$, in which $A$ and $B$ are cations with a total charge of $+6$. The lower valence $A$ cations (such as, $\text{La}$, $\text{Sr}$, $\text{Ca}$, $\text{Pb}$, etc.) are larger and coordinated to twelve oxygen anions, while the $B$ cations (such as, $\text{Ti}$, $\text{Cr}$, $\text{Ni}$, $\text{Fe}$, $\text{Co}$, $\text{Zr}$, etc.) occupy the much smaller space and are coordinated to six oxygen anions. Full or partial substitution of $A$ or $B$ cations with cations of different valence is possible. When the overall valence of the $A$-site and $B$-site cations $(n + m)$ adds up to less than six, the missing charge is made up by introducing vacancies at the oxygen lattice sites. Figure 3.8 shows the typical structure of the cubic perovskite $\text{ABO}_3$.

![Figure 3.8. Unit cell of the $\text{ABO}_3$ perovskite structure](image)

For most of the perovskite materials used as cathodes in SOFCs, the $A$-site cation is a mixture of rare and alkaline earths (such as $\text{La}$ and $\text{Sr}$, $\text{Ca}$ or $\text{Ba}$), while the $B$-site cation is a reducible transition metal such as $\text{Mn}$, $\text{Fe}$, $\text{Co}$, or $\text{Ni}$ (or a mixture thereof). Therefore, in most cases, a redox catalytic mechanism is usually provided by $B$-site cations. The octahedral symmetry around the transition metal often promotes a metallic or semiconducting band.
structure at high temperatures leading to high electronic conduction. With a rational choice of \(A\)- and \(B\)-site cations, a large and stable number of oxygen ion vacancies can be introduced at SOFC operating conditions, thus facilitating significant bulk ionic oxygen transport [53].

For \(A_{1-x}A_{x}BO_3\) perovskite-type oxides resulting in sub-stoichiometric oxygen-to-metal regions, an oxygen vacancy scenario results, e.g. in \(Ln_{1-x}^{3+}Sr_{x}^{2+}M^{3+}O_{3-\delta}\), the oxygen vacancies arise either from substitution of \(A^{3+}\) by \(A^{2+}\) or from the partial reduction of \(B^{3+}\) or \(B^{4+}\) to \(B^{2+}\) and \(B^{3+}\), respectively. Oxygen mobility through vacancies is the basis of oxide ion conductivity. In some compositions of perovskite-type oxides, the oxide ion conductivities are as high as those observed in solid electrolyte materials, e.g. the ionic conductivity of \(Sr_{0.9}Ce_{0.1}CoO_3\) reaches 13.3 S m\(^{-1}\) at 800 °C in air [75]. In general, most cathode materials rely on doping of both the \(A\)- and \(B\)-sites to improve electrical conductivity and electrocatalytic performance.

Besides the electrical and structural characteristics mentioned above, thermodynamic data is essential for evaluating and predicting the longer term stability of perovskite cathode materials and their compatibility with other components at SOFC operating temperatures [76]. Considering these physical-chemical and structural requirements, a summary of the materials most commonly used as SOFC cathodes is presented below.

- **Lanthanum manganite(\(LaMnO_3\))-based cathodes**

For lanthanum manganite, the most commonly used dopant is strontium because its size matches with lanthanum. The strontium dopant in \(La_{1-x}Sr_{x}MnO_{3-\delta}\) (\(x \leq 0.5\)) does not increase the oxygen vacancies concentration, a common phenomenon in most of the other perovskite cathode materials studied, but rather oxidizes the manganese ion according to:

\[
Mn^{x+}_{Mn} + SrO \xleftarrow{LaMnO_3} \rightarrow Sr^{2+}_{La} + Mn^{3+}_{Mn} + O^{\delta}_O
\]  

(3.3)

This reaction effectively increases the electron-hole concentration and improves the electrical conductivity of this cathode material. The electronic conductivity of \(LSM\) increases approximately linearly with increasing the strontium concentration up to a maximum around 50 mol% [77]. 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 [78]. 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% [78]. Therefore, a \(Sr\) content of 30 mol% is considered as optimal against the formation of unwanted electronically insulating
phases (LZ and SZ present conductivities two or three orders of magnitude lower than that of YSZ).

The absence of oxygen vacancies in LSM restricts the reduction of oxygen to the triple phase boundary regions. This limitation is the primary reason why LSM does not have acceptable performance at temperatures below 800 °C. Two approaches have been taken to improve the performance of LSM cathodes [79]: (1) addition of a second ionically conducting phase to LSM in order to extend the surface area over which the oxygen reduction can occur; (2) replacement of lanthanum with other rare earth elements (\(Ln = Pr, Nd, Sm\) and Gd) or dope LSM with a cation (such as \(Co, Fe\) or \(Ni\)) in order to promote the formation of oxygen vacancies when strontium is doped on the A-site.

- Lanthanum cobaltite (LaCoO\(_3\)) and ferrite (LaFeO\(_3\)) cathodes

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. \(La_{1-x}Sr_xCoO_3\delta\) has a marked electrode activity due to high oxide ions diffusivity and high dissociation ability of oxygen molecules [80]. However, a large amount of cobalt results in an increased thermal expansion coefficient (TEC), which may result in delamination at the cathode | electrolyte interface or cracking of the electrode [81]. By substituting the La cation with an alternative one, such as Gd or Pr, a decrease in the area specific resistance (ASR) and the TEC can be expected to occur.

Besides the disadvantage of high thermal expansion coefficient, cobaltite cathodes react readily with YSZ to form insulating compounds during the sintering process, which degrades their performance. Therefore, a diffusion barrier layer is necessary for the cells consisting of cobaltite-based cathodes and the YSZ electrolyte [82, 83].

Lanthanum ferrite (LaFeO\(_3\)) is expected to be more stable than cobaltite perovskites because the \(Fe^{3+}\) ion has a stable electronic configuration \(3d^6\). Sr-doped LaFeO\(_3\) (LSF) cathodes have shown promising performance with respect to the power density and stability at 750 °C [84-86]. In iron-based cathodes, reactivity with YSZ electrolyte is significantly reduced. In addition, TECs of the ferrite-perovskite are relatively close to those of the YSZ and CGO electrolyte. By incorporating La deficiency in \(La_{0.8}Sr_{0.2}FeO_3\), Ralph et al. [84] found that the ASR of this cathode was significantly reduced and reached 0.1 Ω cm\(^2\) at 800 °C. The thermal expansion coefficient of the \(La_{0.7}Sr_{0.25}FeO_3\) cathode closely matches with those of CGO and YSZ. This cathode has demonstrated no degradation over 500 hours of operation indicating a promising material for lower temperature SOFCs.
Finally, lanthanum ferro-cobaltite cathodes \((La_{1-x}Sr_xFe_{1-y}Co_yO_3, \text{LSCF})\) show good electrical conductivity, a high oxygen surface exchange coefficient, and a good oxygen self-diffusion coefficient between 600 and 800 °C [87, 88]. At lower temperatures, \text{LSCF}-based cathodes are superior to \text{LSM}-type cathodes due to a lower area-specific resistance. However, \text{LSCF}-type perovskites are generally incompatible with \text{YSZ} electrolytes due to undesirable interface reactions. Therefore, a \text{CGO} diffusion barrier layer is used to prevent the formation of low conductive compounds without negatively affecting the electrochemical performance [89, 90]. Another cause of higher degradation rates for cells with \text{LSCF} cathodes lies in the diffusion of strontium out of \text{LSCF}, which leads to a strontium depletion in the cathode and significantly lower performance. This process of partial decomposition of the perovskite usually has greater influence on the cell degradation than interface reactions during the operation [91, 92].

- \textit{K}_2\textit{NiF}_4 \text{type structure cathodes}

\(La_{2}NiO_{4+δ}\)-based compounds have a \textit{K}_2\textit{NiF}_4-type structure and are usually formulated as \(A_2BO_{4+δ}\), which is described as a stacking of perovskite \(ABO_3\) layers alternating with rock salt \(AO\) layers along the \(z\)-direction [93]. Such oxides are of interest as an oxygen electrode material for applications in various solid electrolyte devices. This is primarily associated with the high electronic conductivity of \(A_2BO_{4+δ}\) \((B = \text{Co, Ni, Cu})\) compounds and solid solutions based on them due to the mixed valence of the \(B\)-site metal. In addition, a high concentration of oxygen interstitials offers the possibility of rapid oxide ions transport through the ceramic material and thus provides a new type of mixed ionic-electronic conductor.

The electrical conductivities of the \(A_2BO_{4+δ}\)-type nickelates and cobaltites reach nearly 10 000 S m\(^{-1}\) at 800 °C under high oxygen partial pressures. At lower oxygen partial pressures, their conductivities decrease slower than that of some perovskite oxides [94]. The oxygen diffusivity of \(La_{2x}Sr_xNiO_{4+δ}\) is higher than that of \text{LSCF}, particularly at lower temperatures, but lower than that of \text{LSC} [95]. In addition, \(La_{2x}Sr_xNiO_{4+δ}\) appears to be more stable than either of these two materials in terms of thermal behaviour at high temperatures. The thermal expansion coefficient of \(La_{2}NiO_{4+δ}\) is 13.7 × 10\(^{-6}\) K\(^{-1}\), which matches well with those of possible electrolyte materials such as \text{YSZ} or \text{CGO}.

- \textit{Noble metals-based cathodes}

As the operating temperature is reduced, electrode polarization losses increase. The cathode thus becomes the limiting component for further progress. One way to overcome
this limitation may be adding a certain amount of noble metal, such as, palladium, silver, or platinum to the cathode. The addition of noble metals phases to an active cathode layer is mainly used to enhance the oxygen reduction reaction. Nevertheless, it should be pointed out that the addition of noble metals, in particular Pt, does not seem a good solution to improve the performances of cells since one target for commercialization of SOFC is to decrease the prices.

Considering that its melting point is 961 °C, metallic silver is a potential component for the cathode in SOFCs operated at less than 800 °C because of its good catalytic activity, high electrical conductivity, and relatively low cost. An example of use of Ag in SOFCs cathode is the coating of this metal on the electrode which improves the oxygen exchange reaction activity of LSCF-YSZ-Ag composite cathode and interface conductivities at 600 °C [96]. Palladium (Pd) is another noble metal widely used to improve the cathode performance in SOFCs, for example by adding it to a LSCF cathode to obtain a decrease in the cell resistances of 15 % at 650 °C and 40% at 550 °C [97].

Although the electrochemical performance of some alternative cathode materials is significantly higher compared with LSM, problems persist in the areas of chemical stability and thermal expansion match with other fuel cell components, especially when extreme operating conditions are required (e.g. temperatures above 800 °C). Considering this, a trade-off between electrochemical performance and thermal expansion may be necessary to identify an optimum cathode composition and microstructure. With this objective in mind, a more profound understanding of the reaction mechanisms and the kinetic aspects of the oxygen reduction processes taking place at the SOFC cathodes is highly desirable in order to achieve a rational design of the materials used for fabrication of this electrode.

3.1.3. SOFC Anodes and Fuels

As stated in Section 3.1.1 and Section 3.1.2, when a SOFC operates in the range of temperature between 800 and 1 000 °C the electrolyte used is normally yttria-stabilized zirconia (YSZ), which offers good oxide ion transport while blocking electronic transport. In this manner, the oxygen reduced at the air electrode, which is typically a composite of lanthanum strontium manganese oxide (LSM) with YSZ, is transported across the electrolyte to the fuel electrode where oxidation of the fuel gas occurs.

The material to be selected as SOFC anode must fulfil the following conditions: (1) be electronically conductive in order to promote the electrochemical oxidation of the fuel at the
electrode | electrolyte interface; (2) maintain its structural integrity over the whole temperature range to which the component is exposed (minimize shrinkage during sintering and thermal expansion during operation) and be compatible with other cell components (absence of solid-state contact reactions); and (3) present chemical stability when operating in contact with the fuel and fuel cell components, especially when the concentration of oxidant species increases undesirably. In normal operating conditions the ambient oxygen partial pressure at the anode is low, but it can vary over several orders of magnitude if accumulation of intermediate species or products occurs during the process. To accommodate the system to these fault conditions, the ability of the materials to recover even after brief exposure to air at high temperature would be advantageous.

Additionally to the characteristics listed above, the anode also has to be sufficiently electro-catalytically active to sustain a high current density with low overpotential losses and selective to avoid the promotion of unwanted side reactions (e.g. hydrocarbon pyrolysis followed by deposition of vitreous carbon when this type of fuel is used).

As in the case of the cathode | electrolyte interface, an intimate contact between the two solid phases (anode | electrolyte) and pore sites are required to promote the triple phase boundaries (TPBs) where the oxidation reaction takes place. Low-loss operation implies that these TPBs are not dimensionally limited to a planar interface of solid materials but are delocalized to provide a ‘volumetric’ reaction region porous for gas diffusion and permitting both electron and ion transport. As stated in Section 3.1.2, one option is to provide a single electrode with mixed conductivity permitting both oxide ion and electron mobility within the electrode material. The alternative is to use a porous composite such as nickel-based cermets which have typically been used in SOFCs to date when hydrogen is used as fuel [98, 99].

In this section a review of the main aspects related to the SOFC anode is presented, including a description of the reaction mechanisms involved in the oxidation processes occurring at this electrode and a brief overview of the most suitable anode materials to be used when hydrogen is replaced by carbonaceous fuels.

3.1.3.1. Fuels for SOFCs

Each of the many applications for fuel cells in electricity generation (industrial and domestic power generation, automobile sector, electronic devices) has its own characteristic fuel requirements or preferred fuel. Fuels can range from hydrogen to methane to diesel to coal, however most fuel cells can work only with fairly pure hydrogen and those that can use
other fuels still typically work best with it [100-102]. This mismatch between desired and/or available fuel and the fuel cell has limited their commercial implementation. In addition, most of the hydrogen currently produced comes from hydrocarbons, which makes fuel cell commercialization even more sensible considering that to produce energy directly from hydrocarbon fuels is more economical. Nonetheless, reversible fuel cells/electrolysers using hydrogen as the storage medium should be viable in the near future for matching distributed generation electricity supply with widely varying demand levels [98, 103].

Based on the widespread availability of natural gas (methane with small amounts of other hydrocarbons), several stationary fuel cell systems have been designed/fabricated for the use of this hydrocarbon [100, 104, 105]. Although direct introduction of either dry natural gas (direct hydrocarbon operation) or steam-natural gas mixtures (internal reforming) to SOFC anodes has been reported, in most cases partial external reforming is used. By this means, the fuel mixture arriving at the fuel cell anode is primarily methane, hydrogen and carbon monoxide. Additionally, hydrogen sulphide (contained typically in natural gas in small amounts) is introduced to the fuel cell, which can accumulate in the anode microstructure resulting in most of the cases in poisoning of the electrode and degradation of the fuel cell performance [106, 107].

Liquid hydrocarbons, such as propane and butane, are also used for a number of stationary and portable power generation, and transportation applications because of their high energy densities and widespread availability [101, 102]. Similarly, gasoline and diesel could be used considering their widespread application in the automobile sector. However, all of these liquid fuels are characterized by a fairly broad range of molecular weights and substantial sulphur-containing impurities, which cause similar anode degradation problems than in the case of natural gas. Alcohols (such as methanol and ethanol) have been widely considered for use in portable fuel cell applications because they are readily available from industrial processes, and have reasonably high energy density and negligible content of undesired impurities. Nevertheless, these fuels have the disadvantage of being relatively expensive because of processing costs compared to oil and natural gas by-products.

Finally, due to its worldwide abundance, there is a substantial interest in environmentally friendly use of coal in fuel cells [108, 109]. The problems of its applicability are related once again to the large amount of impurities present in many of the coal resources, including sulphur and chlorine, and the high degree of carbon dioxide emission produced by its combustion in comparison to hydrocarbons. In addition, in most of the cases coal gasification is needed to produce a gaseous fuel that can be introduced into the fuel cell.
Clearly there is a diverse range of fuels that could be used in fuel cells. For high temperature fuel cells, such as the SOFC, there is the important possibility of using these fuels without pre-processing, or at least with only partial pre-processing. To achieve this, it is essential to appropriately select and tailor the fuel electrode components and structure. To date, most of the efforts have been pointed in the direction of developing an anode that can perform optimally when hydrogen is used as the fuel and therefore most of the kinetics and reaction mechanisms studied are associated with this gas. In the following subsection, a brief overview of the main reaction mechanisms proposed for hydrogen oxidation on nickel anodes is presented, being this latter the material most commonly used for SOFC anodes fabrication.

3.1.3.2. Kinetics and Reaction Mechanisms of SOFC Anodes

The kinetics of the SOFC anode cannot be effortlessly understood due to its complicated three-dimensional microstructure and the diverse chemical/electrochemical reactions taking place on its surface. In order to simplify its study, the microstructure of the anode can be simplified into a two-dimensional Ni-YSZ contact, such as a Ni pattern [110, 111], a Ni point [112, 113], or a porous Ni [114, 115] electrode. In all these cases, interface reactions are studied based on the results obtained applying DC and AC electrochemical techniques (polarization and impedance plots) and its analysis by means of equivalent circuits fitting (see Chapter 4 and Chapter 6 for more details about these methods).

Figure 3.9 presents some of the electrochemical models suggested by different authors to characterize the anode reaction mechanisms based on these experimental techniques. It can be observed that all the mechanisms suggested agree with the adsorption/desorption behaviour of hydrogen and the formation of hydroxyl (OH). However, major diversity is found regarding to the location where the chemical and the electrochemical reactions take place (either on the Ni surface or equally on the Ni and the YSZ surface), which are the reactions related to the interstitial oxygen in the YSZ, the adsorption and desorption behaviour of water, and the charge transfer steps.

Mizusaki et al. consider exclusively the Ni surface to be electrochemically active, while Jiang et al. include surface reactions on the YSZ surface. Furthermore, de Boer et al. and Holtappels et al. suggest that interstitial hydrogen and hydroxyl are formed. The removal of oxygen from the YSZ is assumed to proceed rather differently: it becomes either adsorbed onto the YSZ surface as shown in Figure 3.9(a), forms a hydroxyl interstitial as shown in Figure 3.9(b) and Figure 3.9(d) or a negatively charged hydroxyl on the Ni surface as shown
in Figure 3.9(d), or water is immediately formed without any intermediate step as shown in Figure 3.9(c). In conclusion, a large number of reaction steps are supposed to take place at the triple phase boundaries where Ni, YSZ and the gas phase converge.

![Electrochemical models for the kinetics of SOFC anodes](image)

**Figure 3.9.** Electrochemical models for the kinetics of SOFC anodes: (a) Mizusaki et al. [111], (b) de Boer et al. [116], (c) Jiang et al. [114], (d) Holtappels et al. [117, 118]

Alternatively to Ni, other elements/compounds have been studied to be used as SOFC anodes when hydrocarbons fuels are used instead hydrogen. The following subsection presents a review of the most promising materials for fabrication of this fuel cell electrode.

### 3.1.3.3. Materials for SOFC Anodes

After some early investigations using single-phase anodes, nickel-zirconia cermets have been the dominant materials used for fabrication of this electrode in the last forty years. Single-phase materials investigated in the earliest SOFC developments included graphite, the platinum group, and transition metals such as iron, cobalt and nickel [119]. While graphite is corroded electrochemically when the fuel cell is operational, platinum spalls off presumably due to water vapour evolution at the metal | oxide(electrolyte) interface. Similarly, iron is no longer protected by the reducing activity of the fuel gas once the partial pressures of oxidation products in the anode compartment of an operating cell exceed a critical value, resulting in corrosion and formation of red iron oxide. Finally, cobalt is somewhat more stable than iron but also more costly, while nickel shows a significant
thermal expansion mismatch to stabilized zirconia and at high temperatures it aggregates by grain growth obstructing the porosity of the anode and eliminating the triple phase boundaries required for cell operation.

In view of the limitations presented by these materials, nickel-zirconia cermet anodes were introduced as an stable alternative for fuel cell electrodes fabrication [120]. Combining nickel with the stabilized zirconia material used for electrolyte fabrication, the two problems mentioned above are confronted: the difference of thermal expansion that would mechanically stress any nickel anode-electrolyte bond and the aggregation of the metallic electrode during operation. The metal content in the cermet guarantee the electronic conduction whereas the ceramic retains the dispersion of the metal particles and the porosity of the anode during longer term operation. The provision of oxide ion mobility complementary to the electronic conductivity and electro-catalytic action of the metal is a very important secondary role of the ceramic, enhancing the electrochemical performance by the delocalization of the electrochemically active zones previously mentioned.

The major disadvantage of the nickel-cermet electrodes is their ability to promote the competitive catalytic cracking of hydrocarbons. The rapid deposition of carbon at nickel cermets means that direct oxidation of methane is not technically viable in nickel-containing SOFCs. Unless sufficient amount of steam is present along with the hydrocarbon to remove carbon from the nickel surface at a rate faster than that of carbon precipitation, the anode will be destroyed [107]. In addition, impurities in the fuel stream, particularly sulphur, also inhibit the anode functionality and affect its performance as it was stated in Section 3.1.3.1.

Most research aimed at overcoming the limitations of nickel-based anodes has focused on the development of alternative materials that are catalytically active for oxidation of methane or higher hydrocarbons, and inactive for cracking reactions that can lead to carbon deposition. This latter criterion is a difficult one, and rules out most transition metals with the possible exception of Cu, Ag and Au. However, these metals make good current collectors but are not highly active oxidation catalyst. Therefore, considering that many metal oxides are excellent oxidation catalysts and are not active for catalytic cracking, the use of composite ceramic anodes has been suggested as one possibility for optimizing both the transport (ionic and electronic conduction) and catalytic properties of ceramic anodes.

Interest has largely been focused on ceria as a replacement of zirconia and copper as a replacement of nickel. One approach is to alloy copper with nickel in order to reduce the catalytic activity of nickel for hydrocarbon cracking [106]. The influence of adding nickel to (Ce, Zr)O₂ or (Ce, Y, Zr)O₂ to form a cermet was also studied and cerium oxide is reported
as a promising support [105]. In a series of publications, Gorte et al. reported that noble metals (Pd, Pt, Rh) had much higher specific rates for water gas shift, steam reforming and carbon dioxide reforming of methane when supported on ceria than when supported on silica or alumina [121, 122]. Gadolinium doped ceria, $\text{Ce}_{0.9}\text{Gd}_{0.1}\text{O}_{1.95}$ has been studied as an anode material at 900 °C in 5% $\text{CH}_4$ with steam/methane ratios between 0 and 5.5 [123]. This material revealed itself to be resistant to carbon deposition, although the reaction rate was controlled by slow methane adsorption. The same catalyst has been studied for methane oxidation, and it was demonstrated that ceria has a low activity for methane oxidation but high resistance to carbon deposition [104]. It was proposed to add a catalyst ($\text{Ni, \text{Rh, \text{Ru}}}$) to break the C-H bond more easily. Another approach being used in the development of cermet anodes that allows the use of fairly dry hydrocarbons, is to use a relatively inert metal such as copper for electrical conductivity and a metal oxide to provide catalytic activity and ionic conductivity. Examples of this type of composite anode include $\text{Cu/\text{CeO}_2/YSZ}$ and $\text{Cu/YZT}$ (titania-doped yttria zirconia) [101, 124]. The $\text{Cu/\text{CeO}_2/YSZ}$ anode system is particularly interesting and has been shown to be effective for the direct use of a variety of hydrocarbon fuels including butane and decane, and highly resistant to deactivation through carbon deposition [102].

Table 3.4 presents some typical candidate oxide materials for anode fabrication and its more relevant properties. $\text{La}_{1-x}\text{Sr}_x\text{CrO}_3$ has been thoroughly investigated as an interconnect material for SOFCs and also as a potential anode material due to its relatively good stability in both reducing and oxidizing atmospheres at high temperatures [27, 76]. The acceptor doping gives high p-type conductivity in air but, as with all p-type materials, this decrease under reducing conditions. Addition of reducible transition metals such as $\text{Ti}$ can introduce significant n-type contribution at low partial pressure of oxygen, but the dilution of $\text{Cr}$ on the B-site generally has a greater effect [125]. Substitution of mid-transition metals such as $\text{Mn}$ and $\text{Fe}$ does not have such a dilution effect, indicating some complimentary of electronic function, and affords an extension of the p-type domain to lower partial pressures, although conductivities are still below 1 000 S m$^{-1}$ under reducing conditions [126]. Finally, rutile structures such as $\text{NbO}_2$ or $\text{Nb}_2\text{TiO}_6$ have been investigated, resulting in materials that offer very high electronic conductivity under fuel conditions, but with very low thermal expansion coefficient [127].

The performance of the anodes developed for operation of SOFCs directly on hydrocarbons is still not at the level obtained with $\text{Ni-YSZ}$ cermets operating on hydrogen, which allow a higher generation of energy. Consequently, there is still much room for improvement in the catalytic properties of these alternative SOFC anode materials.
Table 3.4. Summary of properties of some potential oxide anodes at 800 °C under reducing conditions [128]

<table>
<thead>
<tr>
<th>Material</th>
<th>Electronic conductivity[a] / S m(^{-1})</th>
<th>Ionic conductivity / S m(^{-1})</th>
<th>Oxygen diffusivity / cm(^2) s(^{-1})</th>
<th>Redox stability[b]</th>
<th>Polarization resistance[c]</th>
<th>CTE / p.p.m K(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)</td>
<td>50 – 100</td>
<td>10 – 20</td>
<td>1.0 x 10(^{-6})</td>
<td>XX</td>
<td>**</td>
<td>12</td>
</tr>
<tr>
<td>Zr(_{1-x})Ti(_x)Y(_y)O(_2)</td>
<td>10</td>
<td>1.0</td>
<td>?</td>
<td>**</td>
<td>*</td>
<td>10</td>
</tr>
<tr>
<td>La(<em>{0.8})Sr(</em>{0.2})Cr(<em>{0.95})Ru(</em>{0.05})O(_3)</td>
<td>60</td>
<td>Low</td>
<td>?</td>
<td>*</td>
<td>**</td>
<td>10</td>
</tr>
<tr>
<td>La(<em>{0.8})Sr(</em>{0.2})Fe(<em>{0.8})Cr(</em>{0.2})O(_3)</td>
<td>50</td>
<td>?</td>
<td>1.0 x 10(^{-8})</td>
<td>*</td>
<td>**</td>
<td>12</td>
</tr>
<tr>
<td>La(<em>{0.25})Sr(</em>{0.75})Cr(<em>{0.5})Mn(</em>{0.5})O(_3)</td>
<td>300</td>
<td>?</td>
<td>?</td>
<td>**</td>
<td>***</td>
<td>10</td>
</tr>
<tr>
<td>Sr(<em>{0.86})Y(</em>{0.06})TiO(_3)</td>
<td>8 000</td>
<td>Low</td>
<td>?</td>
<td>***</td>
<td>*</td>
<td>11-12</td>
</tr>
<tr>
<td>La(<em>{0.33})Sr(</em>{0.66})TiO(_{3.166})</td>
<td>4 000</td>
<td>Low</td>
<td>?</td>
<td>***</td>
<td>* / *** [d]</td>
<td>10</td>
</tr>
<tr>
<td>Nb(_2)TiO(_7)</td>
<td>20 000</td>
<td>Very Low</td>
<td>?</td>
<td>X</td>
<td>---</td>
<td>1-2</td>
</tr>
<tr>
<td>Gd(_2)Ti(Mo, Mn)O(_7)</td>
<td>10</td>
<td>Reasonable</td>
<td>?</td>
<td>XXX</td>
<td>*</td>
<td>?</td>
</tr>
</tbody>
</table>

\[a\] Should only be considered as a rough guide as factors such as partial pressure of oxygen, density and microstructure are not standardized

\[b\] ***: excellent, to XXX: very poor

\[c\] 1 – 10 Ω cm\(^2\)

\[d\] High performance for composite with ceria
Understanding the mechanisms of the surface reactions occurring on the anode near the triple phase boundaries is likely to be the key for further advances in this area. Unfortunately, fundamental insight into these reaction mechanisms is rather limited considering the high complexity of the multiple elementary steps and reaction intermediates involved in the oxidation process, and therefore more efforts have to be devoted for the development of experimental techniques and mathematical methods that helps to elucidate these phenomena.

3.2. Carbon-Air Fuel Cells

Electrochemical coal oxidation in carbon-air fuel cells, also known as direct carbon fuel cells (DCFCs), offers the potential of significantly higher conversion efficiencies than conventional coal-fired power plants. Higher efficiencies naturally means smaller amounts of coal consumed and proportionately less amounts of $CO_2$ emitted for the same amount of electrical power generated. To achieve this goal, electrochemical conversion of carbon has been pursued for more than a century using many different types of carbon-air fuel cell systems, based on molten hydroxides, molten carbonates, solid oxides and molten metal anodes [13, 14, 129].

This section presents an overview of the main carbon-air fuel cell technologies based on the different delivery modes and vehicles that have been adopted for engaging the solid fuel and oxygen at the electrochemical interface to achieve efficient oxidation of carbon.

3.2.1. Carbon-Air Fuel Cells with Oxidant Mass Transport

A large portion of the early carbon-air fuel cell efforts adopted and explored the strategy of transport the oxidant to the solid fuel surface (electrochemical interface), starting with Becquerel nearly 150 years ago [130] and by others during the turn of the century [131]. In general, this method involves three main stages: (1) delivery of oxygen to the solid fuel particle in the form of a chemical vehicle present in the electrolyte; (2) electrochemical oxidation of carbon at the anode and reduction of oxygen at the cathode; and (3) collection of electrons on the current collector managed by the electrical connectivity created for fine particles of solid fuel which are dispersed in the molten electrolyte. Figure 3.10 shows this mechanism and the elements involved.

In an oxidant mass transport configuration, the reaction sites reside at the solid fuel particle | molten electrolyte interface (molten hydroxide or carbonate), provided that the electrical connectivity of the reaction sites to the current collector is maintained. When the
solid fuel particle is physically disconnected from the neighboring particles (see the isolated particle on the right side in Figure 3.10), then no electrochemical reaction can take place at that particle | molten electrolyte interface, leading to the loss of capacity and efficiency. This situation becomes increasingly complex as the solid fuel particles are gradually being consumed while the oxidation reaction proceeds and connection among them is lost. Moreover, most solid fuels usually have poor electrical conductivity (it ranges from $10^2$ to $10^3$ S m$^{-1}$ [132]) and their transport in a viscous melt can be sluggish, being the performance of the cell limited by surface kinetics and diffusion, respectively.

Figure 3.10. Schematic of oxidant delivery vehicle(s) for carbon oxidation in molten electrolyte

Considering the problems associated to continuous delivery of the solid fuel to the electrochemical cell, avoiding disruption of the electrical connectivity of the particles in the molten bed and contamination of the cell components, some practical designs have been developed in order to employ coal in fuel cells.

3.2.1.1. Oxide/Carbonate Hybrid Vehicle Mechanism

The mechanism of this hybrid vehicle includes daisy-chaining$^{[4]}$ of the oxide ions in series with the carbonate ions to supply the oxygen needed to react with the solid fuel, as shown in Figure 3.11. It couples a SOFC element in series with the molten salt electrolyte, which contains densely dispersed carbon particles above the percolation limit which allow maintaining the electrical connectivity in the melt and serve as a distributed or extended anode [133, 134].

$^{[4]}$ Electrical connection in which $A$ is connected to $B$, $B$ connected to $C$, and successively. It avoids the connection between each pair of components in the system.
Figure 3.11. Schematic of the oxide ion/carbonate ion hybrid vehicle mechanism

In the hybrid scheme showed in Figure 3.11, an auxiliary YSZ electrolyte is contacted with the molten electrolyte bath, which is typically made of the lithium-potassium carbonate eutectic mixture and contains the dispersed carbon particles (the system operates at temperatures up to 900 °C). The external wall of the YSZ electrolyte is coated with an appropriate porous cathode material (e.g. LSM/YSZ) that is exposed to ambient air so oxygen is incorporated into the YSZ lattice as oxide ions in accordance with reaction:

$$O_2 + 4e^- \rightarrow 2O^{2-} \quad (3.4)$$

The oxide ions, $O^{2-}$, migrate through the YSZ to the anode under the electrochemical driving force. Therefore, the delivery path of the oxygen from air to the carbon particles inside the molten bath involves at least two chemical vehicles, namely, oxide and carbonate ions. An understanding of the details of the transfer mechanism between the oxide and carbonate ions and the intermediate species participating in this transformation are not clear at all. However, the preferred reaction at the carbon | molten electrolyte interface can be represented by equation:

$$C + 2CO^{2-} \rightleftharpoons 3CO_2 + 4e^- \quad (3.5)$$

Furthermore, it is possible to have partial oxidation of the carbon at the anode by the reactions of the type:

$$C + CO^{2-} \rightleftharpoons CO + CO_2 + 2e^- \quad (3.6)$$

$$2C + CO^{2-} \rightleftharpoons 3CO + 2e^- \quad (3.7)$$
In several studies, the reported values of the open circuit cell potential and the operating temperature regime suggest a possible formation of $CO$ at the anode compartment indicative of reaction (3.6) and/or reaction (3.7), or even the reversed Boudouard reaction$^5$, but this aspect remains speculative because gas analysis is usually not provided or performed [135].

3.2.1.2. Metal Oxide/Chemical Looping Mechanism

This mechanism involves a suitable metal-metal oxide redox couple to supply the oxidant to the solid fuel in the form of a reducible metal oxide. The scheme employs an YSZ electrolyte in contact with a molten metal bath, while the external wall of the YSZ ceramic is coated with an appropriate porous cathode material (e.g. LSM/YSZ) and exposed to ambient air. The molten metal bath, typically made of a metal with a low melting point such as tin, serves as the anode and contains the dispersed carbon particles [136, 137]. Similarly, two studies aimed at modeling this approach consider ing metals with a high melting point such as silver [138] and iron [139] for the anode. A typical cell configuration for this approach is schematically shown in Figure 3.12.

![Figure 3.12. Schematic depiction of the metal oxide chemical looping mechanism](image-url)

The oxygen from air is reduced to oxide ions at the YSZ-cathode interface by reaction (3.4), and transported through the YSZ electrolyte to the YSZ-molten metal (anode) interface forming a metal oxide, which blocks further electronic and ionic transport. As a consequence, the fuel cell could cease to operate due to the build-up of this blocking layer, but the carbon in the molten bath reduces the oxide to the metallic form restoring the fuel cell operation.

In a molten tin anode cell, the process steps can be expressed by reactions:

$^5$ The Boudouard reaction corresponds to: $2CO \rightleftharpoons CO_2 + C$
In this scheme, oxygen delivery to carbon is in the form of \(O^2\) ions supplied by the chemical looping of \(SnO_2\), which serves as the chemical vehicle. A similar chemical looping mechanism is also valid in the molten iron anode \([139]\). However, in molten silver \([138]\) the delivery vehicle is dissolved oxygen in the molten silver bath. At the elevated operating temperatures employed in this scheme, silver is thermodynamically stable against oxidation and does not form an oxide. Furthermore, it transports dissolved oxygen quite fast, with a diffusion coefficient of \(1.5 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}\) at 700 °C \([140]\). This makes silver an attractive but expensive molten medium for solid fuel conversion.

### 3.2.2. Carbon-Air Fuel Cells with Solid Fuel Mass Transport

The earliest attempt to convert a solid fuel in a SOFC configuration was in 1937, reported by Baur and Preis, who suggested the use of a tubular YSZ solid electrolyte to circumvent the chemical stability issues related to the use of molten electrolytes \([14]\). They demonstrated a 0.90 V open circuit voltage and a volumetric power density of 10 mW cm\(^{-3}\) using coke as the consumable anode and \(Fe_3O_4\) as the air cathode. However, it became clear that engaging the solid carbon at the anodic reaction sites for oxidation requires a good solid-to-solid contact extended over large areas.

The reaction sites at the cermet anodes of a SOFC, defined in Section 3.1.2 as the triple phase boundaries (TPBs), are usually of nanometer size and located in the porous anode | electrolyte interface, which makes it almost impossible for bulky solid fuel particles to gain access to it. Figure 3.13 shows the dimensional mismatch and size incompatibility between the TPBs and the carbon particles, which is almost insurmountable with the possible exception of the in situ pyrolysis of carbon deposited from the gas phase over the anode surface and deep into the pores close to the TPBs, which becomes a first vehicle mechanism.

The second vehicle mechanism devised to overcome this dimensional hurdle is to deliver the solid fuel in the form of a gaseous vehicle to the TPBs. The solid fuel is gasified with an appropriate agent, usually with steam (wet method) or with \(CO_2\) (dry method), to form intermediate gaseous fuel species that can diffuse to the TPBs where electrochemical oxidation takes place.
3.2.2.1. Pyrolytic Vehicle Mechanism

An effective way to supply the solid fuel to the TPBs at the anode is by thermal pyrolysis from a gaseous hydrocarbon fuel, such as methane [141-143] and propane [144], as shown in Figure 3.14. The surface carbon deposited from the gas phase inside the pores of the anode structure is an effective fuel that can electrochemically be oxidized but once depleted needs to be regenerated by further pyrolysis under open-circuit conditions.

Ihara and Hasegawa [144] reported that this cycle can be repeated six times without loss of power, after which degradation sets in. In that sense, this type of carbon-air fuel cell operates much like a battery that needs recharging. This is perhaps the only scheme that, at the nanoscale, has the ability to supply the carbon particles directly to the anode surface sufficiently close to the TPBs that may possibly be within distances readily accessible to lattice oxygen by diffusion. For this reason, it may be the closest process to a direct conversion. However, the maximum peak power density demonstrated with this scheme was only 52 mW cm\(^{-2}\) at 900 °C [144], suggesting that this approach may be limited by the amount, the size and the proximity of the carbon deposits to the TPBs.
3.2.2.2. Fuel Delivery Mode via Steam Gasification

The difficulty of supplying the solid fuel particles to the triple phase boundary of a SOFC can be circumvented by steam gasification of the solid fuel to generate $H_2$ and $CO$ [145] in accordance with reaction:

$$C + H_2O \rightleftharpoons H_2 + CO \quad (3.10)$$

Steam gasification of carbon, or other solid carbonaceous fuels, is an endothermic process, so oxygen and steam are injected into the gasifier to burn part of the carbon and supply the heat necessary for the gasification reaction. The carbon monoxide produced usually reacts catalytically with additional steam to produce more $H_2$ in accordance with the reaction:

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \quad (3.11)$$

Therefore, the net reaction after reactions (3.10) and (3.11) is given by:

$$C + 2H_2O \rightleftharpoons 2H_2 + CO_2 \quad (3.12)$$

With or without the water gas shift step in equation (3.11), the syngas produced is free of contaminants (sulphur, chlorine, and heavy metals) before it is fed into a SOFC. In this scheme, solid fuel delivery to the anode TPBs is accomplished by chemical vehicles $H_2$ and/or $CO$, which are electrochemically oxidized. At the anode TPBs, the half electrochemical reactions are:

$$2H_2 + 2O^{2-} \rightleftharpoons 2H_2O + 4e^- \quad (3.13)$$

$$2CO + 2O^{2-} \rightleftharpoons 2CO_2 + 4e^- \quad (3.14)$$

The concept of gasification of solid carbon in a fuel cell using steam has recently gained renewed interest and constitutes the backbone of the emerging integrated gasification fuel cell (IGFC) technology [146, 147].

3.2.2.3. The CO Shuttle Mechanism

In a recent study, Gür et al. [14] proposed that a more plausible scenario for carbon conversion would involve the surface oxygen on the carbon (or graphite) desorbing as $CO$
into the anode compartment and subsequently undergoing electrochemical oxidization to $CO_2$ at the TPBs. Due to the physical proximity of the carbon particles (or bed) to the anode surface, $CO_2$ that is formed at the anode has a short distance to diffuse out to a neighboring carbon particle and to undergo the reversed Boudouard reaction to generate additional $CO$, as shown in Figure 3.15. The newly formed $CO$ diffuses back to the anode TPBs where it is electrochemically oxidized to $CO_2$, starting the cycle again. Therefore, $CO$ shuttles between the nearby carbon particle and the active sites at the anode TPBs.

![Figure 3.15. Schematic depiction of the CO shuttle mechanism](image)

Gür proposes that as long as the anode surface is either in direct contact with or in close physical proximity of the carbon bed or particles, the $CO$ shuttle mechanism could play an important role in the fuel cell behavior observed in all studies using cell elements immersed either in a fixed [148-150] or a fluidized [151, 152] carbon bed with either a flowing or a stagnant inert gas environment, as well as for the pyrolytic vehicle mechanism, as assumed earlier by Ihara [142, 144]. The proposed $CO$ shuttle mechanism may also play a role in the reaction pathways in other fuel cell arrangements that employ a molten anode or a molten electrolyte, as discussed in Section 3.2.1, where the oxidant is delivered to solid carbon fuel via a chemical vehicle.

Currently five types of carbon-air fuel cells are being comprehensively studied and developed by various research groups globally [129]. These include one based on molten hydroxide electrolyte [153, 154], one based on molten carbonate electrolyte [155, 156] and three based on solid oxide electrolytes. For the three based on solid oxide electrolytes, there are different methods of fuel delivery: carbon mixed with molten carbonates [133, 157], carbon mixed with a molten metal [137, 138] and solid carbon as a fluidized bed of carbon particles [142, 148]. For each type of carbon-air fuel cell there are a number of design variations, different technical issues and performance outcomes (power density, lifetime, etc.). In addition, there is the complication whether the fuel cell involves total direct carbon
oxidation or partial direct carbon oxidation both in electrochemical reactions or indirect conversion, first to CO via molecular processes and then electrochemical reaction of CO to produce CO$_2$.

In this research project a carbon-air fuel cell with a molten tin anode has been selected as the subject of study considering that this metal is non-toxic, has a low melting point, high boiling temperature and low vapour pressures. In addition, considering the low reactivity of tin with some species such as sulphur, arsenic and chlorine, direct oxidation of any gaseous, liquid or solid carbonaceous fuel is possible in this system without previous treatment to remove fuel contaminants.

The following section presents a comprehensive review of the physical-chemical properties of tin and the preliminary results obtained by other authors using these carbon-air fuel cell technologies.

### 3.3. Carbon-Air Fuel Cells with Molten Tin Anodes

As stated in Section 3.2.1.2, when molten tin is used as the anode of a solid oxide fuel cell the metal oxide produced at the anode | electrolyte interface acts as the chemical vehicle transporting the oxygen atoms from the interface to the fuel particles surface. The fuel can be dissolved in the melt or placed in an external combustion unit where the metal oxide is reduced and clean molten tin is recirculated to the anode | electrolyte interface in order to maintain the fuel cell operational.

Considering that tin, oxygen and the metal oxide produced are the species involved in the electrochemical process occurring at the carbon-air fuel cell anode, it is essential to identify the main physical-chemical properties of these anode material and its interactions with the oxidizing environment.

#### 3.3.1. Physical-Chemical Properties of Tin and Tin-Oxygen Systems

Tin is a good candidate liquid metal anode material for SOFCs because of its combination of low melting point (~231.88 °C) and high boiling point (2 603 °C) [158]. The melting point of 232 °C is low relative to a typical SOFC operating temperature between 800 – 1 000 °C and facilitates higher oxygen solubility. In addition, the high boiling point provides low vapour pressures (ca. 0.16 Pa at 900 °C) and therefore low risks when operating. Table 3.5 compares the melting and boiling point of tin with those of various common metals with melting points below 1 100 °C.
Table 3.5. Properties and abundances of common metals [159]

<table>
<thead>
<tr>
<th>Metal</th>
<th>Melting point / °C</th>
<th>Boiling point / °C</th>
<th>Abundance / ppm of crust</th>
<th>Annual production / tons</th>
<th>Price / $ kg⁻¹</th>
</tr>
</thead>
<tbody>
<tr>
<td>Aluminium</td>
<td>660</td>
<td>2 520</td>
<td>83 000 (8.2%)</td>
<td>36.9 million</td>
<td>1.72</td>
</tr>
<tr>
<td>Antimony</td>
<td>631</td>
<td>1 587</td>
<td>0.20</td>
<td>187 000</td>
<td>5.06</td>
</tr>
<tr>
<td>Bismuth</td>
<td>271</td>
<td>1 564</td>
<td>0.063</td>
<td>7 300</td>
<td>16.28</td>
</tr>
<tr>
<td>Cadmium</td>
<td>321</td>
<td>767</td>
<td>0.10</td>
<td>18 800</td>
<td>2.68</td>
</tr>
<tr>
<td>Copper</td>
<td>1 085</td>
<td>2 563</td>
<td>79</td>
<td>15.8 million</td>
<td>5.21</td>
</tr>
<tr>
<td>Indium</td>
<td>157</td>
<td>2 073</td>
<td>0.05</td>
<td>600</td>
<td>390.00</td>
</tr>
<tr>
<td>Lead</td>
<td>328</td>
<td>1 750</td>
<td>7.9</td>
<td>3.9 million</td>
<td>1.74</td>
</tr>
<tr>
<td>Tin</td>
<td>232</td>
<td>2 603</td>
<td>2.5</td>
<td>307 000</td>
<td>13.88</td>
</tr>
<tr>
<td>Silver</td>
<td>962</td>
<td>2 163</td>
<td>0.079</td>
<td>21 400</td>
<td>470.63</td>
</tr>
<tr>
<td>Zinc</td>
<td>420</td>
<td>907</td>
<td>79</td>
<td>11.1 million</td>
<td>1.72</td>
</tr>
</tbody>
</table>
It can be seen that indium and lead also present a low melting point and high boiling temperature. However, they represent a less attractive alternative for SOFC anodes fabrication considering that lead is highly toxic and indium presents an excessive price. Bismuth is another metal that appears as an interesting alternative for SOFC anodes. Gorte et al. compared its performance with the molten tin anode operating in a solid oxide fuel cell in absence of fuel [160]. It was demonstrated that when using a molten bismuth anode the fuel cell generated higher current densities than when a molten tin anode was used, which was associated to the higher conductivity that bismuth oxide ($B_2O_3$) presents for oxide ions in comparison to tin dioxide ($SnO_2$). However, the SOFC with molten bismuth anode presented a lower open circuit voltage than the SOFC with molten tin anode, which can be an undesirable condition if oxidation of carbonaceous fuels wants to be accomplished in an external combustion reactor. In addition, bismuth oxide could react with $Y_2O_3$ affecting the structure and properties of the electrolyte, as stated in references [48, 49].

