Operando Localized Probing of Model Electrodes for Solid Oxide Electrolysis/Fuel Cells

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Operando Localized Probing of Model Electrodes for Solid Oxide Electrolysis/Fuel Cells

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Preface

This work is presented to the evaluation committee and the Ph.D. school of the Technical University of Denmark in candidacy for a Ph.D. degree. It is the result of three years of experimental work, funded through the ECoProbe project by the Danish Independent Research Council (Grant DFF – 4005-00129). The work was performed under the supervision of Dr. Karin Vels Hansen and co-supervision of Dr. Christodoulos Chatzichristodoulou, Prof. Mogens Bjerg Mogensen and Dr. Kion Norrman.
Abstract

The need for efficient large scale energy storage is becoming more and more pressing as entire nations are planning to move away from fossil fuels and intend to harvest more renewable energy sources. Electrochemical technologies such as solid oxide fuel cells (SOFC) and solid oxide electrolysis cells (SOEC), collectively called solid oxide cells (SOCs), are being considered as potential technologies to be used to balance the grid and establish a sustainable transportation system\[1–4\]. However, SOCs remain economically unfeasible as a result of their fast degradation and short durability. Due to the complexity of the microstructure of the SOCs, operando localized probing of SOCs is necessary to further our understanding of the reaction mechanisms at the electrodes as well as their degradation. The purpose of this work was to investigate the electrochemical reactions that occur at the gas/electrode and electrode/electrolyte and to investigate the chemical and microstructural change of the different interfaces as a result of different conditions such as polarizations, atmosphere, temperature, impurity content etc. An operando localized probing approach was used to investigate model electrode systems by using a controlled atmosphere high temperature scanning probe microscope (CAHT-SPM) which was combined with electrochemical measurements at conditions close to the operating condition of SOCs. Scanning electrode microscopy (SEM) and time of flight secondary ion mass spectrometry (ToF-SIMS) were also used to investigate any surface microstructural and chemical changes.

This work is divided into two parts, consisting of the investigation of the fuel electrode and the air electrode. The first part of this study was on the impact of strong cathodic polarization on Ni\(|\)YSZ and Pt\(|\)YSZ microelectrodes using a high temperature scanning probe microscope. Ni and PtIr sharp tips were used as working electrodes to perform electrochemical measurements at 650 °C in
an atmosphere containing 3 % H₂O in a 9 % H₂ in N₂ gas mixture. The influence of impurities was investigated by testing different samples which contained different amount of silica impurities. The impedance spectra under different DC cathodic polarizations revealed that electronic conductivity was introduced into the YSZ, in both the Ni and PtIr cases, a decrease in the high frequency resistance was observed with increasing cathodic polarization. This was further supported by the appearance of high conductance regions close to the metal|YSZ contact. The introduction of electronic conductivity also increased the active area where the water reduction reaction occurs. Additionally, the polarization influenced the distribution of impurities containing Si. With the purpose of investigating the microstructural changes of the metal|YSZ interface, which was challenging due to the small contact area between the tip and the YSZ sample, a similar study was performed using macro electrodes. The electrochemical measurements mainly consisted on cyclic voltammetry (CVs), chronoamperometry and a little of impedance spectroscopy. The second part consists of the investigation of the electrode surface reaction (La$_{0.6}$Sr$_{0.4}$)$_{0.99}$FeO$_{3-δ}$ (LSF) and changes in its stochiometry. This study was performed on model electrodes which were fabricated by using pulsed laser deposition to deposit dense LSF films and photolithography to micro-pattern the film into microelectrodes with different diameters. The electrochemical measurements were performed in synthetic air at different temperatures starting from 500 °C up to 700°C. The microstructure and surface chemistry were inspected after each step. The CV measurements indicate that at low temperature a change in the oxygen stochiometry occurs and as the temperature increases the oxygen evolution reaction becomes more dominant. These results were in agreement with the electrochemical impedance spectroscopy (EIS) measurements which indicate that the electrodes were completely blocking at low temperatures and the surface reaction was a rate determining process.
Behovet for effektiv energilagring på stor skala bliver i stigende grad vigtigere, da flere lande planlægger at opgive fossil brændstof og bruge flere vedvarende energikilder. Elektrokemiske teknologier, som faststofoxid-brændselsceller (SOFC) og -elektrolyseceller (SOEC), fælles betegnet som faststofoxid-cellers (SOC) bliver taget i betragtning som potentielle teknologier til at udjævne belastningen på elnettet og etablere et bæredygtigt transportsystem. Imidlertid er SOC endnu ikke en økonomisk holdbar løsning på grund af deres hurtige degradering og korte holdbarhed. På grund af kompleksiteten af mikrostrukturen i SOC er lokaliserede målinger ved operando betingelser nødvendige for bedre at forstå reaktionsmekanismerne på elektroderne såvel som deres degradering. Formålet med dette arbejde var at undersøge de elektrokemiske reaktioner, der foregår på grænsefladerne mellem gassen og elektroden eller elektroden og elektrolytten ved hjælp lokaliserede operando studier, og at analysere de kemiske og mikrostrukturelle ændringer af de forskellige grænseflader som resultat af forskellige betingelser, herunder ændringer i polarisering, atmosfære, temperatur, indhold af urenheder osv. Hovedinstrumentet, som blev brugt i dette studie, var et scanning-probe-mikroskop med mulighed for kontrolleret atmosfære og høj temperatur (CAHT-SPM), som blev kombineret med elektrokemiske målinger på mikroelektroder under betingelser tæt på SOC driftsbetingelser. Scanning-elektronmikroskop og time of flight secondary ion mass spectroscopy blev brugt til at undersøge mikrostrukturelle og kemiske ændringer på overfladen. Arbejdet er delt i to hoveddele, bestående af undersøgelser af brintelektroder og iltelektroder. Den første del omhandler indflydelsen af stærk katodisk polarisering på Ni|YSZ og PtIr|YSZ mikroelektroder med CAHT-SPM. Tynde prober af Ni og PtIr blev brugt som arbejdslektroder til at gennemføre elektrokemiske målinger ved 650 °C i en atmosfære af 3 % H₂O i en blanding af 9 % H₂ i N₂. Indflydelsen
af urenheder blev undersøgt ved at teste prøver, som indeholdt forskellige mængder af silica. Impedansspektrene fra forskellige DC katodiske polariseringer viste at en elektronisk ledningsevne blev introduceret i YSZ, da der både for Ni og PtIr blev observeret et fald i højfrekvensmodstanden med stigende katodisk polarisering. Dette blev også støttet af tilsynekomsten af områder med høj ledningsevne tæt på kontakten mellem metal og YSZ. Introduktionen af elektrisk ledningsevne øgede det aktive område, hvor vandreduktionssreaktionen foregår. Derudover påvirkede polariseringen også fordelingen af urenheder som indeholdt Si. Et lignende studie blev foretaget med makroelektroder, for at evaluere mikrostrukturerne af grænsefladen mellem metal og YSZ i større skala. I dette studie bestod de elektrokemiske målinger primært af cyklisk voltammetri (CV), kronoamperometri og impedansspektroskopii. Den anden del af arbejdet bestod i undersøgelsen af overfladereaktionerne på \((\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{FeO}_{3-\delta}\) (LSF) og ændringer i dets støkiometri. Denne undersøgelse blev gennemført på modelelektroder, som blev fremstillet med pulsed laser deposition og fotolitografi til at fremstille tyndfilmsemielektroder med forskellige diametre. De elektrokemiske målinger blev gennemført i syntetisk luft ved temperaturer mellem 500 og 700 °C. Mikrostrukturer og overfladeekologi blev undersøgt ved hvert trin. CV-målingerne viser, at der sker en ændring i iltstøkiometriien ved lav temperatur, og når temperaturen stiger bliver iltudviklingsreaktionen mere dominerende. Disse resultater er i overensstemmelse med EIS-målingerne, som viste at elektroderne var helt blokerende ved lav temperatur og at overfladereaktionen var en hastighedsbestemmende proces.
Acknowledgements

The hard work of three long years came to an end, and it has been materialized in the form of this thesis. I would like to take a few lines and thank everyone without whom this work would have not been possible. Apparently, it takes a village!

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List of publications

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<th>Description</th>
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<tbody>
<tr>
<td>AC</td>
<td>Alternate Current</td>
</tr>
<tr>
<td>AFM</td>
<td>Atomic Force Microscopy</td>
</tr>
<tr>
<td>AP-XPS</td>
<td>Ambient Pressure-X-ray Photoemission spectroscopy</td>
</tr>
<tr>
<td>BSCF</td>
<td>$(\text{Ba, Sr})(\text{Co,Fe})\text{O}_3$</td>
</tr>
<tr>
<td>CAHT</td>
<td>Controlled Atmosphere High Temperature</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CGO</td>
<td>Gadolinia doped Ceria</td>
</tr>
<tr>
<td>CPE</td>
<td>Constant Phase Element</td>
</tr>
<tr>
<td>ct</td>
<td>Charge Transfer</td>
</tr>
<tr>
<td>CV</td>
<td>Cyclic Voltammetry</td>
</tr>
<tr>
<td>DC</td>
<td>Direct Current</td>
</tr>
<tr>
<td>EDS/EDX</td>
<td>Energy Dispersive X-ray Spectroscopy</td>
</tr>
<tr>
<td>EIS</td>
<td>Electrochemical Impedance Spectroscopy</td>
</tr>
<tr>
<td>ESM</td>
<td>Electrochemical Strain Microscopy</td>
</tr>
<tr>
<td>HF</td>
<td>High Frequency</td>
</tr>
<tr>
<td>IBE</td>
<td>Ion Beam Etching</td>
</tr>
<tr>
<td>IV</td>
<td>Current-Voltage</td>
</tr>
<tr>
<td>LF</td>
<td>Low Frequency</td>
</tr>
<tr>
<td>LSCF</td>
<td>$(\text{La, Sr})(\text{Co,Fe})\text{O}_3$</td>
</tr>
<tr>
<td>LSF</td>
<td>$(\text{La, Sr})\text{FeO}_3$</td>
</tr>
<tr>
<td>LSM</td>
<td>$(\text{La, Sr})\text{MnO}_3$</td>
</tr>
<tr>
<td>mg</td>
<td>Migration</td>
</tr>
<tr>
<td>OCV</td>
<td>Open Circuit Voltage</td>
</tr>
<tr>
<td>PLD</td>
<td>Pulsed Laser Deposition</td>
</tr>
<tr>
<td>RC</td>
<td>Resistor in parallel with a capacitor</td>
</tr>
<tr>
<td>Acronym</td>
<td>Description</td>
</tr>
<tr>
<td>---------</td>
<td>-------------</td>
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<tr>
<td>RE</td>
<td>Reference Electrode</td>
</tr>
<tr>
<td>RL</td>
<td>Resistor in parallel with a inductor</td>
</tr>
<tr>
<td>RQ</td>
<td>Resistor in parallel with a CPE</td>
</tr>
<tr>
<td>SEM</td>
<td>Scanning Electron Microscopy</td>
</tr>
<tr>
<td>SiYSZ</td>
<td>SiO₂ added Yttria Stabilized Zirconia</td>
</tr>
<tr>
<td>SOC</td>
<td>Solid Oxide Cells</td>
</tr>
<tr>
<td>SOEC</td>
<td>Solid Oxide Electrolysis Cells</td>
</tr>
<tr>
<td>SOFC</td>
<td>Solid Oxide Fuel Cells</td>
</tr>
<tr>
<td>SPM</td>
<td>Scanning Probe Microscopy</td>
</tr>
<tr>
<td>SR</td>
<td>Surface Reaction</td>
</tr>
<tr>
<td>SSC</td>
<td>(Sm, Sr)CoO₃</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission Electron Microscopy</td>
</tr>
<tr>
<td>ToF-SIMS</td>
<td>Time of Flight Secondary Ion Mass Spectrometry</td>
</tr>
<tr>
<td>TPB</td>
<td>Triple Phase Boundary</td>
</tr>
<tr>
<td>UV</td>
<td>Ultra Violet</td>
</tr>
<tr>
<td>WE</td>
<td>Working electrode</td>
</tr>
<tr>
<td>XRD</td>
<td>X-ray Diffraction</td>
</tr>
<tr>
<td>YSZ</td>
<td>Yttria Stabilized Zirconia</td>
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<tr>
<td>YSZ100</td>
<td>Single crystal Yttria Stabilized Zirconia</td>
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Introduction

The technological developments of the last few centuries have increased our demand for energy substantially. Fossil fuels are currently the main source of energy in the world. They are non-renewable and have a huge impact on the environment \[5-8\] and our health \[9, 10\] due to the large amount of green house gases, toxic gases \[11, 12\] and particulates matter that are produced during their combustion. Therefore, recent efforts have been made into moving towards more renewable and cleaner energy sources. As a result of these recent efforts, the technology on which renewable energy sources, such as wind and solar, are based has improved greatly making the harvesting of wind and solar energy more efficient and economically more affordable. However, the dependency of these energy sources on weather conditions poses a challenge for the grid stability. The increased use of these renewable sources would require the implementation of large scale, efficient and low cost energy storage devicess. Hence, several different energy storage technologies are being developed \[13\]. Solid oxide cells (SOC) are promising energy conversion and storage devices \[14\]. SOCs are electrochemical devices which can be operated in two different modes: in fuel cell mode for power generation (SOFC) or in electrolysis mode for energy storage (SOEC).

1.1 SOFC and SOEC working principle

The main working principle of SOFCs and SOECs is shown in Fig.1.1 a) and b), respectively. In the fuel cell mode, the chemical energy of the fuel, which has a high free energy (e.g H\(_2\), CO) is converted into by-product chemicals such as H\(_2\)O and CO\(_2\) with lower free energy and electricity. The reactions occurring at the
1.1. SOFC and SOEC working principle

Figure 1.1: The main working principle of a) SOFC and b) SOEC.

anode and cathode of a fuel cell which uses H\textsubscript{2} as fuel are:

\begin{equation}
\text{Cathode} : O_2(g) + 4e^- \rightarrow 2O^{2-} \tag{1.1.1}
\end{equation}

\begin{equation}
\text{Anode} : 2H_2(g) + 2O^2_0 \rightarrow 2H_2O + 4e^- \tag{1.1.2}
\end{equation}

In the electrolysis mode electricity is used to convert the H\textsubscript{2}O and/or CO\textsubscript{2} into H\textsubscript{2} and/or CO. The co-electrolysis of CO\textsubscript{2} and H\textsubscript{2}O is quite beneficial \cite{15} since the gas mixture of H\textsubscript{2} and CO (also called syngas) is a high energy mixture which can be used to synthesize liquid fuel \cite{1, 2, 16}.

\begin{equation}
\text{Anode} : 2O^{2-} \rightarrow O_2(g) + 4e^- \tag{1.1.3}
\end{equation}

\begin{equation}
\text{Cathode} : 2H_2O + 4e^- \rightarrow 2H_2(g) + 2O^{2-} \tag{1.1.4}
\end{equation}
1.2 Motivation for the current work

Even though it is possible to achieve very high efficiency with SOCs, their efficiency depends on multiple factors, and it is determined by the difference between the real cell potential from the Nernst potential. In the case of a SOFC, the efficiency can be expressed as follows [17]:

\[ V_{\text{Nernst}} = V^0 + \frac{RT}{2F} \ln \left( \frac{P_{H_2} \sqrt{P_{O_2}}}{P_{H_2O}} \right) \]  

(1.2.1)

where the \( F \) is the Faraday’s constant, \( R \) is the gas constant, \( T \) is the temperature in Kelvin, \( n \) is the number of electrons taking part in the reaction and \( V^0 \) is the standard potential. The real cell potential is usually lower than the Nernst potential due to probable losses which can originate from the following factors [17]:

1. Ohmic losses, which occur usually due to the electrolyte because of its low electronic conductivity, while the ohmic drops at the electrodes are usually very small due to the fact that high electronic conductivity is a prerequisite for good electrode materials.

2. Current leaks and/or fuel crossovers.

3. Mass transport of gas reactants. These potential losses occur when there is a concentration gradient from the electrode to the electrolyte, causing a lower concentration of reactants than the concentration used in the Nernst’s equation.

4. Slow reaction kinetics for the electrode reactions.

Reducing these losses and enhancing the power density has been an important task for the scientific environment, and great improvements have been made by carefully designing the microstructure of the components of the SOCs, resulting in a very complex structure. Given the high structural and morphological complexity of the SOCs, investigating the source of the potential losses can be challenging. A lot of studies utilize electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and current-voltage curves (IV-curves) [18]22 at different operating conditions in combination with characterization techniques such as scanning electron microscopy (SEM), sometimes combined with focused ion beam milling (FIB-SEM), to perform post mortem analysis of the cells. These measurements give valuable information about the overall performance of the cell.
1.2. Motivation for the current work

However, the different gradients in gas composition and temperature, as well as the varying microstructure and the compositional heterogeneity can cause the cell to fail in different locations [23]. To date our understanding of the physical processes that lead to potential losses as well as the implications of spatial heterogeneities in the cell durability remain limited; therefore, the development and use of operando localized spatially resolved techniques is vital for separating microstructural effects from the intrinsic properties of materials. Recent efforts have resulted in the development of different in-situ or operando techniques such as in-situ XRD [24], ambient pressure x-ray photoelectron spectroscopy (AP-XPS) [25], in-situ transmission electron microscopy (TEM) [26], controlled atmosphere high temperature scanning probe microscopy (CAHT-SPM) [27], operando Raman etc. [23].

In the presented work the CAHT-SPM has been used to investigate different degradation mechanisms of SOC electrodes. Using these spatially resolved techniques requires the use of model systems; therefore, for the study of the hydrogen electrode, point contact microelectrodes were used to investigate the impact of strong cathodic polarizations on Ni|YSZ and Pt|YSZ, where YSZ is yttria stabilized zirconia. The Ni|YSZ system under strong cathodic polarization is relevant for SOECs which are operated at high current densities. Different studies of SOECs operated under strong cathodic polarizations reveal several degradation mechanisms, such as precipitation of silica nanoparticles into the Ni as reported by Tao et al. [28], or the formation of ZrO$_2$ nanoparticles on the Ni surface [29], the nature of which remains speculative. Additionally, reverse current treatments show remarkable improvements in the electrode performance [30]. It is possible to not only perform very localized strong cathodic polarization, but obtain surface conductance images that reveal changes in the conductance in sub-micron resolution utilizing the CAHT-SPM. The combination of this technique with surface chemistry and microstructural imaging techniques can help us gain a better understanding of the impact of strong cathodic polarizations. The air electrodes exhibit different degradation mechanisms as well, which among other things, can limit the oxygen exchange rate at the electrode. The oxygen exchange rate is dependant on a number of factors such as surface chemistry, microstructure, overpotentials etc. The CAHT-SPM is a great technique to investigate surface related phenomena. The work presented in this thesis was performed on model LSF microelectrodes which were fabricated using pulsed laser deposition (PLD) and photolithography using the CAHT-SPM.

Below is a brief overview of the chapters in this thesis, followed by an introduction of the existing literature in related fields to provide the general motivation for the conducted research.
1.3 Thesis structure

Chapter 2 gives a description of the experimental techniques used for sample preparation as well as testing and characterization. Working principles of the used instruments are also briefly described.

Chapter 3 gives a description of the sample preparation procedures including the preparation of the different yttria stabilized zirconia (YSZ) pellets, PtIr and Ni probes as well as the thin film microelectrode samples.

Several different aspects of fuel cells were investigated in the presented work; therefore, the chapters where the main body of the experimental work is presented (i.e. Chapter 4, 5 and 6), contain individual introduction, theoretical background, results, discussion and conclusions.

Chapter 4 examines the reduction of YSZ as a result of strong cathodic polarizations in Ni|YSZ and Pt|YSZ systems using a simplified point microelectrodes. The CAHT-SPM has been used to perform point contact electrochemical measurements as well as to trace the evolution of the surface conductance after applied polarizations. In this study the impact of impurities is also investigated by examining YSZ with different level of silica impurities. In order to perform a comprehensive study, complementary techniques are utilized for chemical and microstructural studies on the tested samples.

To gain better insights about the impact of the strong cathodic polarization, a different set up, where the Ni|YSZ and Pt|YSZ contact area was larger than the ones obtained in the CAHT-SPM, was used and the results are presented in Chapter 5. The larger point electrodes, with diameters in the some hundreds µm range compared to micron or sub-micron diameters point electrodes used in Chapter 4, were mainly used to overcome challenges which are intrinsic to the set up in Chapter 4, such as difficulties of finding the contact area for post mortem analysis, avoiding temperature gradients etc.

In Chapter 6, the focus is shifted to the oxygen electrode. This study utilizes a similar approach as in Chapter 4, i.e. a microelectrode approach. The experiments presented in this chapter were performed on dense circular \((\text{La}_{0.6}\text{Sr}_{0.4})_{0.99}\text{FeO}_{3-\delta}\) microelectrodes, which were fabricated using pulsed laser deposition (PLD) combined with photolithography. The electrochemical measurements, such as impedance spectroscopy at different polarization and cyclic voltammetry were performed with the purpose of investigating the reaction mechanism at the oxygen electrode. The work done here, in addition to the electrochemical measurements investigates microstructural and chemical changes of the surface of the microelectrodes which were exposed to different polarization.
1.4 Literature review

Finally, the last chapter, Chapter 7 summarizes the most important conclusions and observations obtained from this work.

1.4 Literature review

This literature review section is used to provide an overview of the most important findings from other groups to contextualize the presented work.

1.4.1 In-situ scanning probe microscopy studies for SOCs

Scanning probe microscopy (SPM) represents a group of microscopy techniques which use very sharp probes to obtain local information. Depending on the properties of the probe and specific set up one can detect electrical, electrochemical, mechanical, magnetic etc. properties. Due to the versatility of SPM, some effort is being made into using these techniques for SOC investigation. Solid oxide cells operate at elevated temperatures and gasous environments, which are relatively inconvenient conditions if one would like to perform in-situ or operando scanning probe microscopy studies. The high temperature complicates SPM measurements due to the low stability of the piezoelectic elements under a thermal load [31]; therefore, thermal drifts are usually observed in high temperature SPM measurements. Additionally, the used probes should be stable at the elevated temperature as well as in reducing and/or oxidizing environments. The transport in SOCs is not only limited by electrons, but it relies on ionic and electronic conduction which poses additional difficulties. Due to these difficulties the number of studies that use in-situ/operando SPM techniques for SOCs remains rather limited. Some of in-situ/operando SPM studies are summarized by Nonnenmann in his review paper "A hot tip: imaging phenomena using in situ multi-stimulus probes at high temperatures" [31]. Different types of in-situ/operando SPM techniques in synergy with other characterization techniques have been used in the last decade to investigate high temperature electrochemical phenomena in fuel cells. Nonnenmann et al. [32] for example, used scanning surface potential microscopy (or otherwise called Kelvin force microscopy) to quantify local potential at electrode/electrolyte interfaces in operating solid oxide fuel cells at 600 °C using two different symmetric cells composed of LSM/YSZ/LSM and LSF/YSZ/LSF. With this technique, they were able to map local potential variations on cross-sectional surfaces with a spatial resolution of approximately 100 nm in operating conditions. Direct observation of the local surface potential at the interface has
1.4. Literature review

given important insight on the electrochemical processes that occur in nanometer resolution [32].

Katsiev et al. [33] utilize scanning tunneling microscopy/spectroscopy (STM/STS) up to 580 °C in 10⁻³ mbar oxygen pressure to observe the characteristics of the tunneling current on La₀.₇Sr₀.₃MnO₃ (LSM) thin-film surfaces. They observed a sharp drop, resembling a thresholdlike drop in the tunneling current at positive bias in STS, which they attributed to the activation polarization in cation-oxygen bonding on LSM cathodes. By combining Auger electron spectroscopy to identify Sr-enriched areas, with STS where they observed a decreased tunneling current, they could conclude that Sr-terminated surfaces are less active for electron transfer in oxygen reduction compared to Mn-terminated surfaces on LSM [33].

Another work that uses a combination of STS with focused ion beam milling (FIB) was performed by Chen et al. [34] to obtain microscopic level understanding of why La₀.₈Sr₀.₂CoO₃/(La₀.₅Sr₀.₅)₂O₄ (LSC₁₁₃/LSC₂₁₄) hetero-interfaces exhibit orders of magnitude faster oxygen reduction reaction (ORR) kinetics compared with either single phases at 300 °C. By measuring the energy gap of the heterostructure at different temperatures (RT, 250 and 300 °C), they observed that the LSC₂₁₄ layers are electronically activated through an interfacial coupling with LSC₁₁₃ [34].

Electrochemical strain microscopy (ESM) has also been implemented in energy materials research including SOC materials. ESM is a technique where the SPM probe concentrates an electric field in a small volume near the sample-tip contact, inducing some electrochemical reaction and ionic motion which causes strain in the sample and hence surface displacement [35]. Therefore, the change in the topography of the sample gives information about the electrochemical reaction. There are few examples of in situ studies relevant for SOCs, where this technique has been successfully implemented [36–39]. These studies [36–39] investigate biased induced oxygen reduction reaction at room temperature, as well as the temperature dependent measurements which span from room temperature to 160 °C.

The controlled atmosphere scanning probe microscope (CAHT-SPM) is another instrument used for SOC studies. The first prototype of this instrument was developed in 2006 and since then several studies relevant for SOCs have been published [40]. This instrument has the capability of measuring the surface conductance of materials at elevated temperatures at a controlled atmosphere. For example, Hansen et al. [41] has investigated the surface reduction of NiO-YSZ-Al₂O₃ into Ni-YSZ-Al₂O₃ cerments at temperatures from 312 to 525 °C by monitoring the change of surface conductance. This study also explores the
influence of water in the atmosphere in the reduction rate of NiO. The conductance mapping capabilities in synergy with complementary techniques such as time of flight secondary ion mass spectrometry (ToF-SIMS) and scanning electron microscopy (SEM) were used in the investigation of the chemical changes which influence the electrochemical performance of \((\text{La}_{0.75}\text{Sr}_{0.25})_{0.95}\text{MnO}_3\) electrodes \(^{12}\). The CAHT-SPM can also be used to perform highly localised electrochemical measurements \(^{12, 13}\) as well as Kelvin probe microscopy \(^{40, 44}\).

Despite the challenges, the in-situ/operando SPM techniques are being developed and used for SOC investigation, providing answers to fundamental questions in regard to the electrochemical reactions occur during the operation of SOCs. In this work, I explore the capabilities of a controlled atmosphere scanning probe microscope to investigate model electrodes (microelectrodes) with the purpose of revealing possible degradation mechanisms which could possibly help with the improvement of SOCs.

### 1.4.2 Microelectrode studies for SOCs

In the last two decades, microelectrodes have become an interesting tool for SOC research \(^{45-47}\). One of the reasons is that the performance of SOCs does not depend only on material’s properties but also on the microstructure, geometry and morphology of the electrodes. Therefore, microelectrodes, which have very simple and well defined geometry, have been used in an effort to obtain information about the electrochemical performance purely from materials properties. An additional advantage of microelectrodes is that one can perform multiple measurements on the same sample using multiple identical microelectrodes which enables statistical analysis and reproducibility checks \(^{46}\). Microelectrodes are oversimplified systems, therefore, sometimes they are so far from the real application that it is hard to apply the knowledge gained into the further development of devices. Two main types of microelectrodes are usually employed \(^{45}\):

1. Circular microelectrodes fabricated from dense films using photolithography. In the contexts of this thesis, this type of microelectrode was utilized to perform the experiments shown in Chapter 6.

2. The use of a sharp needle pressed against the surface of the sample. In this case the sharp needle acts like a microelectrode. This approach was used to obtain the results described in Chapter 4, where Ni and PtIr SPM probes were pressed on the YSZ sample and served as working electrodes.
1.4. Literature review

The first type is characterized by well defined geometry, which makes the quantitative analysis relatively simple. When a sharp needle is used, however, the contact geometry depends on the deformation of the tip which does not result in a well defined sample-tip contact area, and in this situation quantitative analysis is more complex.

Most of the microelectrode studies have been performed using different experimental set ups; however, a common feature is the use of an extended counter electrode which is positioned faraway from the microelectrodes. Such configuration implies that any voltage applied between the microelectrode and the counter electrode drops very close to the microelectrode \[45\]. One can calculate the bulk resistance (usually called spread resistance) as follows:

\[
R_{spr} = \frac{1}{2d_{me}\sigma_{bulk}}
\]  

(1.4.1)

where \(d_{me}\) is the diameter of the microelectrode and \(\sigma_{bulk}\) is the conductivity in the vicinity of the microelectrode. This equation is valid if there is no variation of conductivity on the length scale of the microelectrode and there are no blocking regions between the the microelectrode and the counter electrode \[45\]. Microelectrodes have been used to produce conductivity maps \[42\], to investigate inhomogeneous bulk conductivity, high or low conductive grain boundaries \[48\] as well as the kinetics of the electrochemical reactions that occur at the electrodes \[42, 49–51\].

J. Fleig \[52\] obtained information about the homogeneity of the grain boundaries, by measuring the impedance between two microelectrodes (Ag coated dense YBa\(_2\)Cu\(_3\)O\(_{6-x}\) microelectrodes deposited on SrTiO\(_3\) polycrystalline substrate) which were positioned in adjacent grains. By repeating this process in different locations they were able to obtain statistical information about the grain boundary conductivity. Their results showed that in the case of SrTiO\(_3\) the grain boundary resistivity shows a very narrow distribution around the grain boundary resistance calculated from conventional impedance measurements using the brick layer model \[53\]. However, this was not the case for Mn-Zn ferrite polycrystals \[54\].

Fleig et al. \[48\] and Skapin et al. \[55\] were able to detect highly conductive grain boundaries in AgCl by comparing the impedance between the extended electrode and a microelectrode position on a grain, with the impedance between the extended electrode and a microelectrode positioned on the grain boundary. Highly conductive grain boundaries cannot be detected by means of normal impedance, given that these grain boundaries form current paths parallel to the bulk, which in a simplified equivalent circuit would result in a resistance parallel to the bulk resistance \[48\]. In other words, the highly conductive grain boundaries
1.4. Literature review

give a response in the high frequency arc, same as the bulk response. Therefore, the deconvolution of the bulk and grain boundary properties is not possible, making this technique valuable.

In addition to the above mentioned applications, microelectrodes have been used extensively to investigate the reaction mechanisms occurring at the SOC electrodes. Some of the works relevant to this thesis will be summarised in the sections below. Particular interest will be given to Ni or Pt point electrode studies and microelectrode studies on perovskite materials.

1.4.2.1 Ni and Pt point electrode studies

In Chapter 4 and 5 of this thesis, the reduction of YSZ as a result of strong cathodic polarizations in Ni|YSZ and Pt|YSZ systems has been studied using simplified point microelectrodes. A number of studies of the metal/YSZ system have been previously done utilizing point contact electrodes [56–63], often by using a metal wire either bended or melted to a ball-shaped end. A general motivation behind the use of microelectrodes to study the Ni or Pt electrodes is that there are many discrepancies in the reported data, making the reaction mechanism difficult to be determined. A number of mechanisms have been proposed and they are summarised by Mogensen et al. [64].

Graves in his PhD thesis [58] for example, systematically characterized model systems for solid oxide cells using different metal wires contacting polished YSZ samples. The use of the point contact configuration allowed him to compare the performance of different metals such as Ni, Pd, Pt and Cu for H₂/H₂O and CO/CO₂ oxidation/reduction. The different metals showed different impedance response, shedding light into the differences in the reaction mechanism of the different metals [58].

Jensen et al. [65] and Mogensen et al. [60] have investigated the impact of impurities by carefully examining the Ni-YSZ contact of a simplified geometry where a bent Ni wire was pressed against the YSZ. They observed that an impurity phase consisting of silica, alumina and alkali oxides was present at the edge of the contact, where Ni and YSZ are simultaneously in contact with the gas phase, otherwise called the triple phase boundary (TPB). In these works they emphasise the importance of impurities in the system which is technologically important and relevant.

Hansen et al. [57] investigated the effect of strong cathodic polarization on Ni-YSZ interface. Compared to other studies where the focus has been understanding the H₂/H₂O reduction/oxidation reaction, this work was mainly focused on the effect
1.4. Literature review

that strong cathodic polarizations have on the Ni-YSZ interface. Their study revealed major changes in the microstructure of the Ni-YSZ interface, resulting in a large affected volume with a complex microstructure and phase distribution [66].

1.4.2.2 Model electrode studies on perovskite thin films

Oxygen electrodes of SOCs possess a very complex microstructure. They consist of porous structures with different particle sizes, which help enhance the performance of the cell. Several studies have been performed on realistic porous electrodes of different potential oxygen electrodes. However, it is very difficult to separate the influence of microstructure from the intrinsic properties of the material when working with these complex structures. Dense microelectrodes, which have a very well defined geometry, reduce the geometrical factors which cannot be easily measured or controlled, thus making microelectrodes a valuable tool for the investigation of reaction mechanisms occurring at the oxygen electrode. Microelectrode studies have been performed on different oxygen electrode materials and they have proven to provide important information about the oxygen reduction kinetics of perovskite materials [42, 49, 50, 67]. For example, dense microelectrodes with well defined geometrical shape were used to investigate the oxygen reduction reaction on Sr-substituted LaMnO$_3$ (LSM) microelectrodes [42, 68, 73], Sr- and Co- substituted LaFeO$_3$ (LSCF) [50, 51], Co-substituted LaFeO$_3$ (LSC) [74, 75], Sr-substituted LaFeO$_3$ (LSF) [70], Sr- and Co-substituted BaFeO$_3$ (BSCF) [49]. Usually, these microelectrodes are fabricated from dense thin films (produced by pulsed laser deposition) using photolithography and etching to obtain the final patterned samples. Impedance spectroscopy measurements performed on these microelectrodes have revealed important information about the effect of the DC bias, oxygen partial pressure and microelectrode size on the electrode kinetics. Brichzin et al. [72], for example, performed microcontact impedance spectroscopy to measure the dependency of the electrode polarization resistance on the electrode diameter. They used circular, thin film LSM microelectrodes. The change of the electrode polarization resistance with varying electrode diameter was found to be bias-dependent: in the cathodic regime the polarization resistance was proportional to the inverse area, while in the anodic regime it scaled with the inverse diameter. Such results indicated that the applied bias cause the reaction mechanism to transition from bulk path to surface path [73].

Hansen et al. [42] have investigated the influence of oxygen partial pressure and polarization on the electrical, electrochemical and surface chemistry of (La$_{0.75}$Sr$_{0.25}$)$_{0.95}$MnO$_3$ (LSM) dense film microelectrodes. By performing
impedance spectroscopy and cyclic voltammetry at different temperatures in air, N\textsubscript{2} and O\textsubscript{2} on microelectrodes with different sizes, they observed that there was a transition from triple phase boundary reaction zone, to a reaction zone covering the entire area of the microelectrode at $pO_2$ lower than 1e-6 bar. In situ conductance mapping revealed low conductance areas at the perimeter and on the surface of the microelectrodes at elevated temperatures. By further investigating these microelectrodes using ToF-SIMS and SEM, Norrman et al.\[76\] could differentiate among segregation phenomena which occurred due to sintering, long term heat treatment and electrochemical measurements.