Table 3.6 is a compilation of the physical-chemical properties of tin, including available values for oxygen, sulphur and hydrogen solubility. The high solubility of sulphur in tin is an interesting aspect considering that an important issue in carbon-air fuel cells is the tolerance of the anode material to the contaminants contained in the fuel stream. Sulphur can be oxidized as an additional fuel since it does not immediately hinder the catalytic properties of the liquid tin, in contrast with nickel-based anodes.

**Table 3.6.** Physical-chemical properties of tin [159]

<table>
<thead>
<tr>
<th>Property</th>
<th>Temperature</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Surface tension</td>
<td>231.88</td>
<td>544 mN m$^{-1}$</td>
</tr>
<tr>
<td>Viscosity</td>
<td>231.88</td>
<td>1.85 mN s m$^{-2}$</td>
</tr>
<tr>
<td>Density</td>
<td>800</td>
<td>6.58 g cm$^{-3}$</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>6.48 g cm$^{-3}$</td>
</tr>
<tr>
<td>Resistivity</td>
<td>800</td>
<td>62.1 $\mu$Ω cm</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>67.1 $\mu$Ω cm</td>
</tr>
<tr>
<td>Gas solubility – oxygen</td>
<td>536</td>
<td>0.00018 wt%</td>
</tr>
<tr>
<td></td>
<td>750</td>
<td>0.0049 wt%</td>
</tr>
<tr>
<td>Gas solubility – hydrogen</td>
<td>1000</td>
<td>0.04 cm$^3$ H$_2$/100 g Sn</td>
</tr>
<tr>
<td>Gas solubility – sulphur</td>
<td>800</td>
<td>4.5 at%</td>
</tr>
<tr>
<td></td>
<td>1000</td>
<td>8.0 at%</td>
</tr>
</tbody>
</table>
The electronic resistance of liquid tin is very small at SOFC operating temperatures. Consequently, electron flow through the tin anode to the current collector should be sufficient to maintain the fuel cell operational with low ohmic losses at the electrode. On the contrary, high surface tensions seem to represent an undesirable obstacle for the good performance of the system. Yuan et al. [161] reported the surface tension of liquid tin as a function of temperature and oxygen partial pressure. Surface tensions between 540 and 450 mN m\(^{-1}\) were reported between temperatures of 250 and 750 °C at low oxygen partial pressure. These elevated values affect the tin | electrolyte contact angle (poor wettability) if thin layers of molten metal are used for the fuel cell design. Therefore, extra pressure may be required to improve the contact between both cell components which can be obtained using a plug-type structure [160, 162] or an electrolyte-shaped holder for the anode [137, 163]. Finally, viscosity values are pertinently low if circulation of the liquid tin is required, for example, for slag removing or reduction in an external combustion chamber [164].

The phase diagram for oxygen and tin provides fundamental information of the possible states of oxygen in the liquid anode. A recent version of the phase diagram for the Sn-O system determined by Cahen et al. [165] is presented in Figure 3.16. The solubility limit of oxygen in accordance with this diagram is ca. 2 at% at 1 000 °C above which tin dioxide (SnO\(_2\)) begins to precipitate.

![Figure 3.16. Phase diagram for the O-Sn system at 1 bar (by Cahen et al. [165]).](image)
The solubility of oxygen in molten tin was also investigated by Ramanarayanan and Rapp using electromotive force (emf) measurements in the range of temperature from 748 to 964 °C [166]. Based on the experimental data obtained, the following expression was derived:

\[ N'_O(Sn) = 1.3\times10^3 \exp\left(-\frac{30,000}{RT}\right) \]  

(3.15)

where \( N'_O(Sn) \) is the solubility of oxygen in units of at%, \( R \) is the gas constant in units of calories, and \( T \) is the absolute temperature. If a temperature of 1000 °C is replaced in the previous expression an oxygen solubility of 0.91 at% is obtained, which is nearly half of the value reported by the phase diagram in Figure 3.16.

Recently, experimental work was performed by Abernathy et al. in an attempt to validate the oxygen solubility in a molten tin anode in order to potentially narrow down the range of values found in the literature [159]. These authors suggested that conversion of tin to tin dioxide occurs below 0.78 V, thus oxygen concentration \([O]_{Sn}\) can be calculated by the oxide ions flux through the electrolyte when different current values are applied to the system operating under this limiting voltage. Based on this experimental method, the oxygen solubility was shown to be closer to 0.8 at% at 1000 °C which is fairly similar to the value obtained using equation (3.15). Additionally to the experimental approach, Abernathy et al. determined the oxygen solubility in the Sn-O system using the thermodynamic modelling software FactSage™ 5.6. The phase diagram obtained is presented in Figure 3.17, which shows the oxygen solubility calculated in the temperature range between -173 and 2727 °C. In this case, a maximum oxygen concentration of ca. 10 at% was obtained at 1600 °C and ca. 0.5 at% at 1000 °C, which again is closer to the value predicted by equation (3.15) than using the phase diagram in Figure 3.16.

The authors indicated that differences in the phase diagrams demonstrate the variability of the understanding of the solubility limit of oxygen and other species in tin. In fact, the thermodynamic modelling does not account for a second liquid phase or intermetallic compounds, as evident in Figure 3.17, and the gas phase region show some differences in the maximum oxygen solubility compared to Figure 3.16. In addition, there is a shape inconsistency in the \((Sn\text{-liq} + \text{gas})\) boundary calculated which is attributed to the assumptions used for the gas phase mixture and the thermodynamic data available in the software.
Considering that molten tin anode acts as a conduit for oxygen between the electrolyte and the fuel, the oxygen solubility limit in the liquid metal is a significant operating parameter. Differences in solubility from 0.5 to 2.0 at% represent a fourfold increase in the oxygen carrying capability, which could result in an enhanced energy output of the fuel cell considering that oxygen saturation and precipitation of oxide species at the electrolyte | anode interface would be less probable. From Figure 3.16, it can be inferred that \( \text{SnO}_2 \), \( \text{Sn}_x\text{O}_{1+x} \), or \( \text{SnO} \) could precipitate when oxygen is added beyond the solubility limit. However, differential scanning calorimetry measurements made by Bonicelli et al. confirmed that only tin dioxide, \( \text{SnO}_2 \), is found in the system when operating temperature higher than 525 °C were applied \([167]\). Tin dioxide is an n-type wide gap semiconductor with a bulk conductivity on the order of 30 S m\(^{-1}\) at 1 000 °C \([168]\). However, this number reflects dense \( \text{SnO}_2 \) since a less dense layer can exhibit a conductivity that is multiple orders of magnitude lower, especially at high temperatures \([169]\). This decline in conductivity could explain why the power output of a tin-based SOFC would significantly decline even with the formation of thin layers of \( \text{SnO}_2 \). Kamp et al. \([170]\) reported the following chemical diffusion coefficient for oxygen in \( \text{SnO}_2 \) valid in the range of temperature between 700 and 1 000 °C:

\[
D_0 = 0.02 \text{ cm}^2\text{s}^{-1} \exp\left(-\frac{0.9 \text{ eV}}{kT}\right)
\]  

(3.16)

where \( k \) is the Boltzmann constant and \( T \) is the absolute temperature. The density of \( \text{SnO}_2 \) at room temperature is 7.0 g cm\(^{-3}\) (compare to 7.3 g cm\(^{-3}\) for metallic tin at 25 °C).
Nevertheless, at high temperatures tin dioxide is denser than molten tin: density for SnO$_2$ is calculated to be approximately 6.98 g cm$^{-3}$ while that for molten tin is 6.6 and 6.5 g cm$^{-3}$ at 800 and 1 000 °C, respectively [171, 172]. Since SnO$_2$ is denser, the operating voltage of the cell must be closely monitored to avoid the formation of the oxide at the electrolyte | anode interface (especially in planar designs with the tin bath resting on top of the electrolyte), as the oxide layer will not float to the top to allow for its possible removal.

3.3.2. Current Research on Solid Oxide Fuel Cells with Molten Tin Anodes

Between the research groups currently working on solid oxide fuel cells with molten tin anodes (Sn$_{10}$-SOFC), the most renowned approach is the one developed by CellTech Power Inc. [137, 163]. This company has been testing the technology since 1998, using different carbonaceous fuels and improving the design of their system. The latest versions of their Sn$_{10}$-SOFC, the Gen3.0 and Gen3.1 cells, achieve maximum power densities of 400 W m$^2$ and 1 200 W m$^2$, respectively, operating on JP-8 fuel (kerosene-based jet fuel).

The Gen3.0 and Gen3.1 cells were constructed around a closed-end 8YSZ tube with nominal thickness between 160 and 200 µm, which was used as the electrolyte. The cathode was made of doped lanthanum manganites, such as LSM or LCM (lanthanum cobalt manganite), and coated the inside of the YSZ tube, while the cathode current collector corresponded to a non-specified in-house produced material. The half-cell assembly described before was attached with ceramic cement to an alumina cap which sealed and separated the cathode from the molten tin anode encapsulated in an alumina porous separator (65% porosity, less than 200 µm average pore size) holding the 200 µm thick layer of liquid metal against the electrolyte. Finally, the single cell was sealed within an external closed-end alumina tube containing the fuel, which was constantly fed through ceramic tubes positioned in the top of the process chamber where additional ducts were attached for delivery of oxygen into the cathode and removal of by-products gases (for example, CO, CO$_2$ or SO$_2$).

Figure 3.18(a) presents a comparison between the Gen3.0 and Gen3.1 cell designs. As can be seen, the main difference lies on the size and weight of both approaches. This change was associated with the evolution in the design of the alumina porous separator, as can be seen in Figure 3.18(b) where improvements on the geometry and thickness of the ceramic structure are presented. In addition, the porosity, pore size and pore configuration were found to be critical parameters for the diffusion of fuel molecules through the separator wall to the reaction sites in the molten tin anode. It is very likely that the reduction process of tin dioxide at the anode occurred via carbon monoxide oxidation, considering that CO could
be produced in the external alumina tube via the reversed Boudouard reaction. However, CellTech Power Inc. has not presented a more profound experimental analysis of the chemical mechanisms and kinetic aspects involved in the combustion processes taking place in their Sn(l)-SOFC.

![Figure 3.18. (a) Comparison of the Gen 3.0 and the Gen 3.1 Sn(l)-SOFCs, (b) Porous separator evolution. From left to right: square cross-section, circular cross-section with 3 mm wall thickness and circular cross-section with 2 mm wall thickness [163]](image)

A comparison of the performances of the Gen3.0 and Gen3.1 cells at 1,000 °C is presented in Figure 3.19. It is clear that the power and current densities were significantly higher in the Gen3.1 cell than in the Gen3.0 cell, which Celltech Power Inc. associated with the improved porous separator used in the former. The porous separator used in the Gen3.1 cell presented better diffusion paths and was thinner than the porous separator used in the Gen3.0 cell, which should have affected positively the transport of the reducing agent from the external chamber to the anode reaction sites. In addition, it was considered that heavy hydrocarbon molecules could have moved freely through the porous separator wall and reacted directly with the tin dioxide to produce light hydrocarbons going into internal shifting reactions with CO₂ and H₂O. However, as it was mentioned above, no further experimental analysis has been done in order to elucidate the reaction mechanisms involved in the oxidation and combustion processes taking place in this fuel cell. Recently, White et al. presented a one dimensional model of a Sn(l)-SOFC based on the results obtained by CellTech Power Inc. [173]. This model accepts the assumptions stated before regarding to the reduction reactions taking place in the anode and studies the effects of the separator and cathode porosities, YSZ content and tortuosity in the cathode, and fuel feed frequency, in the performance of the Sn(l)-SOFC. Although this study gives some information about the cell kinetics, it does not explain majorly the reaction mechanisms involved in the oxidation and combustion processes.
Figure 3.19. Polarization and power density curves obtained for the Gen3.0 and Gen3.1 Sn(l)-SOFCs operating on hydrogen (a similar trend was observed operating on JP-8) [163]

Gorte et al. [160, 162, 174, 175] examined the molten tin anodes performance at 700 °C and compared it with other molten metals (bismuth, indium, lead and antimony). These authors were mainly interested in the study of the electrochemical reaction of oxidation taking place at the anode | electrolyte interface in absence of fuel. An YSZ wafer, with one side porous and one side dense, was used as the electrolyte. The dense layer was approximately 900 µm thick and had a 1 cm diameter while the porous layer was 50 µm thick and had a 0.67 cm diameter. An LSF-YSZ cathode was impregnated in the porous side of the electrolyte and the resulting half-cell was mounted on an alumina tube using ceramic cement. In order to produce a ca. 1.5 mm thick anode, 800 mg of metal were placed inside the one end-closed alumina tube in contact with the dense side of the YSZ electrolyte. A ceramic wafer of either La$_{0.3}$Sr$_{0.7}$TiO$_3$ (LST) or La$_{0.8}$Sr$_{0.2}$CrO$_3$ (LSCr) was attached to an alumina tube and suspended in the molten metal above the electrolyte for current collection and to ensure the proper contact between the electrode and the electrolyte using pressure. A silver wire was passed through the alumina tube for electrical contact with the ceramic current collector. Figure 3.20 presents the design of the SOFC with a molten metal anode (M(l)-SOFC) used by these authors to characterize the performance of the system.

It was observed that for tin and indium, which form oxides with high melting points, the performance of the cell dropped due to the formation of a thin layer of solid oxide on the YSZ surface which blocked the transport of oxide ions and prevented further oxidation of the
anode (the maximum current density obtained using a liquid tin anode was ca. 250 A m\(^{-2}\) at ca. 0.40 V). For bismuth, such a drop was not observed because its oxide is conductive for oxide ions, while for lead operating above the melting point of lead oxide (\(\text{PbO}, \text{m.p.} 888 \, ^\circ\text{C}\)) the oxide no longer hampered the cell performance. The use of antimony, which forms low melting point antimony oxide (\(\text{Sb}_2\text{O}_3\), m.p. 656 °C), resulted in low anode impedances and the metal oxide was readily reduced by most types of solid fuels at 700 °C. Considering these results, the authors suggested that antimony is the best option to be used as anode of a solid oxide fuel cell. However, this suggestion did not consider the high vapour pressure of antimony and its toxicity, which makes it a non-desirable material to be used in this technology, similarly to lead.

![Figure 3.20. Schematic of the experimental system used by Gorte et al. [160]](image)

As in the case of CellTech Power Inc. technology, Gorte et al. have not presented further experimental analysis of the kinetics and reaction mechanisms of the oxidation processes taking place in the \(\text{Sn}_{(l)}\)-SOFC when no-fuel is being used during its performance.

Lvov et al. [176] studied the performance of a \(\text{Sn}_{(l)}\)-SOFC operating at 900 °C using a variety of fuel feeds, including argon, hydrogen, coal and a coal-water slurry. Their fuel cell design consisted of a 6 YSZ crucible with a 2.54 cm diameter base and 0.15 cm thickness used as the oxide ions conductive membrane. The external base of the crucible was painted with \(\text{LSM}\) paste and sintered onto the crucible to produce the cathode, while gold wires attached to the \(\text{LSM}\) electrode using silver paste were used as cathode current collectors. The resulting half-cell was mounted onto a machined YSZ support tube using ceramic cement and the interior of the crucible (total volume of ca. 12.9 cm\(^3\)) was partially filled with solid tin shot. Rhenium wires were placed into the tin melt to be used as current collectors, while an alumina tube supported above the anode fed argon, hydrogen, coal or coal-water...
slurry, as required. Figure 3.21 presents a schematic of the solid oxide fuel cell with molten tin anode used by these authors.

![Schematic of the liquid metal anode-solid oxide fuel cell used by Lvov et al.][1]

Lvov et al. stated that the open circuit voltage (OCV) generated by the Sn(l)-SOFC operating with the molten tin anode under an argon atmosphere (ca. 0.841 V) resulted from the oxidation of liquid tin to tin dioxide, and is nearly equal to the theoretical standard voltage of 0.877 V for this reaction at 900 °C. The OCV generated by the hydrogen fuelled Sn(l)-SOFC increased to the hydrogen oxidation potential of ca. 1.117 V and indicates that at small current densities a direct electrochemical oxidation of the fuel can be observed. Additionally to the open circuit measurements, the authors did some electrochemical analysis of the reaction mechanisms involved in the fuel cell processes using impedance measurements (see Chapter 4 and Chapter 6 for more details about this technique). From this study Lvov et al. inferred that oxygen is transported from the anode | electrolyte interface through the molten tin layer to be reacted with the hydrogen fuel present at the liquid metal surface. When using dry coal the OCV measured was ca. 0.885 V, which was considered to be not indicative of a direct electrochemical reaction with coal but a partial chemical reduction of tin dioxide in the liquid metal anode. This assumption was confirmed by the authors using impedance measurements in the same way than when hydrogen and argon were fed into the anode chamber. The use of coal-water slurry resulted in similar results than coal with a lower OCV value of ca. 0.852 V.

Finally, the authors studied the durability of a liquid tin anode applying a series of linear potential sweeps when hydrogen was used as fuel. The result of these measurements
showed a decreasing current response with each successive cycle as it can be seen in Figure 3.22. The cause of this degradation was believed to be tin dioxide deposition in the anode | electrolyte interface, but no further analysis of the cell products was presented to support this hypothesis. During the linear potential sweep a sharp increase in the current response to potential change is seen below approximately 0.875 V. Lvov et al. associated this behaviour to the primary electrochemical reaction shifting from fuel oxidation to tin oxidation. In order to overcome the limitations of the oxygen-liquid tin system, the authors proposed a molten tin-lead alloy as an alternative anode material where direct oxidation of carbon particles was observed [177]. However, the use of lead is not recommended taking into account the high toxicity of this metal and the hazards associated with handling it at high temperatures.

![Figure 3.22](#).

**Figure 3.22.** Cell potential (right) and current response (left) produced by a Sn(l)-SOFC fuelled by hydrogen at 900 °C. Potential controlled sweep from OCV = 1.117 V to cell voltage 0.40 V at a rate of 24 mV min⁻¹ [176]

Pal et al. [178] studied the performance of a molten tin anode in a solid oxide electrolyser, using a nickel(Ni)-YSZ cermet as the cathode. Steam-rich gas was fed to the Ni-YSZ cathode, while graphite in the form of a 0.7 cm diameter rod was immersed into the liquid metal anode to act as a reducing agent and current collector. The Ni-YSZ cermet cathode was coated on the outer wall of a one end-closed 6YSZ tube acting as the electrolyte, while the required amount of tin shots were placed inside this tube to serve as the anode. A nickel mesh, welded to a nickel wire, was attached to the Ni-YSZ cathode using a nickel based adhesive and served as the cathode current collector. The resulting solid oxide electrolyser with molten tin anode (Sn(l)-SOE) was placed inside a stainless steel crucible as shown in Figure 3.23 and was held in position using alumina spacers cemented together with a ceramic adhesive also applied to seal the cathode side and separate it from the anode.
The performance of the Sn(SO2) SOE developed was studied using electrochemical polarization and impedance measurements at different steam contents in the cathode inlet gas. The current-voltage curves obtained at 900 °C and 1000 °C are presented in Figure 3.24(a) and Figure 3.24(b), respectively. As it can be seen from the results obtained by Pal et al., high potentials had to be applied to the system in order to produce hydrogen at a reaction rate similar to the one associated with a conventional solid oxide electrolyser where LSM-YSZ cermet is used as the anode. In effect, a potential of 3.0 to 4.0 V have to be applied in the Sn(SO2) SOE to produce a current density of 4000 A m⁻², while the same outcome can be obtained in a conventional SOE applying ca. 0.8 V [179, 180]. These significant differences between both technologies make the system proposed by Pal et al. not really attractive in terms of energy consumption, which added to the reports showing that YSZ electrolytes present some degradation when potentials over ca. 1.8 V are applied to the system [181], results in a non-promising scenery for the application of molten tin anodes in solid oxide electrolyzers.

Finally, Doraswami [182, 183] developed a 2-D model of a micro-tubular hollow fibre Sn(SO2) SOFC operating at 900 °C, where oxygen is dissolved into a molten metal anode continuously circulated into an external combustion unit to be reduced while depleted liquid tin is recycled back into the electrochemical reactor in order to maintain the cell operational (see Figure 3.25). The objective of Doraswami model was analysing the distribution of...
dissolved oxygen along the cell and determining the operational limit (cell potential and current density) at which precipitation of tin dioxide occurs at the anode | electrolyte interface.

**Figure 3.24.** Current-voltage curves at various steam contents obtained by employing potentiodynamic sweeps at (a) 900 °C and (b) 1 000 °C [178]

**Figure 3.25.** Schematic of a Sn\(_{10}\)-SOFC coupled to an external combustion reactor

The model was based on the kinetic data presented by White et al. for the 1-D modelling of the CellTech Power Inc. technology previously discussed [173] and assumed an oxygen solubility limit in accordance with the phase diagram presented in Figure 3.16. The dimensions and geometry of the hollow fibre Sn\(_{10}\)-SOFC modelled and the polarization/saturation curves obtained are presented in Figure 3.26(a) and Figure 3.26(b), respectively. Supposing, in accordance with White et al. kinetic study, that the anode charge transfer coefficient corresponds to 0.5 and the exchange current density is ca. 1 200 A m\(^{-2}\), it was predicted that below ca. 0.42 V the oxygen concentration at the exit of the hollow fibre cross the limit of solubility and precipitation of tin dioxide occurred depending on the degree
of supersaturation. The shaded area in Figure 3.26(b) shows the ‘safe’ operating zone identified by the minimum cell potential and maximum current density that can be applied in order to avoid tin dioxide formation at the anode | electrolyte interface. Considering the limitations stated before, a peak power density of ca. 1 600 W m$^{-2}$ was predicted at an average current density of ca. 4 200 A m$^{-2}$.

![Figure 3.26. (a) Schematic of the 2-D hollow fibre Sn$\|l$-SOFC modelled by Doraswami, (b) Predicted effect of the current density on the cell potential and the maximum percentage saturation of dissolved oxygen in the molten tin at the cell exit [182, 183]](image)

It is important to notice that the kinetic parameters used by Doraswami in his modelled hollow fibre Sn$\|l$-SOFC were obtained by White et al. fitting the polarization curves produced by the CellTech Power Inc. Sn$\|l$-SOFC operating at 1 000 °C in the presence of a carbonaceous fuel acting as reducing agent at the anode. These differences between two approaches could introduce significant inconsistencies in the results presented in Figure 3.26(b), especially taking into account the observations made by other authors (Gorte et al. and Lvov et al.) indicating that kinetics of a system without fuel utilization can be more sluggish and unstable than in the presence of a metal oxide reductant [160, 162, 174, 176]. In addition, the use of a maximum oxygen solubility obtained from the Sn-O phase diagram could be counted as another source of error considering that there is a large difference between the values reported by this diagram and the experimental measurements made by some authors [159, 166], as stated in Section 3.3.1.

During the research project for which results are presented and discussed in this thesis, the thermodynamics and kinetics of a Sn$\|l$-SOFC were studied when the fuel cell was operated at 900 °C in battery mode (with a quiescent anode) and fuel cell mode (with a stirred anode and activated carbon particles or hydrogen acting as fuels).
3.4. Project Objectives

The aim of this thesis was the development of a solid oxide fuel cell with a molten tin anode (Sn\textsubscript{(l)}-SOFC) capable of producing energy when fuelled with a carbonaceous fuel (carbon-air fuel cell), without degradation of the electrodes and electrolyte during its performance. To achieve this aim, the specific objectives were:

- Design and manufacture of a pellet-type Sn\textsubscript{(l)}-SOFC using the following components selected from the literature review: (1) an LSM-YSZ cathode at which atmospheric oxygen (O\textsubscript{2}) is reduced to oxide ions (O\textsuperscript{2-}); (2) a YSZ dense electrolyte through which the oxide ions are transported from the cathode | electrolyte interface to the anode | electrolyte interface; and (3) a molten tin anode where oxygen is dissolved into the melt (\{SnO\}) to produce tin dioxide (SnO\textsubscript{2}). A carbonaceous fuel (activated carbon) or hydrogen was fed into the molten tin anode when fuel cell mode measurements were performed.

- Experimental characterization of the performance of a Sn\textsubscript{(l)}-SOFC based on electrochemical measurements (cyclic voltammetry, chronoamperometry, and electrochemical impedance spectroscopy) for the study of the thermodynamics and kinetics of the reduction/oxidation processes, and X-ray techniques (SEM, EDX and XRD) for stability analysis of the fuel cell components.

- Development of mathematical models in MATLAB R2013a and COMSOL Multiphysics 4.3a to determine the thermodynamic and kinetic parameters associated with operation of a Sn\textsubscript{(l)}-SOFC in battery mode and fuel cell mode, and to study the current and potential distributions across the electrolyte.

- Simulation and analysis of the Sn\textsubscript{(l)}-SOFC performance (operating in battery mode and fuel cell mode) with a 200 µm thick YSZ electrolyte and neglecting contact potential losses, based on the thermodynamics and kinetic parameters obtained experimentally and its comparison with the performance of other fuel cell technologies (conventional SOFCs and CellTech Power’s Sn\textsubscript{(l)}-SOFC).
4. Experimental Methods and Equipment

As stated in Chapter 3, the electrochemical conversion of carbon has been pursued for more than a century using many different types of fuel cells systems, based on molten hydroxide, molten carbonate, solid oxide and alkaline electrolytes, and molten metal anodes. The advantage of carbon-air fuel cells over conventional coal-fired power plants is that the former can generate the same amount of electrical power energy consuming smaller amounts of carbon (higher conversion efficiencies) and proportionally producing less \( CO_2 \) emissions.

Considering the benefits presented by carbon-air fuel cells, in this research project an electrochemical system based on a solid oxide ion conducting membrane and a molten metal anode was studied in order to compare its performance with a conventional solid oxide fuel cell (SOFC). The fuel cell developed with this purpose used a \( LSM/YSZ \) cermet cathode, a \( YSZ \) electrolyte and a molten tin \((Sn(l))\) anode. Activated carbon particles, graphite and hydrogen were used as fuels during performance. Oxygen was fed to the cathode as reactant to be reduced at the triple-phase boundaries (TPBs: gas-\( LSM-YSZ \)), resulting in formation of oxide ions incorporated into the electrolyte membrane and transported to the anode in accordance with equation (3.1). At the interface between the molten tin anode and the \( YSZ \) electrolyte, oxygen ions were oxidized according to reaction:

\[
O^{2-}(YSZ) \Leftrightarrow [O]_{Sn} + 2e^- (Sn) \tag{4.1}
\]

The dissolved oxygen species \([O]_{Sn}\) can diffuse through the molten metal and remain dissolved or can react with it (saturation) to produce a metal oxide \( (SnO_2) \). In both cases, the oxygen and the metal oxide can be removed using a reductant \((R)\) immersed in the molten anode or placed in an external combustion reactor, according to reaction:

\[
[O]_{Sn} + R \Leftrightarrow RO(g) \tag{4.2}
\]

This chapter describes the electrochemical cell designed for this research project, detailing the materials, experimental techniques and equipment used for its fabrication. In addition, the experimental methods used to characterize its performance are presented, including electrochemical methods for kinetic characterization and microscopic techniques for analysis of the materials stability.
4.1. SOFCs with Molten Tin Anodes: Design and Fabrication

In this research project, the thermodynamics and kinetic aspects of the reactions occurring in a solid oxide fuel cell with molten tin anode (Sn\(_{\text{l}}\)-SOFC) operating at 900 °C were characterized and analysed. For this purpose, an electrochemical device based on an 8YSZ dense electrolyte-pellet of 30 mm diameter and 2.0 mm thickness (Pi-Kem Ltd.) was used. One of the planar faces of this ionic conductive structure was coated with a LSM-YSZ cermet to produce the cathode, while molten tin was placed directly in contact with the opposite face of the pure electrolyte to produce the anode.

Selection of 8YSZ as the electrolyte material was based on the high ionic conductivity and thermal stability reported for this stabilized oxide at temperatures higher than 800 °C [184, 185]. The thickness of the dense pellets used had to be 2 mm in order to provide the fuel cell with a strong support for the column of molten tin (anode) placed on the surface of the electrolyte (see Section 4.1.2).

In the next sub-sections materials selection and details on the fabrication of the electrodes and their current collectors are presented. In addition, the experimental equipment and operating conditions used for testing the performance of the Sn\(_{\text{l}}\)-SOFC are described.

4.1.1. LSM/LSM-YSZ Cathode and Reference Electrode

It was stated in Section 3.1.2 that in order to favour the reduction process occurring at the gas/cathode/electrolyte triple-phase boundaries (TPBs) of a composite (cermet) cathode, and consequently optimize the SOFC performance, it is necessary the use of electrodes which present both ionic and electronic conductivity and an optimized microstructure. Considering this, double layered LSM/LSM-YSZ cathodes were fabricated using commercial terpineol-based inks of the electrolyte (8YSZ) and/or electrode (20LSM) materials (NexTech Materials).

Table 4.1 presents the solid composition and formulation details of LSM20-I and LSMYSZ-I, which corresponds to the inks used to produce the LSM and LSM-YSZ electrode layers, respectively. The selection of 20LSM as the electronic conductive material at the cathode is based on similar reasons than those for selecting 8YSZ as the electrolyte: it presents higher electronic conductivity than other cathode materials at temperatures above 800 °C (see Section 3.1.2), and is chemically and thermally stable when is in contact with YSZ [185].
Table 4.1. Compositions of the inks used for fabrication of the $\text{LSM/LSM-YSZ}$ electrodes

<table>
<thead>
<tr>
<th>Product name</th>
<th>Solid composition</th>
<th>Solid loading</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{LSM20-I}$</td>
<td>100 wt% $\text{(La}<em>{0.80}\text{Sr}</em>{0.20})<em>{0.95}\text{MnO}</em>{3-x}$</td>
<td>62 – 72 wt%</td>
</tr>
<tr>
<td>$\text{LSMYSZ-I}$</td>
<td>50 wt% $\text{(La}<em>{0.80}\text{Sr}</em>{0.20})<em>{0.95}\text{MnO}</em>{3-x}$</td>
<td>60 – 70 wt%</td>
</tr>
<tr>
<td></td>
<td>50 wt% $\text{(Y}_2\text{O}<em>3)</em>{0.08}(\text{ZrO}<em>2)</em>{0.92}$</td>
<td></td>
</tr>
</tbody>
</table>

The $\text{LSM-YSZ}$ layer was applied directly on the clean surface of the electrolyte using a doctor blade to spread the ink uniformly with an initial thickness of 300 µm. An adhesive frame was used to cover the zones of the electrolyte that were expected to be clean after the printing process. Once the electrode was printed on the surface of the YSZ electrolyte, the adhesive frame was removed and the half-cell was placed on a hot plate to be dried in air at 120 °C during 10 minutes. The second $\text{LSM}$ layer was applied on the top of the $\text{LSM-YSZ}$ electrode using the same methodology described above. Once both layers were applied and dried, the printed electrolyte disc was placed in a horizontal tubular furnace (Carbolite STF15/75) to be subjected to a second drying process at 50 °C for 1 hour, followed by sintering at 1100 °C for 3 hours (ramping rate of 4 °C min⁻¹). The final half-cell obtained is schematized in Figure 4.1(a), where next to the cathode is shown the reference electrode made using the same materials and fabrication method than for the cathode. The areas of the cathode and reference electrode were 3.26 cm² and 0.31 cm², respectively.

![Figure 4.1.](image)

(a) Schematic of an electrolyte supported half-SOFC with $\text{LSM-LSM/YSZ}$ cathode and reference electrode; (b) Schematic of the half-SOFC presented in (a) including current collectors

Current collection for the cathode and reference electrode was made using platinum mesh and wires (Alfa Aesar) attached via spot-welding. The mesh was cut in the shape of

---

[6] The final thickness of the double-layered cathode was determined using SEM techniques and resulted to be ca. 130 µm (see Chapter 5 for more details).
the electrodes and electrically connected to the pure LSM top layer of each using platinum ink (NexTech Materials) as shown in Figure 4.1(b), which was dried in air at 100 °C for 1 hour and sintered at 1 000 °C for 2 hours (ramp rate of 3.5 °C min⁻¹). Specifications for the materials used for current collection are presented in Table 4.2.

Table 4.2. Specifications for platinum mesh, wire and ink used for current collection at the cathode

<table>
<thead>
<tr>
<th>Product name</th>
<th>Specifications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Platinum gauze</td>
<td>52 mesh woven from 0.1 mm diameter wire, 99.9% (metals basis)</td>
</tr>
<tr>
<td>Platinum wire</td>
<td>300 mm length and 0.5 mm diameter, annealed, 99.95% (metals basis)</td>
</tr>
<tr>
<td>Pt-I (platinum ink)</td>
<td>Terpineol-based ink with a solid loading of 70 wt% platinum</td>
</tr>
</tbody>
</table>

The use of double-layered electrodes is related with the requirements of having a mixed electronic-ionic conductor (LSM-YSZ) next to the electrolyte, which improves the kinetics at the triple-phase boundaries (TPBs), and a good electronic conductor (LSM) next to the current collectors, which optimize the transport of electrons through the electrochemical cell. Both conditions guarantee a good performance of the Sn⁺⁻⁻⁻SOFC since the ohmic losses at the cathode are reduced and less overpotential is wasted in the charge transport processes (see Chapter 5 and Chapter 6 for more details).

4.1.2. Molten Tin Anode

In Section 3.3 it was stated that tin is the best option to be used as the anode material since it is non-harmful, has a low melting point (232 °C), and has a very low vapour pressure in comparison with other alternative metals. Additionally, during this research project it was observed that tin is non-reactive with the YSZ electrolyte (see Chapter 6), contrarily to the cases of silver and bronze which showed high reactivity with the electrolyte and the ceramic sealant.

Considering the properties stated above, a molten tin anode of ca. 5.0 mm thickness was fabricated using granulated tin (Sigma Aldrich) and a 99.7% alumina tube of 250 mm length, 32 mm outer diameter and 25 mm inner diameter open at both ends (Multi-Lab). The half-SOFC presented in Figure 4.1(b) was attached to one end of the alumina tube using an alumina-based ceramic adhesive (Aremco Ceramabond 552) with the cathode and reference electrode facing outside. After curing the adhesive in air in two stages at 94 °C and 260 °C for 2 hours each (ramping rate of 3.5 °C min⁻¹), the resulting one-end closed tube was filled
with ca. 17 g of granulated tin to produce a column of ca. 5 mm thickness over the clean surface of the YSZ electrolyte when the metal was melted. Figure 4.2(a) presents the experimental rig fabricated following this methodology. A 99.9995% (metals basis) graphite rod of 305 mm length and 3.05 mm diameter (AlfaAesar) was immersed in the molten tin anode and used as current collector.

Leakage of atmospheric air into the alumina tube containing the molten metal anode was undesirable since additional oxygen would have been dissolved into the melt, interfering with the electrochemical oxidation processes taking place at the anode | electrolyte interface (see Chapters 5 and Chapter 6 for more details). Therefore, to avoid this side reaction during the experimental measurements, the stainless steel cap presented in Figure 4.2(b) was used to make the anode chamber gas-tight. This stainless steel cap (manufactured at the Chemical Engineering Workshop, Imperial College London) consisted of 2 flanges and a lid pulled together using screws. In addition, Viton o-rings (Polymax Ltd.) were sandwiched between each part to improve the sealing of the system.

![Figure 4.2](image)

**Figure 4.2.** (a) Schematic of a Sn(l)-SOFC with the molten tin anode enclosed in an alumina tube; (b) Schematic of the stainless steel cap used for making the anode chamber gas-tight

The top lid presented four metallic fittings where tubing could be held to feed or exhaust gases into the anode chamber. The central fitting was used to feed helium into the system to maintain an inert atmosphere over the molten tin anode during the experimental process, removing any trace of undesired oxygen inside the chamber. In addition, approximately 5 g of activated carbon particles of ca. 2 mm diameter were placed on the surface of the molten tin to give major protection to the liquid anode from oxidation. Two of the lateral fittings in the top cap were used to hold alumina tubes that go down inside the anode chamber but did not
make contact with the melt. These tubes were used for exhausting the helium leaving the system and holding the current collector, respectively. The third lateral fitting was maintained sealed using an alumina tube blocked with high temperature silicone (RS), except when it was used to add helium or a second gas, such as hydrogen, directly into the melt in order to stir the molten metal and facilitate the transport of carbon particles to the anode | electrolyte interface.

4.1.3. Experimental Equipment and Operating Conditions

The experimental rig fabricated following the methodology described in Section 4.1.1 and Section 4.1.2 was used to study the thermodynamics, kinetics and stability of a solid oxide fuel cell with molten tin anode operating at 900 °C. With this purpose, a vertical tubular furnace (Carbolite VST/HST-12/200) with a working tube of 320 mm length, 60 mm inner diameter, 70 mm outer diameter, and feedback temperature controller was used. The electrochemical cell was held from the outside of the furnace using clamps attached to its external structure and positioned in such a way that the YSZ electrolyte was placed in the centre of the working tube. This condition was necessary because, in accordance with the temperature profiles measured (see Appendix A), the maximum temperature of the tubular furnace was found in this position. Quartz wool was used to isolate the system from the surroundings. Figure 4.3 presents a schematic of the electrochemical system used for experimental measurements at high temperatures.

![Figure 4.3. Schematic of the furnace arrangement used for testing the Sn(II)-SOFC performance](image)
The desired operating temperature was reached heating the system from room temperature up to 900 °C at a ramping rate of 3.5 °C min\(^{-1}\). The same ramping rate was used when the system was cooled to room temperature after finishing the electrochemical measurements. This practise was necessary to avoid an excessive thermal stress of the components of the fuel cell that could have caused cracking and irreversible damage of the experimental rig. Additionally to the furnace temperature controller, an N-type thermocouple connected to an YCT RS-232 data logger (YC-747D) was used to measure the real temperature during the experiments.

Air and helium were fed into the system during performance of the electrochemical cell using digital mass-flow controllers (Bronkhorst F-201 CV). At the cathode an alumina tube of 250 mm length, 9 mm outer diameter and 6 mm inner diameter was held using clamps from the outside of the furnace and maintained close to the cathode surface in order to feed air continuously during the electrochemical measurements at a flow rate of 60 mL min\(^{-1}\). A column filled with silica particles was used to extract any molecule of water from the air before being fed into the mass-flow controller. At the anode chamber helium was fed at a flow rate of 30 mL min\(^{-1}\) using plastic tubing connected directly to the mass-flow controller. The helium flow-rate was maintained continuous during the entire processes of heating and cooling and the exhausting anodic gas was passed through water to avoid any leakage of atmospheric oxygen into the system. Figure 4.4 presents a schematic of the equipment and controllers used for temperature and mass-flow control.

![Figure 4.4. Schematic of the experimental equipment used for testing the Sn\(_0\)-SOFC performance](image)
Finally, the performance of the Sn\(_{l0}\)-SOFC was tested connecting the electrochemical cell to an Autolab PGSTAT 100 potentiostat switching the working, sense, counter and reference electrodes between the anode, cathode and reference electrode depending on the electrochemical technique applied (go to Section 4.2.2 for more details). As an example, Figure 4.4 shows the particular case of the connections used to obtain the impedance plot of the anode and electrolyte together.

### 4.1.4. LST and LCST: Alternative Anode Current Collectors

Graphite rods were selected as anode current collectors after observation of its higher ‘shorter term stability’ during performance of the Sn\(_{l0}\)-SOFC, compared with other metal-based current collectors (Inconel and Tungsten wires) that were previously tested during this research project. In effect, Inconel and tungsten rapidly reacted with the molten tin anode when temperatures over the melting point (232 °C) were reached (even under open-circuit conditions), resulting in dissolution of these current collectors in the melt or formation of alloys. However, in the longer term operation (3 hours or more) of the Sn\(_{l0}\)-SOFC, the section of the graphite rod in contact with the molten tin anode started to show some degradation as well, which affected the performance of the current collector and, consequently, of the fuel cell (see Chapter 6 for more details about this phenomenon). Therefore, alternative materials were studied in order to find a current collector more stable in the longer term.

Titanate perovskites and especially donor-doped \(SrTiO_3\) have been considered in replacement of graphite rods because of their redox stability and high resistance towards reducing or sulphured atmospheres [186, 187], which can be present in the anode chamber if the fuel is fed directly into it. To increase the too low conductivity displayed by \(Sr^{2+}Ti^{4+}O_3\), the partial substitution of \(Sr^{2+}\) by a trivalent ion such as \(La^{3+}\), is judged at the best way up to now [186-188]. The additional substitution of \(La^{3+}\) by \(Ce^{4+}/Ce^{3+}\) in the structure of the \(La_0.3Sr_{0.7}TiO_{3+\delta}\) perovskites shows an additional enhancement of the conductivity of this ceramic [189].

Compounds of stoichiometry \(La_{0.2}Sr_{0.7}TiO_{3+\delta}\) (LST) and \(La_{0.2}Ce_{0.1}Sr_{0.7}TiO_{3+\delta}\) (LCST) were synthesized using the standard Pechini route or polimerizable complex method [190]. This method consists in the use of multifunctional organic acids capable of chelating metal ions into the stable complexes and a diol, which serves as a solvent during complex formation step and later participates in the polyesterification reaction to form three-dimensional polymer network with incorporated metal complexes mixed, as assumed, on the atomic
scale. The essential steps of the polymerizable complex method are presented in Figure 4.5. Suitable metal salts are introduced into the ethylene glycol (EG) after dissolution of citric acid (CA), which is added in a large excess to form metal-citrate complex. Then the temperature should be increased to 100 – 130 °C to speed up the formation of polyester due to the reaction between free citric acid and ethylene glycol. After the formation of the plastic-like gel, the temperature is increased further to remove the excess of ethylene glycol. The obtained relative hard substance should be treated at 450 – 600 °C to oxidize organic compounds. Precursor powders thus obtained contain a mixture of homogeneously distributed metal oxides, carbonates or sometimes an intermediate single phase compound with the proper stoichiometry of the metal ions.

![Scheme of polymeric gel method](image)

**Figure 4.5.** Scheme of polymeric gel method

The materials used in this research work for the synthesis of LST and LCST powders are listed in Table 4.3. The first stage of the synthesis process was conducted in a 500 mL flask.
placed on a magnetic stirring plate at 60 °C, where the starting solution was prepared. Titanium(IV) isopropoxide was mixed with ethylene glycol and citric acid in the molar proportion 1 : 20 : 5. Dissolution of the solid components was obtained adding deionized water in a proportion of 0.5 mL per gram of citric acid. When dissolution was completed, lanthanum oxide, strontium carbonate and cerium carbonate were added in stoichiometric amount to produce $\text{La}_{0.3}\text{Sr}_{0.7}\text{TiO}_3$ (LST) or $\text{La}_{0.2}\text{Ce}_{0.1}\text{Sr}_{0.7}\text{TiO}_3$ (LCST), correspondingly. Nitric acid (65 – 68 wt%, Sigma Aldrich) was added in a proportion of ca. 3 drops for every 100 mL of mixture to dissolve the oxides and carbonates in the mixture. After homogeneous mixing of the reactants was completed, evaporation of solutions was conducted increasing the temperature of the system up to 100 °C until a perfect gel was obtained (4 – 5 hours). The product was placed in an Elite BCF11/8 box furnace to be dried and pyrolyzed in air during 8 hours at 250 °C using a ramping rate of 2 °C min$^{-1}$. The resulting powder was grinded and calcinated in air at 700 °C during 5 hours using the same ramping rate than in the previous process.

**Table 4.3.** Chemicals used for synthesis of LST and LCST powders

<table>
<thead>
<tr>
<th>Chemical</th>
<th>Specifications</th>
<th>Company</th>
</tr>
</thead>
<tbody>
<tr>
<td>Titanium(IV) isopropoxide</td>
<td>$\text{Ti[OCH(CH}_3}_2\text{]}_4$, ≥ 97.0% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Ethylene glycol</td>
<td>$\text{HOCH}_2\text{CH}_2\text{OH}$, ≥ 99% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Citric acid</td>
<td>$\text{HOC(COOH)(CH}_2\text{COOH)}_2$, 99% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Strontium carbonate</td>
<td>$\text{SrCO}_3$, &gt; 99.9% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Lanthanum oxide</td>
<td>$\text{La}_2\text{O}_3$, 99.99% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Cerium carbonate</td>
<td>$\text{Ce}_2\text{(CO}_3\text{)}_3\times\text{H}_2\text{O}$, 99.9% purity</td>
<td>Sigma Aldrich</td>
</tr>
<tr>
<td>Nitric acid</td>
<td>$\text{HNO}_3$, ≥ 65% purity</td>
<td>Sigma Aldrich</td>
</tr>
</tbody>
</table>

The powders synthesized were pressed in a stainless steel die at 5.0 tons for 1 minute to produce pellets of 11 mm diameter and 1.0 mm thickness. These pellets were sintered in air in an Elite BRF16/5 box furnace at 1 400 °C for 12 hours (ramping rate of 3 °C min$^{-1}$). The final product was analysed using X-ray techniques to study its structure and chemical composition (see Section 4.2.3 for more information).

Using the LST and LCST pellets produced, the alternative current collectors were assembled as shown in Figure 4.6. This ceramic plug was fabricated using an alumina tube.
of 5 mm outer diameter, 3 mm inner diameter and 300 mm length and a cylinder of 15 mm outer diameter, 5.1 mm inner diameter and 10 mm height made of pyrophyllite\(^7\) (machinable ceramic fired at 1 000 °C during 2 hours at a ramping rate of 3 °C min\(^{-1}\)). The \(LST\) or \(LCST\) pellet was attached to a platinum wire of 350 mm length using platinum ink (as described in Section 4.1.1 for the cathode current collector) and pasted to the bottom of the plug with the platinum wire going along the alumina tube for external electrical connection. All the ceramic pieces were stick together using Aremco Ceramabond 552.

![Diagram](image)

**Figure 4.6.** Schematic of the plug system used for \(LST\) and \(LCST\) current collectors

The electrical conductivity of both current collectors, \(LST\) and \(LCST\), was determined at different temperatures using the 4-point probe method described in Section 4.2.1.

### 4.2. Experimental Methods: Electrochemical and Structural Analysis

The performance of the \(Sn\)\(_{11}\)-SOFC described along Section 4.1 and the electrical properties, composition and structure of its components were studied using electrochemical methods (cyclic voltammetry, chronoamperometry, electrochemical impedance spectroscopy) and X-ray analysis (SEM, EDX, XRD). In this section the fundamentals of these experimental techniques and the objective of their application are presented.