F.S. Baumann\[77\] in his PhD work performed a variety of impedance experiments mainly on La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3−δ} (LSCF) microelectrodes. His experiments covered a wide range of parameters such as variations in temperature, DC bias, oxygen partial pressure and microelectrode size. By using an equivalent circuit developed by Jamnik and Maier\[78\], three different resistive processes were identified and they were assigned to the charge transfer at the microelectrode surface, the bulk transport and the oxygen transfer at the electrode/electrolyte interface. The rate limiting step was found to be the surface reaction, while the bulk transfer was negligible compared to the interfacial processes.

Baumann et al.\[79\] report a comparative study on the polarization resistance of mixed conducting SOFC cathodes. Using microelectrodes they were able to perform direct comparison of the electrochemical parameters of different perovskite materials such as La\textsubscript{0.6}Sr\textsubscript{0.4}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3−δ} (LSCF), Ba\textsubscript{0.5}Sr\textsubscript{0.5}Co\textsubscript{0.8}Fe\textsubscript{0.2}O\textsubscript{3−δ} (BSCF) and Sm\textsubscript{0.5}Sr\textsubscript{0.5}CoO\textsubscript{3−δ} (SSC). They observed that the influence of the Fe/Co ratio has a small effect in the surface oxygen exchange in LSCF. Additionally, they report an activation phenomenon that occurred after a cathodic pulse was applied to the Co-rich LSCF\[79\].
Chapter 2

Experimental and characterization techniques

2.1 CAHT-SPM

Atomic force microscopy (AFM) is a branch of scanning probe microscopy (SPM) which was founded in 1981 with the development of the scanning tunnelling microscope (STM) by Binning and Rohrer, who received a Nobel prize for its design in 1986 [80]. SPM has given an immense impact on numerous fields, such as material science, electrochemistry, semiconductor physics, biology, surface thermodynamics, organic chemistry etc. The reason that this technique is so widely used in all these different fields lies in the fact that it can provide three dimensional, real space images of the surface at very high resolution. In addition, SPM is a non-destructive technique, which provides a great advantage. The main concept behind the scanning probe microscopy is the detection of interactions between the surface of the sample and a small probe tip. Depending on the interaction type, the images obtained from this technique can represent surface topography, electronic structure, electric or magnetic fields etc.

An atomic force microscope is comprised of the following components [81]:

- **A sharp tip on a flexible cantilever.** The characteristics of the cantilever and the tip are crucial. The resonance frequency of the cantilever for example needs to be high (in the order of several tens or hundreds kHz) so that very small forces can be detected.

- **A detection system** which is usually composed of a laser beam which is reflected off the cantilever into a photo-diode detector that has the capability
of detecting the position of the laser reflection in pico-meter resolution.

- **A feedback system** which is used to monitor the cantilever motion, therefore the amplitude, phase or force.

- **A scanning system.** To obtain an image the tip and the sample move very precisely relative to each other. The very precise motion is established by piezoelectric motors. There are two different scanning systems: a sample scanner and a probe scanner.

- **A visualization system**

Two different methods are usually employed to establish the force between the probe and the sample, and they are generally referred to as contact mode and tapping mode. In contact mode, the cantilever scans the sample surface at a fixed deflection, i.e. at a fixed force. The optimization of the feedback loop parameters is crucial for the force to be constant. The contact mode is typically used to scan hard surfaces with a resolution lower than 50 nm. In addition to the relatively low resolution, this technique is associated with substantiation tip wearing as well as sample surface damage.

In tapping mode, on the other hand, the probe is vibrated while it scans the sample surface. The cantilever of the probe has a given resonance frequency $\omega_0$ which depends on the force constant of the cantilever:

$$\omega_0 = c\sqrt{k} \quad (2.1.1)$$

where $c$ is the proportionality constant. At the resonance frequency a 90 degree phase shift occurs. As the tip interacts with the sample surface, the resonance frequency changes toward lower values. The feedback loop during tapping mode tries to keep either the phase or the amplitude of a given frequency constant. With this technique one can obtain higher spatial resolution as well as less damage to the probe and to the scanned samples. However, in some type of measurements, such as scanning spreading resistance or scanning capacitance measurements, it is impossible to use tapping mode, since it is necessary to have good electrical contact between the sample and the probe.

When dealing with SOFC materials, controlled atmosphere and high temperature environments are necessary if one wants to perform in-situ or in-operando measurements. Hence, two different instruments developed by DME (Danish Micro Engineering a/s, now Semilab) in collaboration with DTU Energy were used. These instruments were designed to perform electrical and electrochemical measurements as well as microstructural characterization at elevated temperatures.
(up to 650 °C and 850 °C, respectively) in different atmospheres (flowing N\textsubscript{2}, 9\%H\textsubscript{2} in N\textsubscript{2}, O\textsubscript{2}, mixture of N\textsubscript{2} and O\textsubscript{2} and CO\textsubscript{2}). Both instruments are table top devices and a 3D diagram is shown in Fig. 2.1. To make a distinction between the two instruments, when necessary, they will be referred to as CAHT1 and CAHT2. Since most of the experiments in this thesis were performed in CAHT2, this section will be dedicated only to CAHT2. Detailed description of both instruments can be found in the following references \[27, 82\].

The CAHT-SPMs were built as a normal AFM containing all features listed in section 2.1 including the laser, photo-detector, sample scanner, the feedback system and a tip holder as shown in Fig. 2.2. The CAHT1 only supports contact mode measurements. Both instruments are equipped with CCD cameras so that one can navigate the sample during the experiments and adjust the laser spot on the cantilever. The CAHT2 is divided in three chambers, so that the sample chamber is separated from the upper chamber containing the laser and detector and lower chamber containing the scanner [27]. The sample chamber itself is equipped with a small furnace (Model 101275 from HeatWave Labs Inc., USA) which is positioned on top of the sample scanner. The sample is placed on top of the furnace and is held in place by three alumina pins as shown in Fig. 2.1. The scanner which is in the lower chamber must operate at temperatures below 50 °C; therefore, the furnace is mounted on a Macor disc. Additionally, water cooling is used to cool down the scanner as shown in Fig. 2.1. Since the separation from the lower chamber and the sample chamber is not completely gas tight, the gas flow can be controlled in both chambers separately. The sample chamber pO\textsubscript{2} is monitored throughout the experiments by connecting the gas outlet to a pO\textsubscript{2} monitor. Additionally, gas humidification is also possible by bubbling the gasses through a millipore water flask. The humidification levels change with the temperature of the water in the flask. The temperature of the flask was not controlled; therefore, during the experiments the water temperature varied between 25 and 30 °C depending on room temperature.

The probe holders for both instruments are designed so that one can mount custom made probes which will be described in detail in Chapter 3. The probe itself can be electrically connected to the probe holder, which makes it possible to use the probe as an electrode. Additionally, platinum wires were used as counter-electrodes. The platinum wires were pressed against the top surface of the sample using one of the alumina pins. The other end of the wire was connected to the electrical connectors which are located within the sample chamber. The instrument is externally connected to devices which make it possible to perform electrical and electrochemical measurements. For the purpose of this thesis, two different modes were used: scanning mode which
2.1. CAHT-SPM

Figure 2.1: 3D representation of the CAHT2 instruments

Figure 2.2: Schematic drawing of the CAHT2 showing three different chambers
includes conductance and topography measurements performed in contact mode and electrochemical characterization mode, where the probe is used as a working electrode for electrochemical measurement. Since no scanning is used for the electrochemical measurements, this is referred to as the static mode.

2.1.1 Scanning modes

Topography and conductance images were collected simultaneously in contact mode. Conductance maps cannot be obtained using tapping mode, since good electrical connection between the tip and the sample is necessary. To obtain the images shown in this thesis, home-made electrically conductive probes were fabricated from either high purity PtIr or Ni wires. Since the conductance/topography scans were obtained in contact mode, the resolution of these images depends on the tip sharpness. Additionally, the quality of the conductance images depend also on the quality of the electrical contact between the sample and the tip; therefore, relatively large forces were used to ensure electrical contact throughout the scanning process. These large forces caused extensive tip modifications, which further lowered the resolution one could obtain with such measurements.

![Diagram of CAHT for scanning mode measurements](image)

Figure 2.3: Simplified diagram of the CAHT for scanning mode measurements showing the 1 Mohm resistance which has the purpose of protecting the lock in amplifier from any overload.

In a conductance map each pixel of the image essentially represents a single frequency impedance measurement. Considering that the impedance using a contact point configuration depends on the contact circumference, the images
2.1. CAHT-SPM

obtained using different probes cannot be compared. Therefore, throughout
the thesis, elements within the same conductance map are discussed without
comparing absolute values across different samples.

Localized measurements give rise to very small currents due to the large contact
resistance of such configuration; therefore, a Stanford RS830 lock-in amplifier
was used to perform surface conductance measurements. The lock-in amplifier
singles out part of a signal at a particular reference frequency and phase, rejecting
this way any noise signals away from the reference frequency. The reference
alternating voltage signal was generated by a Stanford RS830 lock-in amplifier
and was applied across the Pt counter electrode and the home made probes. For
all the conductance measurements shown in this work, unless mentioned otherwise,
an AC voltage signal with reference frequency of 10 kHz and 0.5 V rms was used.
The current response was measured by the lock-in amplifier through a 1 MΩ
resistor connected in series with the counter electrode (Fig. 2.3). The resistance
has the purpose of protecting the lock-in amplifier from any overload [42]. Since
these measurements are conducted in contact mode the resolution of the technique
is determined by the electrical probe-sample contact area.

2.1.2 Static mode

Electrochemical measurements such as cyclic voltammetry (CV), chronoamper-
ometry and electrochemical impedance spectroscopy (EIS) were obtained using
the conductive probe as a working electrode. To perform such measurements, the
tip was pressed in selected positions against the surface of the sample and was
kept static throughout the duration of the measurements, hence the name static
mode. It was crucial to obtain a stable contact between the tip and sample since
the electrochemical measurements lasted from 30 s up to 6 hours. Therefore, in
contrast to the tip requirements for conductance scanning, the tip size was not
important for these measurements. As a matter of fact, the blunter tips offered
better contact stability. Due to discrepancies in the tip properties requirements
between the two modes, sometimes it was not possible to obtain both optimal
electrochemical measurements and conductance maps using the same probe. The
electrochemical measurements were carried out using a two-electrode set up. Due
to the large size difference between the working electrode (the probe’s micro-sized
tip) and counter electrode (Pt wire-sample macro-contact), the polarization of the
counter electrode is negligible. This assumption has been tested and the results
are shown in Appendix A. Consequently, the Pt wire can be used as a reference
electrode as well. Several different types of counter electrodes were considered
and the resistance of the counter electrode was measured. These measurements
2.2. Time of Flight Secondary Ion Mass Spectrometry

indicated that all counter electrode configurations had smaller resistance than 5 kΩ, which can be considered negligible in comparison to the large resistance obtained with the working electrode. Considering the local measurements that are performed with the CAHT, where the working electrode size varies from a couple of hundreds of nanometers up to 100 μm in diameter, the CAHT is coupled with electrochemical measuring systems that can detect low currents/high resistances. To perform these electrochemical measurements a Gamry Instrument FAS2 Femtostat potentistat was used, which can resolve current fluctuations of 1 femtoamp ($10^{-15}$ A).

2.2 Time of Flight Secondary Ion Mass Spectrometry

Secondary Ion Mass Spectrometry (SIMS) is the mass spectrometry of secondary ions emitted from the surface of a sample when it is bombarded with high energy particles, usually ions [83]. This technique was first developed by Herzog et al. in the late 1940’s, while the Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) was introduced by Benninghoven et al. in the late 1960’s [84]. When a beam of ions (for example Bi⁺, Ar⁺, Ga⁺, Cs⁺) or neutral species with energy between 1 and 25 keV hits the surface of a sample, the energy of the incoming particle is transferred to the atoms in the solid and a cascade of collisions occurs between the atoms in the sample. Some of the energy is transported back to the surface, resulting in the dislodge of atoms or atom clusters when they overcome the surface binding energy. Some atoms get ionized when leaving the surface. The technique seems to be destructive, but a very low concentration of primary ions (less $10^{13}$ ions per cm²) is used to hit the sample, hence in the experiment time period less than 1% of atoms in the top surface are impacted [83]. ToF-SIMS is a SIMS technique which uses the fact that the emitted species have different kinetic energies to detect the secondary ions. The kinetic energy distribution depends on the following factors: the primary ion energy, the angle of incidence of the primary ions and their atomicity, the binding energy of the detected species to the surface of the sample, i.e the number of bonds to be broken. A ToF-SIMS instrument is composed of a primary ion generation system (ion gun), a sample chamber, a vacuum system, a time of flight mass analyzer and a detector. The ions produced from the ion gun are bunched to create a pulsing incoming beam. The pulsing of the primary ion beam is the starting signal for the time measurement. The secondary ions, which are produced almost instantaneously are accelerated by an accelerating voltage ($V$) to essentially the same kinetic energy. Then they enter
2.3. Scanning electron microscopy

the field free drift zone. By measuring the time necessary to reach the detector, the mass to charge ratio can be calculated as follows:

\[ K_e = \frac{1}{2} m v^2 \leftrightarrow t = L \sqrt{\frac{m V z}{2}} \leftrightarrow m \frac{z}{z} = 2V \left( \frac{t}{L} \right)^2 \]  (2.2.1)

where \( K_e \) is the kinetic energy, \( m \) is the mass of the particle, \( v \) is the velocity, \( t \) is the time of flight, \( L \) the length of flight and \( z \) the charge \[83\]. When performing a ToF-SIMS measurement one collects the mass to charge ration versus counts. It is important to mention that the ToF-SIMS is a qualitative technique and all the ToF-SIMS measurements shown in this work have a purely qualitative purpose.

The ToF-SIMS analyses were performed using a ToF-SIMS IV (ION-TOF GmbH, Münster, Germany). 25 ns pulses of 25 keV Bi\(^+\) (primary ions) were bunched to form ion packets with a nominal temporal extent of \(<0.9 \text{ ns} \) at a repetition rate of 10 kHz, yielding a target current of 1.0 pA. These primary ion conditions were used to obtain mass spectra, ion images, and depth profiles using a lateral resolution of \(<10 \mu m\). High-resolution images were acquired using a lateral resolution of 200 nm and a target current of 100 fA. 256×256 pixels were used for images up to 500×500 \(\mu m^2\). For images above 500×500 \(\mu m^2\) a stich mode was employed using five frames per patch (one shot/pixel) producing a pixel resolution of 1280×1280 pixels. Depth profiling was performed using an analysis area of 200×200 \(\mu m^2\) centered in a sputter area of 300×300 \(\mu m^2\). 30 nA of 3 keV Xe\(^+\) were used as sputter ions. For all analyses electron bombardment (20 eV) was used to minimize charge built-up at the surface. Desorbed secondary ions were accelerated to 2 keV, mass analyzed in the flight tube, and post-accelerated to 10 keV before detection. Data evaluation was performed using the software suite SurfaceLab (version 6.7, build 83192) from ION-TOF GmbH.

2.3 Scanning electron microscopy

Scanning electron microscopy (SEM) is considered to be a very versatile instrument for morphological and chemical composition characterization. The SEM images are obtained by scanning a focused electron beam and acquiring the signal resulting from the interactions of the specimen with the electrons. Depending on the type of interactions, one can get information about the topography, chemical composition or crystallographic orientation of the sample. The sample-electron interactions are divided in two main categories: elastic and inelastic interactions \[85\]. Elastic scattering which results from the deflection of the incoming electrons from the nuclei or the outer shell electrons which have similar energy, is characterized by
negligible energy loss and are mainly scattered at a wide angle. Electrons scattered at angles wider than 90° are called backscattered electrons (BSE). The inelastic scattering on the other hand occur when energy is transferred from the incident electrons to the sample, causing the scattered electrons to have lower energy. The energy loss is dependent on the electron binding energy to the atom as well as whether the electrons are singularly or collectively excited. The excited electrons cause the generation of secondary electrons which are also detected and used for imaging. Several other signals, such as characteristic X-rays, Auger electrons and cathodoluminescence are produced as a result of the interaction of the electron beam with the sample. As the incident electrons hit the surface, a large number of them penetrate into the sample before they encounter a collision, forming this way an interaction volume which has the shape of a teardrop. The size of the interaction volume depends on the energy of the incoming electrons as well as the nature of the atomic number of the atoms in the sample.

Zeiss Supra and Merlin were the microscopes used for the SEM images taken in this work. In addition to imaging, energy dispersive x-ray spectroscopy (EDS) and electron backscatter diffraction (EBSD) were used in the same instruments for chemical and crystallographic characterization of the samples.

2.3.1 Energy Dispersive X-ray Spectroscopy

Energy Dispersive X-ray Spectroscopy (EDS or EDX) is an analytical technique which uses characteristic x-rays produced as a result of the interaction between the incoming electron beam and the specimen. The analysis of these x-rays provides important chemical information. Characteristic x-rays are produced when an incoming electron transfers energy to an atom causing inner shell electrons to be ejected from the atom leaving a vacant lower energy level. Therefore, the outer shell electrons decay to the vacant lower energy levels, producing x-rays with well defined energies which are characteristic to the specific elements. EDS was used as a post-mortem technique to chemically characterize sample surfaces, when chemical information was needed.

2.4 Electrochemical Impedance Spectroscopy

Electrochemical Impedance Spectroscopy (EIS) is a widely used technique to investigate electrochemical systems. It is used to measure dielectric and transport properties of materials as well as investigate interfaces and mechanisms of electrochemical reactions. In principle, EIS measures the response of a system
2.4. Electrochemical Impedance Spectroscopy

when it is subjected to a small oscillating current or voltage. The frequency of the perturbation can be varied (depending on the instrument) in a range from 82 kHz to 1 mHz. The amplitude of the perturbation signal is very small, around 10-20 mV for potentiostatic EIS, or in the case of galvanostatic EIS a small percentage of the direct current. Since all the measurement shown in this thesis are potentiostatic EIS, let’s consider a small amplitude sinusoidal potential perturbation:

\[ E(t) = E_o \cdot \sin(\omega t) \] (2.4.1)

If the amplitude \( E_o \) of the perturbation signal is small enough so that the voltage-current relation can be considered linear, the current response will be a sinusoidal wave with the same frequency but phase shifted as shown by Eq. 2.4.2.

\[ I(t) = I_o \cdot \sin(\omega t + \phi) \] (2.4.2)

In Eq. 2.4.1 and Eq. 2.4.2 \( E_o \) and \( I_o \) are the amplitudes of the alternating potential and alternating current, \( \omega \) is the angular frequency, \( t \) is the time and \( \phi \) is the phase shift. Using the generalized Ohm’s law one can calculate the impedance \( Z \) response:

\[ Z = \frac{E(t)}{I(t)} = \frac{E_o \cdot \sin(\omega t)}{I_o \cdot \sin(\omega t + \phi)} \] (2.4.3)

The vector representation in the complex plane of the impedance, as shown in Eq. 2.4.4, is quite convenient since most electric components such as capacitors and inductors give an out of phase current response to a sinusoidal potential perturbation.

\[ Z(\omega) = Z_o (\cos \phi + j\sin \phi) = Z_{re} + (-jZ_{im}) \] (2.4.4)

The complex plane where the real and imaginary part of the impedance are used as axes, is called a Nyquist plot. Routinely, the modulus of the impedance plotted versus the log frequency (Bode plots) are used as graphical representations as well. In this thesis, mainly Nyquist plots and the log \( Z_{Re}/Z_{imag} \) versus log frequency are shown. An example of a Nyquist and the corresponding \( Z_{imag} \) versus log frequency plot is shown in Fig. 2.4.

Impedance interpretation and modelling is a crucial step into obtaining important information about the different processes that occur during the operation of an electrochemical process. Electrical circuits can sometimes produce similar impedance spectra as an electrochemical system; therefore, they are used for modelling electrochemical systems. These electrical circuits are called equivalent circuits and they are used to obtain quantitative information about the studied system.
2.4. Electrochemical Impedance Spectroscopy

Figure 2.4: Example of a a) Nyquist plot and b) Imaginary impedance versus log frequency

Table 2.1: List of circuit elements used for building equivalent circuit models

<table>
<thead>
<tr>
<th>Element</th>
<th>Description</th>
<th>Impedance</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Resistor</td>
<td>R</td>
</tr>
<tr>
<td>C</td>
<td>Capacitor</td>
<td>( \frac{1}{j\omega C} )</td>
</tr>
<tr>
<td>CPE or Q</td>
<td>Constant phase element</td>
<td>( \frac{1}{Q_o(j\omega)^n} )</td>
</tr>
<tr>
<td>L</td>
<td>Inductor</td>
<td>( j\omega L )</td>
</tr>
<tr>
<td>RC</td>
<td>Resistor-Capacitor in parallel</td>
<td>( \frac{R}{1+Rj\omega C} )</td>
</tr>
<tr>
<td>RQ</td>
<td>Resistor-CPE in parallel</td>
<td>( \frac{R}{1+RQ_o(j\omega)^n} )</td>
</tr>
<tr>
<td>RL</td>
<td>Resistor-Inductor in parallel</td>
<td>( \frac{j\omega LR}{R+j\omega L} )</td>
</tr>
</tbody>
</table>

Table 2.1 shows some of the elements which are used for equivalent circuits. The impedance responses of these elements are shown in Fig. 2.5 a) through e). The simplest response is obtained by a resistor since its impedance is independent of
2.4. Electrochemical Impedance Spectroscopy

Frequency and has no imaginary compound. The impedance of a capacitor has no real component; therefore, it is just a straight line in the Nyquist plot (Fig. 2.5a) with negative $Z_{\text{imag}}$. Electrochemically speaking, a capacitor can represent a non-Faradaic process such as double layer charging. The impedance of an inductor does not have a real component either; therefore, its response is a straight line as well, but with positive imaginary impedances. It is very common that the wires in the instruments used for performing the impedance spectroscopy would give an inductive response in the high frequency region. Therefore, it is important to distinguish actual physical phenomena from instrumental effects. The constant phase element (CPE) has no electrical equivalent, and its interpretation depends on the value of $n$. A CPE is a perfect capacitor for $n=1$ and a resistor if $n=0$. It is usually used to represent double layer charging in imperfect surfaces.

![Impedance response diagrams](image)

Figure 2.5: Impedance response of a) capacitor in series with a resistor b) R-RC circuit, c) R-RQ circuit with varying $n$, d) inductor in series with a resistor, e) R-RL circuit, f) R-RQ-RQ-RL

A resistor connected in parallel with a capacitor or CPE (RC or RQ) is used to represents a double layer charging effect coupled with a charge transfer process of
2.5 Pulsed Laser Deposition

Pulsed Laser Deposition (PLD) is a thin film deposition technique which can be used to grow a large variety of materials. This technique was first discovered by Smith and Turner in 1965 [87], but it was not until the 1980s, when PLD was reconsidered for the growth of high temperature superconducting materials (YBa$_2$Cu$_3$O$_{7-\delta}$) [88], that the technique started to get exploited more. To this day, PLD is used for the growth of high-quality complex oxides mainly for research purposes.

The deposition process can be described as follows [87, 89, 90]: PLD uses a high energy pulsed laser to ablate the target material. Due to the high energy of the laser, target material evaporates creating a plasma of atoms (referred to as the plume). The plume interacts with the substrate thus creating a thin film. A PLD instrument is schematically shown in Fig.2.6. Even though the PLD working principle might seem very simple and rudimentary, there are several parameters that strongly influence the quality of the deposited films. These parameters include: laser wavelength and energy, pulse duration and frequency, substrate temperature, gas pressure and of course target and substrate quality.

The above mentioned parameters influence the thin film deposition in the following ways:

1. **Laser frequency**: Once the particles are adsorbed on the surface of the...
2.5. *Pulsed Laser Deposition*

[pul ped laser deposition instrument image]

Figure 2.6: Schematic drawing of a pulsed laser deposition instrument

target, a certain amount of time is necessary for the particles to rearrange themselves. Therefore, a very high laser frequency would result in a porous thin film.

2. **Substrate temperature**: The substrate is usually heated so that the adsorbed species can diffuse easily on the surface of the substrate. Limitations on the temperature of the substrate usually rise from the risk of interactions between the thin film species and the substrate.

3. **Chamber pressure**: The presence of gases in the chamber reduces the kinetic energy of the species of the plume; therefore, it would directly influence the deposition rate. In cases when oxides are deposited the presence of oxygen is used to maintain the stoichiometry of the target.

4. **Target and substrate quality**: The quality of the target and substrate have a very obvious influence in the film quality. A porous target would result in non-uniform ablation of the target, which can result in a non-uniform deposition. Similarly, a polycrystalline substrate would result in a polycrystalline thin film and so on.

Therefore, the parameters of the deposition depend on the requirement of the thin film. In the case presented in this thesis, a uniform dense film was required.
Sample preparation

This chapter is an overview of the preparation methods for all the used samples including: YSZ pellets, PtIr and Ni probes as well as the fabrication of model microelectrode samples.

3.1 YSZ samples

In the experiments performed in this work, two types of polycrystalline and one type of single crystal yttria stabilized zirconia (YSZ) samples were used. The polycrystalline samples were produced in-house, while the single crystals were purchased from MTI Corporation. The procedure for fabricating the YSZ polycrystalline pellets was optimized to obtain the densest samples (Appendix B). 8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (8YSZ) powder (TZ8Y, Tosoh) was pressed uniaxially and isostatically using 87 and 275 MPa pressure, respectively. For the uni-axial press, a 14 mm steel mold was used. The first pressed sample was always discarded to avoid any contamination from the steel mold. Then the green pellets were sintered in air at 1550 °C for 2 hours. The final pellets were approximately 10 mm in diameter and 1 mm in thickness. They were polished on one side, using a multi step polishing procedure which included two SiC grinding (piano200 and piano1200) while reverse osmosis water was used as a cooling agent. The grinding was followed by several polishing steps using silk plates with diamond suspension, finishing with 0.1 µm diamond suspension. The samples were cleaned in ethanol in ultrasound between each step.

Additionally, YSZ samples with 1000 ppm of Si were produced following the same procedure. The Si was introduced in the sample by mixing YSZ powder with 0.2 wt% SiO$_2$ (Alfa Aesar) (0.43 mol%). The powder mix was diluted in ethanol to
3.2. Probe fabrication

ensure a uniform mixture and was dried while being mixed on a hot plate at 60 °C for 24 hours. After sintering and polishing, all the pellets were cleaned using 37 % hydrochloric acid in ultrasonic bath for 2 min, then milli-Q water and later ethanol in ultrasonic bath for 5 min each, and finally they were dried using a nitrogen gun.

8 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (8YSZ) single crystals were purchased from MTI corporation with the size 10 x 10 x 1 mm$^3$. The polished surface had the (100) orientation. The lattice parameter was 5.125 Å according to the supplier. The 8 mol% YSZ single crystals were only used for polexperiments on the CAHT-SPM. A zigzag scratch was applied to the sample using a diamond tip with the purpose of tracking the polarization spots. The crystals were cleaned in ethanol in ultrasonic bath for 5 min, with the purpose of removing any particles resulting from the scratch, and then they were dried using a nitrogen gun. For the fabrication of the microelectrodes, 10 x 10 x 0.5 mm$^3$ 9.5 mol% Y$_2$O$_3$ stabilized ZrO$_2$ (9.5YSZ) single crystals purchased from Crystal were used.

3.2 Probe fabrication

SPM probes were fabricated from high purity PtIr (80/20) and Ni wires using electrochemical etching.

The production of both types of probes involved the following steps: electrochemical etching of the wire, pressing and bending of the tip and finally the welding of the probe to the probe holder as shown in Fig.3.1. For both the Ni and PtIr probes processes are the same, except for the electrochemical etching of the wire. After each wire was etched, it was immediately rinsed with distilled water and ethanol. For better cleaning, an ultrasound bath was used. The tip was held so that it did not touch the walls of the beaker. The tips were then inspected under a Deltapix optical microscope. The tips that seemed sharp and not curled, were pressed to create a flat surface (the cantilever), which serves as a reflecting surface for the laser beam in the Scanning Probe Microscope (SPM). The sharpened wires were carefully placed between two polished stainless steel blocks. Using a uniaxial press a 1 ton weight was applied to the blocks. The end of the tip was then bent so that it formed roughly a 75 degree angle from the cantilevers body. Another 15 degree inclination was offered by the probe holder on which the probe was welded. The tip geometry was verified before the experiments using SEM.
3.2. Probe fabrication

3.2.1 PtIr probe fabrication

The sharp Pt-Ir tips were produced using 100 $\mu$m (99.999% purity) Pt$_{0.8}$Ir$_{0.2}$ alloy wires. The etching procedure was the same as the one described by Melmed [91]. The electrolyte solution for the electrochemical etching was prepared using 240 g of CaCl$_2$, 16 g of HCl and 400 g of water, which was then diluted in the same volume of water. A carbon black rod was used as a counter electrode. A 10 mm long PtIr wire was cut, and one end was bent to form a 'Z' shape, which was intended to facilitate the handling of the thin wire. The 'Z' shaped end was clamped and mounted on a tripod. The height of the tripod was adjustable using a micrometer screw. An AC voltage of 35 V was applied across the PtIr wire and the carbon counter electrode. Using the micrometer screw the PtIr wire was lowered into the electrolyte solution. Once the wire was in contact with the electrolyte the etching started and oxygen bubbles would appear on the surface of the electrolyte. The wire was lowered 30 $\mu$m into the electrolyte. Once the reaction was finished, the tip was lowered once more, this time 300 $\mu$m into the electrolyte.
3.2. Probe fabrication

The nickel probes were produced in-house, using 250 µm (99.98 % purity, Alfa Aesar) or 100 µm diameter Ni wires (99.994 % Ni, Alfa Aesar). The 250 µm wire contains less than 10 ppm of Al, Si, Co, Mg, Co, Cr and Fe and 23 ppm of C. The impurities in the 100 µm thick Ni wire consist of 12 ppm of Fe, 10 ppm of C, 5 ppm of O, 2 ppm of Cr and S, and 1 ppm of Co. The sharpening of the tip was done by electrochemical etching of the Ni using 2 M KCl as electrolyte and Pt wire as cathode \[92\]. The Ni wire itself served as the anode. Two different set ups were used to produce the tips, but fundamentally they use the same principle. When a DC potential of 2.5 to 3 V was applied across the Ni and the Pt wire, the following reactions took place:

\[
\text{Cathode : } 2\text{H}_2\text{O}(l) + 2e^- \rightarrow \text{H}_2(g) + 2\text{OH}^- \quad (3.2.1)
\]

\[
\text{Anode : } \text{Ni}(s) + 2\text{Cl}^- \rightarrow \text{NiCl}_2 + 2e^- \quad (3.2.2)
\]

The first set up was the same as the one described by Cavallini and Biscarini \[92\]. A 6 cm long Ni wire was bent in both ends in a 'Z' shape so that it was easier to handle the tips. The Ni wire was clamped on one end and placed vertically in the middle of a 10 mm Pt ring. The lower end of the tip was left free. A thin film of KCl solution was suspended on the Pt ring by surface tension as shown in Fig.3.3 b). Two tips were produced out of one etching. The Ni and Pt were connected to a power supply. A multimeter was used to measure the applied voltage during the etching. As the etching was in progress, a NiCl\(_2\) ring was forming around the Ni wire. Additionally, small bubbles of H\(_2\) gas were observed close to the Pt ring. When the reaction was too fast, usually when potentials higher than 3 V were applied, the electrolyte thin film would burst due to the
3.2. **Probe fabrication**

Figure 3.3: Diagram of the Ni etching instrument

A high amount of H$_2$ bubbles at the Pt ring. When the etching was complete, two tips were formed. The bottom tip would just slide off center and most of the time it remained attached to the suspended thin film due to the surface tension. The sliding of the bottom wire off the center of the Pt ring was an indication to immediately turn off the applied potential, since the etching of the upper tip would follow past the separation time.

The difficulties encountered while using this technique were the following:

1. Burst of the KCl electrolyte solution film during the etching, either due to the high etching rate or due to the long etching time. Therefore, the low and high end of the applied potential were not very successful. Another reason for the bursting of the film was gravity. If the Pt ring was a bit tilted, the liquid would gravitate towards one side causing the solution film to break.

2. Difficulty in handling the lower tip. More often than not, the lower tip dropped when trying to remove it with tweezers after the etching was finished.

Therefore, the same approach as for the fabrication of the PtIr tips was applied. Instead of suspending a thin film on the Pt ring, the Pt ring was dipped in a 2 molar KCl solution, very close to the surface. The Ni wires were cut in pieces of 3 cm in length and bent in a 'Z' shape in only one end. Using a clamp which was attached to a micro-manipulator, the Ni wire was slowly lowered until it reached the solution (in the middle of the ring). When the tip had reached the surface, a current was drawn (measured with the multimeter). Then the tip was lowered for another 300-400 µm into the solution. The current measurement was used as an
3.2. Probe fabrication

indication of when to stop the etching. If the tip was left too long in the solution, it became bold. Even though this technique is supposed to give reproducible tip shapes, a variety of shapes and thicknesses were obtained. Only the sharpest tips were pressed, bent and welded on the probe holders. The final probes were produced from about 10% of the cut wires, meaning that only one in ten trials resulted in a usable Ni probe.

3.2.3 Ni an PtIr tip reproducibility and modification

Two different types of measurements were performed using the CAHT-SPM: two-electrode electrochemical measurements in the static mode and conductance scans in scanning mode. As mentioned in Chapter 2, these types of measurements have slightly different requirement for the SPM probe. The conductance scans require a sharp tip that can maintain electrical contact with the sample during scanning, without deforming (i.e. hard material). On the contrary, for the electrochemical measurements, it is not necessary to have a sharp tip. From experience, I noticed that the blunter the tip the more stable the contact between the sample and the tip was, and the electrochemical measurements were less noisy. Considering the unused Ni tips shown in Fig.3.4 one could guess that the tips in a) and c) would be more suitable for static measurements and not for scanning while the tip in b) could be good for scanning. However due to the design of the instrument, the same tip had to be used for both measurements which caused huge modifications of the tip. The shape of the tip, which is determined by the etching procedure, is not the only indicator of a good tip. Other qualities that are as important in establishing if the tip-sample contact will be stable or not, are: the quality of the reflecting part of the cantilever, the cantilever geometry, the angle at which the tip contacts the surface, the twisting of the tip, as well as the quality of the welding on the probe holder. Since none of the steps for preparing the tips was automated, it was difficult to be consistent and obtain identical tips. For the PtIr tips the etching procedure was better optimized, hence obtaining similar tip

![Figure 3.4: SEM images of three different as fabricated Ni tips](image)

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3.2. Probe fabrication

Figure 3.5: SEM images of three different as fabricated PtIr tips

Figure 3.6: SEM images of three different as fabricated PtIr tips

shapes was easier as shown in Fig. 3.5, however, all the other steps could introduce differences between the tips. Unable to control all these factors, the tips which had a reasonable shape, decision made based on the SEM images of the tips prior to an experiment (examples of unusable tips are shown in Fig. 3.6), were used. If it was not possible to obtain electrochemical measurements or conductance scans, the tip was changed and the experiment was repeated with a different tip. It was a trial and error approach.