#### 4.2.1. Conductivity Measurements: 4-Point Probe Method

The Van der Pauw or 4-point probe method is a technique commonly used to measure the resistivity of a sample. Its power lies on its ability to accurately measure the electrical

\(^7\) Pyrophyllite is a machinable ceramic which after heat treatment assumes many of the properties of fired ceramics.
properties of a sample of any arbitrary shape, so long as the sample is approximately two-
dimensional (i.e. it is much thinner than it is wide) and the electrodes are placed on its
perimeter. The method appears as an alternative to the direct use of an ohmmeter for the
measurement of the resistance of a sample located a significant distance away from the
instrument\[^8\]. Such a scenario would be problematic, because an ohmmeter measures all
resistance in the circuit loop, which includes the resistance of the wires ($R_{\text{wire}}$) connecting
the instrument to the component being measured ($R_{\text{subject}}$).

An ingenious method of measuring the subject resistance in a situation like this involves
the use of both an ammeter and a voltmeter. It is known from Ohm’s Law that resistance is
equal to voltage divided by current ($R = E/I$), thus it is possible to determine the resistance
of the subject component measuring the current going through it and the voltage dropped
across it. Since current is the same at all points in the circuit, its value can be measured from
a distance without any problem, but the voltage loss of the sample resistance cannot be
isolated from the connecting wires. However, upon closer inspection it is seen that the
voltammeter wires carry minuscule current and thus those long wires connecting the
instrument across the sample resistance will drop insignificant amounts of voltage, resulting
in a voltammeter indication that is very nearly the same as if it were connected directly
across the sample resistance.

In order to make the conductivity measurements of the $LST$ and $LCST$ samples studied
in this research work, four ohmic contacts were placed on the border of the pellets and made
as small as possible, as suggested in literature [191, 192]. The experimental probe used is
presented in Figure 4.7, where the electrical contacts are named from A to D in a counter-
clockwise order beginning from the top contact. An Autolab potentiostat controlled using a
Nova 1.5 interface was used to obtain $I-V$ curves for each sample applying the cyclic
voltammetry technique described in Section 4.2.2.2. The slopes of these curves represent
the electrical resistance of the analysed sample and were calculated for two different cases:

(1) The DC current $I_{AB}$ injected into contact A and taken out of contact B was measured
in amperes (A), while the DC voltage $V_{CD}$ between contact C and D was measured in
volts (V). The sample resistance $R_{AB-DC}$ was calculated in ohms (Ω).

\[^8\] The experiments described in this thesis were done using a sample placed inside a furnace at high
temperature (between 600 and 1 000 °C). Therefore, it was impossible locating the measurement
instruments close to the sample.
(2) The DC current $I_{BC}$ injected into contact $B$ and taken out of contact $C$ was measured in amperes (A), while the DC voltage $V_{DA}$ between contact $D$ and $A$ was measured in volts (V). The sample resistance $R_{BC-DA}$ was calculated in ohms ($\Omega$).

![Figure 4.7. Contacts placement in LST and LCST pellets for conductivity measurements](image)

The resistances obtained were used to determine the sample resistivity solving the equation [191, 192]:

$$\rho = \frac{\pi}{\ln 2} \frac{R_{AB,CD} + R_{BC,DA}}{2} f \left( \frac{R_{AB,CD}}{R_{BC,DA}} \right)$$  \hspace{1cm} (4.3)

where $f$ is a function of the ratio $R_{AB,CD}/R_{BC,DA}$ only and satisfies the relation:

$$\ln \left( \frac{R_{AB,CD} - R_{BC,DA}}{R_{AB,CD} + R_{BC,DA}} \right) = \frac{\exp \left( \frac{\ln 2}{f} \right)}{2}$$  \hspace{1cm} (4.4)

Details on the deduction of these equations are presented in Appendix B. Solution of equations (4.3) and (4.4) were obtained using the optimization tool Solver of Microsoft Excel 2010. The conductivity of the sample corresponds to the inverse of its resistivity: $\sigma = 1/\rho$.

4.2.2. Electrochemical Analysis of Thermodynamic and Kinetic Aspects

The performance of the Sn$0\text{°}$-SOFC was characterized based on the thermodynamics and kinetics of the electrochemical reactions occurring at each electrode. Analysis of this information was essential to obtain the parameters used in the development of the mathematical models on which the optimization of the fuel cell operation was based.
In order to obtain the information required for this characterization, electrochemical methods were used to represent the thermodynamics and kinetics of the system based on the electrical potentials applied to the fuel cell and the electrical currents obtained. In this research project, three electrochemical techniques were used to study the phenomena occurring in a Sn\(_{(l)}\)-SOFC:

1. **Cyclic Voltammetry**: this technique was used to obtain the polarization curves used to determine the kinetic parameters of the activation and concentration polarizations (see Chapter 2 and Chapter 5 for more information).

2. **Chronoamperometry**: this technique was used to analyse the stability of the Sn\(_{(l)}\)-SOFC when operating at constant potential during a longer term process.

3. **Electrochemical Impedance Spectroscopy**: this technique was used to determine the ohmic losses associated to each fuel cell component and to identify possible reaction mechanisms.

Additionally to these electrochemical techniques, measurements of the open circuit voltage (OCV) were done at different temperatures during the heating process with the objective of analysing the equilibrium of the system.

In the following sub-sections is presented a brief description of the electrochemical techniques used to study the thermodynamics and kinetics of a Sn\(_{(l)}\)-SOFC.

### 4.2.2.1. Open Circuit Voltage (OCV)

The potential difference measured between two terminals of an electrical device when disconnected from any circuit (no external load/no current flows) is known as open circuit voltage (OCV). In an electrochemical cell this concept corresponds to the Nernst potential, defined in Chapter 2 as the electrical voltage measured under equilibrium conditions. Therefore, the open circuit voltage of a Sn\(_{(l)}\)-SOFC depends on the operating temperature, pressure and activities of the species involved in the half-reactions occurring at each electrode (equation (5.3) and equation (5.4)).

The electrical connections used during this research project for measuring the OCV of the fuel cell are presented in Figure 4.8, where the anode current collector is connected to the sense and working electrodes, and the cathode current collector to the counter and reference electrodes. Using this configuration it was possible the measurement of the cell potential (\(E\)), since the cathode was acting as the reference and then the voltage measured between the two terminals is the total potential of the fuel cell.
The OCV was registered at different temperatures maintaining constant all the other operating conditions during the heating and cooling stages. These measurements were made using the GPES interface of the AUTOLAB potentiostat in order to obtain the cell potential as a function of temperature, which was information necessary to understand the thermodynamics of the electrochemical system and to determine the possible reaction mechanisms involved in the process.

4.2.2.2. Cyclic Voltammetry (CV)

Cyclic voltammetry is a potentiodynamic electrochemical measurement in which the working electrode potential is ramped linearly versus time from an initial potential $E_i$ until it reaches a set potential ($E_a$). At this point the working electrode potential ramp is inverted in a process that can happen multiple times during a single experiment and where the current at the working electrode is plotted versus the applied voltage to give the cyclic voltammogram diagrams.

Figure 4.9(a) presents the potential applied to the cell as a function of time to obtain the voltammograms of the system. The output of the system at this signal is represented in Figure 4.9(b) as a curve of current against potential. During the experimental measurements of this research project, potential $E_i$ corresponded to the open circuit voltage (OCV), while potential $E_a$ was the minimum potential that could be applied to the cell without reverting the direction of the current flow (in this case it corresponded to $E = 0$ V).

All the current-potential curves presented in this thesis were obtained using a scan rate of 10 mV s$^{-1}$ and a number of cycles between 2 and 4. The electrical connections used in this case were the same presented in Figure 4.8 for OCV measurements.
CHAPTER 4. EXPERIMENTAL METHODS AND EQUIPMENT

Figure 4.9. (a) Cyclic potential sweep ($\lambda$: potential switching time), (b) Resulting cyclic voltammetry

In this research project, cyclic voltammetry was used to obtain the kinetic parameters associated to the activation ($\eta^\text{act}$) and concentration ($\eta^\text{conc}$) polarization components of the fuel cell. These parameters were fit minimizing the error between the experimental polarization curves and the cell voltage calculated using the mathematical model presented in Chapter 5.

4.2.2.3. Chronoamperometry

Chronoamperometry is an electrochemical technique in which the potential of the working electrode is stepped and the resulting current from faradaic processes occurring at the electrodes is monitored as a function of time. The charging current generated decay exponentially with time while the species in the electrochemical cell reacts and the gradient of the concentration profiles decays. This result provides a notion of the depletion/saturation processes occurring at each electrode surface and their effect in the performance of the electrochemical cell.

Figure 4.10(a) presents the potential step applied to the electrochemical cell as a function of time, while Figure 4.10(b) shows the resulting current versus time curve. The open circuit voltage ($E_r$) was applied during 5 seconds before the chosen cell potential ($E_w$) was applied to the working electrode using the same electrical connections presented in Figure 4.8 for OCV measurements. This working potential was selected considering the maximum power density output of the Sn$_{0.02}$-SOFC studied (see Chapter 5 for more information).

In this research project, chronoamperometry was used to study the stability of the fuel cell performance when a constant potential was applied to the system during an extended period of time (3 hours in this case).
4.2.2.4. Electrochemical Impedance Spectroscopy (EIS)

It is probably easier to understand the measurements of impedance by considering the classical approach with an impedance bridge [193]. The electrochemical cell is inserted as the unknown impedance into one arm of an impedance bridge, and the bridge is balanced by adjusting the resistance \( R \) and the capacitance \( C \) in the opposite arm of the bridge, as shown in Figure 4.11. This operation determines the values of \( R \) and \( C \) that, in series, behave as the cell does at the measurement frequency. The impedance is measured as a function of the frequency of the ac source, being the job of theory to represent this data in equivalent resistance and capacitance values related to the interfacial phenomena occurring at the cell electrodes. The complexity of the equivalent circuit obtained is related to the number of phenomena occurring in parallel or series at each electrode, including double layer and charge transfer effects (see Section 6.2 for more details).

![Figure 4.11](image-url)
In this research project, three different electrical connection modes were used for making EIS measurements. The first of them corresponds to the configuration presented in Figure 4.8 used for measuring the total cell impedance or total ohmic losses ($\Delta \phi_{\text{total}}^{\text{IR}}$). The ohmic losses at the cathode were measured connecting the cell as shown in Figure 4.12(a), while the anode plus electrolyte losses were measured connecting the cell as shown in Figure 4.12(b). The results obtained using this technique provided information about the distribution of ohmic losses in the cell components and the parallel reactions occurring at the electrodes and current collectors interfaces (see Chapter 5 and Chapter 6 for more information).

**Figure 4.12.** Electrical connections used for measuring (a) ohmic losses at the cathode, and (b) ohmic losses at the anode and electrolyte

### 4.2.3. X-Ray Analysis of Composition and Microstructure of Materials

The stability of the components of a Sn$_{1-x}$-SOFC during its performance was an important aspect to be studied during this research project since it is a determining factor in their longer term applications. In view of that, X-ray techniques were applied to analyse the fuel
cell components after performance (post-mortem analysis) and the \textit{LST/LCST} materials synthesized for anode current collection. The results obtained served to determine the dimensions and reactivity of the fuel cell components, and were used in the development and analysis of the mathematical models discussed in Chapter 5 and Chapter 6. In addition, the analysis of the reactivity between the fuel cell components served to define the feasibility of their use and the need of a replacement if it was necessary.

The fuel cell components analysed and the objective of their analysis were:

1. \textbf{Cermet cathode}: the microstructures of the \textit{LSM} and \textit{LSM/YSZ} layers were analysed to determine their porosity and thickness.
2. \textbf{Anode | electrolyte and anode | current collector interfaces}: the microstructures of the current collectors and the YSZ electrolyte surfaces in direct contact with the molten tin anode during performance of the fuel cell were subjected to post-mortem analysis to detect accumulation of undesired compounds on them and their consequent degradation.

In addition, the composition of the \textit{LST} and \textit{LCST} powders synthesized was analysed in order to detect the presence of secondary phases that could affect their electrical properties. The by-product powders produced at the anode | electrolyte interface were analysed as well to determine its composition and its effects on the kinetics of the fuel cell.

The following sub-sections present a brief description of the X-ray techniques used during this research project to analyse the stability and reactivity of the \textit{Sn}(_{10})-SOFC components.

\textbf{4.2.3.1. Scanning Electron Microscopy (SEM)}

The scanning electron microscope (SEM) is an electronic device which allows analysing the surface structure and composition of a sample by scanning it with a high-energy beam of electrons in a raster scan pattern. The electrons interact with the atoms that make up the sample producing signals that contain information about the surface topography, composition and other properties of the sample, such as its electrical conductivity.

In a typical SEM, the types of signals produced include secondary electrons, back-scattered electrons (BSE), characteristic X-rays, light (cathode-luminescence), specimen current and transmitted electrons \cite{194}. When the scanning process and image formation starts, these signals are obtained by emitting thermo-ionically an electron beam towards the
sample from an electron gun fitted with a tungsten filament cathode\(^9\). The electron beam, which typically has an energy ranging from 0.5 to 40 keV, is focused by one or two condenser lenses to a spot about 0.4 to 0.5 nm in diameter, which guides the beam to pass through pairs of scanning coils or deflector plates in an electron column. This deflection of the electron beam in the \(x\)-\(y\) axes allows it to scan in a raster fashion over a rectangular area of the sample surface. Figure 4.13 presents a simplified schematic of a SEM and its main components.

![Schematic diagram of a scanning electron microscope (SEM)](image)

**Figure 4.13.** Schematic diagram of a scanning electron microscope (SEM)

The energy exchange between the electron beam and the sample results in the reflection of high-energy electrons by elastic scattering, emission of secondary electrons by inelastic scattering and the emission of electromagnetic radiation, each of which can be detected by specialized detectors to create digital images [194].

In the present research work, the scanning electron microscope was used to provide information about the microstructure of the Sn\(_{90}\)-SOFC components and how stable they were under the operating conditions.

### 4.2.3.2. Energy-dispersive X-ray Spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDX) is an analytical technique used for the elemental analysis or chemical characterization of a sample. It is based on the examination of a set of peaks obtained when the sample is excited using a high-energy beam of charged particles.

\(^9\) Tungsten is normally used in thermo-ionic electron guns because it has the highest melting point and lowest vapour pressure of all metals, thereby allowing it to be heated for electron emission, and because of its low cost.
particles, such as electrons or protons, or an x-rays beam. The characterization capabilities of this technique are due in large part to the fundamental principle that each element has a unique atomic structure allowing unique set of peaks on its X-ray spectrum [194].

At rest, an atom within the sample contains ground state (or unexcited) electrons in discrete energy levels or electron shells bound to the nucleus. The incident beam may excite an electron in an inner shell, ejecting it from the shell while creating an electron hole where the electron was. An electron from an outer, higher-energy shell then fills the hole, and the difference in energy between the higher-energy shell and the lower energy shell may be released in the form of an X-ray. The number and energy of the X-rays emitted from a specimen can be measured by an energy-dispersive spectrometer. As the energy of the X-rays is characteristic of the difference in energy between the two shells, and of the atomic structure of the element from which they were emitted, this allows the elemental composition of the specimen to be measured.

Any EDX equipment presents four primary components: (1) the excitation source (electron beam or X-ray beam), (2) the X-ray detector, (3) the pulse processor, and (4) the analyser. Electron beam excitation is used in scanning electron microscopes (SEM), which means that usually SEM and EDX techniques can be applied using the same apparatus, as in the case of this research project.

For this thesis, EDX measurements provided a preliminary elemental analysis of the compounds formed at the anode | electrolyte interface after polarization of the Sn_{0.75}-SOFC. In addition, this technique was used for preliminary elemental characterization of the LST and LCST perovskites produced as alternative current collectors for the anode. A complementary compositional analysis of these samples was provided by X-ray diffraction methods to identify the chemical compounds formed in each case.

4.2.3.3. X-ray Diffraction (XRD)

X-ray diffraction (XRD) is a method of determining the atomic and molecular structure of a polycrystalline specimen using the diffracted pattern produced when an X-ray beam strikes the electrons (scatterers) contained in the atoms of the crystals. A regular array of scatterers produces a regular array of spherical waves which can cancel one another in most directions (destructive interference) or constructively interfere in a few specific directions producing a diffracted beam characterized by Bragg’s law [31]:

\[ 2d \sin \theta = n\lambda \]  

(4.5)
Here $d$ is the spacing between diffracting planes of the crystal, $\theta$ is the incident angle of the X-ray beam, $n$ is any integer, and $\lambda$ is the wavelength of the beam.

Bragg’s law is a simple expression relating the x-ray wavelength and interatomic spacing to the angle of the diffracted beam. If Bragg’s law is not satisfied, then the interference will be non-constructive in nature so as to yield a very low-intensity diffracted beam. X-rays are used to produce the diffraction pattern because their wavelength $\lambda$ is typically the same order of magnitude ($1 – 100$ angstroms) as the spacing $d$ between planes in the crystal, which is necessary to produce significant diffraction.

Figure 4.14 represents schematically the features of the apparatus (diffractometer) used to determine the angles at which diffraction occurs for powdered specimens. The sample ($S$) is supported in a flat plate and rotated about the axis labelled $O$, which is perpendicular to the plane of the page. A monochromatic X-ray beam is generated at point $T$, and the intensities of diffracted beams are detected with a counter labelled $C$ in the figure. The counter is mounted on a movable carriage that also can be rotated about the $O$ axis, in such way that carriage and specimen are mechanically coupled in order that a rotation of the specimen through $\theta$ is accompanied by a $2\theta$ rotation on the counter. This assures that the incident and reflection angles are maintained equal to one another.

![Schematic diagram of an X-ray diffractometer](image)

**Figure 4.14.** Schematic diagram of an X-ray diffractometer [31]

Collimators and filters are incorporated within the beam path to produce a well-defined, focused and monochromatic beam. As the counter moves at constant angular velocity, a recorder automatically plots the diffracted beam intensity (monitored by the counter) as a
function of $2\theta$ which is measured experimentally. The diffraction pattern obtained is characteristic of the crystalline structure and composition of the specimen analysed.

In this research work, XRD analysis was used to identify the composition of the deposits formed at the anode | electrolyte interface after the performance of the fuel cell and the perovskites produced as alternative current collectors ($LST$ and $LCST$).
5. Thermodynamics and Kinetics of Sn(l)-SOFCs Operating in Battery Mode

This chapter presents the experimental study of the performance of the Sn(l)-SOFC described in Chapter 4 when helium was fed into the anode chamber without stirring of the molten tin. The results presented include the variation of open circuit voltage (OCV) with temperature, and the impedance and polarization curves obtained at 900 °C under equilibrium and non-equilibrium conditions, respectively.

Using the theoretical treatment presented in Chapter 2 for thermodynamic analysis of a SOFC system, the OCV plots were used to determine the global reaction controlling the electrochemical process of generation of energy in the Sn(l)-SOFC studied. Kinetics of this fuel cell were analysed using an optimization model based on the equations presented in Section 2.2 in order to fit the experimental polarization curves. Impedance plots were used as a source of information to determine the distribution of the ohmic losses in the fuel cell.

Based on the modelling results obtained, an optimization of the fuel cell performance was implemented modifying some characteristics of the fuel cell components, such as using a thinner electrolyte or less resistive current collectors. The performance of this enhanced Sn(l)-SOFC was compared with a conventional SOFC, in which the molten tin anode was replaced by the traditional Ni-YSZ cermet.

Finally, results of experimental characterization of the LST and LCST alternative current collectors are presented. X-ray analysis and conductivity measurements at different temperatures were undertaken in order to determine the feasibility of using either LST or LCST as a replacement for the graphite rods in the anode chamber. Graphite rods are progressively oxidized by the dissolved oxygen present in the molten tin, whereas LST and LCST were predicted to be stable under such oxidising conditions. Modelling of the Sn(l)-SOFC performance using these alternative current collectors is presented in order to compare it with the performance of the Sn(l)-SOFC using a graphite rod.

A study of the stability and longer term performance of the Sn(l)-SOFC is presented in Chapter 6. Mechanisms of reaction are proposed in that chapter based on the post-mortem analysis of the fuel cell components and modelling of the impedance plots obtained for the anode | electrolyte arrangement and cathode performance at different overpotentials.
5.1. X-ray Analysis of Sn\textsubscript{0} SOFC Structure

An SEM analysis of the cross section of the \(\text{YSZ/LSM-YSZ/LSM}\) half-cell component of the Sn\textsubscript{0} SOFC studied was done in order to determine the thickness, porosity and average pore size of the \(\text{LSM-YSZ}\) and \(\text{LSM}\) layers. Figure 5.1 presents the micrograph obtained with a magnification of x800, showing some large size pores and a non-homogeneous distribution of them, which might be due to the method used for the fabrication of the cathode (see Section 4.1.1). These deficiencies could affect the structure of the triple-phase boundaries (TPBs), which can result in a poor performance of the fuel cell. Therefore, better electrode structures should be produced using improved deposition techniques\[195-197\]. In addition, further SEM micrographs of different half-cell cross sections and repeats of these analyses would have been desirable in order to determine values of thickness, porosity and average pore size based on a statistical distribution analysis of the data. However, since the main objective of this thesis was the understanding of the anode kinetics, analysis and enhancement of the other fuel cell components was considered a secondary matter that could be addressed in depth in a future research project.

![SEM micrograph of the YSZ/LSM-YSZ/LSM half-cell component of the Sn\textsubscript{0} SOFC studied](image)

**Figure 5.1.** SEM micrograph of the \(\text{YSZ/LSM-YSZ/LSM}\) half-cell component of the Sn\textsubscript{0} SOFC studied

Table 5.1 presents the dimensions and structural characteristics of the Sn\textsubscript{0} SOFC and SOFC components used for modelling and comparison of their performances. In the case of the former, porosity and average pore size of the \(\text{LSM-YSZ}\) and \(\text{LSM}\) layers were estimated using the image processing free-software ImageJ\[10\], while tortuosity was obtained from the data used for modelling of a tubular SOFC \[198\]. The SOFC modelled in this chapter had

\[10\] \url{http://rsbweb.nih.gov/ij/}
identical electrolyte and cathode than the Sn(l)-SOFC studied, but the molten tin anode was replaced by a Ni-YSZ cermet with the same characteristics of that used in reference [198].

Table 5.1. Dimensions and structural characteristics of the Sn(l)-SOFC and SOFC modelled

<table>
<thead>
<tr>
<th></th>
<th>Sn(l)-SOFC</th>
<th>SOFC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Electrolyte</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness / m</td>
<td>2.0 x 10^3</td>
<td>2.0 x 10^3</td>
</tr>
<tr>
<td><strong>Anode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness / m</td>
<td>5.0 x 10^3</td>
<td>100 x 10^6</td>
</tr>
<tr>
<td>Porosity / %</td>
<td>---</td>
<td>50</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>---</td>
<td>3.0</td>
</tr>
<tr>
<td>Average pore size</td>
<td>---</td>
<td>1.0 x 10^6</td>
</tr>
<tr>
<td><strong>Cathode LSM-YSZ cermet</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness / m</td>
<td>90 x 10^-6</td>
<td>90 x 10^-6</td>
</tr>
<tr>
<td>Porosity / %</td>
<td>15</td>
<td>15</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>3.0 (reference [198])</td>
<td>3.0 (reference [198])</td>
</tr>
<tr>
<td>Average pore size / m</td>
<td>5.0 x 10^-6</td>
<td>5.0 x 10^-6</td>
</tr>
<tr>
<td><strong>Cathode LSM current collector</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Thickness / m</td>
<td>40 x 10^-6</td>
<td>40 x 10^-6</td>
</tr>
<tr>
<td>Porosity / %</td>
<td>20</td>
<td>20</td>
</tr>
<tr>
<td>Tortuosity</td>
<td>3.0 (reference [198])</td>
<td>3.0 (reference [198])</td>
</tr>
<tr>
<td>Average pore size / m</td>
<td>5.0 x 10^-6</td>
<td>5.0 x 10^-6</td>
</tr>
</tbody>
</table>

5.2. Open Circuit Voltage and Thermodynamics of the Sn(l)-SOFC

The open circuit voltage (OCV) of the Sn(l)-SOFC studied was measured at 7 different temperatures (600, 650, 700, 750, 800, 850 and 900 °C) while the system was heated from room temperature to 900 °C at a ramping rate of 3.5 °C min⁻¹. Each temperature was maintained constant during 15 minutes, while the OCV was monitored every 10 s. Data presented in Figure 5.2 correspond to the mean values of the OCVs measured at each of these temperatures, of which the standard deviation was not higher than 2.70 mV[^11]. The

[^11]: Since these measurements were done using the anode as working electrode and the cathode as counter and reference electrodes, the OCV values measured experimentally were negative. In this section and the rest of this thesis all the OCV values presented will be positive to be in agreement with theory.
additional straight lines showed in Figure 5.2 correspond to the theoretical OCVs calculated for reactions (5.1) and (5.2) using the thermodynamic approach presented in Section 2.1.

\[ \text{Sn}(l) + \frac{1}{2} \text{O}_2(g) \rightleftharpoons \text{SnO}_2(s) \]  

(5.1)

\[ \frac{1}{2} \text{O}_2(g) \rightleftharpoons [\text{O}]_{\text{Sn}} \]  

(5.2)

Equations (5.1) and (5.2) have been considered by other authors to be the most likely global reactions occurring in a solid oxide fuel cell with a molten tin anode before the fuel oxidation process takes place [138, 139, 160, 162].

Figure 5.2. Comparison of the OCV values measured experimentally for the Sn(l)-SOFC studied and calculated using the thermodynamic data of reactions (5.1) and (5.2)

The Nernst potentials for reactions (5.1) and (5.2) correspond respectively to:

\[ E_{N,\text{Sn-SnO}_2} = \Delta E_{rev,T}^{(5.1)} + \frac{RT}{4F} \ln \frac{a_{\text{Sn}(l)} P_{\text{O}_2}}{a_{\text{SnO}_2(s)}} \]  

(5.3)

\[ E_{N,[\text{O}]_{\text{Sn}}} = \Delta E_{rev,T}^{(5.2)} + \frac{RT}{2F} \ln \frac{P_{\text{O}_2}^{1/2}}{a_{[\text{O}]_{\text{Sn}}}} \]  

(5.4)

The reversible potential of reaction (5.1) was determined using MATLAB codes based on the thermodynamic data presented in Appendix C for Sn, O\(_2\) and SnO\(_2\). The equation obtained using the Curve Fitting Toolbox is:
\[ \Delta E^{(5.1)}_{\text{rev.,r}} = -4.86 \times 10^{-4} T + 1.457 \]  

(5.5)

where the reversible potential is calculated in V and \( T \) is the absolute temperature. The activities of pure \( \text{Sn} \) and \( \text{SnO}_2 \) were assumed to be 1.0 at any temperature, while the oxygen partial pressure was 0.21 bar considering that air was being fed continuously to the cathode as stated in Section 4.1.3.

For reaction (5.2), the reversible potential was determined using the following equation to calculate the Gibbs free energy change [166]:

\[ \Delta G^{(5.2)}_T = -167.47 + 6.87 \times 10^{-3} T \]  

(5.6)

where \( \Delta G^{(5.2)}_T \) is calculated in kJ mol\(^{-1}\) and \( T \) is the absolute temperature. Based on equation (3.15), the activity of oxygen dissolved in the molten tin anode can be calculated as:

\[ a_{[O]} = \frac{N^o_D(Sn)}{100 V_{m,Sn}} \]  

(5.7)

where \( a_{[O]} \) is the activity of oxygen in units of concentration (mol L\(^{-1}\)), \( N^o_D(Sn) \) is the solubility of oxygen in at\%, and \( V_{m,Sn} \) corresponds to the molar volume of molten tin at the operating temperature (1.81 \( \times 10^{-2} \) L mol\(^{-1}\)). It is important to notice that the activity values obtained using equation (5.7) correspond to the saturation concentration of oxygen in molten tin. Therefore, the OCVs determined when they are introduced in equation (5.4) are the minimum values that could be obtain for reaction (5.2).

In principle, no presence of oxygen should be detected while helium is being fed continuously into the anode chamber. However, considering that helium is less dense than air [199, 200] and that oxygen could be adsorbed in some fuel cell components, such as the surface of the graphite rod [201, 202], it is very likely that a complete removal of oxygen from the system is not feasible. Therefore, the assumption of a Sn\(_{(l)}\)-SOFC with an initial OCV associated with the global reaction (5.1) or (5.2) is not unreasonable. What does seem to be unreasonable is the assumption of oxygen saturation in the molten tin anode, particularly when it was demonstrated experimentally via chronoamperometric measurements that this condition is reached after ca. 50 min when a constant cell voltage of 0.42 V was applied (see Chapter 6 for more details). The previous result is an indication of an electrochemical system
in which saturation cannot be achieved, unless a constant external potential is applied to take it out of equilibrium. Therefore, the OCV of reaction (5.2) as presented in Figure 5.2 cannot correspond to a possible initial situation in the Sn$_{(l)}$-SOFC studied. What does seem to be more likely, and agrees with the good fitting observed between the OCVs measured experimentally and the curve associated with equation (5.1), is that injection of oxygen in the form of $[O]_{Sn}$ into the molten tin anode is immediately followed by the formation of $SnO_2$, which indicates that equation (5.1) corresponds to the global reaction occurring in the fuel cell. This deduction agrees with results reported by Gorte et al. [160, 162] and Abernathy et al. [159], who considered that oxidation of the molten tin anode to form tin dioxide is the process occurring when the fuel cell is operational. In addition, from Figure 5.3 it can be seen that the Gibbs free energy change for reaction (5.1) is lower than the corresponding values for reaction (5.2) under saturation conditions. This means that oxidation of molten tin is more favourable than dissolution of atomic oxygen, unless its concentration in the anode is low enough to promote a greatly negative Gibbs free energy change for reaction (5.2). Considering that the saturation concentration of atomic oxygen in molten tin is ca. 0.33 at% at 900 °C [166], the amount of oxygen dissolved in the anode should be virtually zero in order to reach these very low values of Gibbs free energy changes, which is a difficult condition to achieve in the experimental system studied.

![Graph showing Gibbs free energy changes with temperature](image)

**Figure 5.3.** Predicted effect of temperature on Gibbs free energy changes for reactions (5.1) and (5.2)

The small differences observed in Figure 5.2 between the experimental results and the theoretical line obtained for reaction (5.1) could be explained assuming that the granular tin
particles used in the experiments contained some traces of metals, such as copper and iron\textsuperscript{[12]}. Nevertheless, the most probable explanation for that is the instability of the graphite rod used as current collector in the anode, which can be oxidized to produce CO and/or CO$_2$ and presents a certain level of reaction with the molten tin anode, as discussed in Chapter 6. In any case, the maximum relative error observed between the experimental and theoretical results is ca. 2.03\% with respect to the former values, which is considered to be acceptable.

If the tin dioxide formed at the anode | electrolyte interface is reduced using a fuel such as coal or hydrogen, the global reaction would be represented by one of the following equations:

\[
2C(s) + O_2(g) \rightleftharpoons 2CO(g) \tag{5.8}
\]

\[
C(s) + O_2(g) \rightleftharpoons CO_2(g) \tag{5.9}
\]

\[
2H_2(g) + O_2(g) \rightleftharpoons 2H_2O(g) \tag{5.10}
\]

Reactions (5.8) and (5.9) correspond to the incomplete and complete combustion of carbon, respectively. Using the approach presented in Section 2.1, the Gibbs free energy changes for reactions (5.8) to (5.10) were calculated using MATLAB codes based on the thermodynamic data presented in Appendix C for C, H$_2$, O$_2$, CO, CO$_2$ and H$_2$O. The lines obtained are presented in Figure 5.4 in the range of temperature between 550 to 950 °C. The Gibbs free energy changes were calculated using the following equations obtained using the Curve Fitting Toolbox:

\[
\Delta G_f^{(5.8)} = -(16.49 \times 10^{-2} T + 232.8) \tag{5.11}
\]

\[
\Delta G_f^{(5.9)} = 7.53 \times 10^{-4} T - 395.6 \tag{5.12}
\]

\[
\Delta G_f^{(5.10)} = 12.41 \times 10^{-2} T - 502.9 \tag{5.13}
\]

where the Gibbs free energy values $\Delta G_f$ are calculated in kJ mol$^{-1}$ and $T$ is the absolute temperature.

\textsuperscript{[12]} From the information obtained in www.sigmaaldrich.com the granular tin used contained:

$Bi \leq 200$ mg kg$^{-1}$, $Cu \leq 100$ mg kg$^{-1}$, $Fe \leq 200$ mg kg$^{-1}$, $Pb \leq 500$ mg kg$^{-1}$ and $Sb \leq 500$ mg kg$^{-1}$. 
As can be seen in Figure 5.4, when carbon is used as the reducing agent incomplete combustion would be the dominant reaction at temperatures higher than ca. 709 °C, since its Gibbs free energy is lower than that for reaction (5.9). However, carbothermal reduction of tin dioxide occurs via oxidation of carbon monoxide, CO, to produce CO₂ (see Section 8.1). Therefore, the main reaction by-product/emission of a system operating with carbon as fuel would be carbon dioxide.

To calculate the Nernst potentials of reactions (5.8) to (5.10), the following equations can be used:

\[
\Delta E_{COJC} = \Delta E_{\text{rev},T}^{(5.8)} + \frac{RT}{4F} \ln \frac{p_{CO(g)}}{p_{O_2(g)}}
\]

(5.14)

\[
\Delta E_{COJC} = \Delta E_{\text{rev},T}^{(5.9)} + \frac{RT}{4F} \ln \frac{p_{CO_2(g)}}{a_{C(s)} p_{O_2(g)}}
\]

(5.15)

\[
\Delta E_{H_2O/H_2} = \Delta E_{\text{rev},T}^{(5.10)} + \frac{RT}{4F} \ln \frac{p_{H_2(g)} p_{O_2(g)}}{p_{H_2O(g)}}
\]

(5.16)

As in the case of the oxidation reactions (5.1) and (5.2), the reversible cell potentials in equations (5.14) to (5.16) can be calculated using the Gibbs free energy changes.
determined thermodynamically. Figure 5.5 presents the reversible potentials obtained for reactions (5.8) to (5.10).

![Graph showing reversible potentials vs. temperature](image)

**Figure 5.5.** Predicted effects of temperature on reversible potentials for reaction (5.8) to (5.10)

Results shown in Figure 5.4 and Figure 5.5 for oxidation of carbon have been presented in this section merely to demonstrate that the OCVs obtained experimentally were not related to complete reduction of oxygen in the molten tin via oxidation of the activated carbon particles situated on the surface of the melt (see Section 4.1.2) or the graphite rod used as current collector. In fact, the reversible potential associated to complete oxidation of carbon is ca. 1.03 V, independent of the operating temperature, which is a higher value than the experimental OCVs reported in Figure 5.2. This is a reasonable result considering that reduction of tin dioxide using activated carbon or graphite particles is a sluggish process \[203\] that could take longer than the electrochemical oxidation processes occurring at the anode | electrolyte interface (see Chapter 8), so that formation of tin dioxide was the cell reaction occurring preferentially in the Sn\(_{10}\)-SOFC. In addition, in the case that some carbon monoxide, CO, or carbon dioxide, CO\(_2\), products were formed in the molten metal anode during the performance of the fuel cell, their partial pressure can be considered constant and equal to 1.0 bar, since they form bubbles that do not dissolve in the liquid tin \[204\], and thus the Nernst potentials (5.14) and (5.15) were even higher than the reversible potential (considering that the activity \(a_{C(1)}\) is equal to 1.0 since Sn did not dissolve the carbon particles, and the partial pressure \(P_{O_2}\) is 0.21 bar).
Hydrogen was used as a reducing agent in some experiments, for which results are presented and discussed in Chapter 8. For the case of the SOFC modelled in Section 5.3.3, a mixed flow of H$_2$ and H$_2$O was fed to the Ni-YSZ cermet anode with a humidity content of 80%.

Based on the observations that suggested the formation of tin dioxide, SnO$_2$, as the most likely global reaction occurring in the Sn$_{(l)}$-SOFC, the following electrochemical and molecular reactions are proposed as the chemical processes occurring at each electrode:

**Cathode**

Electrochemical half-reaction: \[ O_2 + 4e^- \rightleftharpoons 2O^{2-} \] (5.17)

**Anode**

Electrochemical half-reaction: \[ 2O^{2-} \rightleftharpoons 2[O]_{Sn} + 4e^- \] (5.18)

Molecular bulk reaction: \[ Sn + 2[O]_{Sn} \rightleftharpoons SnO_2 \] (5.19)

Anode global reaction: \[ Sn + 2O^{2-} \rightleftharpoons SnO_2 + 4e^- \] (5.20)

It is important to notice that, based on the experimental results discussed in this section, dissolution of atomic oxygen (reaction (5.18)) is expected to occur prior to tin dioxide formation (reaction (5.19)), considering that in a non-saturated system atomic oxygen can be dissolved in the melt up to its solubility limit. When saturation is reached, direct oxidation of molten tin to produce tin dioxide by reaction (5.20) should occur at the anode, since no more atomic oxygen can be dissolved into the melt.

### 5.3. Kinetic Aspects of the Sn$_{(l)}$-SOFC

The kinetics of a Sn$_{(l)}$-SOFC operating at 900 °C were studied experimentally by cyclic voltammetry and electrochemical impedance spectroscopy (EIS). A zero-dimensional model was developed to determine the kinetic parameters related to the activation and concentration polarizations of the fuel cell. This mathematical approach is based on the operating conditions described in Section 4.1 and the structural and thermodynamic data presented in Section 5.1 and Section 5.2, respectively.
In this section the experimental and modelling results obtained for kinetic characterization of the Sn\(_{(l)}\)-SOFC studied are presented and discussed.

5.3.1. Experimental Results: Sn\(_{(l)}\)-SOFC Polarization Curves and Ohmic Losses

Cyclic voltammetric measurements on the fuel cell were carried out at constant temperature and gas flow rates. The average temperature measured next to the pellet-cell during all the experimental sessions was ca. 900 °C, while the flow rates of helium at the anode and air at the cathode were 30 mL min\(^{-1}\) and 60 mL min\(^{-1}\), respectively. The OCV measured under these conditions was stable at ca. 0.85 V, except during the subsequent 10 minutes after a cyclic voltammetric measurement. During this time the OCV value recovered gradually from ca. 0.83 V to the initial OCV value of ca. 0.85 V.

As stated in Section 4.2.2.2, cyclic voltammetric measurements were made using the anode as working electrode and the cathode as counter and reference electrodes, which imply that the (oxidation) current values obtained were positive, according to convention. Figure 5.6 shows the cyclic voltammograms obtained when 4 cycles of potential with a scan rate of 10 mV s\(^{-1}\) were applied to the cell, each starting from the OCV value and finishing at zero volts\(^{13}\). This last value corresponds to the case at which the polarization and ohmic losses are equal to the OCV (see equation (2.18)), which is equivalent to saying that this is the minimum potential that can be applied in order to operate the fuel cell in galvanic mode.

The voltammograms in Figure 5.6 exhibited slight hysteresis that decayed as the number of cycles was increased. This phenomenon could be related with the formation of tin dioxide at the anode | electrolyte interface, which affected the kinetics of the fuel cell since some active sites would have been blocked modifying temporarily the previous OCV value. Tin dioxide in its pure form is an n-type semiconductor which, due to its electrical properties, is widely used in solid state gas sensors and mixed with various catalytic additives in photovoltaic devices [205, 206]. Hence, the tin dioxide layer formed at the anode | electrolyte interface would not have been expected to affect the oxide ions transport during the performance of the Sn\(_{(l)}\)-SOFC. However, when the oxide formed corresponds to a non-stoichiometric phase with an irregular crystallographic structure, such as the intermetallic Sn\(_3\)O\(_4\), its conductivity can be decreased [207]. In addition, as stated previously in Section 3.3.1, non-dense layers of SnO\(_2\) can exhibit a conductivity that is many orders of

\(^{13}\) The area used to determine the current densities and the area specific resistances (ASR) presented in this chapter corresponds to the surface of the working electrode. This value was equal to 4.91 cm\(^2\) in the case of the anode and 3.26 cm\(^2\) in the case of the cathode.
magnitude lower than that of a dense layer [169]. These two conditions were observed in the case of the Sn\(_{\text{(l)}}\)-SOFC studied when post-mortem analysis of the anode | electrolyte interface product was done (see Chapter 6).

![Graph](image)

**Figure 5.6.** Cyclic voltammograms for the Sn\(_{\text{(l)}}\)-SOFC operating at 900 °C (scan rate: 10 mV s\(^{-1}\))

Additionally to the oxide deposit affecting the conductivity of the electrochemical cell, the graphite rod used as current collector at the anode presented some level of reaction when it was immersed in the molten metal (see Chapter 6), which could influence adversely the longer term operation of the Sn\(_{\text{(l)}}\)-SOFC.

In order to understand the kinetics of the fuel cell studied, the voltammogram for the first cycle in Figure 5.6 was assumed to represent the response of a Sn\(_{\text{(l)}}\)-SOFC before any alteration in the system could affects its performance. Figure 5.7 shows the polarization curve extracted from these experimental results and the resulting power densities, which exhibited a maximum of ca. 159 W m\(^{-2}\) at a cell potential of ca. 0.42 V and a current density of ca. 380 A m\(^{-2}\). However, these results depended strongly on the ohmic losses associated with the Sn\(_{\text{(l)}}\)-SOFC, which were analysed based on the results obtained using EIS measurements.

Figure 5.8 shows the impedance spectra obtained under open circuit conditions (OCV or OCP) for the whole fuel cell (a), anode | electrolyte arrangement (b) and cathode (c)[14]. For

---

[14] In general, OCV (open circuit voltage) refers to the equilibrium voltage of the whole cell, while OCP (open circuit potential) refers to the equilibrium potential of an electrode.
all these measurements, a signal of 10 mV p-p amplitude was applied in a range of frequencies varying from 0.01 Hz to 15 kHz. The electrical connections used in each case were presented in Figure 4.8 for the whole fuel cell impedance measurements and in Figure 4.12 for the cathode and anode | electrolyte arrangement. The OCV measured in fuel cell and anode | electrolyte mode was ca. 0.85 V, while the OCP measured in cathode mode was approximately zero volts\textsuperscript{[15]}. 

![Polarization curve and power density obtained experimentally for the Sn\textsubscript{(l)}-SOFC operating at 900 °C](image)

**Figure 5.7.** Polarization curve and power density obtained experimentally for the Sn\textsubscript{(l)}-SOFC operating at 900 °C

From the results shown in Figure 5.8(a) it can be established that the total ohmic resistance of the Sn\textsubscript{(l)}-SOFC was about 1.98 Ω, as determined from the high frequency intercept on the real impedance axis $Z'$ according to the theory presented in Chapter 6. This value corresponds to a whole cell area specific resistance (ASR) of 9.70 Ω cm$^2$, of which almost 78% corresponds to the cathode resistance $R_{\text{cathode}} = 1.54$ Ω (ASR = 5.01 Ω cm$^2$ as can be seen in Figure 5.8(c)). This result could seem inconsistent considering that the cathode is a well-known material that presents usually low impedance during the performance of conventional SOFCs \textsuperscript{[208]}. Nevertheless, usually ohmic losses are related to a poor contact between the current collectors and the cathode; this was very probable in this case, considering that the platinum mesh used as current collector was attached to the LSM

\textsuperscript{[15]} The cathode OCP value measured was due to the use of the same material (LSM-YSZ/LSM) at the cathode and reference electrode, which determined that identical half-reactions were taking place at both surfaces. In the case of the anode | electrolyte arrangement, the OCV measured was equal to the whole cell OCV since the reference electrode was positioned in the cathode side.
layer of the cathode using only some drops of platinum ink. In addition, the length of the platinum wire leading the current from the pellet cell inside the furnace to the outside was large enough to produce a significant resistance, estimated as ca. 0.54 Ω using the mathematical model presented in Section 5.3.2.

**Figure 5.8.** Impedance plots obtained at open circuit conditions (OCV or OCP) for: (a) Sn(l)-SOFC, (b) molten tin anode and electrolyte, and (c) LSM-YSZ/LSM cathode

Figure 5.8(b) presents the impedance spectrum obtained for the anode and electrolyte together. From modelling, it was determined that the ASR associated to the YSZ electrolyte used was ca. 2.75 Ω cm², which was higher than the ca. 1.78 Ω cm² at which the curve intercepts the real axis Z’ but in the same range of magnitude. This experimental result can be understood considering the combination of two effects: (1) the anodic ohmic losses of the Sn(l)-SOFC under operating conditions were very low compared to the electrolyte, thus can be ignored; and (2) an inductive phenomenon occurred at the graphite rod when the fuel cell was operational and influenced the position at which the impedance plot intercepts the real axis Z’ and its shape. The former effect is discussed in the next section based on the mathematical model developed in MATLAB for characterization of the fuel cell kinetics, while
the latter is studied in Chapter 6 which reports results of post-mortem analyses and a more extensive interpretation of the impedance spectra in order to understand better the processes occurring at each electrode.

5.3.2. Modelling Results: Characterization of the Kinetics of a Sn(l)-SOFC

The open circuit voltage (OCV) corresponds to the maximum potential difference (electromotive force, emf) that can be obtained from a galvanic electrochemical cell. When this device is connected to an external circuit, part of the OCV is used by the chemical reactions and charge transfer promoted at the cell components. Therefore, only a fraction of the initial electromotive force can be transformed into useful electrical energy.

In a fuel cell the useful fraction of the OCV, referred from now on as the cell potential $E$, can be represented as a function of the operating current density using equation (2.18). This equation includes the losses related to electrode processes (activation and concentration polarizations) and to the resistivity of the cell components (ohmic losses). In Chapter 2, a general description of the cell potential components was presented for the case of a conventional SOFC using hydrogen as the fuel. In this section, the equations used for mathematical modelling of the Sn(l)-SOFC kinetics are deduced and described.

5.3.2.1. Nernst Potential

In Section 5.2, the experimental OCV data suggested that the global reaction occurring in the Sn(l)-SOFC corresponds to the oxidation of molten tin by reaction (5.1). Therefore, the equilibrium potential of the fuel cell could be represented mathematically using equations (5.3) and (5.5) for a partial pressure of oxygen equal to 0.21 bar at the cathode. Nonetheless, considering that a difference was observed between the experimental and the modelled OCVs (see Figure 5.2), the former values were used for the mathematical characterization of the fuel cell kinetics to reduce the cumulative error in the parameters fitting results.

Considering that the operating temperature of the system studied was 900 °C, an OCV value of 0.85 V was used as the Nernst potential input in the MATLAB codes developed, in accordance with the experimental results presented in Section 5.2.

5.3.2.2. Activation Polarization

The low solubility of oxygen in molten tin (see equation (3.15)) added to the formation of tin dioxide at the electrode | electrolyte interface, suggests that mass transfer controlled
kinetics would be observed at the anode. In order to represent properly this phenomenon, a
modified version of the Butler–Volmer equation (2.19) which includes the mass transfer
effects [16, 193] was used for modelling the activation polarization at the molten tin anode.
Thus, the current density \( j \) can be expressed as a function of the activation overpotential
\( \eta_{\text{act}} \) using the equation:

\[
j = j_{0,\text{an}} \frac{C_{\text{bulk}}^{(a)}}{C_{\text{react}}^{(a)}} \left[ \exp \left( \frac{\alpha_{\text{an}} v_e F}{RT} \eta_{\text{an}}^{\text{act}} \right) - \exp \left( - \frac{(1-\alpha_{\text{an}}) v_e F}{RT} \eta_{\text{an}}^{\text{act}} \right) \right]
\]

(5.21)

where \( \alpha_{\text{an}} \) is the charge transfer coefficient, \( v_e \) is the reaction electron stoichiometry, \( j_{0,\text{an}} \)
is the exchange current density, and \( C_{\text{bulk}}^{(a)}/C_{\text{react}}^{(a)} \) is the ratio between the oxygen
concentration at the bulk of the molten tin anode and the oxygen concentration at the anode
\| electrolyte interface. A relation between this ratio and the current density \( j \) is derived in
Section 5.3.2.3 (equation (5.31)), while the solution of equation (5.21) is presented in
Appendix D.

Reaction (5.20) implies that the formation of one molecule of tin dioxide requires that 4
electrons \( (v_e) \) are transferred from the anode to the cathode. The kinetic parameters \( \alpha_{\text{an}} \)
and \( j_{0,\text{an}} \), and the ratio \( C_{\text{bulk}}^{(a)}/C_{\text{react}}^{(a)} \) were determined minimizing the mean square error
between the experimental polarization curve presented in Figure 5.7 and the \( j - E \) curve
obtained using the mathematical model described along this section. More details about the
computer routine used to solve this optimization problem are presented in Section 5.3.2.5.

In the case of the cathode, the kinetics of reaction (5.17) has been well studied by other
authors [209, 210] considering a reaction electron stoichiometry \( v_e = 2 \). In these references,
the Butler-Volmer equation (2.19) was used for calculation of \( \eta_{\text{ca}}^{\text{act}} \) with a charge transfer
coefficient \( \alpha_{\text{ca}} = 0.5 \) and the exchange current density \( j_{0,\text{ca}} \) defined by:

\[
j_{0,\text{ca}} = 7.0 \times 10^3 \left( \frac{P_{O_2}}{P} \right)^{0.25} \exp \left( - \frac{120 000}{RT} \right)
\]

(5.22)

where \( P_{O_2} \) is the oxygen partial pressure in the bulk and \( P \) is the total pressure.
Replacement of the reaction electron stoichiometry $\nu_e = 2$ and the charge transfer coefficient $\alpha_{ca} = 0.5$ in the Butler-Volmer equation (2.19) results in equation:

$$\eta_{ca}^{act} = \frac{RT}{F} \sinh^{-1}\left(\frac{j}{2J_{0,ca}}\right)$$

(5.23)

Equation (5.23) is representative of the kinetics of an electrochemical process under kinetic control and is the expression most commonly used to represent the activation polarization of an LSM electrode in a SOFC [209, 210].

5.3.2.3. Concentration Polarization

In Section 2.2.2, the concentration polarization was defined as the difference between the OCV at the reaction sites, or triple phase boundaries (TPBs) in the case of cermet electrodes, and the OCV in the bulk of the electrodes. Considering that the anodic half-reaction occurring at the reaction sites corresponds to equation (5.18), the concentration polarization at the anode can be written as:

$$\eta_{an}^{conc} = \frac{RT}{2F} \ln\left(\frac{a_{[O]_{an}}^{react}}{a_{[O]_{an}}^{bulk}}\right)$$

(5.24)

where $a_{[O]_{an}}^{react}$ is the activity of atomic oxygen at the reaction sites and $a_{[O]_{an}}^{bulk}$ is the activity of atomic oxygen in the bulk of the molten tin anode. At the cathode, the concentration polarization can be determined using equation (2.22). The activity of atomic oxygen and partial pressure of oxygen gas in the bulk of the anode and cathode, respectively, were considered to be rather constant during the experimental measurements. The oxygen partial pressure in the bulk of the cathode was ca. 0.21 bar, while the value of the 'pseudo-constant' oxygen concentration in the bulk of the molten tin anode was an output of the mathematical model described in this section. The activities at the reaction sites were determined using a mass balance based on the Fick’s model described below.

As the electrochemical half-reactions take place at the electrode | electrolyte interfaces, the mass of each participating component in the electrodes is conserved in a steady state, which can be represented by the equation [211]:

$$\nabla \cdot N_i = 0$$

(5.25)
where \( N_i \) is the rate of mass transfer for species \( i \). This hypothesis is valid for an assumed constant concentration (activity) of the reacting species in the bulk of the electrodes. As stated in Section 4.1.3, air was fed at the cathode surface at a flow rate sufficiently high to maintain a constant oxygen partial pressure of 0.21 bar at the bulk of the electrode. At the anode, the oxygen concentration in the bulk increased with time when the fuel cell was operational. However, considering that during cyclic voltammetry measurements current was applied to the system during short times (a scan rate of 10 mV s\(^{-1}\) implies a total measurement time of ca. 3 minutes) and that the experimental fuel cell was controlled mainly by ohmic losses (as discussed in Section 5.3.1), the assumption of a (mean) bulk concentration rather constant is acceptable.

Mass transport of atomic oxygen from the anode | electrolyte interface to the molten metal bulk is controlled by diffusion, so the rate of mass transfer can be expressed (approximately) by Fick’s first law:

\[
N_i = -D_{[O]} \frac{\partial C_{[O]_{\text{an}}}}{\partial x}
\]

(5.26)

where \( x \) is the depth measured from the bulk of the electrode, \( C_{[O]_{\text{an}}} \) is the concentration of atomic oxygen dissolved in the molten tin anode, and \( D_{[O]} \) is the diffusion coefficient of this species in molten tin. Substituting equation (5.26) into equation (5.25), the equation governing steady state mass transport of oxygen in the anode is obtained:

\[
\frac{\partial}{\partial x} \left[ -D_{[O]} \frac{\partial C_{[O]_{\text{an}}}}{\partial x} \right] = 0
\]

(5.27)

In the steady state, the rate of atomic oxygen diffusing away from the interface is equal to the atomic oxygen generation rate at the anode | electrolyte interface, which is governed by the current density \( j \) in accordance with the equation:

\[
N_{[O]_{\text{an}}} = -\frac{j}{2F}
\]

(5.28)

Therefore, the Neumann boundary condition of equation (5.27) for the anode | electrolyte interface can be obtained as:
where $\delta_{an}$ is the thickness of the diffusion layer at the molten tin anode. Additionally, the Dirichlet boundary condition can be applied for the concentration in the bulk:

$$C_{[\varrho]}_{|x=0} = C_{\text{bulk}}^{\varrho}$$

(5.30)

Solving equation (5.27) with the boundary conditions (5.29) and (5.30), the concentration of atomic oxygen at the anode | electrolyte interface can be derived:

$$C_{\text{react}}^{\varrho} = C_{\text{bulk}}^{\varrho} + \frac{j}{2FD_{[\varrho]}_{\text{an}}} \delta_{an}$$

(5.31)

Hence, substituting equation (5.31) into equation (5.24) the anodic concentration overpotential results to be:

$$\eta_{\text{an}}^{\text{conc}} = \frac{RT}{2F} \ln \left(1 + \frac{j}{j_{\text{bulk}}} \right)$$

(5.32)

where $j_{\text{bulk}}$ is a ‘hypothetical’ current density at the bulk of the molten tin anode given by:

$$j_{\text{bulk}} = \frac{2FC_{\text{bulk}}^{\varrho} D_{[\varrho]}_{\text{an}}}{\delta_{an}}$$

(5.33)

The diffusion coefficient can be determined using equation [166]:

$$D_{[\varrho]}_{\text{an}} = 9.9 \times 10^{-8} \exp \left(\frac{-6300}{RT} \right)$$

(5.34)

The ratio $C_{\text{bulk}}^{\varrho}/\delta_{an}$ was determined as part of the solution obtained from the minimization of the mean square error between the experimental and modelled fuel cell current densities.

Finally, the limiting current density at the anode is obtained when the oxygen concentration at the anode | electrolyte interface reach the saturation value $C_{\text{sat}}^{\varrho}$. Therefore,
using equation (5.31) it can be obtained that the limiting current density at the molten tin anode corresponds to:

\[ j_{\text{L},\text{an}} = \frac{2FD_{\text{Sn}}\left[\text{Sn}\right]_{\text{an}}}{\delta_{\text{an}}} \left( \epsilon_{\text{Sn}}^{\text{sat}} - \epsilon_{\text{Sn}}^{\text{bulk}} \right) \]  

(5.35)

In a porous \textit{LSM-YSZ} electrode, the mass transport \( N_i \) is mainly by means of diffusion driven by a partial pressure gradient [209, 212, 213], thus it can be represented by Fick’s model in the case of binary component systems [214]:

\[ N_i = -\frac{D_i^{\text{eff}}}{RT} \frac{\partial p_i}{\partial x} \]  

(5.36)

where \( D_i^{\text{eff}} \) is the effective diffusion coefficient of species \( i \) and \( p_i \) is the partial pressure of species \( i \). In the system studied, the species presented in air are oxygen and nitrogen in a ratio 0.21 / 0.79. Substituting equation (5.36) in equation (5.25) the following equation can be obtained for the case of oxygen gas diffusion:

\[ \frac{\partial}{\partial x} \left[ -D_{O_2}^{\text{eff}} \frac{\partial p_{O_2}}{\partial x} \right] = 0 \]  

(5.37)

In steady state, the diffusion rate of oxygen is equal to the oxygen consumption rate at the cathode | electrolyte interface. Thus, the mass transfer rate can be expressed as:

\[ N_{O_2} = -\frac{j}{4F} \]  

(5.38)

Substituting equation (5.38) into equation (5.36), the Neumann boundary condition of equation (5.37) can be obtained:

\[ \left. \frac{\partial p_{O_2}}{\partial x} \right|_{x=\delta_{\text{ca}}} = -\frac{RT}{D_{O_2}^{\text{eff}}} \frac{j}{4F} \]  

(5.39)

In addition, the Dirichlet boundary condition can be applied for the cathode surface:

\[ p_{O_2} \big|_{x=0} = p_{O_2}^{\text{bulk}} \]  

(5.40)
Solving equation (5.37) with boundary conditions (5.39) and (5.40), the partial pressure of oxygen at the cathode | electrolyte interface can be obtained:

\[ p_{\text{O}_2}^{\text{react}} = p_{\text{O}_2}^{\text{bulk}} - \frac{RT}{D_{\text{O}_2}^{\text{eff}}} \frac{j}{4F} \delta_{ca} \]  

(5.41)

Finally, substituting equation (5.41) into equation (2.22), the cathode concentration overpotential can be obtained:

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

(5.42)

where \( j_{l,ca} \) is the limiting current density of oxygen expressed by the equation:

\[ j_{l,ca} = \frac{4FP_{\text{O}_2}^{\text{bulk}}D_{\text{O}_2}^{\text{eff}}}{RT\delta_{ca}} \]  

(5.43)

Diffusion in a porous electrode is mainly based on two mechanisms, namely, molecular diffusion and Knudsen diffusion. Molecular diffusion is the dominant mechanism if the pore size is much larger than the mean free path of the molecular species. In this case, the molecule-molecule interaction governs the diffusion process. On the other hand, if the pore size is much smaller than the mean free path of the species, the molecule-pore wall interaction dominates over the molecule-molecule interaction. Thus, Knudsen diffusion becomes an important mechanism. In most porous structures both mechanisms are significant and thus the effective diffusion coefficient of oxygen can be expressed by the Bosanquet formula [215]:

\[ \frac{1}{D_{\text{O}_2}^{\text{eff}}} = \frac{\tau}{\varepsilon} \left( \frac{1}{D_{\text{O}_2-N_2}} + \frac{1}{D_{\text{O}_2-k}} \right) \]  

(5.44)

where \( \tau/\varepsilon \) is the ratio of cathode tortuosity to porosity; \( \tau/(\varepsilon D_{\text{O}_2-N_2}) \) is the reciprocal of the effective molecular diffusion coefficient of an \( \text{O}_2-N_2 \) binary system; and \( \tau/(\varepsilon D_{\text{O}_2-k}) \) is the reciprocal of the effective Knudsen diffusion coefficient of oxygen.

The molecular diffusion \( D_{\text{O}_2-N_2} \) can be determined using equation [215]:
\[ D_{O_2-N_2} = 1.43 \times 10^{-2} \frac{T^{1.75}}{P M_{O_2-N_2}^{0.5} \left( V_{O_2}^{1/3} + V_{N_2}^{1/3} \right)^2} \]  

(5.45)

where \( V_{O_2} \) and \( V_{N_2} \) are the Fuller et al. diffusion volumes of \( O_2 \) and \( N_2 \), respectively [216], and \( M_{O_2-N_2} \) is the mean molar mass of the mixture of gases calculated using the equation:

\[ M_{O_2-N_2} = \frac{2}{1/M_{O_2} + 1/M_{N_2}} \]  

(5.46)

where \( M_{O_2} \) and \( M_{N_2} \) are the molar mass of \( O_2 \) and \( N_2 \), respectively.

Knudsen diffusion coefficient \( D_{O_2,k} \) can be obtained using the equation [215]:

\[ D_{O_2,k} = \frac{d_p}{3} \left( \frac{8000 \, RT}{\pi M_{O_2}} \right)^{1/2} \]  

(5.47)

where \( d_p \) is the electrode average pore size. Table 5.2 presents the parameters used in equations (5.45) to (5.47) to determine the molecular and Knudsen diffusion coefficients of oxygen. The values \( M_i \) and \( V_i \) correspond to the species molar mass and Fuller et al. diffusion volume, respectively.

<table>
<thead>
<tr>
<th>Property</th>
<th>Oxygen</th>
<th>Nitrogen</th>
</tr>
</thead>
<tbody>
<tr>
<td>( M_i ) / g mol(^{-1})</td>
<td>31.999</td>
<td>28.014</td>
</tr>
<tr>
<td>( V_i )</td>
<td>16.3</td>
<td>18.5</td>
</tr>
</tbody>
</table>

Table 5.2. Molar mass and Fuller et al. diffusion volume of oxygen and nitrogen [216]

### 5.3.2.4. Ohmic Losses

The total ohmic losses of a fuel cell can be determined using equation (2.25). In the system studied the electrodes, electrolyte and current collectors are the principal components offering resistance to the current flowing through the Sn\(_{0.7}\)-SOFC.
The cathode and electrolyte conductivities exhibit an Arrhenius-type dependence with temperature [198]:

\[
\sigma_i = A \exp\left(\frac{B}{T}\right)
\]  

(5.48)

where \(\sigma_i\) is the conductivity of the component \(i\) (LSM/YSZ or LSM cathode layers, or YSZ electrolyte), \(A\) is a pre-exponential factor, \(B\) is the quotient between the activation energy of component \(i\) and the Boltzmann constant \((1.38 \times 10^{23} \text{ J K}^{-1})\), and \(T\) is the absolute temperature.

The resistivity of the molten tin anode can be calculated from [164]:

\[
\rho_{\text{Sn(l)}} = A + BT
\]  

(5.49)

where \(\rho_{\text{Sn(l)}}\) is the resistivity of molten tin (inverse of conductivity: \(\rho_{\text{Sn(l)}} = 1/\sigma_{\text{Sn(l)}}\), and the coefficients \(A\) and \(B\) are constants. If the molten tin at the anode | electrolyte interface is oxidized to form a dense layer of tin dioxide, its conductivity can be calculated from [206]:

\[
\sigma_{\text{SnO}_2} = A \exp\left(BT\right)
\]  

(5.50)

where \(\sigma_{\text{SnO}_2}\) is the conductivity of tin dioxide, \(A\) is a pre-exponential factor, and \(B\) is a constant. The thickness of the tin dioxide layer formed at the anode | electrolyte interface was considered to have a maximum value of ca. 1.0 mm, in accordance with the experimental post-mortem analysis of the pellet cell (see Chapter 6). The adverse effects of formation of a non-stoichiometric and non-dense oxide layer of \(\text{SnO}_2\) at the anode | electrolyte interface were omitted in this chapter since the experimental data used for determination of the kinetic parameters corresponded to a molten tin anode system at which no degradation of performance was detected (see Section 5.3.1). The perturbations that these phenomena could introduce into the fuel cell kinetics are discussed in Chapter 6.

For the platinum wire used as current collector at the cathode, the conductivity was determined from [217]:

\[
\sigma_{\text{Pt}} = AT^B
\]  

(5.51)

where \(\sigma_{\text{Pt}}\) is the conductivity of platinum, \(A\) is a pre-exponential coefficient, and \(B\) is a dimensionless exponent. The conductivity of the graphite rod used as current collector at the anode was considered to be temperature-invariant and equal to \(1.15 \times 10^5 \text{ S m}^{-1}\) [31, 218].
The value of the constants $A$ and $B$ used in equations (5.48) to (5.51) to determine the ohmic losses at all the Sn$_{10}$-SOFC components are listed in Table 5.3.

Table 5.3. Constants $A$ and $B$ used for calculation of ohmic losses in the Sn$_{10}$-SOFC components$^{[16]}$

<table>
<thead>
<tr>
<th>Fuel cell component</th>
<th>$A$</th>
<th>$B$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pure LSM</td>
<td>$1.23 \times 10^4$ S m$^{-1}$</td>
<td>-600 K</td>
</tr>
<tr>
<td>Pure YSZ</td>
<td>$3.40 \times 10^4$ S m$^{-1}$</td>
<td>-10 350 K</td>
</tr>
<tr>
<td>Molten tin, Sn</td>
<td>$33.98 \times 10^8$ Ω m</td>
<td>$2.63 \times 10^{-10}$ (Ω m) K$^{-1}$</td>
</tr>
<tr>
<td>Tin dioxide, SnO$_2$</td>
<td>$7.0 \times 10^{-5}$ S m$^{-1}$</td>
<td>$1.28 \times 10^{-2}$ K$^{-1}$</td>
</tr>
<tr>
<td>Platinum current collector</td>
<td>$2.0 \times 10^9$ (S m$^{-1}$) K$^{0.929}$</td>
<td>-0.929</td>
</tr>
</tbody>
</table>

5.3.2.5. Optimization Results: Kinetic Parameters for Activation and Concentration Polarization

A set of MATLAB codes were generated to determine the kinetic parameters $\alpha_{an}$, $j_{0,an}$ and $j_{bulk}$ related to the anodic activation and concentration polarizations.

The parameters fit was carried out in two steps: first considering only the charge transfer controlled zone of the anode activation polarization (Butler-Volmer equation (2.19)), and second introducing the mass transfer control term $C^{\text{bulk}}_{[\text{O}]_{\text{an}}} / C^{\text{react}}_{[\text{O}]_{\text{an}}}$ in the anode activation polarization (equation (5.21)). Following this methodology, a reliable initial guess of the parameters $\alpha_{an}$, $j_{0,an}$ and $j_{bulk}$ could be obtained using the equation for charge transfer controlled kinetics, which simplified the resolution of the optimization problem when mass transfer controlled kinetics were introduced.

Figure 5.9 shows a flow chart of the optimization routine used to estimate the parameters in both steps (charge and mass transfer controlled kinetics) when fitting the model to the experimental data presented in Section 5.3.1. In this routine, the constants and operating conditions presented in Table 5.4 were used to calculate the activation and concentration polarization components of the cell voltage $E$ based on the equations derived in Section 5.3.2.2 and Section 5.3.2.3, respectively.

$^{[16]}$ The conductivity of the cathode LSM/YSZ layer (50 wt% of each component as reported in Section 4.1.1) was determined by weighting the conductivities of pure LSM and YSZ by the molar fractions 0.37 and 0.63, respectively.
Figure 5.9. Optimization routine used to estimate the kinetic parameters associated to the anodic activation and concentration polarizations.
Table 5.4. Constants and operating conditions used for modelling of the Sn-
SOFCs operating in battery mode

<table>
<thead>
<tr>
<th>Constant / Operating condition</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$T$</td>
<td>1 173.15</td>
<td>K</td>
</tr>
<tr>
<td>$p_{O_2}$</td>
<td>0.2128</td>
<td>bar</td>
</tr>
<tr>
<td>$P$</td>
<td>1.01325</td>
<td>bar</td>
</tr>
<tr>
<td>$R$</td>
<td>8.3145</td>
<td>J (mol K)$^{-1}$</td>
</tr>
<tr>
<td>$F$</td>
<td>96 485</td>
<td>C (mol-eq.)$^{-1}$</td>
</tr>
</tbody>
</table>

Table 5.5 summarizes the oxygen molecular and Knudsen diffusion coefficients, exchange and limiting current densities calculated using the data and equations presented in Section 5.3.2.2 and Section 5.3.2.3 for the LSM-YSZ cathode.

Table 5.5. Diffusion coefficients, exchange current density and limiting current density of the cermet LSM/YSZ cathode

<table>
<thead>
<tr>
<th>Diffusion coefficient / Kinetic parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D_{O_2-N_2}$</td>
<td>$2.26 \times 10^{-4}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_{O_2,k}$</td>
<td>$1.50 \times 10^{-3}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$D_{O_2,eff}$</td>
<td>$9.80 \times 10^{-6}$</td>
<td>m$^2$ s$^{-1}$</td>
</tr>
<tr>
<td>$\dot{j}_{0,ca}$</td>
<td>2 152</td>
<td>A m$^{-2}$</td>
</tr>
<tr>
<td>$\dot{j}_{1,ca}$</td>
<td>91 703</td>
<td>A m$^{-2}$</td>
</tr>
</tbody>
</table>

Table 5.6 presents the electrical resistances of each component of the molten tin anode solid oxide fuel cell derived from equations (5.48) to (5.51). The total cell resistance presented in Table 5.6 is ca. 0.51 Ω lower than the experimental cell resistance measured using EIS (see Figure 5.8(a)). It is highly probable that this difference is due to the contact losses produced at the interface between the LSM layer of the cathode and the platinum mesh used as current collector, which was not optimally attached to the electrode via platinum ink (see Figure 4.1(b)). Considering this non-negligible error, the anodic kinetic parameters were fitted replacing the calculated cell resistance by the experimental value $R_{total} = 1.98$ Ω, resulting in the parameters presented in Table 5.7.
Table 5.6. Electrical resistances of the Sn(l)-SOFC components

<table>
<thead>
<tr>
<th>Component</th>
<th>Resistance / Ω</th>
</tr>
</thead>
<tbody>
<tr>
<td>LSM/YSZ-LSM cathode</td>
<td>1.18 x 10⁻⁴</td>
</tr>
<tr>
<td>YSZ electrolyte</td>
<td>0.56</td>
</tr>
<tr>
<td>Molten tin anode, Sn(l)</td>
<td>5.28 x 10⁻⁶</td>
</tr>
<tr>
<td>Tin dioxide deposit, SnO₂(α)</td>
<td>8.80 x 10⁻³</td>
</tr>
<tr>
<td>Platinum current collector, Pt</td>
<td>0.54</td>
</tr>
<tr>
<td>Graphite rod current collector, C</td>
<td>0.36</td>
</tr>
<tr>
<td><strong>Total cell resistance, R_{total}</strong></td>
<td><strong>1.47</strong></td>
</tr>
</tbody>
</table>

Table 5.7. Anodic kinetic parameters fitted using the optimization routine described in Figure 5.9

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>α_{an}</td>
<td>0.67</td>
<td>---</td>
</tr>
<tr>
<td>j₀_{an}</td>
<td>353</td>
<td>A m⁻²</td>
</tr>
<tr>
<td>j_{bulk}</td>
<td>1 419</td>
<td>A m⁻²</td>
</tr>
<tr>
<td>j₁_{an}</td>
<td>3 273</td>
<td>A m⁻²</td>
</tr>
</tbody>
</table>

The anode limiting current density was calculated using equation (5.35) considering a diffusion layer thickness δ_{an} = 50 μm. This value corresponds, according to the results presented and discussed in Section 6.1.1, to a critical diffusion layer thickness below which the oxygen concentration at the anode | electrolyte interface can be maintained below saturation (C_{sat}[O]_{an} ~ 183 mol m⁻³) when the fuel cell operates around its maximum power density. The oxygen concentration at the bulk of the anode under these conditions resulted to be approximately 30% of the saturation concentration, and was calculated replacing in equation (5.33) the chosen value of the diffusion layer thickness and the oxygen diffusion coefficient D_{[O]_{an}} = 6.63 x 10⁻⁹ m² s⁻¹ obtained from equation (5.34). The values of the diffusion coefficient and diffusion layer thickness at the molten tin were very similar to the values associated to a quiescent aqueous system [219-222], which is not surprising considering that the viscosity of molten tin at 900 °C is very similar to the viscosity of water.
under standard ambient temperature and pressure conditions [164, 219]. Therefore, it can be considered that the hydrodynamic properties of the molten tin anode are favourable for stirring of the melt using gas bubbles with the objective of contacting the oxides formed at the anode | electrolyte interface with the activated carbon particles used as reducing agent (see Chapter 8 for more details about this approach).

Figure 5.10 presents the experimental and modelled polarization curves. The total relative error with respect to the experimental data was ca. 5.54%, which was considered to be acceptable. Figure 5.11 shows the activation and concentration polarization curves obtained using the mathematical model described previously in this section; the kinetic processes at the anode were predicted to be more sluggish than at the cathode as it was expected considering that the anodic processes were controlled by mass transport. In fact, the limiting current density at the cathode was almost 28 times larger than the anodic value (see Table 5.5 and Table 5.7), resulting in a cathodic concentration polarization almost negligible compared to the value at the anode. In addition, the exchange current density at the cathode was almost an order of magnitude greater than the corresponding value at the anode (see Table 5.5 and Table 5.7), which resulted in a cathodic process under kinetic control with low activation overpotentials.

In view of the relative fast cathodic kinetics and considering the low limiting current density at the molten tin anode, the chemical processes occurring in the fuel cell studied would have been controlled by the oxidation reactions at the anode | electrolyte interface.

![Experimental and modelled polarization curves obtained for a Sn(1)|SOFC operating at 900 °C](image)

**Figure 5.10.** Experimental and modelled polarization curves obtained for a Sn(1)|SOFC operating at 900 °C
At this point it is interesting to remark the results reported by CellTech Power Inc. using a one end-closed tubular Sn\(_{10}\)-SOFC for oxidation of different carbonaceous fuels and hydrogen [137, 163, 223]. These authors obtained a power density of ca. 1 500 W m\(^{-2}\), one order of magnitude higher than that obtained in this project (see Figure 5.7), using a ca. 200 \(\mu\)m thick YSZ electrolyte and a molten tin anode of ca. 200 \(\mu\)m thickness contained between the electrolyte tube and a porous ceramic separator of 2.0 mm thickness between the anode and the fuel (see Section 3.3.2). The better performance of the Sn\(_{10}\)-SOFC developed by CellTech Power Inc. was due to the lower electrical resistances at the fuel cell components and the improved kinetics at the anode, which was enhanced via a continuous reduction of the tin dioxide generated at the anode | electrolyte interface. The anodic exchange current density predicted for this system was ca. 1 200 A m\(^{-2}\) when operating with hydrogen [223], resulting in enhanced electrode kinetics compared with the system studied in this chapter operating in battery mode, which presented an exchange current density of ca. 353 A m\(^{-2}\) (see Table 5.7).

The next section reports the beneficial effects of decreasing the YSZ electrolyte thickness and the contact losses at the current collectors on the predicted performance of the Sn\(_{10}\)-SOFC. The analysis of the enhanced anodic kinetics when a thin molten tin layer is used in the presence of a strong reducing agent (CellTech Power Inc. approach) is reported in Chapter 8.
5.3.3. Optimization and Comparison of the Sn\textsubscript{(l)}-SOFC Performance with a Conventional SOFC

The anode kinetic parameters reported in Table 5.7 were used to model the performance of an optimized Sn\textsubscript{(l)}-SOFC with lower ohmic losses than the electrochemical cell used during experimental measurements. Firstly, the total ohmic losses were calculated considering that the resistance offered to current flow by the current collectors was negligible compared to the resistance of the electrodes and the electrolyte. Secondly, it was assumed that there were no contact losses between the electrodes and the current collectors in the system studied.

Considering these two simplifications (case 1), the total fuel cell resistance $R_{\text{total}}$ is:

$$R_{\text{total}} = R_{\text{cathode}} + R_{\text{electrolyte}} + R_{\text{anode}}$$

(5.52)

where $R_{\text{cathode}}$ is the resistance of the LSM-YSZ and LSM layers of the cathode, $R_{\text{electrolyte}}$ is the resistance of the YSZ electrolyte, and $R_{\text{anode}}$ is the resistance of the molten tin anode and the (dense) tin dioxide layer. Considering the data presented in Table 5.6, the total fuel cell resistance was estimated as ca. 0.57 $\Omega$. The activation and concentration polarizations were determined using the kinetic models described in Section 5.3.2.2 and Section 5.3.2.3, respectively, for which results are shown in Figure 5.11.

If additionally to the negligible ohmic losses at the current collectors the YSZ pellet thickness is decreased from 2.0 mm to 200 $\mu$m (case 2), the electrolyte ohmic resistance $R_{\text{electrolyte}}$ is reduced from 0.56 $\Omega$ to ca. 56.5 m$\Omega$, and therefore the total fuel cell resistance is reduced to ca. 65.3 m$\Omega$. Figure 5.12 shows the effects of current density on the Sn\textsubscript{(l)}-SOFC ohmic potential losses for negligible current collector resistances (case 1) and for negligible current collector resistances plus a thinner electrolyte (case 2).

These results predict that the ohmic losses can be decreased almost 9 times by thinning the 2 mm thick YSZ electrolyte to 200 $\mu$m. However, considering that the column of molten tin used as the anode in the Sn\textsubscript{(l)}-SOFC fabricated for this thesis was 5.0 mm high and weighed ca. 17 g, the thinning of the YSZ pellet is not possible without fracture of it (this corresponds to an experimental observation). Therefore, the use of a thinner layer of molten tin seems to be the first step to improve the kinetics at the molten tin anode, provided that the tin dioxide formed at the anode | electrolyte interface is reduced continuously to maintain
the fuel cell operational. This was the case of the system developed by CellTech Power Inc. [137, 163], which in addition uses a ceramic porous separator to hold the thin molten tin anode layer tightly against the YSZ electrolyte. This is not an arbitrary aspect of their design, since it is related with the low wettability that molten metals (and particularly tin) present when they are in contact with a ceramic surface [161, 224], and therefore the porous separator helps to avoid a poor contact between the anode and the electrolyte. In the case of the Sn(l) SOFC used in this research project, the absence of a secondary structure acting as a plug over the molten tin column (see Gorte et al. [160, 162] approach in Section 3.3.2) explains the use of a thick layer of metal anode so its pressure improved the anode | electrolyte contact.

![Figure 5.12](image)

**Figure 5.12.** Ohmic potential losses of a Sn(l)-SOFC for the cases: (1) negligible ohmic losses at the current collectors, and (2) negligible ohmic losses at the current collectors and 200 µm thickness electrolyte

Figure 5.13 shows the predicted effects of current density on cell voltages and power densities for each case study. When only negligible ohmic losses at the current collectors were considered, a maximum power density of ca. 446 W m\(^{-2}\) was predicted at a cell potential of ca. 0.41 V and current density of ca. 1 082 A m\(^{-2}\). If the ohmic potential losses are additionally decreased by decreasing the electrolyte thickness to 200 µm, the maximum power density is increased to 1 477 W m\(^{-2}\) at a cell voltage of ca. 0.45 V and current density of ca. 3 273 A m\(^{-2}\), corresponding to the anode limiting current density.

The maximum power density of the experimental Sn(l)-SOFC was predicted to increase by a factor of almost nine if the electrolyte thickness could have been decreased to 200 µm.
However, as stated previously, an YSZ membrane of this thickness would have failed mechanically in the pellet cell design used for this thesis and therefore an improved design with a thinner molten tin anode has to be developed in order to improve the energy output of the fuel cell.

![Figure 5.13. Predicted effects of current density on cell potential differences and power densities for Sn(l)-SOFC for the cases: (1) negligible ohmic potential losses at the current collectors, and (2) negligible ohmic potential losses at the current collectors and 200 µm thick electrolyte](image)

To conclude this section, a conventional SOFC was modelled to compare its performance with the Sn(l)-SOFC studied. The structural characteristics used in this case were presented in Table 5.1 for a SOFC using LSM-YSZ/LSM cathode and YSZ electrolyte identical to those in the fuel cell developed in this research project, but replacing the molten tin anode with a porous Ni-YSZ cermet operating in a H₂-H₂O(g) atmosphere with a constant humidity of 80%. At the cathode, the oxygen atmosphere was maintained at 0.21 bar and the ohmic losses at the current collectors were considered negligible in order to compare exclusively the kinetics of the fuel cells.

The global reaction occurring in the SOFC studied corresponds to the combustion of hydrogen represented by equation (5.10), thus the open circuit voltage (OCV) can be determined using equation (2.17). If an operating temperature of 900 °C is considered, the OCV calculated for this system is 0.82 V.

From references [209, 210], a charge transfer coefficient $\alpha_{\text{an}} = 0.5$ was obtained for a porous Ni-YSZ anode. Considering that the reaction electron stoichiometry $\nu_e$ is equal to 2,
the anodic activation overpotential was calculated using equation (5.23) and the exchange current density:

\[ j_{0,an} = 5.5 \times 10^8 \left( \frac{p_{H_2}^{bulk}}{P} \right) \left( \frac{p_{H_2,O}^{bulk}}{P} \right) \exp\left( \frac{-100000}{RT} \right) \]  

(5.53)

where \( j_{0,an} \) is the exchange current density of the Ni-YSZ cermet, \( p_{H_2}^{bulk} \) and \( p_{H_2,O}^{bulk} \) are the hydrogen and water gas partial pressures in the bulk, respectively, and \( P \) is the total pressure.

The anodic concentration polarization was determined using the same approach presented in Section 5.3.2.3 for the porous LSM-YSZ cathode. The equation obtained in this case is:

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

(5.54)

where \( \eta_{an}^{conc} \) is the anodic concentration polarization, \( j \) is the cell current density, and \( j_{H_2} \) and \( j_{H_2,O} \) are defined by the equations:

\[ j_{H_2,O} = \frac{2FP_{H_2,O}^{bulk}D_{H_2,O}^{eff}}{RT\delta_{an}} \]  

(5.55)

\[ j_{H_2} = \frac{2FP_{H_2}^{bulk}D_{H_2}^{eff}}{RT\delta_{an}} \]  

(5.56)

where \( D_{H_2}^{eff} \) and \( D_{H_2,O}^{eff} \) are the hydrogen and water gas effective diffusion coefficients, and \( \delta_{an} \) is the thickness of the anode. Considering that \( j_{H_2} \) is the maximum value that the current density \( j \) can reach before the logarithmic term in equation (5.54) becomes infinite, it corresponds to the limiting current of the SOFC (basically, it means that the maximum difference of \( H_2 \) concentration between the anode | electrolyte interface and the bulk of the anode is reached and, consequently, the concentration polarization becomes dominant).

The diffusion coefficients, exchange current density and limiting current density obtained for the anodic kinetics of a conventional SOFC are presented in Table 5.8. As can be seen,
the exchange and limiting current densities, \( j_{0,an} \) and \( j_{H_2} \), obtained for the Ni-YSZ cermet anode are higher than the values of exchange and limiting current densities calculated for the LSM-YSZ cermet electrode (see Table 5.5). This result suggests that the cell kinetics in the case of a conventional SOFC are controlled by the processes occurring at the cathode, contrarily to what is observed in a Sn\(_\text{(l)}\)-SOFC in which the oxidation reactions control the kinetics.

The resistance offered by the Ni-YSZ anode to the current flow in the fuel cell was determined using equation (5.48) with coefficients \( A = 3.35 \times 10^4 \text{ S m}^{-1} \) and \( B = 1.392 \text{ K} \) \([198]\). The resultant resistance \( R_{\text{mode}} = 1.85 \times 10^{-6} \Omega \) was replaced in equation (5.52) to determine a total cell resistance of ca. 0.56 \( \Omega \) for an electrolyte thickness of 2 mm and ca. 56.5 m\( \Omega \) for an electrolyte thickness of 200 \( \mu \text{m} \).

Table 5.8. Diffusion coefficients for \( \text{H}_2\text{-H}_2\text{O} \) binary system, exchange and limiting current densities of a Ni-YSZ anode

<table>
<thead>
<tr>
<th>Diffusion coefficient / Kinetic parameter</th>
<th>Value</th>
<th>Units</th>
</tr>
</thead>
<tbody>
<tr>
<td>( D_{\text{H}_2\text{-H}_2\text{O}} )</td>
<td>( 9.98 \times 10^{-4} )</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>( D_{k\text{H}_2} )</td>
<td>( 1.20 \times 10^{-3} )</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>( D_{k\text{H}_2\text{O}} )</td>
<td>( 3.91 \times 10^{-4} )</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>( D_{\text{H}_2\text{eff}} )</td>
<td>( 8.99 \times 10^{-5} )</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>( D_{\text{H}_2\text{Oeff}} )</td>
<td>( 4.69 \times 10^{-5} )</td>
<td>m(^2) s(^{-1})</td>
</tr>
<tr>
<td>( j_{0,an} )</td>
<td>3 105</td>
<td>A m(^{-2})</td>
</tr>
<tr>
<td>( j_{H_2} )</td>
<td>( 3.60 \times 10^5 )</td>
<td>A m(^{-2})</td>
</tr>
<tr>
<td>( j_{H_2\text{O}} )</td>
<td>( 7.51 \times 10^5 )</td>
<td>A m(^{-2})</td>
</tr>
</tbody>
</table>

Figure 5.14 shows the predicted effects of current density on cell potential differences and power densities for the conventional SOFC modelled using the mathematical approach described previously in this section for both electrolyte thicknesses. In the case of a 2.0 mm thick electrolyte, the maximum power density was predicted to be ca. 508 W m\(^{-2}\) at a current density of 1 250 A m\(^{-2}\) and a cell voltage of ca. 0.41 V. This result is very similar to that obtained previously for a Sn\(_\text{(l)}\)-SOFC (see Figure 5.13), which is reasonable considering that
in both cases the ohmic potential losses in the electrolyte were high enough to reach the OCV at low current densities and govern the cell potential (see equation (2.18)). When a 200 µm electrolyte was introduced, the maximum power density predicted was ca. 2 487 W m⁻² at a current density of ca. 6 850 A m⁻² and a cell voltage of ca. 0.36 V. This value is approximately 1 000 W m⁻² higher than that obtained for the same case in a Sn(ℓ)-SOFC, which reveals the adverse effects that the mass transfer controlled kinetics can have on the performance of the fuel cell studied. In fact, as can be seen in Figure 5.14, in case 2 the limiting current density of the conventional SOFC was not reached even when the polarization and ohmic losses equalize the OCV, while in the case of the Sn(ℓ)-SOFC the current density at the maximum power density corresponded to the limiting current density of the process (see Figure 5.13).

![Figure 5.14. Predicted effects of current density on cell potential differences and power densities of a conventional SOFC for the cases: (1) electrolyte thickness: 2.0 mm, and (2) electrolyte thickness: 200 µm (in both cases the ohmic losses at the current collectors were considered negligible)](image)

The activation and concentration polarizations at the LSM-YSZ cathode and the Ni-YSZ anode are presented in Figure 5.15(a) and Figure 5.15(b), respectively. As suggested previously in this section, the reduction kinetics at the cathode were more sluggish than the oxidation kinetics at the anode since the exchange and limiting current densities at the cathode are lower (see Table 5.5 and Table 5.8). This is an important aspect to be emphasized since it demonstrates that a conventional SOFC has an anode material offering better performance than the molten tin anode used in this research project when operating with hydrogen as fuel (see Chapter 8 for further information of a Sn(ℓ)-SOFC operating in fuel
cell mode). Nevertheless, the Ni-YSZ cermet is not stable when an (impure) carbonaceous fuel is used instead of hydrogen since its performance is affected by sulphur poisoning and carbon deposition \[128\]. Therefore, molten tin is a promising alternative considering its high stability under these conditions.

![Graph](image)

**Figure 5.15.** (a) Activation overpotential and (b) concentration overpotential at the LSM-YSZ cathode and the Ni-YSZ anode of a conventional SOFC.

### 5.4. LST and LCST Current Collectors

LST and LCST powders were produced following the synthesis method described in Section 4.1.4 (standard Pechini route or polimerizable complex method). The resulting materials were ground at 500 RPM for 1 hour in a Restch PM-100 planetary ball mill using zirconia (ZrO$_2$) balls of 2 mm diameter as the grinding agent and isopropanol as the solvent. The objective of this procedure was comparing the microstructure and electrical properties of the LST and LCST pellets obtained pressing rough (non-ground) and ground powders in a stainless steel die at 5.0 tonnes during 1 minute. The chemical composition of these structures was studied using the X-ray diffractograms presented in Figure 5.16(a) and Figure 5.16(b).

The LST and LCST structures produced could not be differentiated based on the XRD and EDX analyses, since both materials present the same X-ray pattern and have a very similar composition \(La_{0.3}Sr_{0.7}TiO_3\) and \(La_{0.2}Ce_{0.1}Sr_{0.7}TiO_3\), as reported previously \[189\]. In addition, lanthanum and cerium are next to each other in the same group of the periodic table (lanthanides) which indicates that they have similar chemical and physical properties. In view of that, the resulting pellets were identified by simple observation of their colour which differed as can be seen in Figure 5.17.
Figure 5.16. (a) X-ray diffractograms (XRDs) of LST and LCST pellets produced using rough and ground powders, (b) Impurities observed in the LST pellets studied

Figure 5.17. Non-reduced and reduced pellets produced using (a) LST powders, and (b) LCST powders
Darker LST and LCST pellets were obtained when ground powders were used in their fabrication. The change in colour is attributed to a reduction phenomenon occurring during the sintering process of the perovskites, due to the presence of residual organic compounds (isopropanol from the ball mill and lubricant from the stainless steel die) captured in the raw materials. This darkening process has been observed previously \[189, 225, 226\] and is related to the reduction of titanium dioxide (\(TiO_2\)) or highly oxidized residual compounds such as the lamellar family \(La_{4}Sr_{n-4}Ti_{n}O_{3n+2}\). Figure 5.16(b) shows that some of these residual compounds could be observed in the structure of the LST pellets produced with rough powders, while almost all of them were removed when ground materials were used.

The conductivities of the LST and LCST perovskites were measured using the 4-point probe method, described in Section 4.2.1, at 4 different operating temperatures: 700, 800, 900 and 1000 °C. Figure 5.18(a) shows that the conductivity increased exponentially with temperature when rough powders were used to produce the pellets, while the use of reduced raw material resulted in conductivities that increased linearly with temperature, as shown in Figure 5.18(b). This result is related to the mixed semiconductor-metallic behaviour of the reduced ceramics produced. The conductivities of semiconductors increase exponentially with temperature, while the conductivities of metals decrease with temperature. Therefore, the LST and LCST pellets produced using rough powders had the semiconductor behaviour determined by Gorte et al. \[227\] when lightly-reduced LST-YSZ composites were used, while the perovskites produced using ground powders presented an intermediate behaviour between the lightly-reduced materials and the highly-reduced \(La_2Sr_4Ti_6O_{19-\delta}\) studied by Irvine et al. \[226\]. Unfortunately for this research project, it was not possible to maintain the anode current collector working under highly-reducing operating conditions (oxygen was dissolved continuously into the molten tin) and consequently its conductivity could not be increased using the method proposed by these authors.

In addition to the reduction process, the microstructure also affected the conductivity of the perovskites. Figure 5.19 shows the SEM micrographs obtained for the non-reduced and reduced LST and LCST pellets produced. The grinding process favoured the densification of the ceramics, reducing the porosity and making their structures more homogeneous. This affected the conductivity of the perovskites positively, since grain boundary resistances are lower and the charged species can be transported smoothly from the bulk \[227\]. However, the higher conductivity of LCST with respect to LST was not related with its porosity. As can be seen from Figure 5.19(b) and Figure 5.19(d), the former semiconductor was less dense than the latter. Therefore, its improved electrical properties were related with the
replacement of $\text{La}^{+3}$ for $\text{Ce}^{+4}$ which introduces an additional bonding electron to the crystalline structure of the semiconductor, resulting in an increased electrical conductivity of $\text{LCST}$ (n-type doping).

![Figure 5.18. Conductivity measured using a 4-point probe method for the (a) non-reduced and (b) reduced $\text{LST}$ and $\text{LCST}$ pellets](image)

The performance of a $\text{Sn}_0$-SOFC was studied based on the mathematical model presented in Section 5.3, replacing the graphite rod with the $\text{LST}$ and $\text{LCST}$ current collectors described in Section 4.1.4. The resistivities of these alternative materials were calculated using the data presented in Figure 5.18(b) and Table 5.6 for the $\text{LST}$ and $\text{LCST}$ pellets operating at 900 °C and a platinum wire of 300 mm length, respectively. Based on
this information, a resistance of ca. 14.9 mΩ and ca. 4.90 mΩ was obtained for the LST and LCST pellets, which added to the high resistance (0.54 Ω) of the platinum wire used to connect them to an external circuit result in a total resistance between 0.55 and 0.56 Ω at the anodic current collector. This value was ca. 0.20 Ω higher than the resistance of the replaced graphite rod, which had a conductivity 4 orders of magnitude higher than the conductivity of LST and LCST; hence, the maximum power density of the Sn(l)-SOFC when using these alternative current collectors was lower as evident from Figure 5.20. It is important to notice that the results presented here do not include the contact losses existing at the interface between the current collectors and the electrodes, and between the LST/LCST pellet and the platinum wire. In fact, when experimental measurements were done using these alternative current collectors, a cell resistance of ca. 4.50 Ω was measured, which was ca. 2.80 Ω higher than the modelled value. For this reason, in view of the poor electrical connections obtained experimentally between the LST/LCST pellets and the platinum wire, the modelling results are presented instead of the experimental ones in order to illustrate properly the effect of each current collector on the performance of the experimental Sn(l)-SOFC.