SEM images of the used SPM probes were also taken after the experiments with the tip-sample couple were finished. Therefore, the SEM images of the used

Figure 3.7: SEM images of four different Ni tips after they were used in CAHT-SPM for static and scanning measurements.

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3.2. Probe fabrication

Figure 3.8: SEM images of four different Ni tips after they were used in CAHT-SPM for static and scanning measurements.

probes (examples shown in Fig.3.7 for PtIr probes and in Fig.3.8 for Ni probes) give no indication on how individual measurements modified the tips, just the final modification.
3.3 Microelectrode fabrication

3.3.1 Preparation of PLD target

The fabrication of microelectrodes involved the following process: the fabrication of the PLD targets, the deposition of the thin film via PLD, photolithography and etching. The steps are summarized in Fig. 3.9.

The microelectrode thin film samples contain Ce$_{0.9}$Gd$_{0.1}$O$_2$ (CGO) and LSF with nominal composition (La$_{0.60}$Sr$_{0.40}$)$_{0.99}$FeO$_{3-\delta}$. The LSF powder was uniaxialy and
isostatically pressed using a 5 T weight for 20 s and a 300 MPa pressure for 30 s, respectively, and then sintered in air. A two step sintering program was used. First the pellets were baked at 1200 °C for 4 h (ramp rate of 120 °C/h) and then for 16 h at 1150 °C. The furnace was then cooled to room temperature using a cooling rate of 60 °C/h. The CGO powder was also pressed uniaxially and isostatically using a 1.5 T weight and a 300 MPa pressure for 30 s respectively and then sintered for 5 hours at 1600 °C. The furnace was heated using 120 °C/h and cooled using a 60 °C/h heating/cooling rate. The LSF and CGO targets were then roughly polished to on both sides to obtain a smooth surface. The final targets have a diameter of roughly 2.5 cm and 5-6 mm thickness.

3.3.2 Thin film deposition

All thin films were deposited on 9.5 mol % YSZ polished single crystals with a size of 10 x 10 x 0.5 mm³. The deposition was performed on four YSZ samples which were heated to 600°C. The rotating target were irradiated by a 248 nm pulsed laser beam generated from a KrF excimer laser. The fluency of the laser was measured prior to the deposition and it varied from 170 mJ to 200 mJ. First, the CGO barrier layer was deposited using a laser frequency of 5 Hz for 15 min. The \( pO_2 \) was \( 10^{-3} \) mbar. This deposition resulted in roughly 35 nm thick film. Without breaking the vacuum the target was changed to the LSF target. The laser frequency was changed to 10 Hz and the deposition lasted for 160 min resulting in a 300-400 nm thick film. The \( pO_2 \) used for the deposition of LSF was 0.03 mbar.

3.3.3 Photolithography

Once the thin films were deposited, microelectrodes were patterned by standard photolithography. First, a thin layer of positive photoresist (S1818, MicroResist Technology GmbH) was applied on top of the samples using a spin coater. To obtain roughly 2 µm of photoresist layer the samples were spun at 4000 rpm. The samples were then dried for 1 min at 120°C. In the next step, using a UV light combined with a Karl Suss MJB-3 mask aligner, the samples were illuminated for 20 s through a photomask, illuminating this way only the necessary area and hence chemically embedding the geometrical structure of the photomask in the photoresist. After the illumination, the photoresist was developed for 1 min and 15 s in the corresponding developer (MF-319, MicroResist Technology GmbH). The developer essentially removes the part of the photoresist which was exposed to the UV light. To remove any left over developer, the samples were cleaned in distilled water and then dried using a nitrogen gun.

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3.3. Microelectrode fabrication

3.3.4 Etching

To obtain the final microelectrodes, dry ion etching was performed using an argon ion beam etching/sputtering equipment manufactured by Oxford Instrument Plasma Technology. The etching source of this instrument is 30 cm in diameter; therefore, several samples were etched at the same time. The produced argon ions were accelerated using a potential difference of 400 V. The ions were then neutralized as they passed through an electron neutralizing beam with a current of 550 mA. The samples were tilted at a 30 degree angle from the Ar beam and they were rotated at 10 rpm.

![Optical image of a microelectrode sample](image)

Figure 3.10: Optical image of a microelectrode sample

To make sure that the surface of the microelectrodes was intact after etching, the etching rate of the LSF film was compared to the photoresist etching rate. For the used photoresist and film it was found that the film etching rate was approximately 4 times slower than that of the photoresist. Therefore, for a 300 nm LSF film, a photoresist film thicker than 1.2 \( \mu \text{m} \) was necessary. To ensure that all of the LSF film was removed, some of the CGO might have been etched as well; however, this was not important since the barrier layer remained intact under the LSF microelectrode. Once the microelectrodes were produced, a thorough cleaning procedure was performed to the samples ensuring that no photoresist remained on the samples and no further contamination was obtained. An optical image of the surface of one of the microelectrode samples is shown in Fig.3.10. Each microelectrode on the sample can be uniquely identified. The top half of
the microelectrodes are classified as the "a" microelectrodes, while the bottom as the "b" microelectrodes. The "a" and the "b" microelectrode are distinguished from each other by the squares close to the left side macro-electrode (note that the squares are connected to the macro-electrode on the top side and not on the bottom side). The naming of the microelectrode is the following: starting from left to right on the top row: 100a1 through 100a5 on the top row and 100b1 through 100b5 on the bottom row. Similarly, there are the 50a1 through 50a9 and so on.
Investigation of Hydrogen Microelectrodes Under Strong Cathodic Polarization

Gaining a better understanding of the electrochemical processes at the interface of electrode-electrolyte interface is crucial for the improvement of the performance of SOCs. This chapter is focused on the investigation of Ni/YSZ (the results of which were published [43]) and Pt/YSZ (to be published [93]) interface operated under strong cathodic polarization in $\text{H}_2\text{O}/\text{H}_2$ atmosphere. A microscopic point contact configuration was used to simplify the geometry of the cell. The Ni/YSZ and Pt/YSZ systems under strong cathodic polarizations are relevant when a SOEC is operated at high current densities. Impedance spectroscopy with and without DC polarizations as well as cyclic voltammetry were used to investigate the surface electrochemical processes in these systems. As silicate impurities are often claimed to be a main source of SOC performance degradation [94–96], the measurements are carried out on YSZ samples with different concentrations of silica. In addition to the electrochemical measurements, surface chemistry, conductance and microstructure was investigated post mortem by complementary techniques such as ToF-SIMS, SEM and AFM.

4.1 Introduction

The $\text{H}_2\text{O}$ reduction reaction takes place at the fuel electrode when the cell is run in electrolysis mode, and the oxidation of the $\text{H}_2$ when the cell is operated in the fuel cell mode. The reaction mechanism at the fuel electrode has been investigated
4.1. Introduction

Intensively and it is well reported in literature. Different cell configurations such as point electrodes \[58, 59, 61, 63, 97-100\], patterned electrodes \[101-108\], mesh electrodes and porous electrodes \[60, 109, 110\] were used. Most fuel electrodes are made of porous metal-ceramic composite, the most common being Ni-YSZ cermet, which offers an interconnected network of Ni and YSZ. It is shown that under certain conditions, the performance of the Ni-YSZ electrode is very good and long lasting \[111\], however there is still place for improvement. For example, it is economically beneficial to operate an electrolysis cell at high current densities, because the fuel production rate increases. However, the high current density increases the degradation rate of the cell.

Several long-term studies have been performed on SOEC operating at high current densities \[29, 112, 113\]. They have revealed different degradation mechanisms on the fuel electrode. Tao \textit{et al.} \[28\] report silica nano-precipitates inside Ni grains in SOECs which had been operating at current densities higher than 1.5 A/cm\(^2\) for 500-700 h. Chen \textit{et al.} \[29\] have performed post mortem analysis on cells operated for more than 300 hours at 0.75, 1.0 and 1.5 A/cm\(^2\) current densities. They observed formation of ZrO\(_2\) nanoparticles on the Ni surfaces in cells which were operated at current densities higher than 1 A/cm\(^2\) at 850 °C \[29\]. The formation of the nanoparticles was strongly correlated to the cell polarization and lowered the electrode performance due to loss of Ni percolation. The degradation mechanism on highly polarized Ni-YSZ electrodes was also discussed by Mogensen \textit{et al.} \[114\], and they observed that part of the Ni particles lose their electrical contact to the electrode. It was noted that the region close to the electrolyte after testing had lower Ni content and higher porosity. In contrast to the long-term testing of SOEC at high current density, short-term tests with very high current densities \[28, 29, 115\] and also reverse current treatment \[30, 116\], have shown to improve the performance of the cell. With reverse current treatment, it is meant that a SOFC is operated as a SOEC for a short time period and then returned to SOFC operation. Klotz \textit{et al.} \[29\] and Szász \textit{et al.} \[113\] observe that a nanostructured interlayer between Ni and YSZ, was formed after the SOFC was operated as a SOEC at a current density of 2 A/cm\(^2\) for 10 s. They attribute the improvement of the SOFC cell performance to the presence of this nanostructure interlayer which increases the reaction active area.

When an SOEC is operated at high current densities the Ni-YSZ cathode is strongly polarized and electronic conductivity is induced in the YSZ. Electronic conductivity in the YSZ is associated with a partial reduction of zirconia which takes place in two steps. The first occurs at low temperatures where electrons are trapped by impurities (e.g. Fe), resulting in a yellow or gray color, and the second occurs at higher temperatures where the electrons are trapped in oxygen.
vacancies, resulting in blackening of the zirconia \[117\].
4.2. Experimental set up

The reduction of zirconia has been studied extensively and coloration has been observed by several authors [118–120]. As the electronic conductivity is introduced in the electrolyte, the reaction zone spreads from the triple phase boundary to a larger gas/electrolyte interface. Electrochemical reduction of ZrO\textsubscript{2} in Ni-YSZ systems has been studied by several groups and they find that as the cathodic polarization increases, the ZrO\textsubscript{2} will become reduced, resulting in formation of Zr dissolved in Ni and intermetallic Ni-Zr phases [29, 57, 115, 121, 122]. Thermodynamic calculations show that at 650 °C a potential below -2.4 V vs. E(pO\textsubscript{2}=1 bar) is required for the reduction of ZrO\textsubscript{2} into pure Zr [29, 122] (refer to Fig.4.1) whereas solid solution of Zr-Ni and intermetallic phases are formed at lower cathodic polarizations than the ZrO\textsubscript{2} reduction. Thus, YSZ is reduced at higher electrode potentials when in contact with Ni. Additionally, under cathodic polarizations, Ni interacts with silicate impurities. According to the Ni-Si-O phase diagram Si forms intermetallic phases with Ni for pO\textsubscript{2} below 10^{-37} bar [123]. Thus, under cathodic polarizations to potentials below -1.8 V vs. E(pO\textsubscript{2}=1 bar) silica may be reduced.

The aim of the work presented in this chapter is to investigate the impact of strong cathodic polarization on the YSZ when using both Ni and Pt micro-contact. The Ni|YSZ system is very important due to its direct application in SOECs, while the PtIr|YSZ system is used to get more details into the reduction of YSZ under strong cathodic polarizations.

4.2 Experimental set up

4.2.1 Conductance scanning

The electrochemical characterization, the surface conductance and topography measurements were carried out in a controlled atmosphere high temperature scanning probe microscope (CAHT-SPM) [27, 82]. The samples were placed on the heating plate and held down by three alumina pins, which were held in place by steel springs. A platinum wire, used as a macroscopic counter and reference electrode, was attached at the edge of the samples and fixed in place by one of the alumina pins. The conductance images were acquired in scanning mode, where each pixel of the image represents a single frequency impedance measurement. The AC voltage with a 10 kHz frequency and 0.5 V amplitude was generated by a Stanford RS830 lock-in amplifier and was applied across the Pt counter electrode and the probe. The current response was measured by the lock-in amplifier through a 1 MΩ resistor connected in series with the tip. The resistance has the
purpose of protecting the lock-in amplifier from any overload \[124\]. Since these measurements are conducted in contact mode the resolution of the technique is determined by the electrical probe-sample contact area. Surface conductance and topography images are obtained simultaneously.

### 4.2.2 Electrochemical measurements

Electrochemical measurements were performed in the CAHT-SPM, where the SPM tip was used as a working electrode by pressing it against the surface of the sample for the duration of the measurements. For the electrochemical measurements, such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and chronoamperometry, a Gamry Instruments FAS2 Femtostat was used. The surface temperature of the sample was determined utilizing a thermocouple placed at the surface of the sample in a separate calibration experiment. The temperature of the sample|tip contact was most likely underestimated due to the fact that the thermocouple|sample contact was larger than the tip|sample and the cooling effect was probably more pronounced.

Most measurements were carried out at 650 °C in a 9 % H\(_2\)/N\(_2\) mixture humidified at room temperature by bubbling the gas through water. The electrochemical measurements were conducted using a two-electrode set up. Due to the large size difference between the working electrode (Ni or PtIr tip-sample micro-contact) and counter electrode (Pt wire-sample macro-contact), the polarization of the counter electrode was considered negligible (as proven by the measurements in Appendix A). Thus, the counter electrode also served as a reference electrode, and the reference potential in our set-up was the equilibrium potential of the H\(_2\)/H\(_2\)O electrode reaction, at the same temperature (650 °C). The oxygen partial pressure, \(pO_2\), of the exhaust gas was continuously monitored with a YSZ-based oxygen sensor operating at 1000 °C. Once the desired experimental temperature was reached, a waiting time of a minimum 30 min was applied for the temperature and the \(pO_2\) to stabilize. When the \(pO_2\) was stabilized a small decrease in the reference potential of roughly 5-10 mV was observed in a time period of five hours.

For the humidified 9 % H\(_2\)/N\(_2\) atmosphere, the measured oxygen potential of -940 mV vs. air at 1000 °C corresponds to \(pH_2O/pH_2\) ratio of 0.309 at the outlet. In the case where the temperature of the water used to humidify the atmosphere was 25 °C and the gas is saturated, an experimental atmosphere containing 3 % H\(_2\)O, 8.7 % H\(_2\) and 88.3 % N\(_2\) (i.e. a \(pH_2O/pH_2\) ratio of 0.34) was expected. The difference between the measured and the theoretical \(pH_2O/pH_2\) was small, and it corresponded to a change in the reference potential of less than 5 mV, which was insignificant for the purpose of the experiments. From the \(pH_2O/pH_2\)
4.2. Experimental set up

Table 4.1: Sample types and impedance series acquired for each sample using Ni tip. i and d refer to increasing and decreasing potentials. F$_1$ and F$_2$ refer to two different contact forces applied on the tip.

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Tip/sample couple</th>
<th>EIS series name</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>YSZ</td>
<td>A</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B</td>
</tr>
<tr>
<td></td>
<td></td>
<td>C</td>
</tr>
<tr>
<td>Ni</td>
<td>SiYSZ</td>
<td>D</td>
</tr>
<tr>
<td></td>
<td></td>
<td>E</td>
</tr>
<tr>
<td>Ni</td>
<td>YSZ 100</td>
<td>F</td>
</tr>
<tr>
<td></td>
<td></td>
<td>G</td>
</tr>
</tbody>
</table>

ratio determined by the $pO_2$ monitor the reference electrode potential at 650 °C is calculated to be -1.066 V versus oxygen ($E^o$($O_2$)). From one experiment to another, variations of the water temperature were observed, which resulted in fluctuations of the reference potential of less than 20 mV. For dry 9% H$_2$/N$_2$, the measured oxygen potential of -1035 mV at 1000 °C corresponds to a $pH_2O/pH_2$ of 0.055 at the outlet, which corresponds to a reference potential of -1.135 V versus $E^o$(O$_2$) at 650 °C.

Table 4.2: Samples types and impedance series acquired for each sample using PtIr tips. i and d refer to increasing and decreasing potentials

<table>
<thead>
<tr>
<th>Type of sample</th>
<th>Tip/sample couple</th>
<th>EIS series name</th>
</tr>
</thead>
<tbody>
<tr>
<td>PtIr</td>
<td>YSZ</td>
<td>H</td>
</tr>
<tr>
<td></td>
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<td>I</td>
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<td>M</td>
</tr>
<tr>
<td>PtIr</td>
<td>SiYSZ</td>
<td>N</td>
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<tr>
<td></td>
<td></td>
<td>O</td>
</tr>
</tbody>
</table>
4.3. Results

DC polarizations starting from 0 V down to -2 V versus the reference potential with a step size of -0.1 V or -0.2 V were carried out. The current response, later referred as chronoamperometry, of each applied polarization was recorded for 120-300 s before recording the EIS response under continued constant DC polarization. EIS measurements were recorded in the frequency range from 82 kHz to 0.082 or 0.0082 Hz using 10 mV rms with 7 points per decade. Three types of YSZ samples were used, single crystal YSZ (YSZ 100), polycrystalline YSZ (YSZ) and SiO$_2$ added YSZ (SiYSZ). Two different lists of the samples for electrochemical measurements using Ni and PtIr probes are reported in Table 4.1 and Table 4.2 respectively.

4.2.3 Surface chemistry and microstructure

To obtain post-mortem information about the surface chemistry and morphology of the contact region in the YSZ sample, time of flight secondary ion mass spectrometry (ToF-SIMS) imaging and SEM were performed. The ToF-SIMS analysis was performed using ToF-SIMS IV (ION-TOF GmbH, Munster, Germany). The ion beam used for imaging was a 25 keV Bi$^+$ pulsed beam, with a 10 kHz frequency and a pulse length of 100 ns. Prior to imaging, a larger area (750x750 µm$^2$) was sputtered using 30 nA of 3 keV Xe$^+$ for 45 s to remove any hydrocarbon species adsorbed on the surface. The surface was flushed with 20 eV electrons to reduce surface charging. Additionally, the contact surface of the nickel tip was investigated using SEM and energy-dispersive X-ray spectroscopy (EDS) (Zeiss Supra or Zeiss Merlin).