Figure 5.19. SEM micrographs of (a) LST non-reduced, (b) LST reduced, (c) LCST non-reduced, and (d) LCST reduced
Figure 5.20. Effect of current density on cell potential differences and power densities of a Sn$_{(l)}$-SOFC operating with LST/LCST and graphite current collectors at the anode

It is clear from the results presented in Section 5.3 and this section that improvements in the electrical connections between the fuel cell and the outside of the furnace are necessary in order to enhance the performance of the electrochemical cell. In the case of the LST/LCST current collectors, inclusion of less resistive dopants such as iron or chromium could be an alternative to enhance their conductivity in comparison with graphite. Nonetheless, finding solutions to the poor electrical contacts and the extension of the current collectors (excessive length) is a matter of higher priority in order to reduce the cell ohmic potential losses.
5.5. Chapter Summary and Conclusions

The thermodynamics and kinetics of a Sn(\textit{l})-SOFC operating at 900 °C were studied when flow rates of 60 mL min\(^{-1}\) of air and 30 mL min\(^{-1}\) of helium were being fed continuously to the LSM-YSZ cathode and molten tin anode, respectively. Activated carbon particles were present at the surface of the 5.0 mm thick molten metal layer to protect it from undesired oxidation by atmospheric oxygen.

The open circuit voltages (OCVs) measured at different temperatures were compared with the theoretical Nernst potential values determined using the thermodynamic data of the reactive species. From this analysis, it was determined that the most likely cell reaction taking place at the Sn(\textit{l})-SOFC corresponds to oxidation of the molten tin anode via oxide ions being pumped from the cathode through the electrolyte. As a consequence of that, a non-conductive tin dioxide layer (non-stoichiometric and non-dense SnO\(_2\)) was accumulated at the anode | electrolyte interface, resulting in blockage of the oxide ions transport and decay of the fuel cell performance. Therefore, depletion of the excess oxygen at the anode | electrolyte interface is necessary in order to maintain the Sn(\textit{l})-SOFC operational in the longer term. This can be achieved, for example, by feeding continuously a strong reducing agent such as hydrogen into the system and stirring the melt to promote the contact between the tin dioxide particles and the fuel (see Chapter 8).

Cathode kinetic parameters were calculated based on data obtained from the literature and compared with the anode kinetic parameters determined using an optimization routine for fitting of the experimental polarization curves to a mathematical model. An exchange current density of 353 A m\(^{-2}\) and a limiting current density of 3 273 A m\(^{-2}\) were obtained for the anode, which are one order of magnitude lower than those for the cathode. This result confirms that mass transport of oxygen away from the anode | electrolyte interface controlled the Sn(\textit{l})-SOFC performance. Total ohmic losses of ca. 1.98 Ω were measured experimentally, whereas a theoretical value of ca. 1.47 Ω was predicted; the difference was attributed to contact losses at the cathode | cathode current collector interface and reactivity between the molten tin and the graphite rod used as anode current collector (see Chapter 6).

In order to determine the effects of the current collectors and electrolyte conductivities on the fuel cell performance, the behaviour of the Sn(\textit{l})-SOFC was modelled considering negligible ohmic losses at the current collectors and an electrolyte thickness decreased from 2 mm to 200 µm. Under these conditions, a maximum power density of 1 477 W m\(^{-2}\) was predicted at a cell voltage of ca. 0.45 V and a current density of ca. 3 273 A m\(^{-2}\), which
resulted to be almost nine times higher than the experimental value obtained (159 W m\(^{-2}\)) but almost 1 000 W m\(^{-2}\) lower than the maximum power density produced by a conventional SOFC using a 100 µm thick Ni-YSZ cermet anode instead of the molten tin. However, the use of a 200 µm thick electrolyte in the Sn\(_{(l)}\)-SOFC design used for this thesis was impracticable due to the weight of the molten tin anode on top of the pellet cell (17 g), which would have resulted in mechanical failure of the YSZ disc. Therefore, in order to improve the performance of the fuel cell without affecting its physical stability, a thinner layer of molten tin over the YSZ electrolyte could be used, as suggested by CellTech Power Inc., provided that a plug-type structure is introduced into the anode chamber in order to maintain the electronic contact between the molten metal and the electrolyte (due to the low wettability of YSZ by metals).

Additional improvements in the kinetics of the Sn\(_{(l)}\)-SOFC could be introduced if a flowing molten tin anode, such that proposed by Doraswami [182] (see Figure 3.25 and Figure 3.26(a)), is used instead the stagnant electrode studied in this thesis. Unfortunately, due to technical issues, analysis of the kinetics in this type of system was not possible during this research project and remains as something that could be considered for future work.

_LST_ and _LCST_ perovskites were synthesized and analysed as potential alternative anode current collector materials. Two different pellet-type structures were produced using rough (non-ground) and ground powders. It was observed that the presence of residual organic compounds (used during the milling and pressing processes) in the ceramic products affected positively the electronic conductivity of the resulting perovskites. This phenomenon was attributed to reduction of highly oxidized residual compounds such as TiO\(_2\) and the lamellar family \(La_{4} Sr_{n-4} Ti_{n} O_{3n+2}\). In addition, replacement of La\(^{+3}\) for Ce\(^{+4}\) introduces an additional bonding electron to the crystalline structure of the semiconductor, resulting in an increased electrical conductivity of _LCST_.

Finally, modelling of Sn\(_{(l)}\)-SOFCs with _LST_ and _LCST_ current collectors predicted their performances would be lower than that using graphite due to their electronic conductivities being ca. 4 orders of magnitude lower. Further research is suggested to improve the conductivity of these materials using, for example, metallic dopants such as iron and chromium.
6. Stability Analysis of Sn(l)-SOFCs Operating in Battery Mode

This chapter presents the stability analysis of the longer term performance of a Sn(l)-SOFC operating at 900 °C in battery mode. The experimental results studied include: (1) current density transients produced when a cell potential of 0.42 V was applied to the system (maximum power density output according to Chapter 5); (2) post-mortem analysis of the fuel cell components (anode, electrolyte and anode current collector) and by-products (tin dioxide deposits); and (3) the impedance response of the Sn(l)-SOFC when operating under non-equilibrium conditions.

Based on the current density transients obtained when a cell potential of 0.42 V was applied to the Sn(l)-SOFC during 3 h, the total charge transferred through the system before reaching oxygen saturation in the anode was calculated using the trapezoidal rule for numerical integration. This result was converted into concentration of oxygen in the molten tin using Faraday's equation and compared with the value of the saturation concentration obtained using the thermodynamic models presented in Section 5.2. In addition, the reaction mechanisms at the liquid metal anode were inferred from the evolution of the cell current density output as a function of time.

Post-mortem analysis of the Sn(l)-SOFC electrolyte, anode and anode current collector was done using X-ray techniques to determine the effects of tin dioxide formation and growth in their microstructures. SEM micrographs allowed the structural analysis of the surfaces in contact with this by-product during fuel cell operation, while EDX and XRD diagrams helped in the chemical characterization of the tin dioxide deposits. Mechanisms of the metal oxide formation and growth at the anode | electrolyte interface are proposed based on these results.

Finally, the impedance plots obtained when voltages/potentials different to the OCV/OCP were applied to the whole Sn(l)-SOFC, the anode | electrolyte arrangement and the cathode, allowed identifying the phenomena controlling the kinetics at each fuel cell component. Fitting of these impedance plots using equivalent circuits helped to understand better the mechanisms of reactions taking place at the electrodes of the Sn(l)-SOFC.
6.1. Stability Analysis of Sn\(_{(0)}\)-SOFC Components and its Performance

In Chapter 5, thermodynamics and kinetics of the Sn\(_{(0)}\)-SOFC operating in battery mode were studied based on the experimental measurements obtained using cyclic voltammetry and electrochemical impedance spectroscopy. These results offered a good understanding of the steady state response of the fuel cell when a set of potential steps (CV) or an alternating current (EIS) was applied to the system.

In this section the results obtained and discussed in Chapter 5 are used to study the longer term (non-steady state) performance of the Sn\(_{(0)}\)-SOFC based on chronoamperometric measurements and post-mortem analysis of the fuel cell components and by-products using X-ray techniques (SEM, EDX and XRD).

6.1.1. Longer Term Performance of Sn\(_{(0)}\)-SOFCs operating at Maximum Power Density

Current density transients were obtained using a Sn\(_{(0)}\)-SOFC operating at its maximum power density in battery mode. The objective of these measurements was the analysis of the longer term stability of the fuel cell performance when the highest amount of electrical energy was being produced.

In accordance with the polarization curves presented in Section 5.3.1, which were produced using an analogous Sn\(_{(0)}\)-SOFC, the maximum power density was obtained when a cell potential of ca. 0.42 V was applied to the system. At this cell voltage a current density of ca. 380 A m\(^{-2}\) was observed, which is in agreement with the starting current density value shown in Figure 6.1 for the current density response of a Sn\(_{(0)}\)-SOFC operating at its maximum power density. As can be seen in Figure 6.1, a decay of the current density took place during the initial ca. 50 min, which could be associated with the period in which oxygen is being dissolved into the molten tin anode in the form of \(\{\text{SnO}\}\) until saturation is reached (in accordance with reaction (5.18)).

The total amount of charge transported through the electrochemical system during this initial period was determined based on the area under the curve in Figure 6.1 between the initial time (0 min) and the time at which saturation is reached (51.28 min). The corresponding integral was calculated using the trapezoidal rule:

\[
\int_{a}^{b} f(x) \, dx \approx \frac{h}{2} \sum_{k=1}^{N} \left( f(x_{k+1}) + f(x_{k}) \right)
\]  

(6.1)
where \( f \) corresponds to the current as a function of time, \( h \) is the grid spacing (10 s in this case), \( a \) and \( b \) are the initial and final times, respectively, and \( N \) is the number of grid points. A schematic of the method used for calculation of this value using equation (6.1) is presented in Figure 6.2.

**Figure 6.1.** Current and charge density transient obtained at a constant cell voltage of 0.42 V, value at which the Sn\(_{(l)}\)-SOFC studied was operating at its maximum power density as stated in Chapter 5

**Figure 6.2.** Schematic of the method used for calculation of the charge transferred during dissolution of atomic oxygen in the molten tin anode
A total charge of ca. 412.18 C was obtained between 0 and 51.28 min, which was converted into moles of dissolved atomic oxygen, \( n_{\text{[O]_{Sn}}} \), using Faraday’s equation:

\[
n_{\text{[O]_{Sn}}} = \frac{Q_e}{\nu_e F}
\]

(6.2)

where \( Q_e \) is the total charge transferred and \( \nu_e \) is the reaction electron stoichiometry per mole of atomic oxygen (2 electrons in accordance with reaction (5.18)). The concentration of atomic oxygen, \( C_{\text{[O]_{Sn}}} \), was determined using equation (6.2) and the volume of molten tin at the anode, \( V_{\text{Sn}} \):

\[
C_{\text{[O]_{Sn}}} = \frac{n_{\text{[O]_{Sn}}}}{V_{\text{Sn}}}
\]

(6.3)

Considering that the inner diameter of the alumina tube containing the molten tin anode was 2.5 cm and the height of the liquid metal column was 0.5 cm, the volume \( V_{\text{Sn}} \) calculated was 2.45 cm\(^3\). As a result, an oxygen concentration of ca. 0.87 M was determined, which is ca. 0.69 M higher than the theoretical saturation concentration calculated using equation (5.7). This result is in well agreement with the discussion presented in Section 5.2, where it was stated that the atomic oxygen dissolved into the liquid metal anode (reaction (5.18)) tends to form tin dioxide in the bulk of the electrode (reaction (5.19)) even before saturation conditions are reached. Therefore, according to this result, before saturation of oxygen was reached at the anode, an amount of ca. 27 mg of oxygen had reacted with 100 mg of the molten tin anode (approximately 0.59% of the total amount of tin) to form ca. 127 mg of tin dioxide\(^{[17]}\).

The rapid decay of current density shown in Figure 6.1 during the first minute could be related with an initial ‘transient state’ during which accumulation of oxygen at the interface occurred (Figure 6.3(a)). Following this first stage, a smoother decay was evident until ca. 12 minutes which could be associated with the establishment of a ‘steady state’ diffusion process in which continuous removal of atomic oxygen from the reaction sites to the bulk of the molten tin anode occurs preferentially (Figure 6.3(b)). Finally, the current density

\[^{[17]}\] For these calculations were considered an atomic weight of 15.999 g mol\(^{-1}\) for oxygen and 118.71 g mol\(^{-1}\) for tin (Source: Callister W.D. Materials Science and Engineering. An Introduction, 8th Edition. John Wiley and Sons, 2010). In addition, the total amount of tin in the anode corresponded to ca. 17 g as it was stated in Chapter 4 and Chapter 5.
decayed rapidly with a similar slope as that during the first stage of the process, which is followed by a slower decay of the kinetics after ca. 28 minutes. This behaviour may have been associated with a dominant formation of SnO$_2$ at the anode | electrolyte interface according to equation (5.19), which is associated with accumulation (saturation) of oxygen at the anode | electrolyte interface to produce SnO$_2$ (accumulation stage in Figure 6.3(c)) and the consequent rapid decay of the current density. When sufficient tin dioxide had been produced, some of the original reaction sites at the anode | electrolyte interface were blocked and the oxide ions reaching these points had to be transported from the electrolyte surface to the new reaction sites at the SnO$_2$ | anode interface, where atomic oxygen is produced to be dissolved into the melt or to produce more tin dioxide (O$^{2-}$ transport stage in Figure 6.3(c)). This final process can be related with the slower decay of current density occurring close to the saturation time. Figure 6.3 shows a schematic of these phenomena.

Figure 6.3. Transport and reaction of atomic oxygen, [O]$_{Sn}$, at the molten tin anode during performance of the Sn$_{107}$-SOFC at its maximum power density: (a) [O]$_{Sn}$ accumulation at the interface between 0 and 1 minutes; (b) [O]$_{Sn}$ ‘steady state’ transport between 1 and 12 minutes; (c) Tin dioxide formation between 12 and 51.28 minutes (saturation time)
It is important to notice that the oxygen transport and reaction processes described in Figure 6.3(b) and Figure 6.3(c) could have occurred in parallel at any stage of the current density transient. Therefore, even in the case when the dissolution of \([O]_{\text{Sn}}\) species in the bulk of the anode was the dominant process taking place in the system (between 1 and 12 minutes), the local formation of \(SnO_2\) at some active sites in the anode | electrolyte interface could have been observed in a minor scale.

According to equation (5.31), current densities can be defined as a function of the concentration gradient of \([O]_{\text{Sn}}\) species between the anode | electrolyte interface and the bulk of the anode as follows:

\[
j = \frac{2FD_{[O]_{\text{Sn}}}}{\delta_{\text{an}}} \left( C^\text{react}_{[O]_{\text{Sn}}} - C^\text{bulk}_{[O]_{\text{Sn}}} \right)
\]  

(6.4)

where \(C^\text{react}_{[O]_{\text{Sn}}}\) and \(C^\text{bulk}_{[O]_{\text{Sn}}}\) are the oxygen concentrations in the interface and the bulk, respectively, \(D_{[O]_{\text{Sn}}}\) is the diffusion coefficient of oxygen in molten tin and \(\delta_{\text{an}}\) is the thickness of the diffusion layer at the anode | electrolyte interface. The oxygen diffusion coefficient at 900 °C can be calculated using equation (5.34) \((D_{[O]_{\text{Sn}}} = 6.63 \times 10^{-9} \text{ m}^2 \text{ s}^{-1})\), while the diffusion layer thickness and the oxygen concentration in the bulk of the anode can be used as variables, together with the electrode kinetics, in order to understand under which conditions the oxygen concentration at the anode | electrolyte interface can be maintained below its saturation value \((C^\text{sat}_{[O]_{\text{Sn}}} \sim 183 \text{ mol m}^{-3})\) in order to avoid the precipitation of tin dioxide according to equation (5.19).

To provide a general idea of the dependence of the oxygen surface concentration with the diffusion layer thickness (fluid dynamics of the molten tin anode) and the anode electrochemical kinetics, a Tafel behaviour of the anodic current-potential curves will be considered [193]:

\[
j = j_{0,\text{an}} \exp \left( \frac{\alpha_{\text{an}} \nu F}{RT} \eta^\text{act}_{\text{an}} \right)
\]  

(6.5)

where \(j_{0,\text{an}}\) is the exchange current density, \(\alpha_{\text{an}}\) is the charge transfer coefficient, and \(\eta^\text{act}_{\text{an}}\) is the activation overpotential. Equation (6.5) is used considering a stirred or flowing anode.
at which the mass transport controlled kinetics is enhanced by reducing the diffusion layer thickness. Therefore, equalizing equations (6.4) and (6.5) the oxygen concentration at the anode | electrolyte interface can be calculated:

\[
C_{[\Theta]_\text{an react}} = C_{[\Theta]_\text{an bulk}} + \frac{\delta_{\text{an}} J_{0,\text{an}}}{2 F D_{[\Theta]_\text{an}}} \exp\left(\frac{\alpha_{\text{an}} v F}{RT} \eta_{\text{an}}^{\text{act}}\right) \tag{6.6}
\]

Since this analysis aims to provide only an idea of the effects of introducing a stirred or flowing anode in the Sn\(_{\text{l}}\)-SOFC system, the parameters \(\alpha_{\text{an}}\) and \(J_{0,\text{an}}\) replaced in equation (6.6) corresponded to the values reported in Table 5.7 for a quiescent system. This could be considered the ‘worst case’, since the kinetics at the anode should be affected as well by changes in the fluid dynamics [193].

Figure 6.4 shows the variation of oxygen concentration at the anode | electrolyte interface as a function of the diffusion layer thickness and anode activation overpotential for oxygen concentrations in the bulk equal to zero, a fourth and half of the oxygen saturation concentration. As can be seen, even for a negligible oxygen concentration in the bulk of the anode, a diffusion layer thickness lower than a 50 \(\mu\)m is required to operate the Sn\(_{\text{l}}\)-SOFC at anode overpotentials higher than 100 mV. When the oxygen concentration in the bulk is increased to half of the saturation concentration, the diffusion layer thickness must be lower than 50 \(\mu\)m even for anodic overpotentials as low as 80 mV. In Section 5.3 it was predicted that a Sn\(_{\text{l}}\)-SOFC with negligible ohmic potential losses could have reached its maximum power density when an anode activation overpotential of ca. 130 mV (cell voltage of 0.45 V) was applied. It suggests that the anode kinetics are expected to be improved by changes in the fluid dynamics if oxygen saturation at the anode | electrolyte interface needs to be avoided. However, since oxygen accumulation in the bulk of the anode cannot be avoided operating the Sn\(_{\text{l}}\)-SOFC in battery mode, introduction of a fuel would be necessary to maintain the fuel cell operational (see Chapter 8).

As an example of the fluid dynamics conditions that would be required to maintain the diffusion layer thickness under 50 \(\mu\)m, a molten tin anode flowing inside a tubular YSZ electrolyte of 1.0 cm inner diameter and 5.0 cm length was studied. To calculate the rate at which this liquid metal should flow inside the tubular electrolyte avoiding tin dioxide precipitation \((C_{[\Theta]_\text{an react}} < C_{[\Theta]_\text{an sat}})\), correlations between the dimensionless numbers Reynolds (\(Re\)), Schmidt (\(Sc\)) and Sherwood (\(Sh\)) were used for the case of flow in a pipe.
Figure 6.4. Oxygen concentration at the anode | electrolyte interface as a function of the diffusion layer thickness and anode activation overpotential for the cases: (a) $C_{[\theta]_{\text{in}}}^{\text{bulk}} = 0$, (b) $C_{[\theta]_{\text{in}}}^{\text{bulk}} = C_{[\theta]_{\text{in}}}^{\text{sat}} / 4$ and (c) $C_{[\theta]_{\text{in}}}^{\text{bulk}} = C_{[\theta]_{\text{in}}}^{\text{sat}} / 2$
CHAPTER 6.
STABILITY ANALYSIS OF Sn\textsubscript{0}\textsubscript{7} SOFCs OPERATING IN BATTERY MODE

The Reynolds (Re), Schmidt (Sc) and Sherwood (Sh) numbers are defined as follows:

\[
Re = \frac{\nu_{Sn} D_h}{\nu_{Sn}} \quad (6.7)
\]

\[
Sc = \frac{\nu_{Sn}}{D_{[2]a}} \quad (6.8)
\]

\[
Sh = \frac{k_m D_h}{D_{[2]a}} \quad (6.9)
\]

where \( \nu_{Sn} \) is the linear velocity at which the molten tin flows inside the YSZ tube, \( D_h \) is the (hydraulic) diameter of the pipe, \( \nu_{Sn} \) is the kinematic viscosity of molten tin at the operating temperature (it corresponds to \( 1.21 \times 10^{-7} \) m\(^2\) s\(^{-1}\) at 900 °C [164]), and \( k_m \) is the mass transfer coefficient defined as \( D_{[2]a} \delta_{an} \). Reynolds, Schmidt and Sherwood numbers can be correlated by the following equations for laminar and turbulent flow [219]:

Laminar:
\[ Sh = 1.86 \ Re^{\frac{1}{3}} Sc^{\frac{1}{3}} \left( \frac{D_h}{L} \right)^{\frac{1}{3}} \quad (6.10) \]

Turbulent (\( Re > 20,000 \)):
\[ Sh = 0.023 \ Re^{0.8} Sc^{\frac{1}{3}} \quad (6.11) \]

where \( L \) is the length of the tube. Using equations (6.7) to (6.11) and assuming a diffusion layer thickness of 50 µm, it was determined that the flow regime should be turbulent (Re ~ 25 000), which was expected considering the low thickness required for the diffusion layer. Consequently, a linear velocity of ca. 0.30 m s\(^{-1}\) was predicted to be necessary in order to maintain the oxygen concentration at the anode | electrolyte interface below the saturation value. This linear velocity was equivalent to a flow rate of ca. 1.5 L of Sn\textsubscript{0}\textsubscript{7} min\(^{-1}\) inside the YSZ electrolyte, which should be even higher considering that the oxygen concentration in the bulk of the molten tin increases along the tube and therefore a thinner diffusion layer would be required, according to the results exposed in Figure 6.4. This condition would be difficult to achieve using a thin electrolyte tube (e.g. 200 µm) considering the mechanical constraints of this fuel cell component (see Section 5.3). However, since these calculations and analysis are based on the kinetic parameters obtained using a Sn\textsubscript{0}\textsubscript{7}-SOFC with a quiescent anode in absence of a fuel, it can be expected that in reality lower flow rates are
required to avoid saturation at the anode electrolyte interface. Chapter 8 presents preliminary results of a Sn\(_{(\text{l})}\)-SOFC with stirred anode operating in fuel cell mode.

The shape of the data in Figure 6.1 after reaching the saturation time is in good agreement with the shape of the current density transients obtained for electrochemical nucleation of metals and/or oxides on foreign substrates [228-230]. Therefore, it is reasonable to believe that once the system reached its saturation limit after 51.28 minutes, a nucleation process started due to the direct electrochemical formation of SnO\(_2\) by reaction (5.20). Considering this, the initial growth of the current density could be associated to the formation of isolated nuclei (SnO\(_2\)) on the foreign substrate surface (clean YSZ electrolyte), which promoted an increase of the electrolyte | anode area where reaction sites were available for oxidation of the reacting species (O\(^2\)). When the O\(^2\) diffusion zones adjacent to the SnO\(_2\) nuclei started to overlap, a competition for the consumption of the oxide ions was established between the SnO\(_2\) deposits and decay of current density occurred until the foreign substrate was completely covered and the phenomenon of nucleation led to a process of crystal growth [230]. In simple terms, the final stage of the current density transient presented in Figure 6.1 corresponded to the complete coverage of the electrolyte surface via direct electrochemical formation of SnO\(_2\) at the YSZ sites that remained clean during the previous phases of SnO\(_2\) formation via equation (5.19). When this process was concluded, all the original reaction sites at the electrolyte | anode interface were replaced by equivalent reaction sites at the SnO\(_2\) | anode interface and consequently the kinetics of the oxidation process changed.

The noisy peaks observed between ca. 40 minutes and the saturation time, as well as the background noise at the final section of the current density transient in Figure 6.1, were related mainly to the growth of a non-dense and non-stoichiometric layer of tin dioxide on the electrolyte surface and tin dioxide inclusions in the pores of the graphite rod used as current collector at the anode (see Section 6.1.2). These undesired deposits promoted a higher resistance to the transport of oxide ions from the electrolyte surface to the reaction sites and affected the electrical response of the Sn\(_{(\text{l})}\)-SOFC due to changes in the current collector microstructure. Formation and growth of SnO\(_2\) during fuel cell operation are analysed and discussed in the next section.

### 6.1.2. SnO\(_2\) Formation and its Effects on the Stability of the Sn\(_{(\text{l})}\)-SOFC Components

Post-mortem analysis of the Sn\(_{(\text{l})}\)-SOFC components was done using X-ray techniques with the objective of studying the effects of SnO\(_2\) formation on the microstructure of the
electrolyte and graphite rod current collector (SEM), and characterizing the chemical composition of this by-product by XRD and EDX.

Figure 6.5(a) and Figure 6.5(b) shows images of the electrolyte | molten tin anode interface after operation of a Sn(1)-SOFC at its maximum power density for 3 hours, corresponding to the current density transient presented in Figure 6.1. Figure 6.5(c) and Figure 6.5(d) correspond to the electrolyte | molten tin anode interface of a Sn(1)-SOFC used for 3 days for the steady state voltammetric and electrochemical impedance spectroscopic (EIS) measurements presented in Chapter 5.

In both cases, a grey stain can be observed on the area of the YSZ electrolyte which was in contact with the clean (no by-product formed on it) tin anode surface. This phenomenon was examined in detail using SEM and EDX analysis of the stained zone to determine its chemical composition and the possible effects that it could have had on the stability of the electrolyte microstructure. Figure 6.6 shows SEM micrographs at x400 and x6000 magnifications. The x400 SEM micrograph shows that the original stain was formed by several micrometre-scale inclusions on the electrolyte surface, each of them formed by pure tin included on the YSZ surface and several microscopic particles growing at its grain boundaries, in accordance with the results presented in the x6000 SEM micrograph and the
EDX diagram in Figure 6.7. Considering the absence of any visible effect on the surface of the YSZ pellet in contact with the anode surface covered by tin dioxide (white and brownish powder in Figure 6.5(b) and Figure 6.5(d)), it is believed that the microscopic particles produced at the grain boundaries of the electrolyte surface corresponded to SnO₂ growing at these sites in accordance with reaction (5.19). Therefore, it is likely that during operation of the Sn(l)-SOFC the anode reaction mechanism included: (1) inclusion of molten tin on the electrolyte surface; (2) conversion of the liquid metal into SnO₂ at the reaction sites; and (3) transport of SnO₂ from the reaction sites to the bulk of the anode. However, considering that the density of tin dioxide at high temperatures is higher than the density of pure molten tin [171, 172], the SnO₂ produced at the reaction sites did not diffuse into the bulk of the anode but remained sited on the surface of the YSZ electrolyte as can be seen in Figure 6.5.

**Figure 6.6.** SEM micrographs of the tin stains shown in Figure 6.5(a) and Figure 6.5(c) on the surface of the YSZ-pellet electrolyte

**Figure 6.7.** EDX spectra of the tin stains observed in Figure 6.6(a) and Figure 6.6(c) on the surface of the YSZ-pellet electrolyte
The darker (species accumulation) ‘tin stain’ evident on the surface of the electrolyte used for the steady state measurements presented in Chapter 5 (compare Figure 6.5(a) and Figure 6.5(c)) could be related to the higher current densities promoted during operation of the Sn(SOFC when cell potentials lower than 0.42 V were applied (see Figure 5.7). Under these operating conditions, an increased flux of oxide ions was promoted between the cathode triple phase boundaries (TPBs) and the anode | electrolyte interface, in comparison with the case studied in Section 6.1.1. Consequently, greater amount of molten tin had to be included on the electrolyte surface in order to satisfy the charge transfer balance of the system.

From the results discussed above it can be concluded that good contacting of the electrolyte and molten tin is required for acceptable anode kinetics. This was achieved in the experimental Sn(SOFC by using the weight of the 5 mm deep molten tin anode (17 g) on the surface of the YSZ pellet electrolyte. In addition, removal of the SnO₂ product layer deposited on the electrolyte surface is an important aspect to be considered in future designs of the Sn(SOFC in view of its negative effect on the fuel cell performance, as demonstrated in Section 6.1.1.

Figure 6.5(b) and Figure 6.5(d) shows the evolution of SnO₂ formation at the anode | electrolyte interface. In both cases, it grew preferentially from the wall of the alumina tube containing the molten tin anode, which could be associated with the higher current densities at the edges of the electrode (see current distribution analysis in Chapter 7). In addition, the SnO₂ deposit grew preferentially on the side of the anode | electrolyte interface which was parallel to the cathode surface (see Figure 4.1), while the side parallel to the reference electrode remained relatively clean. This phenomenon was related again with the current distribution on the surface of the anode and is discussed in detail in Section 7.2. As can be seen in Figure 6.5(d), in the longer term the complete coverage of the electrolyte surface occurred from the clean boundary of the molten tin anode towards the ‘centre’ of the electrolyte. This boundary, as stated above, corresponded initially to the inner wall of the alumina tube containing the molten tin anode (see Figure 6.8(a)). However, after SnO₂ was formed around this position, the boundary of the electrode moved towards the limit of the SnO₂ deposit, as shown in Figure 6.8(b)).

As can be seen in Figure 6.5(b) and Figure 6.5(d), two types of SnO₂ were formed at the anode | electrolyte interface: (1) a white species, which could correspond to the stoichiometric phase of SnO₂; and (2) a brownish deposit, which could be associated with a non-stoichiometric (non-fully oxidized) SnO₂ species (similarly to the cases presented in
Section 5.4 for non-reduced and reduced LST and LCST). Figure 6.9 shows the XRD diffractogram obtained for both species, the peaks corresponding unequivocally with the theoretical pattern of pure SnO$_2$. In view of this result, no differences between these phases could be detected by XRD, which does not allow differentiating these deposits by other means than pure observation.

**Figure 6.8.** Schematic of the evolution of the border of the molten tin electrode during Sn$_{(l)}$-SOFC operation

**Figure 6.9.** XRD diagram of the tin dioxide product observed in Figure 6.5(b) and Figure 6.5(d) on the surface of the YSZ-pellet electrolyte

To explain the formation of a non-fully oxidized phase of SnO$_2$ at the anode | electrolyte interface, the anode electrochemical process could be considered as a multi-step reaction. Therefore, the oxidation of oxide ions at the anode | electrolyte interface (equation (5.18)) could be represented as a two-step reaction mechanism:
where reaction (6.13) is followed by diffusion of $[O]_{Sn}^-$ species from the anode | electrolyte interface to the bulk of the anode and formation of tin dioxide according to equation (5.19). When oxygen saturation at the anode is reached, as it was stated in Section 5.2 and Section 6.1.1, direct oxidation of tin would occur at the active sites according to equation (5.20). Therefore, the electron-transfer processes now would occur according to the reaction mechanism:

$$Sn + O^{2-}_{YSZ} \rightarrow SnO^-_{ads} + e^-$$

(6.14)

$$SnO^-_{ads} \rightarrow SnO_{ads} + e^-$$

(6.15)

$$SnO^-_{ads} + (1-x)O^{2-}_{YSZ} \rightarrow SnO_{(2-x),ads}^+ + 2(1-x)e^-$$

(6.16)

$$SnO_{(2-x),ads}^+ + xO^{2-}_{YSZ} \rightarrow SnO_2 + 2xe^-$$

(6.17)

Reactions (6.16) and (6.17) would explain the formation of a non-fully oxidized species at the anode | electrolyte previous to the formation of $SnO_2$. Therefore, it is believed that before saturation fully oxidized tin dioxide ($SnO_2$) was formed by oxidation of molten tin in accordance with equation (5.19), while under saturation conditions $SnO_2$ was formed via a non-fully oxidized species in accordance with reactions (6.14) to (6.17). These mechanisms are merely a hypothesis based on observation of Figure 6.5 and need further experimental and mathematical analysis.

Finally, the longer term stability of the anode current collector was studied based on examination of the post-mortem images and SEM micrographs obtained for the graphite rod fragments submerged in the molten tin electrode during operation. Figure 6.10(a) shows the anode current collector of the Sn$_{(l)}$-SOFC used to generate the current density transients reported in Section 6.1.1, while Figure 6.10(b) shows the anode current collector used for the voltammetry and EIS measurements presented in Chapter 5. As can be seen in both cases, the longer term operation had a visible effect on the graphite rod surface, over which growth of a white deposit took place. In the case of a Sn$_{(l)}$-SOFC operating at 0.42 V for 3 hours the deposit was visible but thin, while the anode current collector used for 3 days for
voltammetry measurements (when lower cell potentials were applied resulting in higher current densities) was covered by a thicker deposit which blocked the normal electron transport and promoted noisy measurements and poor Sn\(_{(l)}\)-SOFC performance.

![Figure 6.10](image)

**Figure 6.10.** Post-mortem analysis of the graphite rods used as current collector at the molten tin anode: (a) corresponds to a Sn\(_{(l)}\)-SOFC after operation at its maximum power density for 3 hours, (b) corresponds to a Sn\(_{(l)}\)-SOFC used for cyclic voltammetry measurements for 3 days

With the objective of determining the chemical composition of these deposits and their adverse effects on the current collector microstructure, SEM and EDX analysis of the graphite rod piece presented in Figure 6.10(a) was done. As shown in Figure 6.11, an important change occurred in the surface of the anode current collector after applying a constant cell potential of 0.42 V for 3 hours. In fact, the original flat surface of the graphite rod became porous and several inclusions grew inside these cavities. EDX analysis detected a high content of tin on the graphite rod surface covered by the white deposit, which was related with formation of tin dioxide at the porous sites of the current collector (similar to the phenomenon taking place at the anode | electrolyte interface discussed previously in this section). Porosity in the surface of the graphite rod after operation of the Sn\(_{(l)}\)-SOFC could be associated with oxidation of the current collector in the melt by the reaction:

\[
C + 2[O]_{Sn} \rightarrow CO_2
\]  

However, since oxidation of a carbonaceous fuel in a Sn\(_{(l)}\)-SOFC is a sluggish process (see [176, 177] and Chapter 8), it should not have a dramatic effect on the microstructure of the graphite rod. Consequently, a low porosity is promoted on the current collector surface but high enough to generate the active sites where tin dioxide inclusions can accumulate. It is believed that growth of tin dioxide in the pores occurred from the surface of the YSZ pellet electrolyte, which (for experimental reasons) was in contact with the base of the graphite rod current collector during operation of the Sn\(_{(l)}\)-SOFC, as shown schematically in Figure 4.2(a). Hence, SnO\(_2\) particles would have formed first at the junction between the electrolyte and the current collector, and then the deposit would have grown along the graphite by a mechanism similar to that shown in Figure 6.3(c) for oxide ions transport through the initial
oxide layer produced at the anode | electrolyte interface. Particles would have accumulated inside the pores, due to the higher local current densities at these sites (see Chapter 7) compared to the flat surface of the graphite rod. Figure 6.12 shows a schematic of the mechanism described above for SnO₂ growth on the anode current collector surface.

Figure 6.11. SEM micrograph of surface of graphite rod used as current collector at the molten tin anode (a) before cell operation and (b) after cell operation at maximum power density for 3 hours

Figure 6.12. Schematic of the proposed mechanism of SnO₂ growth on the anode current collector surface

From the results presented in this section, it can be concluded that the Sn₀ₓ-SOFC performance can be affected dramatically by accumulation of tin dioxide at the molten tin anode | electrolyte interface. Therefore, the use of a reducing agent (in-situ or in an external combustion reactor as shown in Section 3.3.2) is essential in order to maintain the fuel cell operational in the longer term and with a stable energy output, as discussed in Chapter 8.
6.2. Effects of \( \text{SnO}_2 \) Formation on \( \text{Sn}_{(0)} \)-SOFC Impedance

Among the major diagnostic tools used in the study of solid oxide fuel cells (SOFCs), electrochemical impedance spectroscopy (EIS) has been used widely for performance evaluation and degradation analysis. Application areas of this technique include: electrode-electrolyte assembly optimization and fabrication, improved fuel cell components selection, and optimization of fuel cell stack performances as a function of the operating conditions (temperature, pressure and fuel/oxidant flow rates) and electrode microstructures [231].

In EIS measurements, a sinusoidal voltage signal:

\[
e(t) = E \cos(2\pi ft + \varphi)
\]

(6.19)
is applied to excite a linear time-invariant (LTI) circuit system, producing an AC current response:

\[
i(t) = I \cos(2\pi ft + \psi)
\]

(6.20)
in accordance with linear system theory [193, 231]. The sinusoidal time-dependant functions (6.19) and (6.20) present the same frequency \( f \), amplitude \( E \) and \( I \), and initial phase \( \varphi \) and \( \psi \) for the voltage and current response, respectively.

Normally, the expressions of voltage and current can be mapped and converted from a time domain to a complex domain \((i: \text{imaginary unit})\) as follows:

\[
e^*(t) = E \exp[(2\pi ft + \varphi) i]
\]

(6.21)
\[
i^*(t) = I \exp[(2\pi ft + \psi) i]
\]

(6.22)
where \( e(t) = \text{Re}[e^*(t)] \) and \( i(t) = \text{Re}[i^*(t)] \). If the angular frequency is defined as:

\[
\omega = 2\pi f
\]

(6.23)
the impedance of the system, \( Z(i\omega) \), can be expressed as:

\[
Z(i\omega) = \frac{e^*(t)}{i^*(t)} = |Z(i\omega)| \exp(i\varphi)
\]

(6.24)
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where \( |Z(i\omega)| = \frac{E}{I} \) reflects the amplitude transfer function between the excitation and response signals \( e^*(t) \) and \( i^*(t) \), respectively, and \( \phi = \varphi - \psi \) corresponds to the phase transfer function between these signals.

As it has been stated and demonstrated along this thesis, SOFCs are complicated electrochemical devices involving multiple charge-transfer, mass-transfer and chemical processes which coupled result in a non-linear system. Strictly speaking, under these conditions the impedance \( Z(i\omega) \) will not directly follow the expressions obtained for a LTI system, particularly when the amplitude of the voltage/current excitation/response is large and the interfacial response of the SOFC is strongly non-linear. Fortunately, when the amplitude \( E \) of the applied AC voltage is less than a given thermal potential (usually between 10 and 50 mV) the basic differential equations that govern the response of the fuel cell system become nearly linear and the theory presented before is applicable [232, 233].

The variation of the expression \( Z(i\omega) \) with frequency is often presented in the form of a Nyquist plot where the couples \( (Z_{Re}, Z_{Im}) \) are displayed for different values of \( \omega \) [193, 232, 233]. These impedance spectra are often associated with equivalent circuits which represents the phenomena taking place at the electrochemical cell using different lumped elements (such as resistances, capacitances and inductances) and frequency-dependent elements (such as Warburg elements, constant-phase elements, bounded frequency-dependent elements, bounded-constant phase elements and unloaded elements) which are connected in series, in parallel or a combination of both [233]. The simplest and most common representation of a conventional SOFC corresponds to the equivalent circuit presented in Figure 6.13(a), where an ohmic resistance \( R_{Electrolyte} \) representing the electrolyte (and possibly other ohmic contributions, such as current collectors and contact losses) is in series with two \( RC \) (resistance-capacitance) components representing the phenomena taking place at the electrodes. The Nyquist plot associated to this equivalent circuit is presented in Figure 6.13(b) for arbitrary resistance and capacitance values.

As shown in Figure 6.13(b), the total ohmic losses of the SOFC correspond to the high frequency intercept on the left hand side of the real axis \( Z' \). This value is associated in Figure 6.13(b) with the ionic area specific resistance (ASR) of the electrolyte and the ionic and electronic ASR at the electrodes. However, in reality these losses include the electronic ASR offered by the current collectors and contact losses between the fuel cell components. The
impedance behaviour of cathode and anode is represented by independent semicircles associated to the equivalent circuits used to model the phenomena occurring at each electrode. Therefore, the whole cell impedance is the result of the addition of both semicircles plus the pure resistance representing the electrolyte, as shown in Figure 6.13(b). The second (low frequency) intercept on the right hand side of the real axis $Z'$ corresponds to the ASR of the total interfacial impedance which includes both ohmic and activation losses within the fuel cell. Finally, values in the imaginary axis $Z''$ are related to the capacitance elements at the equivalent circuit due to double layer capacitances at the electrode | electrolyte interfaces.

Figure 6.13. (a) Equivalent circuit representing a conventional SOFC under working conditions, (b) Nyquist plot for equivalent circuit shown in (a)

Fitting data using equivalent circuits is subject to some uncertainties, as impedance spectra of a particular electrochemical system can be represented by different models [231, 232]. Therefore, it is important to have sufficient knowledge of the physical-chemical processes involved in a SOFC in order to obtain a realistic and simplified representation of the device. For example, an $RC$ (resistance-capacitance) element as the one presented in Figure 6.13(a) for cathode and anode is associated to a perfect semicircle, as shown in Figure 6.13(b) for both electrodes. However, impedance measurements of SOFCs usually produce depressed semicircles which are associated with the existence of a constant phase element due to heterogeneous (porous) electrodes [231]. Therefore, modifications to the simplified equivalent circuit in Figure 6.13(a) have to be introduced in order to represent the SOFC adequately.

Finally, 3-electrode measurements are necessary if the effects of each electrode on the total impedance spectra are to be determined. The presence of a reference electrode for
half-cell measurements at the cathode and anode allows producing data as that presented in Figure 6.13(b), which simplifies the interpretation of the experimental results. Unfortunately, the use of reference electrodes in high temperature solid state and molten metal/salt systems is not yet the norm and only under certain conditions 3-electrode measurements are applicable.

In this section electrochemical impedance spectra (EIS) are reported to determine the Sn\(_{0.7}\)-SOFC ohmic and activation losses when a set of overpotentials, starting from the open circuit condition (OCV/OCP), were applied to anode and cathode separately. In addition, equivalent circuits were fitted to the impedance plots to identify the resistance and capacitance elements representative of the charge and mass transfer processes occurring at the electrodes. The final objective of these measurements and modelling was to elucidate the effects that operation of the Sn\(_{0.7}\)-SOFC could have on the stability of its components and performance.

### 6.2.1. Impedance Response of Sn\(_{0.7}\)-SOFC Electrodes at Different Overpotentials

Impedance spectra of the whole Sn\(_{0.7}\)-SOFC, \textit{LSM-YSZ/LSM} cathode and molten tin anode | electrolyte arrangement were measured at open circuit voltage (OCV) or open circuit potential (OCP) before and after polarization and at different electrode overpotentials using the experimental arrangements described in Chapter 4. In order to obtain the whole fuel cell impedance spectra a 2-electrode arrangement was used with the reference and counter electrodes connected to the \textit{LSM-YSZ/LSM} cathode and the working electrode connected to the molten tin anode. A sinusoidal excitation signal of 10 mV p-p amplitude was applied around the OCV (0.85 V) over the frequencies range 0.01 Hz to 15 kHz. In the cases of the cathode and anode | electrolyte arrangement, 3-electrode measurements were done with the reference input connected to the \textit{LSM-YSZ/LSM} reference electrode printed next to the cathode (see Figure 4.1). Under these conditions, a sinusoidal excitation signal of 10 mV p-p amplitude was applied at different overpotentials when the \textit{LSM-YSZ/LSM} cathode was used as the working electrode using the same range of frequencies applied for the whole fuel cell measurements. Similarly, impedance spectra were obtained using the molten tin anode as working electrode and applying the same excitation signals around different potentials measured between the reference electrode at the cathode side and the anode current collector (see Figure 4.12).

Figure 6.14 shows the results obtained when an excitation signal around the OCV or OCP was applied to: (a) the whole Sn\(_{0.7}\)-SOFC, (b) the anode | electrolyte arrangement and...
(c) the cathode, before and after polarization measurements (cyclic voltammetries as the one presented in Figure 5.6) were done.

![Impedance plots](image)

**Figure 6.14.** Impedance plots obtained at open circuit voltage/potential for (a) whole Sn(l)-SOFC, (b) molten tin anode and electrolyte, and (c) LSM-YSZ/LSM cathode before and after polarization measurements (cyclic voltammetry)

As can be seen for the case of the whole Sn(l)-SOFC, there was a difference of ca. 0.07 Ω cm² between the ohmic losses (high frequency intercept) measured before and after polarization. This value corresponds to approximately 0.7% of the initial total ASR of the fuel cell, which was ca. 9.70 Ω cm², and was probably due to the formation of tin dioxide at the anode | electrolyte interface and the anode current collector (graphite rod) surface. Even though the difference between the total ohmic losses before and after fuel cell operation seemed to be negligible, in the longer term operation this result would be cumulative (SnO₂ accumulation) and would have an adverse effect in the maximum power density output of the system, as stated in Section 6.1. In the case of the anode | electrolyte arrangement, a difference of ca. 0.04 Ω cm² is measured, which was approximately 2.25% the value of the initial anode | electrolyte ASR (ca. 1.78 Ω cm²). Finally, this difference was ca. 0.06 Ω cm² at
the cathode, corresponding to ca. 1.20% of the initial cathode ASR (5.01 Ω cm²). It is important to notice that the cathode impedance spectrum dominates the response of the whole Sn(l)-SOFC (both present a similar shape). This is not surprising considering that in the shorter term accumulation of tin dioxide in the anode chamber should not be high enough to affect the impedance response of the molten tin electrode significantly; consequently, the higher ohmic and activation losses at the cathode controlled the Sn(l)-SOFC performance.

As stated in Section 5.3, since the reference electrode was positioned on the cathode side of the fuel cell, impedance measurements for the anode necessarily included the electrolyte ohmic potential losses associated with transport of oxide ions from the TPBs at the LSM/YSZ cermet to the anode | electrolyte interface. This constant resistance would have not been varied during experimental measurements, so should not have affected the shapes of impedance spectra. Hence, the inductive component at high frequencies shown in Figure 6.14(b) was determined wholly by phenomena occurring at the anode. This will be discussed in more detail in the next section, where an equivalent circuit model is proposed to fit these experimental data. In the case of the cathode, the impedance spectra in Figure 6.14(c) is well fitted by a circuit of the type presented in Figure 6.13(a) replacing the capacitance element with a constant-phase element to represented the depressed semicircles [231, 234].

Figure 6.15 shows the impedance spectra for the anode | electrolyte arrangement at potentials 0.85, 0.79, 0.74, 0.69 and 0.64 V measured between the reference electrode and the anode current collector, as described at the beginning of this section. In order to clarify the relation between these potentials and the kinetics at the molten tin anode, these values were converted into anode activation overpotentials using the mathematical models presented and developed in Chapter 5. The voltages used to obtain the data shown in Figure 6.15 corresponds to the Sn(l)-SOFC Nernst potential (OCV) minus the ohmic, activation and concentration losses at the anode plus the ohmic losses at the electrolyte:

\[
E_{\text{measured, an}} = E_N - \left[ \eta_{\text{an}}^{\text{act}} + \eta_{\text{an}}^{\text{conc}} + I \cdot (R_{\text{an}} + R_e) \right]
\]  \hspace{1cm} (6.25)

Using this approximation, the corresponding anode activation overpotentials 0, 11, 20, 29 and 38 mV were obtained. As shown in Figure 5.11, these values were in the range in which the anode response still can be considered linear if a sinusoidal excitation of 10 mV p-p amplitude is applied.
As can be seen in Figure 6.15, between anode overpotentials 0 and 20 mV the impedance response of the anode | electrolyte arrangement exhibited an inductive component (negative imaginary component) at high frequencies as in Figure 6.14(b). This phenomenon could be associated with the growth of tin dioxide inclusions at the graphite rod (anode current collector) and will be discussed in detail in Section 6.2.2. The range of overpotentials used to obtain these three impedance spectra corresponded to conditions of kinetic rather than mass transfer control in the anodic activation polarization curve (see Figure 5.11), which could explain that the inductive phenomenon dominates the anode impedance response up to 20 mV. However, when 29 and 38 mV were applied in addition to the inductive component a more significant additional capacitive phenomenon occurred, which suggests that some tin dioxide started to grow at the anode | electrolyte interface when these anode overpotentials were reached. Considering that at the maximum power density the cell voltage is ca. 0.42 V, using the mathematical model presented in Section 5.3 it can be predicted that the anode activation overpotential under these operating conditions is ca. 27 mV. Therefore, the impedance response observed at 29 and 38 mV is in agreement with the observations made in Section 6.1 with respect to the adverse effect that tin dioxide formation has on the current density transients of a Sn\textsubscript{(l)}-SOFC operating at its maximum power density output.

Finally, Figure 6.16 shows the impedance spectra for cathode activation overpotentials of 0, -5, -10 and -15 mV. Since the reference electrode was placed next to this electrode, the
overpotentials were measured directly and no transformation was necessary unlike in the case of the anode. The maximum overpotential applied during these measurements (-15 mV) corresponded, in accordance with the kinetic models presented in Section 5.3, to the value at which the Sn\textsubscript{(l)}-SOFC reached its maximum power density. In addition, the cathode kinetics showed a linear behaviour in the entire range of overpotentials used, so validating the amplitude of the sinusoidal excitation applied.

![Graph showing impedance spectra for LSM-YSZ cathode of Sn\textsubscript{(l)}-SOFC](image)

**Figure 6.16.** Effect of overpotential on impedance spectra for LSM-YSZ cathode of Sn\textsubscript{(l)}-SOFC

As evident from Figure 6.16, the cathode impedance response did not change significantly over the range of overpotentials applied, which confirms that the impedance response of the cathode was controlled by the ohmic losses at the cathode current collector and cathode | cathode current collector interface (see Section 5.3), rather than by the electrode kinetics. The slight increase in ohmic potential losses (high frequency intercept) could be related to the increase on the bias potential (cathode overpotential) applied to the electrode, that promoted a higher current density which could have affected the kinetic response of the LSM-YSZ electrode, but with an effect still not comparable to the ohmic losses. These observations demonstrate the need of improving the current collection at the cathode in order to reduce the ohmic losses, which would allow studying the electrode kinetics without the interference of undesirable side effects. The two depressed semicircles were associated with the mass and charge transfer processes occurring at the cathode and will be discussed in detail in the next sub-section.
6.2.2. Equivalent Circuits for the Sn\textsubscript{0.99}SOFC Impedance Response

The anode and cathode impedance spectra presented before for the case of the Sn\textsubscript{0.99}-SOFC operating under open circuit conditions (i.e. zero overpotential) were used to investigate the phenomena controlling the kinetics of the electrochemical system. With this objective, equivalent circuits (EC) are proposed in this section for modelling of the charge and mass transfer processes occurring at each electrode, based on reports in the literature on SOFC cathodes [234] and molten tin anodes [176, 235].

In order to understand the mass and charge transfer processes occurring at the oxygen electrode (cathode) of a SOFC, Kuboyama et al. [234] fabricated a symmetrical \(O_2/O_2\) cell using a thin 8YSZ disc electrolyte with platinum electrodes painted in both sides and a platinum wire as the reference electrode. Figure 6.17(a) presents the equivalent circuit proposed by these authors to represent the phenomena taking place at the oxygen electrode, where \(R_{ct}\) denotes the resistance to charge transfer, \(R_{mt}\) corresponds to the resistance to mass transfer, and \(Q_H (j\omega)^{-\alpha_H}\) and \(Q_L (j\omega)^{-\alpha_L}\) are the constant-phase elements at high and low frequency, respectively. For the case of the Sn\textsubscript{0.99}-SOFC studied in this thesis, the element \(R_{cc}\) was added in series with the proposed cathode equivalent circuit in order to represent the ohmic losses associated with current collection and contact losses.

The introduction of constant-phase elements requires the implementation of a nonlinear least square fitting (NLLSF) procedure for determination of the constants associated to the equivalent circuit presented in Figure 6.17(a). Therefore, the Fitting Tool included in the Nova 1.5 FRA2 module (Metrohm) was used. This method is based on the Boukamp model [236] which uses a combination of an analytical and gradient searches according to the Marquardt algorithm. The values obtained for \(R_{ct}\), \(R_{mt}\), \(Q_H\), \(Q_L\), \(\alpha_L\) and \(\alpha_H\) are presented in Table 6.1, while Figure 6.17(b) shows the theoretical prediction curve fitted to the experimental data obtained for the LSM-YSZ/LSM cathode operating under open circuit conditions. It can be seen that the low-frequency semicircle, associated with the charge transfer phenomenon, shows a better fit to the experimental data than the high-frequency semicircle, associated with mass transfer phenomena. This was evidently due to the higher noise that the measured impedance exhibited over ca. 5.9 \(\Omega\) cm\(^2\) (root mean square error of 0.031 \(\Omega\) cm\(^2\) and higher relative error of ca. 30%) which was probably produced by poor current collection at the cathode and/or uncompensated impedance between the working and reference electrodes resulting in a large error in the controlled electrode potential [231].
Figure 6.17. (a) Equivalent circuit proposed to represent the LSM-YSZ cathode of the Sn$_{0.9}$-SOFC studied, (b) Experimental impedance spectrum obtained under open circuit conditions for the LSM-YSZ cathode (see Figure 5.8(c)) and modelled curve obtained using the Nova 1.5 FRA2 module Fitting Tool

Table 6.1. Parameters associated to the equivalent circuit presented in Figure 6.17(a) obtained using the Nova 1.5 FRA2 module Fitting Tool

<table>
<thead>
<tr>
<th>Circuit 1 (ohmic and charge transfer element)</th>
<th>Circuit 2 (mass transfer element)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{cc}$ / Ω cm$^2$</td>
<td>$R_{cc}$ / Ω cm$^2$</td>
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<tr>
<td></td>
<td>$R_{ct}$ / Ω cm$^2$</td>
</tr>
<tr>
<td>$R_{ct}$ / Ω cm$^2$</td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>$R_{ct}$ / Ω cm$^2$</td>
</tr>
<tr>
<td></td>
<td>$Q_H$ / F cm$^2$ s$^{(α-1)}$</td>
</tr>
<tr>
<td></td>
<td>$Q_L$ / F cm$^2$ s$^{(α-1)}$</td>
</tr>
<tr>
<td></td>
<td>$α_H$</td>
</tr>
<tr>
<td></td>
<td>$α_L$</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>5.00</td>
</tr>
<tr>
<td></td>
<td>0.83</td>
</tr>
<tr>
<td></td>
<td>1.81 x 10$^{-4}$</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
</tr>
<tr>
<td></td>
<td>---</td>
</tr>
<tr>
<td></td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td>7.90</td>
</tr>
<tr>
<td></td>
<td>0.99</td>
</tr>
</tbody>
</table>
Another source of noise in the impedance response of the \( \text{LSM-YSZ/LSM} \) cathode in the low frequency range could be the low partial pressure of oxygen gas (reactive species) in the pores of the electrode. It might be due to two reasons: (1) rapid consumption of the reactant at the triple phase boundaries (TPBs) due to low air flow rates and high current densities at the oxygen electrode, and (2) a defective microstructure of the \( \text{LSM-YSZ} \) and \( \text{LSM} \) layers of the cathode limiting facile transport of reactant to reaction sites. The former situation is unlikely to have occurred considering that air was being fed continuously to the electrode surface at a rate of 60 mL min\(^{-1}\), which is high enough to maintain the partial pressure of oxygen constant next to the \( \text{LSM} \) layer (see Chapter 5). In addition, the current density produced by the \( \text{Sn\(_{0.07}\)-SOFC} \) when an alternating overpotential around zero is being applied to the cathode should be low enough to have no effect on the concentration of \( O_2 \) reactant at the electrode surface. Therefore, the defective microstructure of the cathode is more likely to have been the reason of having a low partial pressure of oxygen at the TPBs. In effect, as shown previously in Figure 5.1 and Table 5.1, the porosity of the cermet cathodes produced in this project was only ca. 15 – 20\% and the distribution of the pores in the \( \text{LSM-YSZ} \) and \( \text{LSM} \) layers was not homogeneous, which could affect the diffusion of the reactive species and the formation of the TPBs as reported previously [237, 238].

From the values presented in Table 6.1 it can be seen that the charge transfer phenomenon presents less resistance than the mass transfer process, which suggest that diffusion of oxygen gas through the porous \( \text{LSM-YSZ/LSM} \) electrode was the kinetics controlling step at the cathode. This result is in good agreement with the discussion offered above where the defective microstructure of the cermet electrode and current collector was identified as responsible for the low mass transport rates at the cathode. In addition, considering that the value of the exponents \( \alpha_H \) and \( \alpha_L \) is nearly 1.0, it can be assumed that both constant-phase elements behave almost like capacitors. Since the argument value of the high frequency constant-phase element \( Q_H \) is around four orders of magnitude lower than its corresponding value \( Q_L \) at low frequency, it could be assumed that an accumulation of charged species is taking place at the cermet structure of the \( \text{LSM-YSZ} \) cathode. This condition could be related with formation of the intermediate species \( O_{ad} \) at the electrode, according to the following reaction mechanism proposed by Kim et al. [239] for oxygen reduction on a \( \text{LSM-YSZ} \) composite:

\[
O_2(g) \rightarrow 2O_{ad}
\]  

(6.26)
Therefore, if diffusion of $O_{ad}^-$ species from the reaction sites in the LSM phase towards the TPBs is considered a sluggish process due to the poor microstructure of the electrode, accumulation of this charged species in the LSM phase could be identified as the responsible of the 'double-layer' effect associated to the constant phase element $Q_L$.

As for the case of the cathode, an equivalent circuit is proposed for modelling of the impedance response of the molten tin anode operating under open circuit conditions. Equivalent circuit models for Sn$_0$-SOFCs have been proposed by Lvov et al. [176] and White et al. [235] for the whole cell and the anode | electrolyte arrangement, respectively. In the first case, a purely experimental analysis was presented based on impedance measurements using the Sn$_0$-SOFC design shown in Figure 3.21 without and with fuel (coal or hydrogen) in the anode chamber. In the second case, a mathematical approach was proposed for modelling of the impedance response of the anode | electrolyte arrangement based on experimental measurements using a Sn$_0$-SOFC design similar to that fabricated for this project (see Section 4.1) using hydrogen as the fuel.

The equivalent circuit model proposed by Lvov et al. is shown in Figure 6.18(a) for the whole Sn$_0$-SOFC operating without and with fuel (coal) at 900 °C. In this approach, $R_s$ represent the ionic resistance of the solid electrolyte, $R_C$ corresponds to the combined anode and cathode charge transfer resistances, and the terms $\frac{1}{Q_{CPE}} (j\omega)^{-\alpha_{CPE}}$ and $\frac{1}{Q_G \sqrt{k_G + j\omega}}$ (Gerischer element, $G$) model the anode and cathode mass transfer resistance coupled with the molecular reactions of adsorption of oxygen and inclusion of molten tin at the cathode TPBs and anode | electrolyte interface, respectively. The equivalent circuit model proposed by White et al. is presented in Figure 6.18(b) for the Sn$_0$
Stability analysis of Sn\(_{l0}\)-SOFCs operating in battery mode

Anode | YSZ electrolyte arrangement of a Sn\(_{l0}\)-SOFC operating at 1 000 °C with hydrogen as the fuel. In this mathematical approach, the components of the circuit are defined as follows:

Ohmic impedance:

\[
R_{\text{ohmic}} = R_{\text{Sn(l)}} + R_{\text{YSZ}}
\]  
(6.31)

Charge transfer impedance:

\[
Z_{\text{ct}} = \frac{1}{\frac{1}{R_{\text{ct}}} + C_j \omega}
\]  
(6.32)

Diffusion impedance:

\[
Z_{\text{diff}} = k_o \left( \frac{1}{R_{\text{ct}}} + C_j \omega \right) nF \sqrt{\frac{j \omega}{D}} \left( \frac{j \omega}{K} - 1 \right)
\]  
(6.33)

Apparatus impedance:

\[
Z_L = L_j \omega
\]  
(6.34)

Figure 6.18. (a) Equivalent circuit model proposed by Lvov et al. for the whole Sn\(_{l0}\)-SOFC operating without and with fuel [176], (b) Equivalent circuit model proposed by White et al. for Sn\(_{l0}\) anode | YSZ electrolyte arrangement operating with fuel [235]

The study presented by Lvov et al. [176] is limited by the absence of a reference electrode, precluding separation of cathode and anode effects on the Sn\(_{l0}\)-SOFC kinetics. Hence, the equivalent circuit model (ECM) shown in Figure 6.18(a) is only a general representation of the Sn\(_{l0}\)-SOFC and does not enable proper understanding of the processes occurring in the molten tin anode. However, there are some interesting suggestions in this approach, such as the introduction of a Gerischer element (G) associated
with the processes taking place at the anode | electrolyte interface. This circuit element is usually associated with molecular reactions (adsorption) taking place in the bulk of porous electrodes before any electrochemical oxidation/reduction occurs [240, 241]. In the case of a molten tin anode, this element can be used to represent the process described in Section 6.1 for inclusion of liquid tin in the microstructure of the YSZ electrolyte prior to the oxidation of $O_2^-$ and formation of tin dioxide.

A key assumption of the mathematical model of White et al. [235] is the diffusion of tin dioxide in the molten tin anode, enabling its continuous removal at the anode | electrolyte interface by its reduction in the surface of the liquid metal using hydrogen gas fed continuously on the top of the melt. This assumption contradicts the results presented in Section 6.1, which demonstrated that tin dioxide accumulates at the electrolyte surface. In addition, White et al. [235] stated that the density of tin dioxide is lower than the density of the molten metal which is in clear contradiction with the information presented by Abernathy et al. (from CellTech Power Inc.) in reference [159] and supported by references [171, 172]. This last inconsistency represents a major conflict considering that the modelling approach developed by White et al. [235] was based on experimental results obtained using the Sn$_{(l)}$-SOFC technologies developed by CellTech Power Inc., which makes this mathematical approach even more questionable.

Considering the discussion presented above about the ECMs available for Sn$_{(l)}$-SOFCs, the impedance analysis presented in this thesis for the anode | electrolyte arrangement was based on that proposed by Lvov et al. [176], as it appears to be more in agreement with the results obtained in this project.

Figure 6.19(a) presents the ECM proposed to represent the anode | electrolyte arrangement of the Sn$_{(l)}$-SOFC studied. The resistance $R_{ecc}$ represents the electrolyte and anode current collector (graphite rod) ohmic potential losses, while the inductance $L_{cc}$ corresponds to the inductive effect evident at high frequencies in Figure 5.8(b) associated to the formation of pores and tin dioxide growth at the graphite rod surface. The rest of the elements (constant-phase element, charge transfer resistance and Gerischer element) are taken from the ECM presented in Figure 6.18(a) and represent the charge and mass transfer processes taking place at the molten tin anode. Table 6.2 lists the values of the parameters $R_{ecc}$, $L_{cc}$, $Q_{CPE}$, $\alpha_{CPE}$, $R_c$, $Q_G$ and $k_G$ obtained using the Nova 1.5 FRA2 module Fitting Tool, while Figure 6.19(b) shows the curve fitted to the experimental data obtained for the molten tin anode operating under open circuit conditions.
Figure 6.19. (a) Equivalent circuit model proposed to represent the anode | electrolyte arrangement of Sn\textsubscript{0.7}-SOFC, (b) Experimental impedance spectrum under open circuit conditions for molten tin anode (see Figure 5.8(b)) and modelled spectrum using the Nova 1.5 FRA2 module Fitting Tool

Table 6.2. Parameters associated with the equivalent circuit presented in Figure 6.19(a) obtained using the Nova 1.5 FRA2 module Fitting Tool

<table>
<thead>
<tr>
<th>Parameter / Units</th>
<th>Value</th>
<th>Parameter / Units</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>$R_{vcc}$ / Ω cm\textsuperscript{2}</td>
<td>1.82</td>
<td>$R_{ct}$ / Ω cm\textsuperscript{2}</td>
<td>4.17 x 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>$L_{cc}$ / H cm\textsuperscript{3}</td>
<td>2.12 x 10\textsuperscript{5}</td>
<td>$Q_{G}$ / F cm\textsuperscript{-2} s\textsuperscript{-1/2}</td>
<td>14.37</td>
</tr>
<tr>
<td>$Q_{CPE}$ / F cm\textsuperscript{-2} s\textsuperscript{(α-1)}</td>
<td>7.78</td>
<td>$k_{G}$ / s\textsuperscript{-1}</td>
<td>4.24 x 10\textsuperscript{-2}</td>
</tr>
<tr>
<td>$\alpha_{CPE}$</td>
<td>1.0</td>
<td>---</td>
<td>---</td>
</tr>
</tbody>
</table>
As can be seen from Figure 6.19(b), the fit using the ECM proposed exhibits an important deviation from the experimental data, especially around the ‘hump-shaped’ section in the vicinity of \( Z'' = 0 \). From this result it is clear that the inductive element introduced in the equivalent circuit did not seem to have the expected effect on the shape of the fitted curve in the high frequency range, which suggests that a different phenomenon is responsible of this result. The constant-phase and Gerischer elements representing the mass transfer phenomena at the molten tin anode were related exclusively with the impedance zone over \( Z'' = 0 \), so could not explain totally the ‘hump-shaped’ section. Unfortunately, due to the absence of a reference electrode measuring data directly from the anode (as in the case of the \( \text{LSM-YSZ/LSM} \) cathode) and the instability of the graphite rod current collector, it is difficult to elucidate which part of the impedance measured was actually related to the phenomena occurring at the anode. This limitation precludes a good fit of the experimental data and therefore the parameters generated using the ECM proposed and listed in Table 6.2 are not fully reliable.

It is important to note that the ECM proposed by Lvov et al. [176] produced a good fit with their experimental data because it represents the impedance response of the whole \( \text{Sn}_{\theta} \)-SOFC. This result could be explained considering that the impedance spectra obtained for the whole fuel cell showed an undeniable similarity with the results obtained for the isolated \( \text{LSM-YSZ/LSM} \) cathode, as discussed in Section 6.2.1. Hence, the effect of the ‘hump-shaped’ zone obtained in the impedance spectra for the anode | electrolyte arrangement was suppressed by the cathode response, so the ECM did not need to incorporate an additional element for modelling this phenomenon. This last observation is clear evidence of the limitations of EIS analysis in general when the electrochemical system studied is not adequately understood and suggests that, despite the experimental difficulties, the use of reference electrodes is necessary in order to obtain good comprehension of the phenomena.

From Table 6.2, it can be seen that the ohmic resistance \( R_{\text{cc}} \) obtained (0.37 \( \Omega \)) was lower than the electrolyte resistance calculated in Section 5.3 based on mathematical models (0.56 \( \Omega \)) and does not include the current collector resistance (0.36 \( \Omega \) in accordance with modelling). In view of these results, it is highly probable that these values are influenced by the uncompensated ‘hump-shaped’ section, so the inductance value \( L_{\text{cc}} \) calculated cannot be considered reliable. The pure capacitance \( \alpha_{\text{CPE}} = 1.0, \quad Q_{\text{CPE}} = 7.78 \text{ F cm}^{-2} \) obtained from the constant-phase element (CPE) can be related with accumulation of oxide...
ions ($O^{2-}$) at the anode | electrolyte interface according to the reaction mechanism proposed in Section 6.1.1 (see Figure 6.3). The charge transfer resistance $R_{ct}$ obtained (8.50 mΩ) is in good agreement with the value calculated using the mathematical models in Section 5.3 for tin dioxide (8.80 mΩ), suggesting that an oxide deposit was formed. However, it should not be thick enough to influence significantly the kinetics under open circuit conditions. Finally, kinetics of inclusion of molten tin in the YSZ electrolyte ($k_G$, $Q_G$) were relatively low, possibly due to the low wettability of zirconia-based ceramics by molten tin [161].

Considering that the inductive component at high frequencies was not well fitted by the ECM presented in Figure 6.19(a), it needs to be redesigned in order to represent accurately the charge transfer processes (high frequencies in impedance spectra) occurring at the anode | electrolyte interface. To achieve this objective, improved impedance measurements need to be made using, for example, a reference electrode and a more stable current collector at the anode side.

From the results presented in this section, it has been demonstrated that the cathode kinetics were controlled mainly by diffusion of oxygen gas through the porous electrode and accumulation of intermediate charged species ($O_{ad}^-$) in the LSM-YSZ cermet structure. These results suggest that the fuel cell kinetics could have been controlled by mass transport phenomena occurring at the cathode due to its poor microstructure. However, analysis of the molten tin anode performance in this section and Section 6.1 suggest that the mass transfer processes occurring in this electrode were more sluggish than at the cathode (compare, for example, the mass transfer components in Table 6.1 with the Gerischer element in Table 6.2). Consequently, the anode kinetics should control the whole fuel cell kinetics.
6.3. Chapter Summary and Conclusions

The longer term stability of a Sn\(_{(l)}\)-SOFC was studied based on current density transients, impedance spectra and post-mortem analysis of the fuel cell components and by-products.

According to chronoamperometric measurements of the Sn\(_{(l)}\)-SOFC operating at 0.42 V (maximum power density), oxygen saturation took place at the anode after ca. 50 min. At this time, a total oxygen concentration of ca. 0.87 M was calculated using Faraday’s equation, which was 0.69 M higher than the saturation concentration determined using equation (5.7). This result suggested that formation of tin dioxide at the anode | electrolyte interface occurred before oxygen saturation was reached in the bulk of the anode. Therefore, it was determined that ca. 127 mg of SnO\(_2\) were formed at the anode | electrolyte interface in 50 min, which corresponded to oxidation of ca. 0.59% of the total weight of molten tin in the anode.

From the shape of the current density transient, the following processes were proposed to explain the different stages of degradation in the longer term performance of the Sn\(_{(l)}\)-SOFC: (1) slow diffusion of atomic oxygen from the anode | electrolyte interface to the bulk of the liquid metal, (2) formation and growth of tin dioxide deposits at the electrolyte surface, and (3) diffusion of oxide ions (O\(^2^-\)) through the tin dioxide deposits from the electrolyte surface to the bulk of the anode.

X-ray analysis (SEM, EDX and XRD) of the tin dioxide deposits formed at the molten tin anode | electrolyte interface and the electrolyte surface suggested that SnO\(_2\) growth occurred by the following steps: (1) inclusion of molten tin at the YSZ electrolyte surface, (2) oxidation of oxide ions to atomic oxygen in the included liquid metal, and (3) formation and growth of tin dioxide at the anode | electrolyte interface. In addition, SEM and EDX post-mortem analysis of the graphite rod current collector established that formation of pores at its surface occurred during Sn\(_{(l)}\)-SOFC operation, enabling SnO\(_2\) growth inside these cavities and resulting in poor electrochemical measurements in the longer term.

The performance stability of the whole Sn\(_{(l)}\)-SOFC, anode | electrolyte arrangement and cathode were studied by impedance measurements at open circuit conditions and different anode and cathode activation overpotentials. From these results, the cathode was shown to be highly stable in the entire range of potentials of fuel cell operation, while the anode was severely affected by any cell potential applied other than open circuit conditions. In addition,
equivalent circuit models (ECMs) were fitted to the impedance spectra obtained for the cathode and anode | electrolyte arrangement operating at $\eta^{act}_{c//a} = 0$. In the case of the cathode, a good fit of the data was obtained using a model which included two parallel circuit elements representing the charge transfer (high frequency) and mass transfer (low frequency) processes taking place at the LSM-YSZ electrode. The cathode exhibited mass-transfer controlled kinetics due to its poor microstructure, which promoted difficult transport of: (1) oxygen gas from the bulk to the active sites of the electrode, and (2) intermediate charged species ($O^{\text{ad}}_{\text{ad}}$) to the TPBs. In the case of the anode, the mass transfer processes were more sluggish than at the cathode, mainly due to poor contacting between the molten tin anode and the YSZ pellet ('slow' inclusion of the liquid metal in the electrolyte surface) and formation of tin dioxide at the anode | electrolyte interface. The ECM proposed for the anode | electrolyte arrangement did not fit well the 'hump-shaped' zone of the impedance spectra at high frequencies (zone of charge transfer control) using an inductive element. Hence, it is suggested that a better system with a reference electrode in the anode side (e.g. embedded platinum wire in the YSZ pellet) and a more stable current collector (e.g. highly conductive perovskites, as discussed in Section 5.4) is used in order to separate the actual phenomena taking place at the anode from the side effects produced by other fuel cell components, such as the electrolyte and anode current collector.
7. Potential and Current Distributions in the Sn(l)-SOFC

In this chapter, an overview of the theory of potential and current distributions is presented in order to incorporate its concepts into the analysis of the results presented and discussed in Chapter 6. The current density and the potential along the electrode | electrolyte interfaces depend on the position, which implies that they are not equal to the mean values of cell voltage (or overpotentials) and current density predicted by the mathematical model described in Chapter 5. This provides an explanation of the form in which the tin dioxide deposit grows at the anode | electrolyte interface, since the current density on this surface (formation rate of the product) depends on the position. In addition, the geometry and conductivities of the fuel cell components determine how the potential is distributed in the system, and therefore the reference electrode used in the experimental Sn(l)-SOFC described in Section 4.1 could not be an ideal equipotential surface as expected. This situation particularly is observed when potentials other than equilibrium values are applied to the electrodes, and which could have a negative impact on the reliability of the EIS measurements analysed in Section 6.2.1.

The potential and current distribution of an electrochemical system can be described as primary, secondary or tertiary, depending on which of the kinetic effects (activation overpotentials, concentration overpotentials, and ohmic losses) are considered in the solution of the charge and mass transport equations. For primary distributions, effects of kinetics at the electrodes are neglected, so only the effects of the geometry and conductivities determine potential/current distributions. Secondary distributions take activation overpotentials at the electrodes into account, which make those distributions more uniform than primary distributions, which hence constitute the worst case. Tertiary distributions consider activation and concentration overpotentials, so in the limit of totally mass transport controlled current densities, these distributions are the most representative.

This chapter presents and discusses only the primary distribution of potential and current of the experimental Sn(l)-SOFC used in this project. Since this result corresponds to the least uniform potential and current distributions, it is useful for the analysis of the results discussed in Chapter 6 and gives support to the theory proposed therein to explain the formation and growth of tin dioxide at the anode | electrolyte interface.
7.1. Theory of Potential and Current Distributions

In general, the current density along the surface of the electrodes and the potential difference at the electrode | electrolyte interface depend on the position and are not equal to the mean current density and cell voltage values predicted by the lumped parameter model discussed in Chapter 5. For example, the current density tends to be larger on the crests of an electrode with a serrated profile (Figure 7.1(a)) or near the edges of an electrode that does not entirely fill the cross section of the electrolyte (see Figure 7.1(b)). This situation is associated with the fact that at these privileged spots, the cross section available for the passage of charges through the electrolyte increases with increasing distance from the electrode, so that the resistance for the current flow from anode to the cathode is smaller at these spots than in other parts of the surface.

Figure 7.1. Schematic of the spots at which the current density tends to be larger in: (a) an electrode with a serrated profile and (b) a planar electrode pair with a cross section shorter than the electrolyte

The potential and current distributions are of great importance for the technical applications of electrochemistry. For example, the current distribution in electroplating determines the local variation of the coating thickness, which is desirable to be minimized in order to avoid an accelerated corrosion of the less protected parts (zones with a thin coating layer). In electrometallurgy, for example in copper refining, the metallic layers deposited on the cathode are much thicker than in electroplating, so a non-uniform current distribution could cause the formation of local protuberances (dendrites) that may promote short-circuits if they come in contact with the anode surface. This situation imposes a lower limit to the inter-electrode distance, which should be as small as possible in order to minimise ohmic potential losses reduce the energetic losses through the Joule effect in the solution. In the case of SOFCs, the potential and current distributions are an important design aspect.
especially considering that the fuel and oxidant consumption along the electrodes depends directly on the current density and is a determining factor for the efficiency of the fuel cell (see Chapter 2).

The main factors on which the current and potential distributions over an electrode depend are: (1) the geometry of the system; (2) the conductivity of the electrolyte and electrodes; (3) the activation overpotentials, which depend on the kinetics of the electrode reactions; and (4) the concentration overpotentials, which are caused by the concentration differences between the electrode | electrolyte interface and the bulk environment where the reactant/product species are present\[^{18}\]. A more detailed description of the conductivity and activation/concentration overpotentials associated with a Sn\(_{0.7}\)-SOFC are given in Chapter 2 and Chapter 5.

Depending on the operating conditions, the influence of one or the other of these factors may be more or less neglected. Accordingly, three main types of current distributions can be distinguished:

- **Primary distribution**: this is established when the influence of the overpotentials is negligible. The absence of concentration overpotentials implies that there are no appreciable concentration gradients between the electrode | electrolyte interfaces and the bulk environments. In addition, the absence of activation overpotentials means that there is no influence of the kinetics of the electrode reactions.

- **Secondary distribution**: in this case, the activation overpotentials at the electrodes are taken into consideration, but the influence of the concentration overpotentials is still neglected.

- **Tertiary distribution**: this takes into account both the activation and concentration overpotentials.

The most general theoretical approach to the problem of potential and current distribution starts from the integration of the fundamental equation of mass and charge transport \([16, 193, 242]\):

\[
\frac{\partial C_B}{\partial t} = D_B \nabla^2 C_B - F \left( RT \right)^{-1} v_B D B \nabla \cdot (C_B \nabla \phi) - \nabla \cdot \nabla C_B + \sum_r u_{r,B}^* 
\]

\(^{(7.1)}\)

\[^{18}\] Depending on the type of electrochemical cell studied, the bulk environment can be referred, for example, to the electrolyte solution in an aqueous system or the gas streams fed into the electrodes chambers in a conventional SOFC.
where the term $D_B \nabla^2 C_B$ is related to the diffusion of species $B$ being generated or consumed in the electrochemical system, $F (RT)^{-1} v_B D_B \nabla \cdot (C_B \nabla \phi)$ is associated with the migration of this species, $\nu \cdot \nabla C_B$ is related to the convective processes taking place into the system, and $\sum_r \nu^*_{B,r}$ is the total number of moles of species $B$ produced (or consumed) per unit of time and per unit of volume through all the homogeneous reactions $r$ taking place in the system.

In practice, more or less simplified versions of this equation are used depending on the type of distribution considered (primary, secondary or tertiary). In the case of primary and secondary distributions, where the influence of the concentration overpotentials is neglected, there are no concentration gradients in the system, i.e. the terms $D_B \nabla^2 C_B$ and $\nu \cdot \nabla C_B$ in equation (7.1) can be neglected. Furthermore:

$$\nabla \cdot (C_B \nabla \phi) = \nabla C_B \cdot \nabla \phi + C_B \nabla^2 \phi = C_B \nabla^2 \phi$$  \hspace{1cm} (7.2)

Finally, if equation (7.1) is multiplied by the reaction electron stoichiometry $\nu_i$ and the sum for all the ionic species $i$ in the system is taken, the terms $\sum_i \nu_i (\partial C_i / \partial t)$ and $\sum_i \sum_r \nu_i \nu^*_{i,r}$ are nil because of the electroneutrality condition: $\sum_j \nu_j C_j = 0$ [16, 193, 242]. Therefore, equation (7.1) is reduced to:

$$\nabla^2 \phi = 0$$  \hspace{1cm} (7.3)

which is Laplace’s equation. The electroneutrality condition, which is implied in the validity of equation (7.3), means that this equation can be applied everywhere except at the electrical double layers at the electrodes. Therefore, the boundary condition for the integration of equation (7.3), which yields the potential field in the electrolyte, can be formulated as a value of the potential prevailing at the electrolyte side limit of the electric double layer. The formulation of this boundary condition is not the same for primary and secondary distributions, as it will be seen in Section 7.1.1 and Section 7.1.2.

In the absence of concentration gradients, the current density $j$ at any point in the electrolyte is proportional to the gradient of the potential $\phi$ at that point and to the conductivity $\sigma_e$ of the electrolyte as follows:
which corresponds to Ohm’s law. The current density is a vector perpendicular to the equipotential surfaces, and thus it is the tangent to the current lines. The latter indicate the direction in which the current flows and show the path followed by electric charges.

The following sub-sections introduce a more detailed description of the three types of potential and current distribution, and the boundary conditions used to solve the corresponding charge and mass transfer equations in each case.

7.1.1. Primary Distribution

The first important assumption made to obtain the primary (and secondary) distribution of potential and current in an electrochemical system is that the conductivities of the electrodes are infinite compared to the conductivity of the electrolyte, which means that there is no potential differences within the cathode/anode and the electrode side of the cathode/anode | electrolyte interface is an equipotential surface. In addition, since the influence of the overpotentials is negligible in the primary current distribution, the potential across the double layer is constant over the electrode. As a result, the electrolyte side of the double layer is an equipotential surface also, which can be taken as a boundary condition for the integration of equation (7.3).

Since the electrolyte is usually bounded not only by the electrodes but also by insulating surfaces, such as the cell walls or the free surface of the electrolyte, a second boundary condition associated with no current flows through an insulating surface is necessary. Therefore, the boundary conditions for the integration of equation (7.3) can be written as follows:

At the electrode surface: \[ \phi = \text{const.} \] \hspace{1cm} (7.5)

At the insulating surface: \[ \frac{\partial \phi}{\partial n} = 0 \] \hspace{1cm} (7.6)

For simple geometries of the electrochemical system, analytical solutions can be derived for equation (7.3), and consequently (7.4), using the boundary conditions (7.5) and (7.6). For example, for the case of a cell with two plane parallel electrodes embedded in insulating
walls as the one presented in Figure 7.2, Newman reported the following expression for the current distribution [243]:

\[
\frac{j_x}{j} = \frac{\varepsilon \cosh \varepsilon / K\left(\tanh^2 \varepsilon\right)}{\left[\sinh^2 \varepsilon - \sinh^2 \left(2x'\varepsilon / l\right)\right]^{1/2}}
\]

(7.7)

where \(\varepsilon = \pi l / 2h\), \(h\) being the distance between the two electrodes, \(l\) the length of the electrode and \(x'\) the distance from the centre of the electrode. The function \(K(m)\) (with \(m = \tanh^2 \varepsilon\)) is the first-order elliptic integral whose numerical values are given in tables [244]. Figure 7.3 presents the current distribution predicted by equation (7.7) for the case of \(h = 2l\).

As can be seen from equation (7.7), the current distribution depends on two characteristic dimensions: \(h\) and \(l\). If a disk electrode is considered instead, the current distribution would depends on the radius \(r_0\) of the disk [245], which makes it clear that the geometry of the system is a determining factor in the solution of the Laplace equation.

The complexity of equation (7.7) shows that even for a relatively simple electrode configuration, calculation of the primary current distribution is an intricate problem which increases in difficulty with increasing complication of the geometry. Therefore, in most of the
cases numerical methods of integration, such as finite-difference or finite-element methods, are needed in order to solve equation (7.3). In Section 7.2, the primary potential and current distributions of the experimental Sn\textsubscript{n0}\textsubscript{-SOFC} used during this research project are presented, based on the numerical solutions obtained from the simulation software COMSOL Multiphysics 4.3a which use finite-element methods to solve the Laplace equation.

![Graph](image)

**Figure 7.3.** Primary current distribution in the cell of Figure 7.2 with $h = 2l$ calculated using Newman’s equation (7.7)

To conclude this section, it is important to notice that equation (7.7) shows that the local current density becomes infinite at the edge of the electrodes ($x' = l/2$). This type of behaviour is always observed in the case of the primary current distribution and can only be avoided when an electrode fills the cross section of the cell completely and is perpendicular to an insulating wall. If the angle between the electrode and the insulating wall is sharp, the current density at the edge is zero; if the angle is obtuse, the current density is infinite. In reality, the local current density does not become infinite because of two main reasons: (1) in practice, the angle is never perfectly even, and (2) the overpotential opposes to very strong variations in the current density, so that it cannot take extreme values, as will be discussed with more detail in Section 7.1.2. This last condition leads to the secondary distribution, in which the kinetics at the electrodes are considered in the solution of the Laplace equation.
and the value of the conductivity of the electrolyte influences the repartition of the potential and current.

7.1.2. Secondary Distribution

As discussed previously in this chapter, near the edges of plane electrodes the current densities tend to be larger because the resistance at current tube A is smaller than that at current tube B in Figure 7.2. If the activation overpotentials at the electrodes are introduced in the current distribution analysis, it would be determined that the large current densities near the edges cause these electrode overpotentials to be higher there than towards the centre of the electrode surfaces (\( \Delta \phi_1 > \Delta \phi_2 \)). Consequently, since the potential difference between the interior of the metal cathode and that of the anode is constant everywhere, the following relation is obtained:

\[
\Delta \phi_m = \Delta \phi_1 + \Delta \phi_A = \Delta \phi_2 + \Delta \phi_B
\]  

(7.8)

Considering the larger value of \( \Delta \phi_1 \), the potential difference \( \Delta \phi_A \) over tube A in Figure 7.2 is smaller than that available for tube B (\( \Delta \phi_B \)). Therefore, the current density at the edge in A does not increase as strongly as it would in the absence of the equalizing action of the activation overpotentials.

In order to make clearer the effect of the activation overpotential in the current distribution, the polarization resistance \( R_{act} \) will be defined as follows:

\[
\frac{d\eta_{act}}{dj} = R_{act}
\]  

(7.9)

This expression represents the slowness of charge transfer across the interface. In addition, since it is in series with the resistance of the electrolyte, \( R_e \), and with the polarization resistance of the counter electrode, \( R_{act}^{'} \), it is related with the kinetics of the overall electrochemical system.

It is clear that if the activation overpotential is a linear function of the current density, the resistance \( R_{act} \) is a constant. In addition, if the kinetic properties of the interface are invariable, the polarization resistance \( R_{act} \) will also remain constant along the interface. It means, for example, that its value will be the same at the crests and recesses of the
serrated cathode profile presented in Figure 7.1(a). In this system, the resistance $R_p$ of the solution at a peak is smaller than the resistance $R_r$ of the solution at a recess, for reasons mentioned at the beginning of this sub-section (equation (7.8)). Hence, the following relation can be obtained:

$$\frac{j_p}{j_r} = \frac{R_r}{R_p} > 1$$ (7.10)

where it is clear that the current density is larger at the peak ($j_p$) than in the recess ($j_r$).

However, if a larger enough constant resistance is added in series to $R_p$ and $R_r$ (which would correspond to the polarization resistance at the electrode), the peak and recess will differ less with respect to the total resistance, i.e., the current distribution is rendered more uniform [242]:

$$\frac{j_p'}{j_r'} < \frac{j_p}{j_r}$$ (7.11)

A similar situation is obtained in the case of a cell with plane electrodes (Figure 7.2) where the resistance at tube A is smaller than that at tube B. Therefore, in accordance with the discussion above, if the same polarization resistances are added in series to both $R_A$ and $R_B$ the difference between the currents flowing through the two sets of resistances decreases.

If the polarization resistance $R_{act}$ is much larger than the electrolyte resistance $R_e$, a uniform current distribution can be obtained, even if the geometry is non-uniform and tends to cause a non-even distribution. On the other hand, if $R_{act}$ is zero, a primary current distribution is obtained, which indicates that in the former case the transfer of charges through the interface is what controls the current distribution, whereas in the latter case the transfer of charges through the electrolyte is controlling. In order to quantify and characterize more precisely the equalizing action of the activation overpotential in the current distribution, the following dimensionless group has been defined:

$$Wa = \frac{d\eta_{act}}{dj} \frac{\sigma_e}{L} = \frac{R_{act}}{R_e}$$ (7.12)
where $\sigma_e$ is the conductivity of the electrolyte and $L$ is a characteristic length equal to the distance $h$ in the case of Figure 7.2. Equation (7.12) is known as the Wagner number and represents the ratio of the polarization resistance to the solution resistance [242]. The larger the Wagner number is the more even the current distribution in spite of a non-uniform geometry.

The principle of the quantitative evaluation of secondary current density distribution is essentially the same as for the primary distribution; this is the solution of the Laplace equation (7.3) with appropriate boundary conditions. The insulating surfaces remain defined by the boundary condition (7.6), but the potential at the electrode surfaces are different from equation (7.5), since in the secondary distribution the influence of the activation overpotential has to be taken into account, which means that the potential difference $\Delta \phi$ over the electrode | electrolyte interface is dependent on the current density. Even if the metallic side of the interface is an equipotential surface ($\phi_m$), the electrolyte side is not because, in general, the local current density varies along the interface. In the case of a single electrode reaction, the boundary condition at the electrode | electrolyte interface can be defined as:

$$\phi_e = \phi_m - \Delta \phi$$  \hspace{1cm} (7.13)

where $\phi_e$ is the potential at the electrolyte side of the electrode | electrolyte interface and $\phi_m$ is the constant value of the potential in the interior of the metal. $\Delta \phi$ is a function of current density which is determined by the kinetics of the electrode reaction, thus it is linked to the overpotential by the relationship:

$$\eta_{act} = \Delta \phi - \Delta \phi_{eq}$$  \hspace{1cm} (7.14)

where $\Delta \phi_{eq}$ is the potential difference at the interface when the electrode reaction is at equilibrium ($j = 0$).

In order to calculate the potential and current density profiles across the electrolyte, an explicit expression for the potential difference $\Delta \phi$ must be used. The most commonly employed relationships are the linear approximation and Tafel equation for the activation overpotential $\eta_{act}$.

In the case of the linear approximation, the overpotential is defined by the equation [193]:
\[
\eta_{\text{act}} = \frac{jRT}{j_0\nu_c F}
\]

which is valid for values of \( \eta_{\text{act}} \) for low ratios of operating current density to exchange current density. In this case, the derivative \( d\eta_{\text{act}}/dj \) corresponds to a constant polarization resistance: \( R_{\text{act}} = RT/j_0\nu_c F \).

In the case of the Tafel equation, the overpotential is defined by equation [193]:

\[
\eta_{\text{act}} = \chi + \beta \ln j
\]

where \( \chi = \ln(j_0)RT/\alpha\nu_c F \) and \( \beta = RT/\alpha\nu_c F \). This equation is valid at sufficiently large values of \( \eta_{\text{act}} \) (either negative or positive) at which one of the exponential terms in Butler–Volmer equation (2.19) becomes negligible.

In some treatments of potential and current distribution, the more complex kinetic equations (2.19) or (5.21) have to be used as boundary condition. Therefore, a more difficult problem than in the case of primary distribution has to be solved and numerical methods are the only alternative to obtain results.

7.1.3. Tertiary Distribution

As stated previously in this chapter, in tertiary current distributions concentration variations within the electrochemical system must be taken into account. Hence, the Laplace equation (7.3) has to be replaced by equation (7.1). In addition, equation (7.4) for the current density is also no longer valid and has to be replaced by the equation:

\[
j = -\frac{F^2}{RT} \nabla \phi \sum_k \nu_k^2 D_k C_k - F \sum_k \nu_k D_k \nabla C_k
\]

which considers the concentration gradient effects on the reaction rate.

The solution of this problem is more complex than those for primary and secondary distributions, but can be simplified making the assumption that the concentration gradients are essentially restricted to the diffusion layers, the thicknesses of which are small compared to the main dimensions of the system. Therefore, the bulk of the electrolyte in a cell such as that presented in Figure 7.2, for example, can be treated in a different manner than the
potential and current distributions in the Sn(l) - SOFC diffusion layers. In the inner zones of the electrolyte, where there are no concentration gradients, the Laplace equation (7.3) can be applied, while in the diffusion layers the potential drop and its influence on the concentration variations can be neglected. In that manner, the current flowing through the electrodes is calculated in two different ways: first by integrating the Laplace equation down to the outer limit of the diffusion layer (i.e. virtually down to the electrode), and second from the mass transport equations for a given interfacial concentration and a given distribution of the latter [16, 242]. Since the two calculated currents must be equal, the interfacial concentration must be adjusted in such a manner that this condition is fulfilled, which means that an optimization problem must be solved in parallel with the solution of the charge and mass transfer equations.

The methodology described above is useful in some cases such as the plane and disk electrodes discussed previously in this section. However, when diffusion processes are occurring in porous or molten metal electrodes, such as those used in the system studied in this project, these approximations are not reliable considering the hardly predictable concentration profiles of the species in the porous structure of the cermet cathode and the growth of a tin dioxide layer in the anode | electrolyte interface. Therefore, numerical methods would have to be used in order to produce an accurate representation of the phenomena taking place at the Sn(l)-SOFC, if the effects of the activation and concentration overpotentials in the system need to be derived.

The following section presents the analysis of the primary distributions of potential and current in the experimental Sn(l)-SOFC used during this research project. This study was based on the results obtained in COMSOL Multiphysics 4.3a for the 3D-model of the fuel cell arrangement described in Section 4.1. The purpose of this analysis was to determine the influence that the potential and current distributions had on the experimental results presented and discussed in Chapter 6, especially these related with the way in which tin dioxide grows at the anode | electrolyte interface (Section 6.1.2) and the reliability of the reference electrode measurements when potentials different to the equilibrium potential are applied at the electrodes during EIS analysis (Section 6.2.1).