4.3 Results

4.3.1 Testing of the Ni probes

The platinum iridium probes have been used for many years in the CAHT-SPM and have shown to be well suited for both topography and conductance measurements at room temperature and at elevated temperatures up to 850 ºC. The Ni probes, however, were developed for this work. Initial experiments using the Ni probes to perform topography measurements at room temperature on a polycrystalline YSZ sample, which was previously exposed to humidified 9 % H$_2$/N$_2$ gas mixture at 650 ºC, showed small features, such as pores and elevated grains as exemplified in Fig.4.2. This indicates that the Ni tips can produce good images at room temperature. The resonance frequency of this particular tip was measured at room
4.3. Results

temperature and it was 27.6 kHz. It was measured in the CAHT by sweeping the oscillation frequency of the tip while monitoring the deflection amplitude. When the deflection amplitude reached its maximum, the cantilever was oscillating at the resonance frequency. The same probe was then used to obtain topography and surface conductance images at 650 °C in humidified 9 % H₂/N₂ and the corresponding images are shown in Fig. 4.3. The resolution and quality of the images is no different that the ones obtained using PtIr probes,

Figure 4.2: A 40x40 µm² topography image obtained at room temperature using a Ni probe fabricated in-house.

Figure 4.3: A 40x40 µm² a) topography images and b) surface conductance of the same area obtained at 650 °C using a Ni probe which was fabricated in-house.

The resonance frequency of the tip decreased from 27.6 kHz at room temperature, to 21.7 kHz at 650 °C, which indicates a decrease in the stiffness of the cantilever at elevated temperatures. However, once at the temperature the resonance frequency of the cantilever did not change. Since the cantilever resonance was measured when the tip was not in contact with the surface of the sample, one would expect
4.3. Results

the stiffness of the cantilever to decrease even further when in contact with the hot sample. Using the same sample but a different Ni probe, the measurement were repeated at 650 °C and similar quality images were obtained as shown in Fig. 4.4.

Figure 4.4: A 40x40 µm² a) topography images and b) surface conductance of the same area obtained at 650 °C using a different Ni probe than the one used to obtain the images in Fig. 4.3.
4.3. Results

4.3.2 EIS measurements on Ni|YSZ

Series of impedance measurements were performed under applied DC potential which were stepped from 0 to -2 V and back to 0 V in steps of 0.1 V or 0.2 V. A conditioning period of 300 s, when the current response of the applied potential was recorded before each spectrum. Fig. 4.5 shows conditioning currents as a function of time at selected polarizations. The behaviour of the current evolves from capacitive to inductive with increasing polarization. In other words, under low cathodic polarization Fig. 4.5a), the cathodic current decreases with time, like the response of a resistor in parallel with a capacitor (RC), while at high cathodic polarization an increasing cathodic current is observed Fig. 4.5c), i.e. like that of a resistor in parallel with an inductor (RL) behaviour.

The impedance spectra acquired upon increasing cathodic polarizations are shown in Fig. 4.6. The EIS evolve significantly with increasing polarization. From 0 V to -0.8 V, only one suppressed arc is present in the impedance spectra. A new arc becomes visible in the low frequency regime at -0.9 V. Furthermore, at low frequency an inductive loop is present at polarizations between -1.1 V and -1.5 V. Other series of impedance measurements with frequencies as low as 0.0082 Hz, reveal inductive loops from -1 V and -2 V, as illustrated in Fig. 4.7.

As the results obtained with frequency range from 82 kHz to 0.082 Hz did not allow a reasonable extrapolation of the

Figure 4.5: The time dependency of the current during different polarizations at a) low cathodic polarizations b) intermediate polarizations and c) high cathodic polarizations for the YSZ-A sample. At low cathodic polarizations the relaxation shows RC behaviour while at high cathodic polarization RL behaviour is observed.
4.3. Results

Inductive loops to DC, the width of the spectra was used as a describing parameter instead of the DC polarization resistance.

![EIS spectra recorded for Ni|YSZ (YSZ-A) under varying DC polarization at 650 °C in humidified 9% H2/N2. The lowest frequency is 0.082 Hz. Summit frequencies and the applied polarizations are given in the figure.](image)

It is referred to as the intercept resistance ($R_{x-L}$) and is determined as the distance from the high frequency extrapolation ($R_s$) to the low frequency intersection of the real axis. In the $R_{x-L}$ notation, $x-L$ stands for real axis intercept at low frequency. Fig 4.8 shows the $R_s$ and $R_{x-L}$ of several different polarization series. The $R_s$ and $R_{x-L}$ values corresponding to the impedance spectra shown in Fig 4.6 are shown in Fig 4.8 a) and b) respectively (YSZ-A). The $R_s$ values were obtained by fitting an equivalent circuit with $R_s$ in series with a RQ parallel combination to
4.3. Results

Figure 4.7: Impedance spectra obtained in the frequency range from 82 kHz to 0.0082 Hz showing inductive loops at low frequencies. These spectra are taken from YSZ-B F2 series.

Figure 4.8: a) The semi-log plot of $R_s$ and b) $R_{x-L}$ of Ni|YSZ as a function of the applied potential versus the reference potential (bottom x-axis). The A, B and C indicate the tip used for the series. The corresponding potential versus oxygen is shown in the top x-axis. The Si/SiO$_2$, Zr/ZrO$_2$ and Y/Y$_2$O$_3$ equilibrium potentials are indicated with red, black and blue dashed lines, respectively. The green triangle in a) indicates the equilibrium relation between potential and $R_s$ when electronic conductivity is introduced in YSZ.

The high frequency data, whereas the $R_{x-L}$ values were read from the impedance graphs. When determining $R_s$ by fitting was not possible, the $R_s$ values were read from the EIS as well. While the cathodic polarization increases from 0 V to -1 V, $R_s$ stays constant. For cathodic polarizations stronger than -1 V, $R_s$ decreases. This decrease varies from an order of magnitude to a factor of two from one polarization series to another as shown in Fig. 4.8. It is important to remember that in a point contact configuration, the properties of a small volume of the sample close the contact is probed, therefore there are two factors that influence the $R_s$: the size of the contact and the conductivity of the small volume around
4.3. Results

the contact, which for the polycrystalline YSZ might have different values if the probe is close to a grain boundary or not. This can justify the variations in the $R_s$ as shown in Fig. 4.8. The intercept resistance, $R_{x-L}$, shows a more consistent behaviour across different data series than $R_s$. Almost one order of magnitude decrease of the $(R_{x-L})$ is observed down to -0.7 V. A steeper decrease of roughly three orders of magnitude of the $R_{x-L}$ follows for polarizations down to -1.4 V. For polarizations between -1.4 V and -1.7 V the $R_{x-L}$ displays an increase followed by a decrease down to -2 V. For an overall increase of the cathodic polarization of two volts, $R_{x-L}$ decreases by four to five orders of magnitude. The $R_s$ and $R_{x-L}$ for the decreasing cathodic polarization are also shown in Fig. 4.8 (YSZ-A) and they show a similar behaviour. It was not possible to extract the values of the $R_{x-L}$ between -0.3 V and 0 V because the summit frequency was too far below the frequency range used for the measurements to obtain a valid extrapolation. However, the extracted $R_{x-L}$ points follow the same trend as for the increasing cathodic polarization. The $R_s$ during the increasing cathodic polarization deviates from the decreasing cathodic polarization, especially at low cathodic polarizations.

4.3.3 EIS measurements on Ni|SiYSZ

Similarly to the Ni|YSZ study, the Ni|SiYSZ system was investigated as well. Fig. 4.9 shows a series of impedance spectra obtained at increasing cathodic polarization on Ni|SiYSZ. The chronoamperometry measurements during the conditioning time exhibit similar behaviour as Ni|YSZ shown in Fig. 4.5. In resemblance to the YSZ system, the impedance spectra show the presence of one arc from 0 V to -0.9 V. At -1 V a clear emergence of a second arc is observed at low frequencies. Contrary to the Ni|YSZ impedance spectra, the two arcs are clearly separated in the SiYSZ system. As the low frequency arc becomes more prominent, the two arcs do not merge but remain very well separated. Additionally, the beginning of the low frequency arc shows a straight line behaviour (45 degree slope) at -1.1 and -1.2 V. The inductive behaviour in the SiYSZ sample is only observed from -1.8 V to -2 V for frequencies down to 0.082 Hz. The inductive loops could be present at cathodic polarization than -1.8 V if lower frequencies were probed.

The values of the high frequency resistance ($R_s$) and the intercept resistance ($R_{x-L}$) for several series were obtained in the same manner as for the Ni|YSZ system and were shown in Fig. 4.10(a) and b), respectively. In addition to the $R_s$ and $R_{x-L}$ extracted from the series shown in Fig. 4.9 (SiYSZ-E), another series with 0.2 V step in both increasing (SiYSZ-Dd) and decreasing (SiYSZ-Di) cathodic polarizations is shown in Fig. 4.10. The $R_{x-L}$ and $R_s$ of the Ni|YSZ and the
4.3. Results

Figure 4.9: a)-d) Impedance spectra of Ni|SiYSZ (SiYSZ-D₁) at different polarization voltages. Frequency range: 82 kHz – 0.082 Hz. This data set was performed using a very sharp tip (sub-micron diameter). e)-f) The corresponding log-log plots of $Z_{\text{im}}$ and $Z_{\text{real}}$ versus frequency.

Ni|SiYSZ system show generally similar behaviours with some minor differences. The $R_s$ vs. potential curve of Ni|SiYSZ does not show a plateau at low cathodic polarization, and a steeper decrease is observed at cathodic polarizations stronger than -1.6 V. The $R_{x-L}$ vs. applied potential behaviour of the SiYSZ shows three different activations, a slow decrease of $R_{x-L}$ at low cathodic polarization (0 V down to -0.5 V), followed by steeper decrease at intermediate (-0.6 V down to -1.4 V) and at high polarization (-1.6 V down to -2 V), where the last two sections are separated by a small increase or a plateau (-1.4 V down to -1.6 V). The $R_{x-L}$ decreases four to five orders of magnitude for both systems.
4.3. Results

Figure 4.10: a) The Ni|SiYSZ semi-log plot of $R_s$ and b) $R_{x-L}$ as a function of the applied potential versus the reference potential (bottom x-axis). The corresponding potential versus oxygen is shown in the top x-axis. The Si/SiO$_2$, Zr/ZrO$_2$ and Y/Y$_2$O$_3$ equilibrium potentials are indicated with red, black and blue dashed lines respectively. The green triangle in a) indicates the equilibrium relation between potential and $R_s$ when electronic conductivity is introduced in the YSZ.

4.3.4 Electrochemical measurements on Ni|YSZ100

Impedance spectra obtained from single crystal YSZ show similar behaviour to the previous two systems. The $R_s$ and $R_{x-L}$ of two different series are shown in Fig 4.11 a) and b), respectively. The YSZ100-D series shows the $R_s$ and $R_{x-L}$ in both increasing (-0.1 V steps) and decreasing (0.2 V steps) cathodic polarizations. The $R_s$ shows an overall decrease of approximately one order of magnitude in the increasing cathodic polarization series, where the steepest decrease is observed from -1.4 V up to -1.8 V. The $R_s$ values at low cathodic polarizations do not return to the same value when the electrode potential is increased. At -0.6 V, the $R_s$ is a factor of two smaller in the decreasing series compared to the same electrode potential in the increasing series. In the decreasing direction the series finishes at -0.4 V due to loss of contact between the tip and the sample. The second series shows an increase in the $R_s$ at low cathodic polarizations, followed by a small decrease from -0.8 V to -1.4 V. The steepest decrease is observed from -1.4 V to -1.8 V. The $R_{x-L}$ for both series show very similar behaviour, where an overall 4-5 orders of magnitude decrease is observed. A small decrease was observed from 0 V to -0.7 V followed by a steep decrease down to -1.6 V. Finally, the $R_{x-L}$ increased by approximately a factor of two from -1.6 V to -2 V. When increasing the electrode potential, $R_{x-L}$ remained suppressed and up to two orders of magnitude difference was observed.
4.3. Results

Figure 4.11: a) The Ni|YSZ100 semi-log plot of $R_s$ and b) $R_{x-L}$ as a function of the applied potential versus the reference potential (bottom x-axis). The corresponding potential versus oxygen is shown in the top x-axis. The Si/SiO$_2$, Zr/ZrO$_2$ and Y/Y$_2$O$_3$ equilibrium potentials are indicated with red, black and blue dashed lines respectively.

4.3.5 EIS measurements on PtIr|YSZ

Impedance spectroscopy measurements where the potential was either stepped upwards or downwards were performed on PtIr|YSZ system using the same set up as for the Ni measurements. Two different series with decreasing potentials are shown in Fig. 4.12 and Fig. 4.13 to illustrate some general features of the EIS for this system. Even though at first glance the impedance spectra look different, one can find common features at closer inspection. The impedance spectra reveal one highly suppressed arc at low cathodic polarizations. At polarizations between -1.2 and -1.3 V vs $E_{Ref}$ two different arcs are present. As the potential is decreased further, an inductive loop appears between the capacitive arcs. It should be noted that the summit frequencies in the series shown in Fig. 4.12 are lower than those in the series shown in Fig. 4.13. The summit frequency of the high frequency arc in Fig. 4.12 (c) is outside of the measured frequency range making the inductive loop appear at high frequencies while in Fig. 4.12 (c) it appears in between the two arcs. At -1.5 V vs. $E_{Ref}$ in Fig. 4.13 (d) the size of the inductive loop has increased. As the polarization is further decreased the inductive loop decreases and it is not present at -1.9 V vs. $E_{Ref}$. In the case of Fig. 4.12 (d) two inductive loops were observed. To test if these inductive loops were not a result of drift in the system during the measurements, impedance spectra with increasing frequency were recorded. The inductive loops were present in these measurements as well showing that the they were not a result of system drift.

Several series with increasing or decreasing potentials were recorded. The high
4.3. Results

Figure 4.12: Impedance spectra from a downward stepping potential series. The minimum potential reached in this series was -1.6 V (PtIr|YSZ-J). The frequency range of these measurements is 82 kHz down to 0.08 Hz. The featured spectra correspond to a) 0 V, b) -1.2 V, c) -1.4 V and d) -1.6 V versus the reference potential. The corresponding potential versus the $E^0(O_2)$ is noted on the right hand corner of each graph. The full line corresponds to the fit to the equivalent circuit shown in Ref. [93].

The frequency resistance ($R_s$) was determined as the extrapolation of the high frequency impedance to "infinite" frequency to the intercept with the x-axis. These values are shown in Fig. 4.14 a) and c) for the decreasing and increasing potentials, respectively. When the polarization was decreased, a 2-4 orders of magnitude decrease in the $R_s$ was observed, while when the potential was stepped upwards, $R_s$ increased only by one order of magnitude. The DC resistance ($R_{DC}$) was determined similarly to the $R_s$, but in the $R_{DC}$ case the extrapolation of the low frequency impedance to the x-axis was used. The $R_{DC}$ are shown in Fig. 4.14 b) and d). A six order of magnitude decrease of the $R_{DC}$ is observed when the potential is stepped downwards. In contrast to the $R_s$ behaviour, the $R_{DC}$ increases by almost 6 orders of magnitude when the potential of the probe is increased. Note that the definition of $R_{DC}$ is different from the definition of $R_{x-L}$. This difference comes from the fact that the Pt|YSZ system exhibits a more complex impedance behaviour and a more complex equivalent circuit (shown in Fig. 4.36) was used to fit the data.
4.3. Results

Figure 4.13: Impedance spectra from a downward stepping potential series. The minimum potential reached in this series was -1.9 V (PtIr/YSZ-J_d). The frequency range of these measurements is 82 kHz down to 0.08 Hz. The featured spectra correspond to a) 0 V, b) -1.3 V, c) -1.4 V, d) -1.5 V e) -1.8 V and f) -1.9 V versus the reference potential. The corresponding potential versus the $E^0(O_2)$ is noted in the right hand corner of each graph. The full line corresponds to the fit to the equivalent circuit shown in 4.36 which is proposed in Ref. [93].
4.3. Results

Figure 4.14: a) High frequency resistance $R_s$ and b) the DC resistance ($R_{DC}$) obtained from EIS series where the potential was stepped downward. c) $R_s$ and d) $R_{DC}$ obtained from EIS series where the potential was stepped upwards.
4.3. Results

4.3.6 EIS measurements on PtIr|SiYSZ

Impedance spectroscopy was used to investigate the PtIr|SiYSZ system as well. Fig. 4.15 and Fig. 4.16 show two series impedance spectra which were recorded without moving the tip position, first in the range from -0.5 V down to -1.8 V with 0.1 V step (PtIr|SiYSZ-N_d) and then from -1.6 V up to -0.2 V vs \( E_{\text{Ref}} \) (PtIr|SiYSZ-N_i). A third series, where the potential was stepped upwards from -2 V up to -0.2 V vs. \( E_{\text{Ref}} \) is shown in Fig. 4.17. These series appear to be different, but they still have the main features as in the PtIr|YSZ, where close to the zero applied potential only one suppressed arc is present, and as the tip-sample polarization is decreased the low frequency arc becomes more dominant. In the series shown in Fig. 4.15, inductive behaviour is observed at low frequencies and as the potential is decreased the inductive loop increases. In the increasing potential series in Fig. 4.16, the inductive loop is only observed at -1.6 V vs. \( E_{\text{Ref}} \) and the two arcs in the mid polarization range do not appear separated. In the series shown in Fig. 4.17 however, the inductive behaviour is not present.