7.2. Primary Potential and Current Distribution in the Sn(l)-SOFC

As stated in Section 7.1, the primary distribution corresponds to the most simplified case of potential and current distributions, thus could be considered as the analysis of the “worst case”. The results presented in this section provide a further explanation to the growth of tin
dioxide from the borders of the clean surface of the molten tin anode during operation of the
fuel cell studied (see Figure 6.5(b) and Figure 6.5(d)), and sustain the hypothesis advocated
in Chapter 6 to explain this phenomenon. In addition, based on the study of the equipotential
surfaces next to the reference electrode, the reliability of the EIS measurements at other
than open circuit conditions (see Section 6.2.1) was analysed. Based on mathematical
models and experimental results, Hill et al. [246] determined that the position and
dimensions of the electrodes in a three-electrode system can have significant effects on
impedance measurements; hence, the need to determine the effect of the particular
Sn(l)-SOFC geometry used during this research project in distorting the results presented in
Section 6.2.1.

Laplace’s equation (7.3) was solved numerically using COMSOL Multiphysics 4.3a for
the 3D geometric model of the experimental Sn(l)-SOFC. The geometry of the LSM-YSZ
cathode | YSZ electrolyte pellet half-cell corresponding to that shown in Figure 4.1(a) was
modelled without the current collectors, which did not affect the primary potential and current
distributions (see Section 7.1). The anode was modelled as a 5 mm thick molten tin layer
positioned over the clean surface of the YSZ pellet electrolyte. Figure 7.4 shows a
cross-sectional view of the modelled Sn(l)-SOFC across a cut plane parallel to the x-y plane
with its z-coordinate placed on the centre of the electrolyte (origin of the coordinate system).

The dimensions of each fuel cell component are summarized in Table 7.1, listing the
diameters and thicknesses of electrodes and electrolyte. The dimension $d_{ca-re}$ corresponds
to the diameter of the circle around the cathode and reference electrode, which were
separated by a gap of constant width $\Delta_{ca-re}$ along the direction perpendicular to the plane
x-y in Figure 7.4.

![Figure 7.4. Cross-section view of the modelled Sn(l)-SOFC across a cut plane parallel to the x-y plane with its z-coordinate placed on the centre of the electrolyte (origin of the coordinate system)](image)

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Table 7.1. Dimensions of the components of the Sn\textsubscript{0.7}-SOFC modelled for analysis of the primary potential and current distribution.

<table>
<thead>
<tr>
<th>Fuel cell component(s) dimension / distance</th>
<th>Dimensions</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anode diameter, $d_{an}$</td>
<td>25 mm</td>
</tr>
<tr>
<td>Anode thickness, $t_{an}$</td>
<td>5 mm</td>
</tr>
<tr>
<td>Electrolyte diameter, $d_e$</td>
<td>30 mm</td>
</tr>
<tr>
<td>Electrolyte thickness, $t_e$</td>
<td>2 mm</td>
</tr>
<tr>
<td>Cathode - reference electrode circle diameter, $d_{ca-re}$</td>
<td>23 mm</td>
</tr>
<tr>
<td>Distance between cathode and reference electrode, $\Delta_{ca-re}$</td>
<td>3 mm</td>
</tr>
<tr>
<td>Cathode/reference electrode thickness, $t_{ca/re}$</td>
<td>90 µm</td>
</tr>
</tbody>
</table>

The conductivities of the LSM/YSZ cathode and the YSZ electrolyte were determined using equation (5.48), while the conductivity of the molten tin anode was calculated based on the resistivity value determined by equation (5.49). The boundary conditions used to solve the primary distribution in the geometry represented by Figure 7.4 are summarized in Table 7.2, based on the 2D boundaries defined in Figure 7.5. The actual problem solved corresponded to a 3D geometry similar to that shown in Figure 4.1(a), so the boundaries defined in Figure 7.5 are a simplification of the real 3D boundaries used. However, the two-dimensional representation along this section was used as it provided a clearer visualization of the problem being solved and its solution.

![Figure 7.5. Two-dimensional representation of the boundaries defined to determine the primary distribution of potential and current in the experimental Sn\textsubscript{0.7}-SOFC system](image-url)
As can be seen from Table 7.2, at the boundaries of the molten tin anode a constant potential equal to 0 V (ground) was assumed, with 0.42 V (cell voltage) at the boundaries of the LSM/YSZ cathode. These conditions were defined to enable the primary distributions of potential and current to be predicted for the Sn_{(l)}-SOFC operating at its maximum power density (“extreme case”), corresponding to the case discussed previously in Section 6.1. The electrolyte free surface and the reference electrode were considered to be insulating elements, since no current should be flowing through their boundaries during fuel cell operation.

Figure 7.6 shows the potential distribution over the cross-sectional view presented in Figure 7.4 (plane x-y with z-coordinate at 0 mm, along the electrolyte centre). As can be seen, the potential decreased across the electrolyte from the surface of the cathode towards the anode, following equipotential surfaces that reached the position of the reference electrode at values < ca. 26 mV. Similar cross-sectional views were generated for x-y cut planes with z-coordinates equal to 3 mm and 6 mm from the electrolyte centre, but they are not shown here since the behaviour of the equipotential surfaces across the electrolyte did not show major differences from the result in Figure 7.6. Figure 7.7 shows the variation of potential along the reference electrode | electrolyte interface (boundary B12 in Figure 7.5) for the z-coordinates: 0 mm, 3 mm, and 6 mm. As can be seen, the potential difference along the reference electrode | electrolyte interface increases towards the centre of electrolyte (z = 0 mm), reaching its maximum at ca. 24 mV along this line. This value corresponds to approximately 5.7% of the cell voltage, which could be considered as a negligible error in the control of the cathode or anode overpotentials in the impedance analysis presented in Section 6.2.1. Nevertheless, upgrading the design of the experimental Sn_{(l)}-SOFC is essential if improved equivalent circuit models are to be achieved leading to improved understanding of fuel cell kinetics (see Section 6.2.2).
Figure 7.6. Primary potential distribution across the electrolyte of the experimental Sn\textsubscript{0.95}-SOFC for the cross-sectional view shown in Figure 7.4

Figure 7.7. Potential distribution along the reference electrode | electrolyte interface (boundary B12 in Figure 7.5) for three z-coordinates: z = 0 mm (centre of the electrolyte), z = 3 mm, and z = 6 mm. The position in the x-axis moves out from the border of the reference electrode which is closer to the cathode (B17 in Figure 7.5)
Figure 7.8(a) and Figure 7.8(b) present, respectively, the current density profile and current lines across the electrolyte for the cross-sectional view presented in Figure 7.4. As discussed in Section 7.1, the current density at the edges of the electrodes should be higher than at the interior positions due to the lower resistance offered by the former to the current flow. Figure 7.8(a) shows that the current densities at the edges of the cathode were markedly greater than at the edges of the anode, probably due to the lower resistance that the thin \( \text{LSM-YSZ} \) layer (90 \( \mu \)m) offers to current flow in comparison to the thick molten tin anode (5.0 mm). This considerable difference in thicknesses promotes current densities about 5 times higher at the cathode edges compared with the average current density at the anode edges and surface. However, this edge effect does not seem to have any consequence in the distribution of current density across the electrolyte. In effect, the current density profile inside the YSZ pellet cross-section appeared rather uniform around \( 1000 \text{ A m}^{-2} \), which is in good agreement with the average current density value of ca. \( 1082 \text{ A m}^{-2} \) predicted by the kinetic model derived in Chapter 5 for the case of a \( \text{Sn(l)} -\text{SOFC} \) operating in fuel cell mode at a cell voltage of ca. 0.42 V.

Figure 7.8(b) shows the current lines across the electrolyte, which represent the paths that \( O^2^- \) ions followed in the operational \( \text{Sn(l)} -\text{SOFC} \). As can be seen, despite the fact that the reference electrode was an insulating element, where no oxygen reduction occurred, the reduced species produced at the cathode moved towards the region of the electrolyte parallel to the zone at which the reference electrode was located. This condition was related to the larger anode diameter, which covered the entire circumference containing the cathode and reference electrode, and suggested that some tin dioxide could be formed at the anode | electrolyte interface parallel to the reference electrode.

Finally, Figure 7.9 shows the current density distribution along the anode | electrolyte interface (boundary B4 in Figure 7.5) for the cross-sectional view shown in Figure 7.4. As can be seen, the current density decayed from boundary B2 to boundary B3 along the x-axis, probably due to the absence of a parallel cathode surface towards the right-hand side boundary (the cathode ended at the x-coordinate equal to 18 mm). This condition indicates that a lower flux of ionic species would have been driven across the electrolyte towards the position of the anode | electrolyte interface neighbouring the boundary B3. Therefore, the tin dioxide layer formed on this interface grew following the irregular shape observed in Figure 6.5(b) and Figure 6.5(d), where it is clear that the formation of \( \text{SnO}_2 \) is more favourable over the section of the electrolyte parallel to the cathode. In addition, this result demonstrates that even though the current lines passed over the reference electrode position, the oxidation
product formed preferentially over the section of the anode | electrolyte interface that was parallel to the cathode, where the local current density was higher.

Figure 7.8. Primary current distribution across the electrolyte of the experimental Sn\textsubscript{10}-SOFC for the cross-sectional view shown in Figure 7.4: (a) current density profile and (b) current lines
Figure 7.9. Current density distribution along the anode | electrolyte interface of the experimental Sn$_{0.01}$-SOFC (boundary B4 in Figure 7.5) in the cross-sectional view presented in Figure 7.4. The position x = 0 mm corresponded to the boundary B2 in Figure 7.5

Before finishing this section, it is important to note that the primary current distribution does not provide a clear explanation to the growth of the tin dioxide product from the edges of the clean surface of the molten tin anode, which in Section 6.1.2 was associated to a displacement of the border of the electrode from the alumina tube wall to the internal border of the SnO$_2$ deposit (see Figure 6.8). This type of phenomena could be included in the analysis of the tertiary distribution of potential and current, since it considers the effects of the chemical reactions occurring in the electrochemical system. However, since the experimental Sn$_{0.01}$-SOFC used in this research project was not optimized, it was considered that improvement of the fuel cell design is the first step to be taken towards developing a more elaborated mathematical model.
7.3. Chapter Summary and Conclusions

The primary distributions of current and potential in the experimental Sn\textsubscript{SnO\textsubscript{2}}-SOFC were analysed to provide a further explanation of the form in which tin dioxide grew at the anode | electrolyte interface when a cell voltage of 0.42 V was applied (maximum power density condition). In addition, the potential distribution on the surface of the reference electrode was modelled to determine the adverse effects that it could have had on the EIS measurements presented and discussed in Section 6.2.1.

The potential across the electrolyte decreased from cathode to anode, as expected, while the calculated shape of the equipotential lines was independent of the cross section considered along the z-coordinate. This resulted in a distribution of potential along the reference electrode | electrolyte interface which exhibited a constant decay along the x-coordinate (from the internal boundary of the reference electrode closer to the cathode). The predicted maximum potential difference over this surface on the line passing through the centre of the electrolyte disc was ca. 24 mV, which corresponds to approximately 5.7% of the cell voltage. It could be considered that the effects of such low potential differences on the reference electrode surface were negligible in the EIS measurements. However, improvements in the design of the experimental system are needed if a more comprehensive understanding of the fuel cell kinetics is to be achieved, based on equivalent circuit models (see Section 6.2.2).

The current distribution was predicted to be quite homogenous across the electrolyte, except at the edges of the cathode where values 5 times higher than the mean current density (ca. 1 000 A m\textsuperscript{-2}) were predicted. This condition is associated with the analysis of the primary current distribution with large differences between the thicknesses of the cathode LSM/YSZ layer (90 µm) and the other cell components (anode: 5 mm, electrolyte: 2 mm), which would have promoted lower resistances to current flow at the electrode edges. In addition, anode current densities decayed along the anode | electrolyte interface from the edge closer to the left-edge of the cathode (boundary B2) to the edge closer to the right-edge of the reference electrode (boundary B3). This phenomenon was due to the shorter radius of the cathode than anode along the x-axis, which resulted in smaller current densities towards the zone of the electrolyte parallel to the reference electrode. Therefore, growth of tin dioxide occurred preferentially along the anode | electrolyte interface parallel to the cathode surface, while positions parallel to the reference electrode remained almost unaffected.
Making the cathode radius equal to or greater than the anode radius would have greatly diminished the potential differences parallel to the reference electrode surface, even for primary potential and current density distributions, and would be even smaller for secondary distributions. Therefore, redesign of the \( \text{Sn}_{0.01}\)-SOFC geometry is suggested if a more comprehensive analysis of the kinetic aspects of the process is attempted.
8. Performance of Sn(l)-SOFCs Operating in Fuel Cell Mode

This chapter reports the results of a brief study of the performance of Sn(l)-SOFCs operating in fuel cell mode, it is when the oxidized species produced at the molten tin anode were removed continuously by oxidation of a fuel. The discussion is based on the thermodynamics and kinetics of tin dioxide reduction by carbon or hydrogen (reducing agent) and the results obtained by CellTech Power Inc. for their Sn(l)-SOFC technology.

The Gibbs free energy changes and equilibria of the reactions of tin dioxide reduction by carbon or hydrogen were determined, including the direct and indirect combustion of carbon and the reversed Boudouard reaction, based on the thermodynamic theory presented in Chapter 2. The kinetic aspects of these processes are discussed based on the results obtained previously by other authors. The performance of the Sn(l)-SOFC technology developed by CellTech Power Inc. was analysed based on these thermodynamic and kinetic data and compared with the experimental and modelling results presented previously in this thesis for a Sn(l)-SOFC operating in battery mode (see Chapter 5 and Chapter 6).

Finally, the performance of a Sn(l)-SOFC operating with a molten tin anode stirred continuously by bubbling a flow rate of gas into the melt, was studied and compared with the results presented in Chapter 5 for a Sn(l)-SOFC with a quiescent anode and with the performance of the system developed by CellTech Power Inc. The effects of current density on cell potential differences and power densities were determined for this fuel cell system operating with helium or hydrogen as the stirring agent. In addition, impedance spectra for the whole fuel cell and the anode | electrolyte arrangement are presented for analysis of the ohmic losses and electrical response of the fuel cell components when operating under these conditions.
CHAPTER 8.
PERFORMANCE OF Sn\textsubscript{(l)}-SOFCs OPERATING IN FUEL CELL MODE

8.1. Reduction of Tin Dioxide and its Effects on the Performance of a Sn\textsubscript{(l)}-SOFC

In this section, a comprehensive study of the reduction of tin dioxide using carbon or hydrogen is presented based on the thermodynamic mathematical models introduced in Chapter 2 and the experimental results obtained previously by other authors for characterization of the kinetics of this process [203, 247, 248]. The objective of this study was to achieve a better understanding of the effects that the presence of a fuel has on the performance of a Sn\textsubscript{(l)}-SOFC and determine how it was related with the improved fuel cell kinetics obtained by CellTech Power Inc. using its Sn\textsubscript{(l)}-SOFC technology [163].

8.1.1. Thermodynamics and Kinetics of Tin Dioxide Reduction using Carbon and Hydrogen

Reduction of metal oxides using carbonaceous materials such as charcoal, graphite and coke, has been historically the most popular and economical method to produce pure metals. For this reason, in the last decades several authors have studied the thermodynamic and kinetic aspects associated with the carbothermal reduction of different metal oxides such as cuprite (Cu\textsubscript{2}O), tenorite (CuO), magnesia (MgO) and zincite (ZnO) [249-251]. The study of carbothermal reduction of tin dioxide, SnO\textsubscript{2}, is not the exception and in the last 10 years renewed interest in this process has emerged due to its promising application as a method for water splitting to produce hydrogen [248, 252].

In 1979, Padilla and Sohn reported an exhaustive analysis of the reduction process of tin dioxide using coconut charcoal and graphite in the temperature range between 800 and 1 000 °C [203]. Their results have been discussed and confirmed by Epstein et al. who studied a similar system using beech charcoal and graphite as reducing agents in the same temperature range [248]. According to Padilla and Sohn, the reduction of tin dioxide with carbon represented by the global reaction:

\begin{equation}
\text{SnO}_2(s) + C(s) \rightarrow \text{Sn}(s,l) + CO(g)
\end{equation}

is a two-step reduction-oxidation process which follows the reaction mechanism:

\begin{equation}
\text{SnO}_2(s) + 2CO(g) \rightarrow \text{Sn}(s,l) + 2CO_2(g)
\end{equation}

\begin{equation}
CO_2(g) + C(s) \rightarrow 2CO(g)
\end{equation}
Equation (8.3) corresponds to the reversed Boudouard reaction and represents the ‘dry gasification’ of elemental carbon to produce carbon monoxide, which is the actual reducing agent in the carbothermal reduction of tin dioxide. The direct reaction between the solid oxide and solid carbon represented by equation (8.1) is possible only when the gaseous products of reaction ($CO$ and/or $CO_2$) are removed from the system and requires contact between the $SnO_2$ and carbon particles. This last condition becomes difficult to achieve once formation of tin by-product occurs, since the direct contact between the solid reactants is lost.

Figure 8.1 presents the Ellingham diagram obtained for oxidation of molten tin to tin dioxide in the temperature range between 550 and 1,000 °C. In addition, the reversed Boudouard reaction is included to compare its energy requirements with the incomplete and complete oxidation of solid carbon (equations (5.8) and (5.9), respectively). The Gibbs free energy changes presented in this plot were calculated using a MATLAB code based on the mathematical approach introduced in Section 2.1 and the thermodynamic data presented in Appendix C.

As can be seen, formation of $SnO_2$ occurs spontaneously in the entire temperature range, thus oxidation of tin cannot be avoided if oxygen is present in the system (as was already confirmed by the experimental results reported in Chapter 5 and Chapter 6). Formation of carbon dioxide, $CO_2$, is preferred until about 709 °C, above which the Gibbs free energy change for incomplete oxidation starts to be more negative, so that formation of carbon monoxide, $CO$, then dominates. At this temperature, the reversed Boudouard reaction becomes spontaneous which means that reduction of tin dioxide in accordance with reactions (8.2) and (8.3) will be promoted. However, according to Figure 8.1 incomplete combustion of carbon should be the reaction occurring preferentially in the system, considering its lower Gibbs free energy change in the entire temperature range compared to the reversed Boudouard reaction. This observation can be considered to contradict the theory exposed by Padilla and Sohn and demonstrated later by other authors [253, 254]. Nevertheless, it has to be taken into account that even though the thermodynamics shows that a reaction is preferred over another in terms of energy demand, ultimately the kinetics will determine which chemical process will actually occur preferentially in the system depending on its activation energy (lower activation energy, higher reaction rate).

Regarding the discussion above, it has been demonstrated that metals have a catalytic effect on the oxidation of carbon via the reversed Boudouard reaction and clearly tin is not an exception [203, 248, 255, 256]. Figure 8.2 presents the results obtained by Epstein et al.
[248] when different amounts of tin were mixed with beech charcoal to be oxidized under a \(N_2-CO_2\) atmosphere at 875 °C\(^{[19]}\). As can be seen, the presence of the metal has a significant catalytic effect even at a molar ratio \(Sn/C\) as lower as 0.025, which proves that the reversed Boudouard reaction is favoured during the carbothermal reduction of tin dioxide.

![Figure 8.1. Ellingham diagram for the oxidation of tin and carbon and reversed Boudouard reaction\(^{[20]}\)](image)

![Figure 8.2. Catalytic effect of tin on the oxidation of beech charcoal in accordance with equation (8.3) at 875 °C for different \(Sn/C\) molar ratios [248]](image)

\(^{[19]}\) The experimental results reported previously by other authors and presented in this chapter were recovered using the data extraction tool GetData Graph Digitizer 2.25 (free software).

\(^{[20]}\) In this plot the Gibbs free energy of the reversed Boudouard reaction is in units of kJ (mol CO\(_2\))\(^{-1}\).
CHAPTER 8.
PERFORMANCE OF Sn$_{0.9}$-SOFCs OPERATING IN FUEL CELL MODE

Figure 8.3 presents the Gibbs free energy changes for the reactions of reduction of tin dioxide using carbon and carbon monoxide in accordance with equations (8.1) and (8.2). In addition, the Gibbs free energy change for the reversed Boudouard reaction is included to compare it with the energy requirements of the carbothermal reduction process. As can be seen, reduction of tin dioxide using CO is preferential until ca. 709 °C, above which the reversed Boudouard reaction becomes spontaneous and the reduction of tin dioxide via solid carbon corresponds to lower Gibbs free energy changes. In principle, this result seems inconsistent with the discussion exposed above where reaction of tin dioxide with carbon monoxide has been stated as the dominant reduction process. However, it is important to notice that the lower Gibbs free energy change values for reaction (8.1) over ca. 709 °C is a result of the addition of the Gibbs free energy changes associated with the spontaneous reactions (8.2) and (8.3), which agrees with the theory of a reduction-oxidation process following a two-step reaction mechanism.

![Figure 8.3](image)

**Figure 8.3.** Effects of temperature on Gibbs free energy changes for the reduction of tin dioxide using solid carbon and carbon monoxide and for the reversed Boudouard reaction

Finally, in order to make completely unquestionable the fact that reduction of tin dioxide in a carbothermal process occurs preferentially via oxidation of carbon monoxide, the theoretical equilibrium ratios $P_{CO_2}/P_{CO}$ for reactions (8.2) and (8.3) were calculated using the Gibbs free energy changes presented in Figure 8.3. The results are presented in Figure 8.4 as a function of the temperature for a total pressure: $P_{CO_2} + P_{CO} = 1.0$ atm. It can be seen that at a temperature of ca. 609 °C simultaneous equilibrium between SnO$_2$, Sn and
solid carbon takes place which means that the metal oxide will be reduced by carbon at any temperature above ca. 609 °C and the resulting gas mixture will present a ratio $p_{\text{CO}_2}/p_{\text{CO}}$ closer to the value associated with the process which has the higher reaction rate. In most of the studies cited previously on the reduction of metal oxides with solid carbon, the reversed Boudouard reaction (8.3) is the rate controlling step in the overall reduction process. Padilla and Sohn measured the equilibrium ratio $p_{\text{CO}_2}/p_{\text{CO}}$ using gas chromatography to analyse the exit gases during the reduction process obtaining the results presented in Figure 8.4 in the temperature range between 800 and 950 °C. The experimental data produced by these authors demonstrates that the controlling step during carbothermal reduction of tin dioxide is the oxidation of carbon via the reversed Boudouard reaction, which confers additional importance to the catalytic effect of tin on the oxidation of carbon.

![Figure 8.4](image)

**Figure 8.4.** Effect of temperature on the theoretical equilibrium ratio $p_{\text{CO}_2}/p_{\text{CO}}$ for the reduction of tin dioxide with CO and for the reversed Boudouard reaction, together with experimental data obtained by Padilla and Sohn using mass spectrometry measurements [203]

The kinetics of tin dioxide reduction by coconut charcoal and graphite were studied by Padilla and Sohn [203] using thermogravimetric analysis for measurement of the weight loss of the SnO$_2$-C samples during the reduction-oxidation process and mass spectrometry to determine the ratio $p_{\text{CO}_2}/p_{\text{CO}}$ in the exit gases [203, 247, 248]. By these means, the extension of the reaction can be expressed in terms of the total weight loss, the amount of oxygen removed from SnO$_2$ or the carbon consumption which are all related for a known
$p_{CO_2}/p_{CO}$ ratio. Figure 8.5 and Figure 8.6 present the results obtained by these authors in terms of the fractional conversion of carbon $\Delta W/\Delta W^0$ when a molar ratio $SnO_2/C = 1/2$ was used in a temperature range between 800 and 900 °C for coconut charcoal and between 925 and 1 000 °C for graphite\[21\].

![Graph showing the effect of temperature on the rate of reduction of tin dioxide using coconut charcoal with a molar ratio $SnO_2/C = 1/2$](image1)

**Figure 8.5.** Effect of temperature on the rate of reduction of tin dioxide using coconut charcoal with a molar ratio $SnO_2/C = 1/2$ [203]

![Graph showing the effect of temperature on the rate of reduction of tin dioxide using graphite with a molar ratio $SnO_2/C = 1/2$](image2)

**Figure 8.6.** Effect of temperature on the rate of reduction of tin dioxide using graphite with a molar ratio $SnO_2/C = 1/2$ [203]

\[21\] The fractional conversion of carbon $\Delta W/\Delta W^0$ corresponds to the weight loss divided by the initial weight of carbon in the sample.
As can be seen from these results, the temperature has an important effect on the kinetics of tin dioxide reduction, decreasing the time of the process in about 20 minutes if the temperature is increased from 850 to 900 °C in the case of coconut charcoal. The type of carbon used is another variable that affects considerably the rate of removal of oxygen from the metal oxide matrix. In the case of coconut charcoal, more favourable kinetics can be observed as complete reduction of tin dioxide can be reached in ca. 9 minutes at 900 °C, while complete reduction takes about 10 extra minutes using graphite, even at temperatures as high as 1 000 °C. An activation energy of 220.9 kJ mol\(^{-1}\) was calculated for the carbothermal reduction of tin dioxide with coconut charcoal in the temperature range between 800 and 900 °C, while for reduction with graphite the activation energy determined was 323.8 kJ mol\(^{-1}\) in the temperature range between 925 and 1 000 °C. These results are not surprising considering the larger active surface (porosity) that coconut charcoal presents compared to graphite, making coconut charcoal highly reactive with any gaseous oxidant present in the system. Epstein at al. obtained similar results to coconut charcoal using beech charcoal, which exhibited even faster kinetics reaching the complete reduction of tin dioxide in approximately 5 minutes at 900 °C [248].

In 1988, Mitchell and Parker proved that the increasing amount of carbon content in \(\text{SnO}_2 / C\) samples enhanced the kinetics of the reduction process only up to a molar ratio \(C / \text{SnO}_2\) of 3.0, above which the curves for fractional conversion of carbon as a function of time did not show changes [247]. The reason of this phenomenon could be that with increasing amount of carbon the ratio \(p_{CO_2} / p_{CO}\) is lowered by excess formation of carbon monoxide via the reversed Boudouard reaction, which is favoured by the greater amount of carbon available in the system. In that way, the rate of the reversed Boudouard reaction is increased up to a value above which it becomes similar to the reaction rate of reduction of \(\text{SnO}_2\) (equation (8.2)), that then becomes the rate controlling step of the process. This result is of particular importance in the study of the performance of \(\text{Sn}_{\text{III}}\)-SOFCs operating with carbonaceous fuels, since it demonstrates that at a certain point removal of oxygen from the molten tin anode cannot be hastened by addition of greater amounts of reducing agent.

To close the discussion about carbothermal reduction of tin dioxide, it is important to mention that formation of the lower oxide of tin, \(\text{SnO}\), during the process has been reported to be thermodynamically unfavourable at the operating temperatures [257]. The solid state of stannous oxide (\(\text{SnO}\)) is unstable and decomposes into tin and tin dioxide at temperatures above ca. 300 °C, while the partial pressure of its gaseous phase was calculated by HSC 5.0 software to be less than ca. 1.0 Pa at 1 000 °C.
As an alternative to carbon-based materials, hydrogen ($H_2$) has been proposed by some authors as a reducing agent for the reduction of metal oxides with the intention of decreasing the large amounts of $CO_2$ emissions produced by the combustion of these carbonaceous compounds [258, 259]. In the case of tin dioxide, Lee et al. [260] and Wright [257] discussed the advantages offered by hydrogen over carbon for production of tin metal, especially on the base of the faster reduction rates presented by the reduction processes when $H_2$ is used.

Reduction of tin dioxide by hydrogen occurs in accordance with reaction:

\[
SnO_2(s) + 2H_2(g) \rightarrow Sn(s, l) + 2H_2O(g)
\]  (8.4)

Considering this, Figure 8.7 presents a comparison of the Gibbs free energies obtained for reactions (8.1) and (8.4) using the MATLAB code mentioned previously based on the thermodynamic data presented in Appendix C. As can be seen from these results, instantaneous reduction of tin dioxide by hydrogen takes place over ca. 665 °C while reduction of tin dioxide by carbon is instantaneous from ca. 621 °C. According to these values, from the thermodynamic point of view carbothermal reduction of $SnO_2$ would occur preferentially in the temperature range between 700 and 1 000 °C. However, as it has been stated before in this section for the case of the oxidation of carbon, it will be the kinetics of the reduction process the aspect that finally will decide which is the most favourable reducing agent.

Similarly to the thermogravimetric measurements done by Padilla and Sohn for determination of the reaction rate of reduction of tin dioxide using coconut charcoal and graphite [203], Lee et al. measured the reduction ratio of tin dioxide, $X_{SnO_2}$, as a function of time using hydrogen at a partial pressure of 101.3 kPa and a flow rate of 11.7 mL s$^{-1}$ in the temperature range between 500 and 750 °C [260]. The results obtained by these authors are presented in Figure 8.8 where it can be seen that the complete reduction of 700 mg of $SnO_2$ can be reached in about 10 min at a temperature of 750 °C. In addition, an activation energy of 62.5 kJ mol$^{-1}$ was calculated for reaction (8.4) in the temperature range previously mentioned. Considering the results presented in this section for carbothermal reduction of tin dioxide using different types of carbon, it is clear that the use of hydrogen as reducing agent promotes a more effective process in terms of time and energy requirements. This information will be determining in the study of the longer term performance and stability of a Sn$_{0.98}$-SOFC and is discussed in the next sub-section based on the results obtained by CellTech Power Inc. using hydrogen and JP-8 fuels.
Figure 8.7. Effect of temperature on Gibbs free energy changes for the reduction of tin dioxide using hydrogen and solid carbon and for oxidation of tin dioxide.

Figure 8.8. Effects of temperature on the reduction of 700 mg tin dioxide using hydrogen at a partial pressure of 101.3 kPa and a flow rate of 11.7 mL s⁻¹ [260]

8.1.2. Discussion of the Results obtained by CellTech Power Inc. using a Sn₀₋SOFC operating with Hydrogen and JP-8 Fuels

The Sn₀₋SOFC technology used by CellTech Power Inc. was described in Section 3.3.2, in which its performance was compared with the results obtained by other authors using...
similar equipment to that fabricated during this research project (see Chapter 3 and Chapter 4). As stated in that section, the main characteristic of the Sn\(\text{(l)}\)-SOFC developed by this company was the use of an alumina porous separator which held the molten tin anode against the wall of the YSZ-tubular electrolyte and allowed the diffusion of the fuel from an external chamber to the tin dioxide particles to be reduced into the melt. Figure 8.9 shows the polarization and power density curves obtained by CellTech Power Inc. using their Sn\(\text{(l)}\)-SOFC technology operating at 1 000 °C with hydrogen and JP8 (kerosene-based jet fuel) fuels. The maximum power densities operating with hydrogen were about one order of magnitude greater than the experimental values reported for the Sn\(\text{(l)}\)-SOFC described in Chapter 4 operating in battery mode and approximately the same than the value obtained by modelling this fuel cell with a thinner YSZ-pellet electrolyte (200 µm thick instead 2.0 mm) and negligible ohmic losses associated with current collection, but at a lower current density (ca. 2 820 A m\(^{-2}\), compared to ca. 3 273 A m\(^{-2}\) in the modelled Sn\(\text{(l)}\)-SOFC).

![Figure 8.9. Effects of current density on cell potential differences and power densities reported by CellTech Power Inc. for a Sn\(\text{(l)}\)-SOFC operating at 1 000 °C with H\(_2\) and JP8 fuels [163]](image)

From these results, it is clear that CellTech Power Inc. managed to produce an optimized design of the fuel cell technology studied in this thesis by using a thin YSZ electrolyte and molten tin anode (200 µm thick both). Nonetheless, even though the improvements introduced by the use of a thin electrolyte in the performance of the Sn\(\text{(l)}\)-SOFC (which are associated with lower ohmic losses) were already demonstrated in Section 5.3, in the particular Sn\(\text{(l)}\)-SOFC fabricated for this research project a pool of ca. 5 mm depth (ca. 17 g)
of molten tin over the pellet electrolyte was required to minimise the electrical consequences of the poor wettability of ceramics by molten metals \[160, 161\]. Consequently, a thick YSZ pellet \((2 \text{ mm thick})\) was necessary to support the molten tin anode without mechanical failure of the electrolyte. In addition, the high thickness of the molten tin anode made the tin dioxide formed at the anode \| electrolyte interface hardly accessible to the reducing agent \(\text{(e.g. activated carbon particles)}\) being fed at the top of the liquid anode, which results in another factor affecting the performance of the fuel cell. Even if the molten metal bath was stirred with a gas, as it is shown in the next section, poor contact between the reducing agent and the metal oxide was promoted due to the excessive turbulence in the melt which could also affect the continuity of the electrical contact between anode and electrolyte.

Another advantage of the system developed by CellTech Power Inc. is that due to the pressure applied by the alumina porous separator against the molten tin anode, it is possible that if \(\text{SnO}_2\) is produced during the fuel cell operation the force acting on it promotes formation of a dense layer that is highly conductive \[169\] compared to the \(\text{SnO}_2\) crystals produced at the anode \| electrolyte interface of the \(\text{Sn}_{(l)}\)-SOFC studied in this project \(\text{(see Section 6.1.2)}\). This aspect is performance determining for the continuous operation of the fuel cell considering that the kinetics of oxidation of the molten metal anode are faster than the kinetics of reduction of tin dioxide using carbonaceous fuels. In effect, from the results obtained for the modelled \(\text{Sn}_{(l)}\)-SOFC operating at \(900 \degree\text{C}\) with thin electrolyte and negligible ohmic losses \(\text{(see Section 5.3.3)}\), tin dioxide was predicted to be formed at the anode \| electrolyte interface at a constant rate of \(7.67 \text{ mg cm}^{-2} \text{ min}^{-1}\) when the fuel cell was operating at its maximum power density output \((1 477 \text{ W m}^{-2}\text{ at a cell voltage of ca. } 0.45 \text{ V and a current density of } 3 273 \text{ A m}^{-2})\). According to the reduction rates reported in Section 8.1.1 for reduction of tin dioxide with coconut charcoal, only \(0.51 \text{ mg } \text{SnO}_2 \text{ cm}^{-2} \text{ min}^{-1}\) would be reduced if ca. \(0.81 \text{ mg cm}^{-2}\) of this reducing agent was mixed homogeneously with the metal oxide. If a mass of \(1.22 \text{ mg cm}^{-2}\) of coconut charcoal is added to the system instead, the kinetics of reduction could be increased from \(0.51\) to \(1.53 \text{ mg } \text{SnO}_2 \text{ cm}^{-2} \text{ min}^{-1}\), which is still not comparable to the oxidation rate. In the case of \(\text{SnO}_2\) reduction using hydrogen, it can be deduced from the results obtained by Lee et al. \[260\] that approximately \(2.55 \text{ mg } \text{SnO}_2 \text{ cm}^{-2} \text{ min}^{-1}\) can be reduced using a \(H_2\) flow rate of ca. \(5.10 \text{ mL cm}^{-2} \text{ min}^{-1}\) at a partial pressure of \(101.3 \text{ kPa}\). These results demonstrate that even operating under a strongly reducing atmosphere of hydrogen, accumulation of tin dioxide in the system cannot be avoided and degradation of the performance of the \(\text{Sn}_{(l)}\)-SOFC will occur if a non-dense layer of this by-product grows at the anode \| electrolyte interface, as was shown previously in Section 6.1.
For obtaining the results presented in Figure 8.9, CellTech Power Inc. used flow rates of 50 µl min\(^{-1}\) and 300 mL min\(^{-1}\) of JP8 and \(H_2\), respectively (the area of the electrodes was not specified). In the case of JP8 fuel, it has been suggested that gasification of the carbonaceous high molecular-weight compounds to produce \(CO\) and \(H_2\) takes place in the external chamber containing the fuel, so that these gases are the actual reducing agents diffusing through the alumina porous separator to reduce the \(SnO_2\) formed in the anode [261]. Unfortunately, there are no further studies which could support this assumption based on the reaction mechanisms taking place in this \(Sn(l)\)-SOFC system. The fuel utilisation efficiencies reported for this technology correspond to 50% for hydrogen and 43% for JP8 [137] which could be related to: (1) excess of fuel being fed into the system and/or (2) incomplete reduction of tin dioxide by-product in the anode. Considering the kinetics reported in Section 8.1.1, it is probable that a combination of both situations could be observed in the system due to the slow \(SnO_2\) reduction rates in comparison to the \(Sn\) oxidation rates and the short residence time of the fuels in the system (due to the high flow rates reported and that no fuel accumulation was observed in the anode chamber).

To conclude this section, it is important to emphasise that the kinetics of the \(Sn(l)\)-SOFC reported in Figure 8.9 seems to be enhanced when operating with hydrogen, in comparison with the results obtained using the mathematical model presented in Chapter 5 for a \(Sn(l)\)-SOFC operating in battery mode. In effect, the fuel cell developed by CellTech Power Inc. reached its maximum power density (ca. 1 520 W m\(^{-2}\)) at a lower current density (ca. 2 820 A m\(^{-2}\)) than the modelled fuel cell (maximum power density of ca. 1 477 W m\(^{-2}\) at a current density of ca. 3 273 A m\(^{-2}\)). This difference suggests that the global electrochemical reaction cannot correspond to the oxidation of tin in accordance with equation (5.1), since if it were so the kinetics of the electrochemical process would not be enhanced by the oxidation of the reductant in the bulk of the anode. Therefore, it could be said that the electrochemical process taking place at the anode is a combination of two parallel oxidation reactions by which tin is oxidised by mechanisms suggested in Section 6.1 and hydrogen reacts with the oxide ions (\(O^2^-\)) to produce steam. This final reaction can take place either at the anode | electrolyte interface, where originally the oxidation processes occur, or at the anode | \(SnO_2\) interface generated during operation of the fuel cell. The performance of the \(Sn(l)\)-SOFC operating on JP8 fuel is compared in Figure 8.10 with the results obtained in Section 5.3.3 for an optimized \(Sn(l)\)-SOFC operating at 900 °C in battery mode\[22\]. The

\[22\] The technology developed by CellTech Power Inc. reported low ohmic losses when operating under JP8 and hydrogen (29 and 34 mΩ, respectively), which is due to the use of a low resistive anode current collector (material not revealed) and a 200 µm thick YSZ electrolyte.
polarization curves for the two cases differ mainly in their OCV values (CellTech Power Inc. fuel cell ca. 0.88 V, modelled fuel cell 0.85 V), probably due to the higher operating temperature used by CellTech Power Inc. (1 000 °C) and the presence of a reducing agent. However, the shapes of the curves does not seem to be affected significantly by the presence of this fuel, suggesting that direct electrochemical oxidation of JP8 is more unlikely to occur than in the case of hydrogen.

Figure 8.10. Effects of current density on cell potential differences and power densities for a Sn(l)-SOFC operating without fuel at 900 °C (modelled) and the CellTech Power Inc. technology operating with JP8 fuel at 1 000 °C

From the results presented in this section, it can be concluded that the use of a fuel for continuous reduction of the SnO₂ by-product during operation of a Sn(l)-SOFC not always will enhance the kinetics of the system. In the case of a Sn(l)-SOFC operating on hydrogen, considering that reduction of SnO₂ by this fuel is slower than the electrochemical oxidation of tin, it is probable that a parallel oxidation reaction of the fuel takes place at the anode | electrolyte interface promoting an improvement in the kinetics of the system. However, due to the lack of information reported by CellTech Power Inc. about their system (there is no data about exit gases analysis, chemical composition of the anode current collector, three electrode measurements or post-mortem analysis of the fuel cell components) it is difficult to determine precisely the reaction mechanisms involved in the total anode electrochemical process.
8.2. Sn(l)-SOFC Operating with a Stirred Molten Tin Anode and a Fuel

As for the results presented in Section 5.3.1 for a Sn(l)-SOFC operating at 900 °C in battery mode, cyclic voltammograms and impedance spectra (EIS) were obtained also for the system when the molten tin anode was stirred by feeding constant flow rates of helium (30 mL min⁻¹) or hydrogen (20 mL min⁻¹) using an alumina tube of 3 mm outer diameter, 2 mm inner diameter and 300 mm length immersed in the melt. In both cases, the weight of tin added to the system was doubled compared with that used in previous experiments (Section 5.3) to produce a molten anode layer of ca. 10 mm height to facilitate the stirring process. The amount of activated carbon particles added on the surface of the liquid anode was maintained to act as a reducing agent of the tin dioxide produced at the anode | electrolyte interface, which should have been accessible to these particles due to the high turbulence promoted in the melt. The viscosity of molten tin at 900 °C is similar to that for water at standard temperature and pressure conditions [164, 219], suggesting that a gas flow rate of 20 to 30 mL min⁻¹ bubbling into the liquid metal contained in the anode chamber can generate significant turbulence. A flow rate of 60 mL min⁻¹ of air was maintained at the cathode side during fuel cell operation.

Cyclic voltammograms were measured using the molten tin anode as the working electrode and the LSM-YSZ/LSM cathode as the counter and reference electrodes. Four consecutive cycles of potential were applied to the system at a scan rate of 10 mV s⁻¹ starting from the corresponding open circuit voltage (OCV) value and finishing at zero volts. Impedance spectra were measured for the whole fuel cell, anode | electrolyte and cathode operating under open circuit conditions when an AC potential difference of 10 mV p-p amplitude was applied in the frequency range between 0.01 Hz and 15 kHz. The electrical connections used for these measurements correspond to the arrangements presented in Figure 4.8 for the whole cell impedance and Figure 4.12 for the anode | electrolyte and cathode impedances.

For the molten tin anode stirred with helium, an OCV of ca. 0.88 V was measured and remained stable during the process except throughout the 7 minutes after a cyclic voltammogram was measured, when the OCV decayed to ca. 0.84 V and recovered gradually to the original value. As can be seen from the thermodynamic results presented in Section 5.2, the open circuit voltage measured in this case was close to the Nernst potential.

[23] The OCV measured at fuel cell and anode | electrolyte modes was the same in both cases, while the OCP at cathode mode was approximately zero.
value obtained for the reaction of direct dissolution of atomic oxygen in the molten tin anode (equation (5.2)) when saturation conditions are assumed ($E_{N,\{O\}_\text{sat}} = 0.87$ V). The difference of 0.01 V observed between the measured OCV (0.88 V) and the Nernst potential calculated for reaction (5.2) is probably related with the assumption of a saturation activity of atomic oxygen in the molten anode, which was clearly not the case since a concentration of oxygen lower than the saturation should be observed before the fuel cell is operational.

The OCV measured is rather distant from the reversible potentials obtained for the incomplete (reaction (5.8)) and complete (reaction (5.9)) combustion of carbon which correspond to 1.10 V and 1.02 V, respectively. This result can be interpreted as a promotion of the atomic oxygen diffusion rate due to the turbulence in the melt which removes the oxidation product from the anode | electrolyte interface, avoiding the immediate formation and accumulation of tin dioxide at the surface of the YSZ pellet (see Section 6.1). In addition, it suggests that the activated carbon particles were not affected significantly by the oxygen dissolved in the melt, which implies that in the longer term operation precipitation of the metal oxide cannot be avoided. This last observation is not surprising considering the discussion presented in the previous section, in which carbothermal reduction of $SnO_2$ was shown to be slow compared to the electrochemical oxidation of molten tin, especially when the operating conditions (contact between the oxide and carbon particles) and the type of carbon used were sub-optimal. Figure 8.11 shows SEM micrographs (magnifications of x4000 and x6000) of the activated carbon particles used in this thesis$^{[24]}$, which presented low porosity and high content of contaminants. These characteristics make this fuel less suitable for reduction of tin dioxide compared to coconut or beech charcoal (see Section 8.1.1).

![Figure 8.11. SEM micrograph of the activated carbon particles used as fuel (reducing agent) at the Sn$_{0.9}$-SOFC](image)

$^{[24]}$ Previously to any Sn$_{0.9}$-SOFC measurement, the carbon particles were subjected to heat treatment at 600 °C during 2 hours for removing any volatile undesired content.
For the molten tin anode stirred with hydrogen, an OCV of ca. 0.90 V was measured and remained stable during the process, except throughout the 2 minutes after a cyclic voltammogram was measured when the OCV decayed to ca. 0.87 V and recovered gradually to the original value. Comparing again the OCV measured with the thermodynamic data presented in Section 5.2, it can be seen that this value was close to the reversible potential calculated for the oxidation reaction of hydrogen gas to produce steam (equation (5.10)), which corresponds to ca. 0.93 V. Due to the absence of exit gas analysis during these experiments, it was not possible to determine with exactitude the value of the Nernst potential, which according to equation (2.17) is affected by the partial pressures of the gases in the system (oxygen, hydrogen and water gas). Therefore, it can be assumed that the difference of 0.03 V observed between the measured OCV (0.90 V) and the reversible potential (0.93 V) was due to this missing partial pressure-dependent term.

In view of the discussion presented above, it can be said that the direct electrochemical oxidation of hydrogen suggested by the results obtained by CellTech Power Inc. (Section 8.1.2) is a valid fuel cell reaction and thus, in addition to the oxidation of molten tin in accordance with equation (5.20), the parallel half-reaction:

\[
2H_2 + 2O^{2-} \rightleftharpoons 2H_2O + 4e^- \quad (8.5)
\]

occurred at the anode active sites during operation. By this means, combination of the half-reaction (5.17) occurring at the LSM-YSZ cathode with the anode half-reaction (8.5) results in the total fuel cell reaction (5.10) for oxidation of hydrogen to produce steam.

The polarization and power density data for the Sn(l)-SOFC operating with an anode stirred with a flow rate of helium or hydrogen is presented in Figure 8.12 and compared with the case of a Sn(l)-SOFC with a non-stirred anode reported in Chapter 5. These data correspond to the first cycle of the voltammograms produced for each fuel cell system before hysteresis was evident, due to accumulation of SnO\textsubscript{2} at the anode | electrolyte interface or the anode current collector surface (see Appendix E). As can be seen, the kinetics of the Sn(l)-SOFC increased slightly by comparison with the quiescent system when helium and hydrogen were bubbled directly into the melt. In the case of a molten anode stirred with the inert gas, a maximum power density of ca. 165 W m\textsuperscript{-2} was obtained at a cell potential difference of ca. 0.42 V and a current density of ca. 395 A m\textsuperscript{-2}. When hydrogen was used for stirring the liquid metal, a maximum power density of ca. 177 W m\textsuperscript{-2} was obtained at the same cell potential and a current density of ca. 420 A m\textsuperscript{-2}. These values did not differ
significantly from the values obtained with a non-stirred system, for which the maximum power density was ca. 159 W m\(^{-2}\) at a cell potential of ca. 0.42 V and a current density of ca. 380 A m\(^{-2}\) (see Figure 5.7). These results suggest that the reducing conditions during these experiments were not optimal compared to the system developed by CellTech Power Inc. for which the flow rate of hydrogen used was 15 times higher. As can be seen in Figure 8.9, this considerable increase in the amount of hydrogen fed to the anode increased the OCV value by about 0.1 V, which clearly affected the power densities of the Sn\(_{0}\)-SOFC.

![Figure 8.12. Effects of current density on cell potential differences and power densities for a Sn\(_{0}\)-SOFC operating with a non-stirred anode, an anode stirred with 30 mL min\(^{-1}\) of helium and an anode stirred with 20 mL min\(^{-1}\) of hydrogen](image)

Even though the improvements introduced by stirring of the melt in the performance of the Sn\(_{0}\)-SOFC were not significant, it can be seen from the shape of the polarization curves presented in Figure 8.12 that the kinetics of the system were affected by this operating condition. In the case of the molten tin anode stirred using a helium flow rate, it can be considered that the dissolution of atomic oxygen in the melt was enhanced due to the removal of this oxidation product from the anode | electrolyte interface. In addition, if SnO\(_2\) was produced during fuel cell operation, which is likely to occur at very high current densities, the turbulence of the melt enabled the removal of this by-product from the electrolyte surface maintaining the kinetics of the Sn\(_{0}\)-SOFC temporarily stable until the amount of SnO\(_2\) produced was high enough to cause precipitation in the anode. In the case of the molten tin anode stirred using a hydrogen flow rate, similar behaviour occurred but the highly reducing effects of this fuel enhanced the kinetics. The previous discussion suggests
that in both cases (anode stirred with helium and hydrogen), the limiting current densities should have been higher than the value obtained for the Sn\(_{0}\)SOFC with a quiescent anode (3 273 A m\(^{-2}\)), which is reflected in Figure 8.12 by the slight curvature in the polarization curves over ca. 400 A m\(^{-2}\). Nevertheless, further experimental work, including current density transients and exit gas analysis, are necessary in order to develop a reliable mathematical model which includes the kinetic effects of the parallel oxidation reactions taking place at the anode.

The ohmic potential losses in the Sn\(_{0}\)SOFC with stirred anode were studied by means of the impedance spectra presented in Figure 8.13 and Figure 8.14 for the whole fuel cell and the anode | electrolyte, respectively. The cathode impedance spectra were similar to that presented in Figure 5.8(c) for the LSM-YSZ/LSM cathode of a quiescent anode system. As can be seen from these figures, the impedance of the system in the presence of hydrogen was slightly higher than that for the system with helium, which agrees with the results obtained previously by Lvov et al. for a Sn\(_{0}\)SOFC operating with a fuel fed over a quiescent liquid anode [176]. Considering that the cathode impedance is the same in both cases, it is clear that this difference should have its foundation in the anode | electrolyte arrangement, as can be seen in Figure 8.14.

It was demonstrated previously from the analysis of the results obtained by CellTech Power Inc. and the Sn\(_{0}\)SOFC system developed in this project, that hydrogen shows some interaction with the anode | electrolyte interface which affects its electrical response, unlike the effects of inert gas. With respect to the impedance response obtained for the anode | electrolyte arrangement of a Sn\(_{0}\)SOFC with a non-stirred anode, it is clear that the inductive loop observed at high frequencies was eliminated by the introduction of a stirring agent, suggesting that the surface of the graphite rod used as current collector for the anode was protected when operating under these conditions. This situation was verified by post-mortem SEM analysis of this fuel cell component, which appeared similar to that presented in Figure 6.11 for a clean surface. In addition, stirring of the system minimised accumulation of oxidant species in the anode | electrolyte interface which could be another reason for the absence of an inductive response in the impedance spectra. However, further studies for the longer term performance of the Sn\(_{0}\)SOFC operating with a stirred anode are required to understand properly the phenomena occurring.

From the results presented in this section, it can be concluded that the performance of the Sn\(_{0}\)SOFC studied can be improved stirring the molten tin anode using an inert gas or a gaseous fuel. In both cases, the anode kinetics were enhanced by constant dispersal of the
oxidant species from the anode | electrolyte interface to the bulk of the melt, while the addition of a highly reducing agent such as hydrogen resulted in a fuel oxidation reaction occurring in parallel with the molten tin oxidation at the anode active sites.

**Figure 8.13.** Impedance spectra obtained at open circuit voltage (OCV) for the Sn\textsubscript{(l)}-SOFC operating with an anode stirred with 30 mL min\textsuperscript{-1} of helium and an anode stirred with 20 mL min\textsuperscript{-1} of hydrogen

**Figure 8.14.** Anode impedance plots obtained at open circuit voltage (OCV) for a Sn\textsubscript{(l)}-SOFC operating with a non-stirred anode, an anode stirred with 30 mL min\textsuperscript{-1} of helium and an anode stirred with 20 mL min\textsuperscript{-1} of hydrogen
8.3. Chapter Summary and Conclusions

The thermodynamics and kinetics of $\text{SnO}_2$ reduction by carbon or hydrogen have been studied based on the mathematical models presented in Chapter 2 and the experimental results reported previously by other authors. For the case of carbothermal reduction, a two-step reaction mechanism was proposed with oxidation of solid carbon producing carbon monoxide (reversed Boudouard reaction) and the subsequent reduction of $\text{SnO}_2$ by $\text{CO}$. The reversed Boudouard reaction, which occurs spontaneously above ca. 709 °C, was the rate limiting reaction. However, the kinetics of the oxidation of solid carbon using carbon dioxide ($\text{CO}_2$) can be enhanced by the presence of the molten metal, which decreased the time for complete conversion in about 10 minutes when tin was present in a molar ratio $\text{Sn} / \text{C}$ as small as 0.025. Beech char produced faster kinetics for carbothermal reduction of $\text{SnO}_2$, complete conversion being achieved in ca. 5 minutes at 900 °C, which was 5 minutes faster than the reduction using coconut charcoal and 15 minutes quicker than the reduction process with graphite. These results demonstrated that the higher porosities of activated carbons enhanced the kinetics of the process. In the case of reduction using hydrogen, which occurs in one direct reaction step and is spontaneous above ca. 665 °C, complete conversion of 700 mg of $\text{SnO}_2$ was achieved in 5 minutes at only 750 °C when a flow rate of 11.7 mL s$^{-1}$ of hydrogen was fed into the system at a partial pressure of 101.3 kPa.

The performance of the Sn$\text{(l)}$-SOFC technology developed by CellTech Power Inc. was discussed based on the thermodynamic and kinetic data summarized above, and compared with the performance of the Sn$\text{(l)}$-SOFC operating in battery mode studied in Chapter 5. In the case of CellTech Power Inc.’s technology, JP8 and hydrogen fuels were fed continuously into the system and contacted with the molten tin anode (200 µm thick) through a porous alumina separator which held the liquid electrode tightly against the electrolyte wall. This design enabled the electrical conductivity of the anode to be maintained relatively constant during fuel cell operation, even when $\text{SnO}_2$ was formed at the anode-electrolyte interface since a dense and highly conductive oxide layer could have been produced. This condition was important considering that, in accordance with the modelling results obtained in Chapter 5, molten tin is oxidized electrochemically to form $\text{SnO}_2$ at a rate of ca. 7.67 mg cm$^{-2}$ min$^{-1}$, which makes precipitation of this by-product unavoidable in the longer term even when a strong reducing agent was being fed into the anode. In effect, the reduction rate of $\text{SnO}_2$ using $\text{H}_2$ was estimated to be ca. 2.55 mg cm$^{-2}$ min$^{-1}$ when a flow rate of 5.10 mL cm$^{-2}$ min$^{-1}$ of this gas was fed into the system at a partial pressure of 101.3 kPa, which reflects the importance of the porous alumina holder in this Sn$\text{(l)}$-SOFC design.
The limiting current and maximum power densities produced by the technology developed by CellTech Power Inc. when operating on JP8 were predicted to be similar to the values obtained in Chapter 5 for a Sn\textsubscript{0}\textsubscript{0} - SOFC operating in battery mode with a 200 µm thick electrolyte and negligible ohmic potential losses at the current collectors. In the case of the fuel cell operated on hydrogen, the maximum power density was obtained at a lower current density, which was associated with the electrochemical oxidation of hydrogen at the anode active sites in parallel to the oxidation of molten tin.

Finally, a Sn\textsubscript{0}\textsubscript{0} - SOFC with a stirred anode was studied in order to determine the effects of this operating condition on the fuel cell performance. With this objective, a constant flow rate of helium (30 mL min\textsuperscript{-1}) or hydrogen (20 mL min\textsuperscript{-1}) was fed into the melt using an alumina tube immersed in it. The maximum power densities for the two cases did not differ significantly from the value obtained with a quiescent anode (Chapter 5). However, some changes were observed in the shape of the Sn\textsubscript{0}\textsubscript{0} - SOFC polarization curves (essentially in the slope at ca. 400 A m\textsuperscript{-2}) and the impedance spectra obtained for the anode | electrolyte which suggested that the stirring of the liquid metal had some effects on limiting current densities. These changes were associated with the continuous dispersal of the oxidation products from the anode | electrolyte interface to the bulk of the electrode and the parallel oxidation reaction of hydrogen at the anode active sites. Nevertheless, further experiments (exit gas analysis and chronoamperometric measurements) are necessary in order to develop a consistent mathematical model which includes these effects in the reaction mechanisms of the process.
Conclusions

This thesis reported and analysed results of the performance of a carbon-air solid oxide fuel cell with a molten tin anode (Sn\textsubscript{\(0\)\textdegree}SOFC) operating at 900 °C in battery mode, with a quiescent anode, or in fuel cell mode, with a stirred anode, using activated carbon particles or hydrogen as fuels. This section summarizes the main contributions of those results to existing knowledge on Sn\textsubscript{\(0\)\textdegree}SOFC systems.

The Sn\textsubscript{\(0\)\textdegree}SOFC arrangement used for experimental measurements consisted of a 2 mm thick yttria stabilized zirconia (YSZ) electrolyte, a 90 µm thick lanthanum strontium manganite (LSM)-YSZ cathode and a 5 mm thick molten tin anode. A 40 µm thick LSM layer was coated on the surface of the cathode for current collection together with platinum mesh and wires attached to the electrode using platinum ink. Graphite rods were used as current collectors at the anode, replaced on occasions by lanthanum strontium titanate (LST) or lanthanum cerium strontium titanate (LCST) pellets for analysis of their stability and performance. A flow rate of 60 mL min\(^{-1}\) of air was fed continuously at the cathode surface, while a flow rate of 30 mL min\(^{-1}\) of helium and activated carbon particles were fed on the surface of the molten tin anode to avoid oxidation by possible ambient air leaks. In the case of the Sn\textsubscript{\(0\)\textdegree}SOFC operating in fuel cell mode, a flow rate of 30 mL min\(^{-1}\) of helium or 20 mL min\(^{-1}\) of hydrogen was used to stir the melt.

- **Sn\textsubscript{\(0\)\textdegree}SOFC operating in battery mode with quiescent anode**

Thermodynamic analysis of the open circuit voltages (OCVs) measured in the temperature range 600 to 900 °C suggested that the global reaction occurring corresponded to oxidation of molten tin to tin dioxide by overall reaction:

\[
Sn(l) + O_2(g) \rightleftharpoons SnO_2(s)
\]  

Limited rates of transport of dissolved \([O]_{\text{Sn}}\) from the Sn anode | electrolyte interface caused accumulation and super-saturation of \([O]_{\text{Sn}}\) at operating current densities of the Sn\textsubscript{\(0\)\textdegree}SOFC, resulting in tin dioxide formation. This caused degradation of its longer term performance due to the low conductivity of the non-dense and non-stoichiometric layer of SnO\textsubscript{2} produced.

A reaction mechanism for the formation and growth of tin dioxide at the Sn anode | electrolyte interface was proposed, based on the analysis of the current density transients.
CONCLUSIONS

produced by a Sn\textsubscript{(l)}-SOFC operating at its maximum power density. This hypothesis was supported by post-mortem analysis of the Sn anode | electrolyte interface using SEM micrographs and EDX/XRD data. The reaction steps determined were: (1) inclusion of molten tin in the electrolyte surface, (2) oxidation of the molten tin inclusions by reaction:

$$2O^{2-} \rightleftharpoons 2[O]_{\text{Sn}} + 4e^-$$ \hspace{1cm} (5.18)

and (3) slow diffusion of $[O]_{\text{Sn}}$ species from the Sn anode | electrolyte interface to the bulk of the anode and formation of tin dioxide at the Sn anode | electrolyte interface by the reaction:

$$Sn + 2[O]_{\text{Sn}} \rightleftharpoons SnO_2$$ \hspace{1cm} (5.19)

The processes of diffusion and tin dioxide formation at stage (3) occurred simultaneously during the time prior to oxygen saturation being reached at the bulk of the anode. When this condition was reached, stage (3) changed into direct oxidation of tin by reaction:

$$Sn + 2O^{2-} \rightleftharpoons SnO_2 + 4e^-$$ \hspace{1cm} (5.20)

During coverage of the electrolyte surface by tin dioxide, the original reaction sites at the Sn anode | electrolyte interface were gradually replaced by the Sn anode | SnO$_2$ interface being formed over it. Therefore, oxide ions ($O^2-$) had to diffuse through the SnO$_2$ deposits to reach the new reaction sites.

Anode kinetic parameters were determined using a mathematical model of the polarization curves based on conductivities of the Sn\textsubscript{(l)}-SOFC components and cathode kinetic parameters reported in the literature. As a result, the following values were determined for the anode charge transfer coefficient, exchange current density and limiting current density under quiescent conditions:

$$\alpha_{\text{an}} = 0.67, \quad j_{0,\text{an}} = 353 \text{ A m}^{-2} \quad \text{and} \quad j_{1,\text{an}} = 3.273 \text{ A m}^{-2}$$

The anode exchange and limiting current densities predicted were one order of magnitude lower than the values predicted for the cathode: $j_{0,\text{ca}} = 2.152 \text{ A m}^{-2}$ and $j_{1,\text{ca}} = 91.703 \text{ A m}^{-2}$. This suggested that the overall fuel cell kinetics were controlled by the relatively slow oxidation reaction occurring at the Sn anode | electrolyte interface, the rate of which was limited by the low diffusion coefficient of oxygen in molten tin ($D_{[O]}_{\text{Sn}} = 6.63 \times 10^{-9} \text{ m}^2 \text{ s}^{-1}$) and formation of tin dioxide at the Sn anode | electrolyte interface.
A maximum power density of ca. 1 477 W m$^{-2}$ at a cell potential of ca. 0.45 V and a current density of ca. 3 273 A m$^{-2}$ (anode limiting current density) was predicted for a Sn$_{0.5}$-SOFC with negligible ohmic losses at the current collectors and a 200 µm thick electrolyte. This value was almost 1 000 W m$^{-2}$ lower than the power density predicted for a conventional SOFC with identical LSM-YSZ cathode and YSZ electrolyte (same dimensions and microstructure), but replacing the molten tin anode by a 100 µm thick Ni-YSZ cermet operating on hydrogen (80% humidity). Even though the resulting power density was lower than that for a conventional SOFC, this value seemed to be promising compared with the results reported previously in the literature and could be enhanced by operating the Sn$_{0.5}$-SOFC in fuel cell mode, i.e. by continuous reduction of the SnO$_2$ formed at the Sn anode | electrolyte interface using a carbonaceous fuel or hydrogen.

Finally, LST and LCST perovskites were studied as alternative anode current collectors to replace graphite rods. These perovskites exhibited electrical conductivities 4 orders of magnitude lower than graphite, but were stable during Sn$_{0.5}$-SOFC operation in the longer term. Post-mortem analysis of the graphite rods using SEM and EDX analysis suggested pore formation and tin dioxide inclusion in the graphite surface in contact with the molten tin anode. Pore formation was due to oxidation of the graphite rod according to reaction:

$$\text{C} + 2\left[\frac{O}{S_{\text{Sn}}}\right] \rightleftharpoons \text{CO}_2$$  \hfill (6.18)

while tin dioxide grew inside these cavities due to the higher current densities promoted at the edges of these cavities and the junction between the base of the graphite rod and the electrolyte.

- **Sn$_{0.5}$-SOFC operating in fuel cell mode (with stirred anode)**

Reduction of tin dioxide using carbon and hydrogen was studied based on results reported previously in the literature. In the case of carbothermal reduction, it has been stated that the reduction process occurs in two steps according to the reaction mechanism:

$$\text{SnO}_2(s) + 2\text{CO}(g) \rightleftharpoons \text{Sn}(l) + 2\text{CO}_2(s)$$  \hfill (8.2)

$$\text{CO}_2(g) + \text{C}(s) \rightleftharpoons 2\text{CO}(g)$$  \hfill (8.3)

Reaction (8.3) corresponds to the reversed Boudouard reaction and is the controlling step of the reduction process. In the case of reduction with hydrogen, the process takes place in one step according to reaction:
According to the kinetics reported in this thesis for a Sn_{l0}\text{-SOFC} operating in battery mode, approximately 7.67 mg SnO$_2$ cm$^{-2}$ min$^{-1}$ were produced at the anode | electrolyte interface during cell operation. From the values reported in the literature, tin dioxide can be reduced at a rate of ca. 1.53 mg SnO$_2$ cm$^{-2}$ min$^{-1}$ using ca. 1.22 mg cm$^{-2}$ of coconut charcoal, while using a flow rate of ca. 5.10 mL cm$^{-2}$ min$^{-1}$ of hydrogen (at a pressure of 101.3 kPa) the reduction rate can be increased to ca. 2.55 mg cm$^{-2}$ min$^{-1}$. These results indicate that formation of tin dioxide cannot be avoided in the system. However, from analysis of the results reported by CellTech Power Inc. for a Sn_{l0}\text{-SOFC} operating at 1000 °C with a quiescent anode (200 μm thick molten tin electrode pressed against a 200 μm thick YSZ electrolyte), it was concluded that the kinetics of the fuel cell were enhanced when hydrogen was used as fuel. It suggested that, together with formation of tin dioxide at the anode | electrolyte interface, this fuel was being oxidized according to reaction:

$$2H_2 + 2O^{2-} \rightleftharpoons 2H_2O + 4e^- \ (8.5)$$

Therefore, the kinetics of the process was enhanced by coupling of these two oxidation half-reactions.

Oxygen concentration at the Sn anode | electrolyte interface was calculated as a function of the oxygen concentration in the bulk, the diffusion layer thickness and the anode activation overpotential, in order to determine the operating conditions at which saturation was reached at this surface, and so tin dioxide was formed. The predictions, based on the kinetic parameters obtained under quiescent conditions, suggested that saturation at the anode | electrolyte interface could not be avoided in a Sn_{l0}\text{-SOFC} operating at its maximum power density at least the diffusion layer thickness was lower than 50 μm. This observation suggested that extreme stirring/flowing conditions were required at the molten tin anode in order to maintain the fuel cell operational. However, further experimental analysis of the kinetics of a stirred/flowing system is required in order to complete this study.

When a Sn_{l0}\text{-SOFC} with a stirred anode was experimentally studied, a slight increase in the current densities of the system was observed (no higher than ca. 100 A m$^{-2}$) using both activated carbon particles and hydrogen as fuels. However, due to the absence of further experiments (e.g. different stirring rates, determination of exit gas compositions and longer term performance analysis), it was not possible to determine quantitatively the effect that stirring could have had on the kinetics.
**Future Work**

From the encouraging results reported for the performances of Sn\textsubscript{0.07}-SOFCs operating in battery and fuel cell modes, future work could focus on:

1. Development of an experimental Sn\textsubscript{0.07}-SOFC arrangement with: thin electrodes and electrolyte (in the order of ca. 100 µm thick), enhanced cathode microstructure (homogeneous pores size and distribution), and current collectors with low ohmic potential losses (shorter and stable during fuel cell operation). As shown in Chapter 5 and Chapter 6, these improvements would enhance the kinetics of the Sn\textsubscript{0.07}-SOFC and would introduce less error in the determination of the electrode kinetics.

2. Use of a reference electrode at the anode side (e.g. embedded platinum wire in the YSZ electrolyte) to isolate the anode electrochemical response from side effects of other cell components. As discussed in Chapter 6, this improvement would help in the determination of a correct equivalent circuit model of the anode and would enable improved understanding of the charge and mass transport phenomena occurring at each electrode.

3. Analysis of the kinetics of the Sn\textsubscript{0.07}-SOFC with an anode operating under controlled and predictable fluid mechanical conditions, to provide reliable information about mass transfer coefficients and their effects on the formation of tin dioxide at the anode | electrolyte interface, completing the study started in Chapter 6 and Chapter 8.

4. Exit gas analysis during Sn\textsubscript{0.07}-SOFC operation in fuel cell mode using different carbonaceous fuels or hydrogen. This would provide information about the kinetics of \( O_{\text{Sn}} \) / SnO\textsubscript{2} reduction and enable their comparison with the anode oxidation kinetics, as suggested in Chapter 8.

5. Determination of the effects of temperature and air flow rates at the cathode.

6. Integration of the information from (1) to (5) to enable design of Sn\textsubscript{0.07}-SOFCs, especially addressing how best to couple fuel oxidation with oxidation at the Sn anode | electrolyte interface, to achieve optimal performance of the whole system.
References


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REFERENCES


REFERENCES


REFERENCES


REFERENCES


REFERENCES


Appendix A.

Carbolite VST/HST-12/200 Furnace Temperature Profiles

In this Appendix are presented the temperature profiles measured in the Carbolite VST/HST-12/200 furnace using an N-type thermocouple connected to an YCT RS-232 data logger (YC-747D). The thermocouple was placed at different positions inside the furnace working tube, starting at 4 cm from the entrance and displacing it every 1 cm towards the centre of the heated chamber located at 16 cm depth.

Figure A.1 presents the temperature profiles obtained when set points of 822, 923 and 1025 °C were adjusted in the furnace controller. These temperatures were chosen in order to obtain temperatures of 800, 900 and 1000 °C, respectively, in the centre of the furnace where the pellet $\text{LSM/LSM-YSZ/YSZ}$ half-cell was placed during the experimental measurements. The temperatures presented in this figure were determined as an average of the temperature values measured during 10 min at each position.

![Temperature profile graph]

*Figure A.1. Temperature profile of the Carbolite VST/HST-12/200 furnace at a set-point temperature of 822 °C, 923 °C and 1025 °C*
Appendix B.

Van der Pauw Equation for Conductivity Measurements

In this Appendix is presented the deduction of the equation introduced in Section 4.2.1 for the calculation of the resistivity of a sample based on 4-point probe measurements. The mathematical approach summarized below was developed in 1958 by Van der Pauw for measuring the specific resistivity and Hall effect on discs and lamellae of arbitrary shape and material (see references [191, 192]).

In many cases the specific resistivity of a conducting material is measured by cutting a sample in the form of a bar where current contacts A and B and voltage contacts C, D, E and F are attached to the bar as shown in Figure B.1. The specific resistance is then derived from the potential difference and the distance between the points C and D or E and F, the current density and the dimensions of the bar.

![Figure B.1. Classical shape of a sample for measuring the specific resistivity](image)

For the measurement of the specific resistivity of a semiconductor a more complicated shape of the sample has often to be used considering that in this case the voltage cannot be determined with sufficient accuracy due to the higher resistances that the contact points present. Figure B.2 presents a bridge-shaped sample which is a typical example of the type of geometry that can be used in order to reduce the contact resistances using current and voltage contacts of large surface area. Unfortunately, the fabrication of a sample with this shape could result rather difficult if a brittle semiconductor material needs to be studied considering the high risk of breakage involved in the cutting process even when special equipment such as ultrasonic tools are used.

In the following section the mathematical derivation of the Van der Pauw method for measuring the specific resistivity of a sample of arbitrary shape and material is presented.
B.1. Mathematical Derivation of the Van der Pauw Equation

Consider a flat sample of a conducting material of arbitrary shape with successive contacts A, B, C and D fixed on arbitrary places along the periphery (see Figure B.3) such that the following conditions are fulfilled: (1) the contacts are at the periphery of the sample, (2) the contacts are sufficiently small, (3) the sample is homogeneous in thickness, and (4) the surface of the sample is singly connected, i.e. the sample does not have isolated holes.

Based on Ohm’s law (see Chapter 2), the resistance $R_{AB,CD}$ is defined as the potential difference between the contacts D and C divided by the current $I_{AB}$ flowing between the contacts A and B in accordance to equation:

$$R_{AB,CD} = \frac{V_D - V_C}{I_{AB}}$$  \hspace{1cm} (B.1)

Similarly the resistance $R_{BC,DA}$ is defined as:

$$R_{BC,DA} = \frac{V_A - V_D}{I_{BC}}$$  \hspace{1cm} (B.2)

In order to determine the resistivity of a material sample based on the experimental measurement of the resistances represented by equations (B.1) and (B.2), Van der Pauw demonstrated that between these values exists the following relation:

$$\exp\left(-\frac{\pi d}{\rho} R_{AB,CD}\right) + \exp\left(-\frac{\pi d}{\rho} R_{BC,DA}\right) = 1$$  \hspace{1cm} (B.3)
where $\rho$ is the specific resistance of the material and $d$ is the thickness of the sample.

**Figure B.3.** Schematic of a sample of arbitrary shape with four small contacts at arbitrary places along the periphery

To prove equation (B.3) first it is necessary to show that it holds for a particular shape of the sample. The second step is to prove that if it holds for a particular shape then it will hold for any shape. For the case of a particular shape a semi-infinite plane will be considered with contacts P, Q, R and S along its boundary, spaced at distances a, b and c respectively as it is shown in Figure B.4(d). If a current $I$ enters the sample at the contact P and leaves it at the contact Q, it will be demonstrated that the following relation holds:

$$V_s - V_r = \frac{I \rho}{2 \pi d} \ln \left( \frac{(a+b)(b+c)}{b(a+b+c)} \right)$$  \hspace{1cm} (B.4)

With this intention, initially a lamellae of thickness $d$ and resistivity $\rho$ which extends to infinity in all directions is considered (see Figure B.4(a)). If a current $2I$ is applied at the contact P and flows to infinity with radial symmetry then at a distance $r$ from P the current density results to be:

$$j = \frac{2I}{2 \pi rd}$$  \hspace{1cm} (B.5)

As a consequence of this condition, the potential field-strength $E$ is radially orientated and according to the generalized form of Ohm’s law it has the value:

$$E = \rho j = \frac{\rho I}{\pi rd}$$  \hspace{1cm} (B.6)

The potential difference between two points R and S lying on a straight line with P is:
\[ V_S - V_R = \frac{\rho I}{\pi d} \int_{s}^{e} \ln \left( \frac{a + b + c}{a + b} \right) \, E \, dr \]  
\[ = \frac{\rho I}{\pi d} \int_{s}^{e} \ln \left( \frac{a + b + c}{a + b} \right) \, r \, dr \]  
\[ = \frac{\rho I}{\pi d} \ln \left( \frac{a + b + c}{a + b} \right) \]  
\( (B.7) \)

Since no current flows in the direction perpendicular to the line through P, R and S, the result obtained remains valid if the part of the lamellae at one side of this line is omitted – yielding a half-plane – and if at the same time the current is halved (see Figure B.4(b)).

\[ \ln \frac{SR}{I b c V V dB} \rho \pi \frac{a + b + c}{a + b} = \frac{\rho I}{\pi d} \ln \left( \frac{b + c}{b} \right) \]  
\( (B.8) \)

Superposition of the cases (b) and (c) yields to case (d) with the current \( I \) being introduced at P and taken off at Q. Therefore, the value for the potential difference \( V_S - V_R \) in this case can be determined by adding equations (B.7) and (B.8) to obtain equation (B.4).
Based on the mathematical approach presented before, the resistances $R_{PQ,RS}$ and $R_{QR,SP}$ can be calculated as:

$$R_{PQ,RS} = \frac{\rho}{\pi d} \ln \frac{(a+b)(b+c)}{b(a+b+c)}$$  \hspace{1cm} (B.9)

$$R_{QR,SP} = \frac{\rho}{\pi d} \ln \frac{(a+b)(b+c)}{ca}$$  \hspace{1cm} (B.10)

In addition, considering that:

$$b(a+b+c)+ca = (a+b)(b+c)$$  \hspace{1cm} (B.11)

equation (B.3) can be derived using equations (B.9) to (B.11).

Having demonstrated the validity of equation (B.3) in the particular case of a semi-infinite plane, the following step is to prove its validity in the general case. With this objective, the technique of the conformal mapping of two-dimensional fields (see reference [262]) is used assuming that the semi-infinite plane considered before coincides with the upper part of the complex $z$-plane where: $z = x+iy$. Additionally, the auxiliary complex function $\omega = f(z) = u(x,y) + i v(x,y)$ is introduced being $u$ and $v$ real functions of $x$ and $y$ with $u$ representing the potential field in the sample. Based on complex variable theory (see reference [263]) it can be demonstrated that the functions $u$ and $v$ in $f$ satisfy the Cauchy-Riemann relations:

$$\frac{\partial u}{\partial x} = \frac{\partial v}{\partial y}$$  \hspace{1cm} (B.12)

$$\frac{\partial u}{\partial y} = -\frac{\partial v}{\partial x}$$  \hspace{1cm} (B.13)

Figure B.5 presents the same semi-infinite sample introduced in Figure B.4(d) but now with the upper part of it coinciding with the complex $z$-plane. Considering that the current now flows from an arbitrary point $T_1$ in the complex $z$-plane to another point $T_2$ in the same plane, the net current which traverses this path from right to left is given by:
where \( E_n \) is the normal component of the field strength. This expression is readily verified to be equal to:

\[
I_{T_1,T_2} = \frac{d}{\rho} \int_{T_1}^{T_2} E_n ds
\]  

(B.14)

Hence, if the current is applied along the real axis from \(-\infty\) to \(+\infty\) the value of \( v \) remains constant until we pass the point P. When passing the point P along a small half-circle in the upper half-plane the value of \( v \) will increase by \( \rho I/d \). Similarly, when passing the point Q the value of \( v \) will decrease by \( \rho I/d \).

In order to generalize this case a sample of arbitrary shape is considered now lying in a different complex plane called the \( t \)-plane as shown in Figure B.6, where \( t = r + is \). By a well-known theorem it is always possible to find an analytic function \( f(z) = k(t) \) such that the upper half-plane in the \( z \)-plane is mapped onto the sample in the \( t \)-plane. In particular, considering that the contact points A, B, C and D in the \( t \)-plane are images of the points P, Q, R and S respectively in the \( z \)-plane, and that \( k(t) = l + im \) is identical with \( f(z) = f(z(t)) = k(t) \), by definition \( m \) remains constant when travelling in counter-clockwise direction along the boundary of the sample in the \( t \)-plane and only increase by \( \rho I/d \) when passing the point A and it decreases by the same amount when passing the point B.
From the theory of conformal mapping it follows that if \( m \) in the \( t \)-plane is interpreted in the same way as \( v \) in the \( z \)-plane, then \( l \) will represent the potential field in the \( t \)-plane. Consequently, if a current \( I' \) enters the sample at the contact A and leaves it at the contact B and if we choose \( I' \rho'/d' = I \rho /d \), where \( \rho' \) and \( d' \) are the specific resistivity and the thickness of the sample in the \( t \)-plane, then the voltage difference \( V_D - V_C \) will be equal to the voltage difference \( V_S - V_R \). Hence \( (d/\rho) R_{AB,CD} \) is invariant under conformal transformation. The same is true for \( (d/\rho) R_{BC,DA} \). From this it follows that equation (B.3) is of general validity.

From the demonstration presented before it follows that for measuring the specific resistivity of a flat sample it suffices to make four small contacts along its circumference and to measure the two resistances \( R_{AB,CD} \) and \( R_{BC,DA} \) in addition to the thickness of the sample.

Equation (B.3) determines uniquely the value of \( \rho \) as a function of \( R_{AB,CD} \) and \( R_{BC,DA} \) and \( d \). In order to facilitate the solution of \( \rho \) from equation (B.3) it can be written as equation (4.3) as follows. First, simplification of the exponential arguments is done using the expressions:

\[
\pi d R_{AB,CD} = x_1 \quad \text{(B.16)}
\]

\[
\pi d R_{BC,DA} = x_2 \quad \text{(B.17)}
\]

Replacing expressions (B.16) and (B.17) in equation (B.3) it can be obtained:
\[ \exp\left(-\frac{x_1}{\rho}\right) + \exp\left(-\frac{x_2}{\rho}\right) = 1 \]  
(B.18)

Second, \( x_1 \) and \( x_2 \) are rearranged as follows:

\[ x_1 = \frac{1}{2} \left\{ (x_1 + x_2) + (x_1 - x_2) \right\} \]  
(B.19)

\[ x_2 = \frac{1}{2} \left\{ (x_1 + x_2) - (x_1 - x_2) \right\} \]  
(B.20)

and replaced in equation (B.18) to obtain:

\[ \exp\left(-\frac{x_1 + x_2}{2\rho}\right) \left[ \exp\left(-\frac{x_1 - x_2}{2\rho}\right) + \exp\left(-\frac{x_1 - x_2}{2\rho}\right) \right] = 1 \]  
(B.21)

which is equivalent to:

\[ \exp\left(-\frac{x_1 + x_2}{2\rho}\right) \cosh\left(\frac{x_1 - x_2}{2\rho}\right) = \frac{1}{2} \]  
(B.22)

If the argument of the exponential function is written as:

\[ \frac{x_1 + x_2}{2\rho} = \frac{\ln 2}{f} \]  
(B.23)

Then equation (B.22) can be written as:

\[ \exp\left(-\frac{\ln 2}{f}\right) \cosh\left(\frac{x_1/x_2 - 1}{x_1/x_2 + 1} \frac{\ln 2}{f}\right) = \frac{1}{2} \]  
(B.24)

Replacing expressions (B.16) and (B.17) in equations (B.23) and (B.24) and rearranging equations (4.3) and (4.4) can be obtained. The variable \( f \) is a function that depends of the ratio \( \frac{R_{AC,CD}}{R_{BC,DA}} \) and varies between 0 and 1. Its value can be determined by solving equation (B.24) for each particular value of \( \frac{R_{AC,CD}}{R_{BC,DA}} \).
Appendix C.

Thermodynamic Data of Chemical Species in Sn(l)-SOFCs

In this Appendix is presented the thermodynamic data used in Chapter 5 and Chapter 8 to determine the enthalpies, entropies, Gibbs free energies, open circuit voltages (OCVs) and equilibrium constants associated to the chemical reactions involved in the operation of the Sn(l)-SOFC.

Table C.1 presents the standard enthalpies and entropies of species Sn(s), O_2(g), SnO_2(s), C(s), CO(g), CO_2(g), H_2(g) and H_2O(l), and the heats of change of phase for Sn(s) and H_2O(l). Table C.2 presents the coefficients of the heat capacity power series of these species, including Sn(l) and H_2O(g), in the range of temperature of interest for the calculations included in this thesis.

Table C.1. Standard enthalpies and entropies of Sn(s), O_2(g), SnO_2(s), C(s), CO(g), CO_2(g), H_2(g) and H_2O(l)

<table>
<thead>
<tr>
<th>Compound</th>
<th>ΔH^o_{298.15} / kJ mol(^{-1})</th>
<th>S^o_{298.15} / J (mol K)(^{-1})</th>
<th>T(<em>{cp}) / ΔH(</em>{cp}) / K and kJ mol(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(s)</td>
<td>0</td>
<td>51.18</td>
<td>505.10 / 7.029</td>
</tr>
<tr>
<td>O_2(g)</td>
<td>0</td>
<td>205.15</td>
<td>---</td>
</tr>
<tr>
<td>SnO_2(s)</td>
<td>-577.63</td>
<td>49.04</td>
<td>---</td>
</tr>
<tr>
<td>C(s)</td>
<td>0</td>
<td>5.60</td>
<td>---</td>
</tr>
<tr>
<td>CO(g)</td>
<td>-110.53</td>
<td>197.66</td>
<td>---</td>
</tr>
<tr>
<td>CO_2(g)</td>
<td>-393.52</td>
<td>213.79</td>
<td>---</td>
</tr>
<tr>
<td>H_2(g)</td>
<td>0</td>
<td>130.68</td>
<td>---</td>
</tr>
<tr>
<td>H_2O(l)</td>
<td>-285.83</td>
<td>69.95</td>
<td>373.15 / 40.7</td>
</tr>
</tbody>
</table>

### Table C.2. Coefficients of heat capacities power series for Sn(s), Sn(l), O$_2$(g), SnO$_2$(s), C(s), CO(g), CO$_2$(g), H$_2$(g), H$_2$O(l) and H$_2$O(g)

#### Tin, Sn(s)

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>298.15 – 505.10</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>21.14</td>
</tr>
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<td>B</td>
<td>20.10</td>
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</table>

#### Tin, Sn(l)

<table>
<thead>
<tr>
<th>Temperature / K</th>
<th>505.10 – 1273</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>27.63</td>
</tr>
<tr>
<td>B</td>
<td>0</td>
</tr>
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</table>

#### Oxygen, O$_2$(g)

<table>
<thead>
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<th>Temperature / K</th>
<th>298.15 – 700</th>
<th>700 – 2000</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>31.32234</td>
<td>30.03235</td>
</tr>
<tr>
<td>B</td>
<td>-20.23531</td>
<td>8.772972</td>
</tr>
<tr>
<td>C</td>
<td>57.86644</td>
<td>-3.988133</td>
</tr>
<tr>
<td>D</td>
<td>-36.50624</td>
<td>0.788313</td>
</tr>
<tr>
<td>E</td>
<td>-0.007374</td>
<td>-0.741599</td>
</tr>
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</table>

#### Tin dioxide, SnO$_2$(s)

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<thead>
<tr>
<th>Temperature / K</th>
<th>298.15 – 1373</th>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>58.36</td>
</tr>
<tr>
<td>B</td>
<td>26.66</td>
</tr>
<tr>
<td>C</td>
<td>-1.06</td>
</tr>
</tbody>
</table>
## APPENDIX C.
THERMODYNAMIC DATA OF CHEMICAL SPECIES IN $Sn_{0.5}$-SOFCs

### Carbon, C(s)

<table>
<thead>
<tr>
<th>Temperature / K</th>
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</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>27.069006</td>
</tr>
<tr>
<td>B</td>
<td>0.457868</td>
</tr>
<tr>
<td>C</td>
<td>-4.536443</td>
</tr>
<tr>
<td>D</td>
<td>-2.183448</td>
</tr>
<tr>
<td>E</td>
<td>0.800572</td>
</tr>
<tr>
<td>F</td>
<td>-0.072207</td>
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### Carbon monoxide, CO(g)

<table>
<thead>
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</thead>
<tbody>
<tr>
<td>A</td>
<td>25.56759</td>
</tr>
<tr>
<td>B</td>
<td>6.096130</td>
</tr>
<tr>
<td>C</td>
<td>4.054656</td>
</tr>
<tr>
<td>D</td>
<td>-2.671301</td>
</tr>
<tr>
<td>E</td>
<td>0.131021</td>
</tr>
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### Carbon dioxide, CO$_2$(g)

<table>
<thead>
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<th>1 200 – 6 000</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>24.99735</td>
<td>58.16639</td>
</tr>
<tr>
<td>B</td>
<td>55.18696</td>
<td>2.720074</td>
</tr>
<tr>
<td>C</td>
<td>-33.69137</td>
<td>-0.492289</td>
</tr>
<tr>
<td>D</td>
<td>7.948387</td>
<td>0.03884</td>
</tr>
<tr>
<td>E</td>
<td>-0.136638</td>
<td>-6.447293</td>
</tr>
</tbody>
</table>
APPENDIX C.
THERMODYNAMIC DATA OF CHEMICAL SPECIES IN SnO\textsubscript{2}-SOFCs

### Hydrogen, $H_2(g)$

<table>
<thead>
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<th>1 000 – 2 500</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>33.066178</td>
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</tr>
<tr>
<td>B</td>
<td>-11.363417</td>
<td>12.257357</td>
</tr>
<tr>
<td>C</td>
<td>11.432816</td>
<td>-2.859786</td>
</tr>
<tr>
<td>D</td>
<td>-2.772874</td>
<td>0.268238</td>
</tr>
<tr>
<td>E</td>
<td>-0.158558</td>
<td>1.977990</td>
</tr>
</tbody>
</table>

### Water, $H_2O(l)$

<table>
<thead>
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<th>Temperature / K</th>
<th>298.15 – 373.15</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>-203.6060</td>
</tr>
<tr>
<td>B</td>
<td>1,523.290</td>
</tr>
<tr>
<td>C</td>
<td>-3,196.413</td>
</tr>
<tr>
<td>D</td>
<td>2,474.455</td>
</tr>
<tr>
<td>E</td>
<td>3.855326</td>
</tr>
</tbody>
</table>

### Steam, $H_2O(g)$

<table>
<thead>
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<th>Temperature / K</th>
<th>373.15 – 1 700</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>30.09200</td>
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<td>B</td>
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<td>C</td>
<td>6.793435</td>
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<tr>
<td>D</td>
<td>-2.534480</td>
</tr>
<tr>
<td>E</td>
<td>0.082189</td>
</tr>
</tbody>
</table>

In the case of Sn(s) and Sn(l) the heat capacity is a lineal function of the temperature represented by the equation:

\[ C_p(t) = A + B \cdot t \]  \hspace{1cm} (C.1)

where \( C_p(t) \) is the heat capacity in J (mol K)^{-1} and \( t = T(K) \times 10^{-3} \), being \( T \) the operating temperature of the process.

In the case of SnO_2(s) the heat capacity is a power series represented by the equation:

\[ C_p(t) = A + B \cdot t + \frac{C}{t^2} \]  \hspace{1cm} (C.2)

For O_2(g), CO(g), CO_2(g), H_2(g), H_2O(l) and H_2O(g) the heat capacity is a power series represented by the equation:

\[ C_p(t) = A + B \cdot t + C \cdot t^2 + D \cdot t^3 + \frac{E}{t^2} \]  \hspace{1cm} (C.3)

Finally, the heat capacity of C(s) follows the power series:

\[ C_p(t) = A + B \cdot t + \frac{C}{t} + \frac{D}{t^2} + \frac{E}{t^3} + \frac{F}{t^4} \]  \hspace{1cm} (C.4)
Appendix D.

Current-Overpotential Equation with Mass Transfer Effect

In this Appendix is presented the solution of the current-overpotential equation:

\[
j = j_{0,\text{an}} \frac{C_{\text{bulk}}^{\text{an}}}{C_{\text{an}}^{\text{react}}} \left[ \exp \left( \frac{\alpha_{\text{an}} \nu_e F}{RT} \eta_{\text{act}}^{\text{an}} \right) - \exp \left( - \frac{(1 - \alpha_{\text{an}}) \nu_e F}{RT} \eta_{\text{an}}^{\text{act}} \right) \right]
\]

(5.21)

used in this thesis for calculation of the activation overpotentials, \( \eta_{\text{an}}^{\text{act}} \), at the molten tin anode.

As it was stated in Section 6.1.1 the current density can be expressed as a function of the gradient of \( [O]_{\text{Sn}} \) species in the molten tin anode using equation:

\[
j = \frac{2FD}{\delta_{\text{an}}} \left( C_{\text{an}}^{\text{react}} - C_{\text{an}}^{\text{bulk}} \right)
\]

(6.4)

Therefore, rearranging equation (6.4) the ratio \( C_{\text{an}}^{\text{bulk}} / C_{\text{an}}^{\text{react}} \) can be derived:

\[
\frac{C_{\text{an}}^{\text{bulk}}}{C_{\text{an}}^{\text{react}}} = \frac{1}{1 + \left( \frac{j}{j_{\text{bulk}}} \right)}
\]

(D.1)

where \( j_{\text{bulk}} \) corresponds to:

\[
j_{\text{bulk}} = \frac{2FC_{\text{an}}^{\text{bulk}} D_{\text{an}}}{\delta_{\text{an}}}
\]

(5.33)

Replacing equation (D.1) in equation (5.21), the following quadratic equation for the current density \( j \) can be obtained:

\[
\frac{j^2}{j_{\text{bulk}}} + j - BV = 0
\]

(D.2)
where $BV$ corresponds to the Butler-Volmer expression:

$$BV = j_0 \left[ \exp\left(\frac{\alpha_m v_e F}{RT} \eta^{\text{act}}_{an}\right) - \exp\left(-\frac{(1-\alpha_m) v_e F}{RT} \eta^{\text{act}}_{an}\right) \right]$$  \hspace{1cm} (D.3)

Therefore, the solution of equation (D.2) corresponds to:

$$j = -1 + \sqrt{1 + 4 \frac{1}{j_{\text{bulk}}} BV}$$  \hspace{1cm} (D.4)

Equation (D.4) was introduced in the mathematical models described in Section (5.3) to determine the activation overpotentials at the molten tin anode when a set of current densities was given.
Appendix E.

Cyclic Voltammetry of a Sn(l)-SOFC with Stirred Anode

In this Appendix are presented the voltammograms obtained during operation of a Sn(l)-SOFC at a temperature of 900 °C using a stirred molten tin anode. An alumina tube of 3 mm outer diameter, 2 mm inner diameter and 300 mm length was used to feed constant flow rates of helium (30 mL min\(^{-1}\)) or hydrogen (20 mL min\(^{-1}\)) into the melt to promote its agitation. In both cases, four cycles of potential were measured at a scan rate of 10 mV s\(^{-1}\) between the corresponding OCV value and zero volts.

Figure E.1 and Figure E.2 present the cyclic voltammetries obtained when helium and hydrogen were used as stirring agent, respectively. The OCV measured in the case of the inert gas was 0.88 V, while for the fuel the OCV resulted to be 0.90 V. Hysteresis is observed in both cases due to the formation of tin dioxide at the anode | electrolyte interface and the anode current collector (graphite rod) surface during operation. This by-product forms non-dense layers which block the continuous transport of oxide ions (O\(^2-\)) from the electrolyte bulk to the anode active sites due to its low conductivity compared to liquid tin.

![Figure E.1. Voltammogram obtained during operation of the Sn(l)-SOFC at 900 °C when the molten tin anode was stirred using a helium flow rate of 30 mL min\(^{-1}\) (scan rate: 10 mV s\(^{-1}\))](image-url)
Figure E.2. Voltammogram obtained during operation of the Sn\textsubscript{(l)}-SOFC at 900 °C when the molten tin anode was stirred using a hydrogen flow rate of 20 mL min\textsuperscript{-1} (scan rate: 10 mV s\textsuperscript{-1})