![Figure 4.15](image)

Figure 4.15: Impedance spectra from a downward stepping potential series. The minimum potential reached in this series was -1.8 V. The EIS series is PtIr|YSZ-N_d. The frequency range is 82 kHz down to 0.08 Hz. The featured spectra correspond to a) -0.5 V, b) -1 V, c) -1.2 V, d) -1.4 V and e) -1.7 V versus the reference potential.
4.3. Results

Figure 4.16: Impedance spectra from an upward stepping potential series. The EIS series is PtIr|YSZ-Ni. The frequency range is 82 kHz down to 0.08 Hz. The featured spectra correspond to a) -0.2 V, b) -0.6 V, c) -1.4 V and d) -1.6 V versus the reference potential.

Figure 4.17: a)-d) Impedance spectra of the series obtained on a PtIr|SiYSZ system (SiYSZ-Oi) where the potential is stepped upwards from -2 V to -0.2 V vs. \(E_{Ref}\). The frequency range of these measurements is 82 kHz down to 0.08 Hz.

The log-log plots of \(Z_{im}\) and \(Z_{real}\) versus frequency of this series are shown in Fig.4.18. The log-log plots indicate that the summit frequency of the high frequency arc shifts towards higher frequencies with decreasing potential, while the summit frequency of the low frequency arc does not change. The \(R_s\) and \(R_{x-L}\) of all the series are shown in Fig.4.19 and Fig.4.20. In the case when the potential was stepped downward and then upwards a small inductive hysteresis is observed in the \(R_s\) behaviour. The \(R_s\) values (shown in Fig.4.19 a) seem to return to the initial values.
4.3. Results

Figure 4.18: The log-log plots of $Z_{im}$ and $Z_{real}$ versus frequency of the series shown in Fig. 4.17 (SiYSZ-O).

Figure 4.19: a) $R_s$ and b) $R_x-L$ for the PtIr|SiYSZ-Ni and PtIr|SiYSZ-Nd.

Figure 4.20: a) $R_s$ and b) $R_{x-L}$ for the PtIr|SiYSZ-O. Note that since there is no inductive behaviour, in this particular case $R_{x-L}$ and $R^{DC}$ are equivalent.
4.3. Results

Approximately one order of magnitude increase of the resistance is observed in the decreasing potential series. The $R_{x-L}$ shown in Fig.4.19 b) behaves the same way when the potential is stepped in either direction. In both cases a four order of magnitude change in the $R_{x-L}$ was observed. The $R_s$ and $R_{x-L}$ of the PtIr|SiYSZ-O$_i$ are Fig.4.20 a) and b) respectively. Since the EIS of these series show no inductive loops a simple R-RQ-RQ equivalent circuit was used to fit the data. Only a four fold increase of $R_s$ is observed with increasing potential, while $R_{x-L}$ increases by four orders of magnitude.

4.3.7 Cyclic voltammetry in all systems

Fig.4.21 a) shows voltammograms recorded on the YSZ, SiYSZ and YSZ100 where Ni probes were used as working electrodes. In Fig.4.21 b) they are shown normalized to their highest cathodic current for better comparison. The voltammograms follow similar trends in all the studied systems, namely in all the CVs inductive hysteresis are observed. With increasing cathodic polarization, in the Ni|YSZ100 system, a strong increase in the cathodic current starts at -1.4 V. This increase starts at lower polarizations (-1.2 V) for the Ni|YSZ while the Ni|SiYSZ system shows a more gradual increase that starts at -0.6 V to -0.8 V followed by a steeper increase down to -1.6 V. The CVs of both the Ni|YSZ and the Ni|SiYSZ have an inflection point at -1.4 V. Indications of an inflection point in Ni|YSZ100 are observed between -1.6 and -1.8 V. In Fig.4.21 c) the inverse $R_{x-L}$ values and the first derivative of the current are compared to better illustrate this behaviour. All data are individually normalized to their highest numerical value. The $R_{x-L}$ values are calculated from the impedance spectra obtained after polarizations of 300 s, while the CVs are obtained with a sweep rate of 10 mV/s. The difference observed between the current values at high cathodic polarizations could be due to the different contact areas. The contact radii are calculated using the Newman formula [125]:

$$R_s = \frac{1}{4\sigma r}$$

(4.3.1)

where $R_s$ is the high frequency resistance, $\sigma$ is the bulk conductivity of YSZ and $r$ is the radius of the contact. This formula is valid for a circular contact area, a homogeneous electrolyte conductivity and negligible contact resistance contribution to the serial resistance, i.e. $R_s$ originates solely from the electrolyte resistance. Thus, using this formula for this system is a crude approximation. The radii are given together with the normalization factors in Fig.4.21 b).
4.3. Results

Table 4.3: Estimated radii of the contact points using $R_s$ at 0 V. The line and area current densities at -2 V were calculated using the estimated radii.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated r (nm)</th>
<th>Current at -2 V (A)</th>
<th>Line current density (A/cm)</th>
<th>Area current density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ 100</td>
<td>235</td>
<td>-1.38·10⁻⁶</td>
<td>-9.35·10⁻³</td>
<td>-795</td>
</tr>
<tr>
<td>YSZ</td>
<td>832</td>
<td>-1.65·10⁻⁶</td>
<td>-3.16·10⁻³</td>
<td>-76</td>
</tr>
<tr>
<td>SiYSZ</td>
<td>515</td>
<td>-4.11·10⁻⁷</td>
<td>-1.27·10⁻³</td>
<td>-49</td>
</tr>
</tbody>
</table>

Figure 4.21: CV for NiSiYSZ-D₄ (purple), Ni|YSZ-A₄ (blue) and Ni|YSZ100-F (orange) in humidified 9% H₂/N₂ at 650 °C. The sweep rate for all CV is 10 mV/s. b) CV curves normalized to the highest cathodic current. c) The first derivative of the CV for all systems (in continuous line) and the inverse ($R_x-L$) obtained from impedance measurements. d) CV in the Ni|YSZ system in dry and wet 9% H₂/N₂. The reference potential in dry 9% H₂/N₂: -1.135 V, in wet: -1.066 V. The corresponding water partial pressures are: 0.055 and 0.306 for the dry and wet respectively.
4.3. Results

Figure 4.22: Cyclic voltammetry series using PtIr probe on YSZ sample. The used sweep rates were: 1 V/s, 500, 200, 100, 50, 20, 10 mV/s. The sweep range used was from -0.5 V down to -1.5 V vs. \( E_{\text{Ref}} \).

The current densities at -2 V (currents used to perform the normalization) are normalized to the tip circumference and to the tip area using the estimated Newman radius and shown in Table 2. The normalized current densities increase with sample purity. The water partial pressure during the measurements has a substantial impact on the cathodic current, as shown in Fig.4.21 d). The voltammograms were acquired using the same sample and the same probe during the same set of experiments, but at two different positions on the sample. The general behaviour is quite similar but in the humidified 9% H_2/N_2 (\( p_{H_2O}/p_{H_2} \) of 0.306) the cathodic current at -2 V is almost twice the value of the current in the dry 9% H_2/N_2 (\( p_{H_2O}/p_{H_2} \) of 0.055).

PtIr probes were also used as working electrodes to perform CVs on YSZ and SiYSZ samples and the corresponding potential sweeps are shown in Fig.4.22 and Fig.4.23 respectively. Both series show very similar behaviour. The maximum cathodic current at the highest cathodic polarization increases with decreasing sweep rate. In both systems a very small inductive hysteresis which becomes more pronounced with decreasing sweep rate is observed as well. The insertion in Fig.4.23 is a zoomed in graph where a step in the current is observed. The raw data revealed that the Gamry Femtostat had changed the current data range, therefore the current step is associated to an instrumental effect.
4.3. Results

Figure 4.23: Cyclic voltammetry series using PtIr probe on SiYSZ sample. The used sweep rates were: 200, 100, 50, 20, 10 and 5 mV/s. The sweeping range used was from -0.8 V down to -1.6 V vs. $E_{\text{Ref}}$.

Figure 4.24: a) Cyclic voltammetry using PtIr probe on SiYSZ sample. The sweeping range used was from 0 V down to -3 V vs. $E_{\text{Ref}}$.

Figure 4.24: b) Cyclic voltammetry using PtIr probe on SiYSZ sample. The sweeping range used was from 0 V down to -3 V vs. $E_{\text{Ref}}$. 

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4.3. Results

Two additional potential sweeps with a range from 0 V to -3 V vs. $E_{Ref}$ for the PtIr|SiYSZ system are shown in Fig. 4.24a. The featured cyclic voltammograms have sweep rates of 200 mV/s (red curve) and 2 mV/s. The features described earlier, i.e. the decrease of the inductive hysteresis with increasing scan rate and the increase in the of the maximum cathodic current at -3 V vs. $E_{Ref}$ with decreasing scan rate are also present in these CVs. It should be noted that at 200 mV/s the hysteresis becomes capacitive from the -2.2 down to -2.8 V vs. $E_{Ref}$. The first derivative of the current in the downward sweep of the 2 mV/s CV is shown in Fig. 4.24b). Note that the features of the first derivative for this system resemble perfectly those of Ni|YSZ and Ni|SiYSZ system shown in Fig. 4.21d) just shifted towards lower potentials.

The maximum currents obtained at -1.5 V vs. the reference potential from the PtIr|YSZ system (for example -0.25 $\mu$A at the 20 mV/s sweep) are almost 5 times smaller in absolute value than the current at the same potential obtained from the PtIr|SiYSZ system (for example -1.2 $\mu$A at the 20 mV/s sweep). This might appear counter-intuitive, but two different tips were used and the y-axis is a measure of the current and not current density.

4.3.8 Conductance mapping

Conductance mapping of the area close to the location where the tip was placed during the different polarization measurements were carried out once the polarization was released.

![Figure 4.25: a) Conductance map of a polarization spot after a polarization of -2 V vs. $E_{Ref}$ for 40 min at 650 °C. This image corresponds to the Ni|YSZ-G probe/sample couple.](image-url)
4.3. Results

Figure 4.26: a) Conductance map (55x55 \( \mu m^2 \)) of the pristine YSZ surface in humidified 9% \( H_2/N_2 \) at 650 °C. b) Conductance map of the same region as in a) after 30 min polarization at -0.8 V vs. the reference potential. c) higher resolution (20x20 \( \mu m^2 \)) conductance map of the region near the Ni|YSZ contact. (The color scale is Log10(G/S), where G is the surface conductance.

The tip used for mapping was the same as the one used for the polarization measurements, therefore if a Ni|YSZ system was under investigation the same Ni tip was used in the scanning mode. In this section several conductance maps for the different systems and conditions will be shown and described. Since a 1 MΩ resistance was used in between the sample and the lock-in amplifier to avoid any overload, in all the conductance maps this resistance has been taken into account. The scale in all the conductance maps is Log10(G/S)), where G is the surface conductance in Siemens (S). Note that this is not a measure of the surface conductivity \( \rho_s \), the unit of which would be S/m². Fig. 4.25 shows a conductance map of a polarization spot on a single crystal YSZ100-G obtained after applying a polarization of -2 V versus the reference for 40 min using a Ni probe.

Figure 4.27: Topography and b) conductance map (20x20 \( \mu m^2 \)) of a region surrounding a Ni|YSZ interface after a 30 min polarization at -0.4 V vs. \( E_{ref} \).
4.3. Results

Figure 4.28: a) Conductance map after 3 subsequent polarizations (1: -1.5 V vs. $E_{Ref}$ for 6 min, 2: -1.5 V vs. $E_{Ref}$ for 10 min and 3: -2 V vs. $E_{Ref}$ for 6 min) using a PtIr probe. b) A detailed conductance map of a high conductive region after 300 s of -2 V polarization. The low conductive regions are outlined with the dotted line.

Figure 4.29: a) Topography and b) conductance map of a region which was polarized at -1.5 V vs. $E_{Ref}$ for 30 min using PtIr probe on YSZ sample.

The image is somewhat blurry due to the bold tip after prolonged contact at a large contact force. However, a low conductance region and a high conductance region can be observed. The difference in conductance between them is more than one order of magnitude. Since -2 V vs. $E_{Ref}$ is well below the reduction potential of zirconia, higher potentials were also investigated. Fig.4.26 shows the conductance map of a polycrystalline YSZ surface prior to and after a 30 min polarization at -0.8 V vs. $E_{Ref}$. A 20x20 µm$^2$ map is shown in Fig.4.26 c). This images also indicates the presence of two regions, a high and low conductance. When the YSZ was polarized for 30 min at -0.4 V vs. $E_{Ref}$, only a low conductive region
4.3. Results

was observed as shown in Fig. 4.27. The PtIr|electrolyte systems also show similar trends, where one or more low and one high conductance regions were observed close to the polarization spots as observed in all examples shown in Fig. 4.28 and Fig. 4.29. The high conductive region were observed for polarizations between -0.8 and -2 V for time periods as short as 30 s. The high and low conductance regions are clearly much different than the YSZ conductance. In some cases, a much larger area is observed to be affected from the polarization, as shown by the slightly higher conductance in a circular area (approximately 20 µm in diameter) around spot 3 in Fig. 4.28 or in Fig. 4.30 d) where a large circular (approximately 60 µm in diameter) lower conductance region.

Figure 4.30: a-b) Topography and conductance of a spot obtained after 10 min of polarization at -2 V vs. \( E_{\text{Ref}} \). c-d) Topography and conductance of the same spot obtained 2 days after. The sample was kept at room temperature during the waiting time and it was reheated for this second measurement. Note that the images in a-b) are 40x40 µm\(^2\) while the ones in c-d) are 70x70 µm\(^2\).

Most of the longer polarizations are also associated with microstructural changes as observed in Fig. 4.29 a) and Fig. 4.30 a) and c). In the case of PtIr|SiYSZ, where -2 V polarization was applied for 30 min, a small region of higher conductance

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was observed which was surrounded by multiple regions of low conductance as shown in Fig. 4.31.

Figure 4.31: Conductance maps of a spot after a polarization of -2 V for 30 min on a SiYSZ sample. a) Higher magnification of the same spot.

Figure 4.32: PtIr tip after polarization measurements and conductance scanning performed on the SiYSZ sample shown in Fig. 4.31. The inset shows the EDX spectra collected at the red and blue points.

Obtaining conductance images after polarization on SiYSZ samples resulted to be more challenging than the other systems. The images obtained on SiYSZ samples after polarizations were usually, blurry and it appeared as impurities were being
4.3. Results

dragged along the scanning direction, which probably was due to the large amount of impurities accumulated at tip during the polarization. An SEM image of the same tip used to obtain the images in Fig.4.31 is shown in Fig.4.32. The insertion in the image shows two EDS spectra obtained at center of the tip (the red point) and at the edge in what seems like impurity. The impurity phase has high content of Si and Al in the oxide form. Additionally, the walls of the tip are contaminated as well.

Considering the modification the tip, as shown in Fig.4.32, it is somewhat surprising that the conductance images shown in Fig.4.31 have such resolution. A possible explanation could be the following: During the 30 min polarization time, a large force was applied which has caused the large deformation of the tip. When in the scanning mode, only 1/3 of the force used during the polarization was applied. Such release could imply that a smaller portion of the tip was in electrical contact during the conductance measurements, making it possible to obtain the resolution shown in Fig.4.31. When looking at these conductance images, it is important to remember that it is impossible to compare conductance maps which were taken using different tips, since conductance (G) depends on the area of the electrical contact. However, assuming that the tip modification that occurs during just one scan is minimal, one can compare different regions within the same image.
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4.3.9 Chemistry and microstructure of the metal|sample contact region

In the samples where it was possible to locate the contact areas, microstructural and chemical changes were observed. It was easier to locate the polarization spots when Ni probes were used, since the Ni signal in the ToF-SIMS is easier to detect than the Pt signal. Two different samples are shown in this section.

The images shown in Fig.4.33 are of a spot obtained after 30 min of -2 V polarization. It was attempted to keep the polarization while cooling the sample, but chronoamperometry data indicate that the contact was lost as soon as the sample started to cool. These measurements were performed using the same probe and sample as for the measurements in Fig.4.25 (i.e. Ni|YSZ100-G). The imaged spots, however, are different but with similar polarization conditions. The SEM images of the contact region are shown in Fig.4.33 a-c) and they display different features. The top region, denoted as Zone 1 in Fig.4.33 a) corresponds roughly to the contact area observed on the Ni tip, and it contains irregular Ni particles. Additionally, the microstructure of the YSZ appears to have been modified and roughened in this region. Zone 1 corresponds to the high conductive region in Fig.4.25. The elongated region (Zone 2 and 3), which appears darker in the SEM images, shows signs of drift signified by striations in the dark region. This drift most probably occurred during the cooling period when the tip was forced to be in contact with the YSZ sample. Further, EDS shows that the dark area contains Si and other impurities such as Na and Fe. The latter are preferentially located along one of the edges and from AFM is it found that this edge is higher than the rest of the area. AFM also shows that the dark region in Zone 1 is elevated 5-10 nm above the polished YSZ surface. This elevated surface could be due to accumulation of impurities or changes to the YSZ. In Zone 2, Ni nanoparticles are abundant in regions in between the impurity phases. In this area bigger lumps of Ni are located where the Ni grains are clearly visible and they seem to be part of the probe which was torn off during drift. ToF-SIMS ion images show the lateral distribution of Zr, Ni, Na and Si (Fig.4.33 d-g) and confirm the EDS measurements regarding the distribution of impurities and Ni.

ToF-SIMS high resolution imaging was performed on a YSZ sample polarized with a Ni probe from 0 V to -2 V with -0.2 V step size. Conductance mapping was avoided to exclude any artifacts on the ToF-SIMS images due to possible spreading of impurities while scanning in contact mode, since the ToF-SIMS is extremely sensitive to surface contamination. A large surface area of the YSZ was mapped by ToF-SIMS, and the Ni signal was used as indicator of the Ni|YSZ contact area. Fig.4.34 a) through f) show ToF-SIMS ion images of the contact
4.3. Results

Figure 4.33: a) SEM image of the polarization spot obtained after 30 min of polarization at -2 V vs. \( E_{\text{Ref}} \) on YSZ100-G the same sample and tip, but different spot, as for the conductance map shown in Fig. 4.25. b) and c) magnified SEM images of Zone1 and Zone3. d-g) ToF-SIMS images of approximately the same region as shown in a).

Area between the Ni probe and YSZ. In addition to the Zr, Y and Ni maps, Si, Na and Ca maps are shown. A lateral distribution of Ni is shown in Fig. 4.34b), which indicate the shape and size of the contact area. Si is enriched in a roughly circular area with a diameter of 50 µm around the contact area, i.e. approximately four times the diameter of the Ni tip. A SEM image of the Ni tip is shown in Fig. 4.34h) and reveals a contact region approximately 12 µm in diameter. Fig. 4.34g) shows a SEM image of the contact area on YSZ. From this SEM image it is obvious that the surface of the YSZ contacted by the Ni tip is substantially roughened. Despite the presence of Ni and Si, both Y and Zr are also observed in the region. Further investigations, such as SEM and EDS of the tips used for the strong polarizations revealed the presence of Si and Al oxide species in the contact region as well as on the walls of the tip.
Figure 4.34: a)-f) ToF-SIMS images (50x50 μm²) of the Ni|YSZ contact area 
g) SEM image of the YSZ at the contact where the dashed line indicates the border of the modified region and 
h) SEM image of the Ni tip after the polarization measurement.
4.4 Discussion

The chronoamperometry measurements at different potentials on the Ni\textasciitilde{}YSZ system, as shown in Fig.4.5, indicate that the current evolves from capacitive to inductive with increasing polarization. This behavior is further supported by the appearance of the inductive loops at low frequencies in the impedance spectra seen in Fig.4.6 and Fig.4.7. Inductive loops have been previously observed in metal\textasciitilde{}YSZ systems \cite{61, 99, 100}, and they have been attributed to either the potential dependency of adsorbed intermediate species \cite{86, 126, 127} or to an increase of the reaction zone \cite{128} by the injection of electrons in the YSZ.

Fig.4.35 a) shows a schematic of the electron concentration (red line) close to the Ni\textasciitilde{}YSZ contact when a high frequency AC signal is applied, while Fig.4.35 b) shows the low frequency case. At low cathodic polarizations, the reaction does not extend far from the tip. Due to the high electrode overpotential and concentration of electrons close to the sample\textasciitilde{}tip contact, it is suggested here that the reaction rate in the region close to the Ni\textasciitilde{}YSZ contact is limited by the water diffusion rate. This region is indicated with continuous black line in Fig.4.35 a) and b). As the cathodic polarization is increased, the reaction zone extends further due to introduction of electronic conductivity in the YSZ. This is represented with the dashed blue line in Fig.4.35. When an AC signal is superimposed on the steady state polarization, a damped electron concentration wave is created. At high frequencies, this concentration wave does not extend beyond the water diffusion-limited area (shown in Fig.4.35 a). Therefore, the high frequency process in the EIS reveals the charge transfer reaction at the tip\textasciitilde{}YSZ interface while the low frequency arc, which appears at higher cathodic polarizations, is attributed to the YSZ\textasciitilde{}gas surface reaction. The impedance measurements for both YSZ and SiYSZ shown in Fig.4.6, Fig.4.7 and Fig.4.9 consistently show a splitting of one arc into two arcs at potentials below -0.8 V and -1.0 V reflecting two series processes as explained above. YSZ100 also exhibit a similar behaviour. However, at lower frequencies, the electron concentration wave extends outside of the diffusion limited region, and thus a modulation on the reaction zone is observed. Such modulation causes an inductive loop at low frequencies as seen in Fig.4.7.

In the series shown in Fig.4.7 (YSZ-B F\textsubscript{2}0), however, there is no splitting of the capacitive arcs. The estimated contact radius for the YSZ-B F\textsubscript{2} is 5 times larger than the contact radius for the YSZ-A\textsubscript{2}. Therefore, the details from the YSZ\textasciitilde{}gas interface impedance may have been overshadowed by a relative increase of the parallel Ni\textasciitilde{}YSZ admittance.
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Figure 4.35: Schematic of the electron concentration (red line) close to the Ni|YSZ contact when an AC signal is applied a) the high frequency case and b) the low frequency case. The gas|YSZ interface is represented using continuous line for the surface where the water diffusion is limiting the surface reaction rate and dashed line for the surface where there is no water diffusion limitation. The electron concentration variation is only illustrative, therefore it is schematically drawn exaggerated.

The impedance behaviour of the Pt|YSZ might appear to be different from the behavior of the Ni|YSZ, SiYSZ, YSZ100 and even from the Pt|SiYSZ system due to the high frequency or double inductive loops as shown in Fig.4.12 and Fig.4.13. Hansen et al. [93] propose an equivalent circuit (Fig.4.36) which can explain the presence of double capacitive and double inductive loops. This equivalent circuit contains nine elements grouped in three blocks, namely: the charge transfer (ct), migration (mg) and YSZ|gas reaction (sr). The electrons are transferred from the probe to the YSZ and at the same time the water reduction reaction takes place at the triple phase boundary (TPB). This combined process is described by a simple R-Q circuit and as mentioned earlier is responsible for the high frequency impedance response. The next block (migration) in the equivalent circuit describes the migration of electrons further into the bulk of the YSZ. When electrons are introduced into the YSZ, charge neutrality requires charge compensation by oxide vacancies, which implies that the electron and vacancy
4.4. Discussion

Figure 4.36: Equivalent circuit proposed by Hansen et al. [93]. The circuit is composed of three blocks: charge transfer (ct) at the probe|YSZ interface, ion and electron migration (mg) and the gas|YSZ surface reaction (sr).

Fluxes are coupled. Therefore, the migration processes are driven by both electric fields and concentration gradients [93]. In other words, a system where a steady state electrodiffusion is superimposed by an AC perturbation is being considered. To understand the electron migration of such system lets consider the following scenarios:

- A high frequency AC perturbation is superimposed to the steady state concentration gradient. In this scenario, the concentration gradient is not influenced by the AC perturbation, and the impedance is defined the electrical resistance through the concentration gradient.

- A very low frequency, quasi stationary perturbation is superimposed to the concentration gradient. In this scenario, the impedance is determined by the slope of the stationary overpotential-current curve.

- An intermediate frequency AC perturbation is superimposed to the concentration gradient. The lower the frequency the higher the wavelength of the perturbation and the impedance transitions from the first scenario to the second.

The last block in the equivalent circuit represents the water splitting reaction at the YSZ|gas surface as a result of the introduction of electronic conductivity into the YSZ. This process was explained earlier in this section.

The behaviour of $R_s$ is semi-quantitatively similar for the three systems when Ni probe was used as shown by Fig 4.8, Fig 4.10 and Fig 4.11 a). Similarly, Fig 4.14, Fig 4.19 and Fig 4.20 a) show the behaviour of $R_s$. Table 4.4 summarizes the changes of $R_s$ and $R_{x-L}/R_{DC}$ for all the investigated systems. From the table,
Table 4.4: A summary table of the behaviour of $R_s/R^\infty$ and $R_{x-L}/R^{DC}$ for all the investigated systems. i and d refer to increasing and decreasing potentials.

<table>
<thead>
<tr>
<th>Probe</th>
<th>Sample</th>
<th>i/d</th>
<th>$R_s$ or $R^\infty$</th>
<th>$R_{x-L}$ or $R^{DC}$</th>
<th>Figure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>YSZ100</td>
<td>d</td>
<td>1 order of magn.</td>
<td>5 orders of magn.</td>
<td>Fig.4.11</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i</td>
<td>up to 3 fold</td>
<td>3 orders of magn.</td>
<td>Fig.4.11</td>
</tr>
<tr>
<td>Ni</td>
<td>YSZ</td>
<td>d</td>
<td>2-3 orders of magn.</td>
<td>3-4 orders of magn.</td>
<td>Fig.4.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i</td>
<td>2 order of magn.</td>
<td>3-4 order of magn.</td>
<td>Fig.4.8</td>
</tr>
<tr>
<td>Ni</td>
<td>SiYSZ</td>
<td>d</td>
<td>&lt;1 order of magn.</td>
<td>4 orders of magn.</td>
<td>Fig.4.10</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i</td>
<td>&lt;1 order of magn.</td>
<td>4 orders of magn.</td>
<td>Fig.4.10</td>
</tr>
<tr>
<td>Pt</td>
<td>YSZ</td>
<td>d</td>
<td>3-4 orders of magn.</td>
<td>6 orders of magn.</td>
<td>Fig.4.14</td>
</tr>
<tr>
<td></td>
<td></td>
<td>i</td>
<td>2-3 orders of magn.</td>
<td>6 orders of magn.</td>
<td>Fig.4.14</td>
</tr>
<tr>
<td>Pt</td>
<td>SiYSZ</td>
<td>d</td>
<td>&lt;1 order of magn.</td>
<td>4 orders of magn.</td>
<td>Fig.4.19</td>
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<tr>
<td></td>
<td></td>
<td>i</td>
<td>&lt;1 order of magn.</td>
<td>3 orders of magn.</td>
<td>Fig.4.19/4.20</td>
</tr>
</tbody>
</table>

one can observe that the $R_s$ change is almost always larger in the decreasing series than in the increasing series, which can be explained by the following possible reasons:

- True steady state is not obtained when the polarization is stepped in the positive direction, which in other words means that the changes in the electrolyte have a longer relaxation time compared to the step rate.

- Irreversible, or slowly relaxing modifications of the YSZ have taken place.

At cathodic polarizations lower than -0.8 V the error on the $R_s$ values can be up to 30%. The standard error of the $R_s$ from the fits in the low polarization region varies from 20% to 30%, even when only the high frequency region is fitted. For the spectra where the uncertainty was higher than 30% the intercept was estimated from the graphs, instead of fitting the EIS. Due to the large spreading of the impedances of more than 2 orders of magnitude, the error for the $R_s$ obtained from the estimation of the intercept is also estimated to be 30%. It should be noted that in this region with high frequency impedance in the megohm range, the values obtained are likely to be influenced by stray capacitances. The stray capacitance of the system was measured to be 0.6 pF, which would give rise to a shunting resistance of 2.65 Mohm at 100 kHz. Therefore, absolute values should be interpreted with care, whereas changes of the $R_s$ with polarization are significant. The extrapolations at higher polarizations are more accurate (< 5%
4.4. Discussion

at -2 V polarization), except for the Ni|SiYSZ samples where the error obtained from the fit was 15% at -2 V.

The ionic conductivity of YSZ, which can be deduced from the $R_s$ at low cathodic polarizations, is independent of the oxygen partial pressure, while the electronic conductivity depends on the local Fermi potential of the YSZ [129]. When a cathodic polarization lower than -1 V vs. $E_{ref}$ is applied, the $R_s$, which is inversely proportional to the conductivity of YSZ, decreases slowly, corresponding to a region where the ionic conductivity is dominant. The cathodic polarization is equivalent to a change in the oxygen partial pressure at the metal|YSZ interface, and as it increases, an exponential decrease of the $R_s$ (or increase in conductivity) is observed, indicating that the electronic conductivity becomes dominating.

Interpolating from the data of Appel et al. [130], the ionic conductivity of 8 mol% YSZ at 650 °C is $9.7 \times 10^{-3}$ S cm$^{-1}$. Using Eq. 4.3.1, the high frequency resistance ($R_s$) at low polarizations and the ionic conductivity, the contact radius is estimated to be 0.8 μm for the series YSZ-Ai in Fig. 4.8. SEM images of the tip show that the geometric radius of the contact area is approximately 7 μm. The discrepancy on the measured versus calculated contact radius is not surprising because, in addition to the irregular and changing shape of the contact area due to modification of the tip during the experiment, the uncertainty of the $R_s$ at low cathodic polarization is the largest. Additionally, SEM images give the final physical contact after the experiment was performed, and the physical area does not necessarily indicate an electrical contact. Therefore, both estimates of the contact area have large uncertainties, and only a semi-quantitative description of the experimental results is possible. For low $pO_2$, in equilibrium conditions, the electronic conductivity of YSZ has a $pO_2^{-\frac{1}{4}}$ dependency as reported by Park and Blumenthal [131]:

$$\sigma = ApO_2^{\frac{1}{4}}$$  \hspace{1cm} (4.4.1)

where $A$ is a constant and $\sigma$ is the electronic conductivity. The ionic conductivity ($\sigma_i$) is independent of the $pO_2$. Considering the Newmann formula the following is obtained:

$$\sigma = \frac{1}{4rR_s}$$  \hspace{1cm} (4.4.2)

where $r$ is the contact radius. For the oxygen reduction the Nernst equation can be written as

$$E = E^o - 2.3026 \frac{RT}{F} \log pO_2^{-\frac{1}{4}}$$  \hspace{1cm} (4.4.3)
4.4. Discussion

where $R$ is the gas constant, $T$ is the temperature and $F$ is Faraday’s constant. Using the above equations one can write the following:

$$\frac{1}{4rR_s} = ApO_2^{1/4} \rightarrow 4rAR_s = pO_2^{1/4}$$

(4.4.4)

$$\log pO_2^{1/4} = \log R_s - \log (4Ar)$$

(4.4.5)

Using Eq. 4.4.3 one obtains

$$\log R_s = \Delta E \left( \frac{2.3026RT}{F} \right)^{-1} + \log (4Ar)$$

(4.4.6)

The linear behaviour with a slope of -1/4 of the log$pO_2$ vs. log$\sigma$ at 650 °C corresponds to a linear behaviour in the log$R_s$ versus applied potential with a slope of

$$\frac{\partial \log R_s}{\partial E} = \left( \frac{2.3026RT}{F} \right)^{-1} = 5.4$$

(4.4.7)

The following assumptions must be true for the above derivation to be correct:

1. The conductivity of the YSZ is purely electronic.
2. The electronic conductivity is constant through out the sample.
3. The electronic conductivity is independent of the oxygen vacancies concentration.

The obtained slopes in all the investigated systems are 2 to 6 times lower than the ideal slope. A factor that might contribute to the flattening of the $R_s$ vs. applied potential can be attributed to the water splitting reaction happening at the surface. If no surface reaction was present, potential distribution in a point contact configuration is shown in Fig. 4.37 a). However, due to the water splitting reaction, the electron concentration in the YSZ surface close to the contact is reduced, thus causing the current lines to loop up to the surface [128] (Fig. 4.37 b). This lowers the volume in which electronic conductivity is introduced in the YSZ, hence causing a decrease the slope of the $R_s$ versus potential. The current and the equipotential lines in Fig. 4.37 b) are qualitative but similar behaviour were simulated by Ciucci et al. [132]. In the case of ceria (CeO$_2$)$_{0.95}$(Y$_2$O$_3$), studies of the variation of conductivity at different temperature as a function of $pO_2$ have
shown that its conductivity flattens out at very low polarizations, which indicates
that the proportionality of the conductivity of ceria with $pO_2^{-1/4}$ breaks for very
low $pO_2$. \[133\] Considering that the used potentials are well below the reduction
of $\text{ZrO}_2$, partial or full reduction of $\text{ZrO}_2$ is expected; therefore the above relation
might not be valid.

Figure 4.37: Qualitative sketch of the electron flux (in dashed lines) and the equipo-
tential lines (continuous lines) near the point contact between YSZ and Ni where a)
no surface reaction is present b) surface reaction is present.

Similar to the high frequency resistance, the $R_{x-L}/R^{DC}$ decreases by almost three
to six decades depending on the system investigated (see Table 4.4), when the
cathodic polarization of is increased. However, in contrast to the high frequency
resistance, it follows the downward curve when returned to the equilibrium
potential, except for the case of Ni\YSZ100 \[4.11\]. The $R_{x-L}$ for all Ni systems
shows reproducible behaviour. For the Ni\YSZ100 and Ni\YSZ there is a low
activation region from 0 V to -0.7 V followed by a steeper activation. For the
SiYSZ system the second more pronounced activation region starts at -0.5 V.
Additionally, all three systems show a tendency to have a local maximum in $R_{x-L}$
at high cathodic polarizations (-1.6 V for the SiYSZ and the YSZ and -1.8 V
for the YSZ100). The shift in the peak towards more negative potentials for the
single crystal indicates that the reaction responsible for the increase in the $R_{x-L}$
is delayed by the slower reducibility of the single crystal in comparison to the
polycrystalline samples. The $R_s$ and $R_{x-L}$ for the decreasing cathodic polarization
series performed in the same spot, immediately after the increasing polarization
series to ensure that the probe-YSZ contact conditions were not changed, are
shown in Fig.4.8, Fig.4.10 and Fig.4.11. For the YSZ100 (Fig.4.11) and the SiYSZ
system (Fig.4.8), the $R_s$ and the $R_{x-L}$ do not return to the initial high values
indicating a permanent or at least a slowly decaying modification of the YSZ close
to the probe contact. For the YSZ system the coincidence of the $R_{x-L}$ between the anodic and cathodic direction does not suggest any irreversible changes. Notice that the biggest hysteresis is observed in the YSZ100, which indicates that the re-oxidation process proceeds slower for the single crystal. Luerssen et al. [119] have observed that it is more difficult to induce electronic conductivity in single crystal YSZ than in polycrystalline samples. This is attributed to the morphology and higher defect density in the polycrystalline sample in comparison to the single crystal [119].

The CV measurements for all Ni systems (Fig 4.21) show inductive hysteresis, and their current densities decrease in absolute value with increasing silica content. This behavior indicates that the quantity of silica in the YSZ impedes the H$_2$O splitting reaction and limits the current. For the SiYSZ and YSZ systems, two different activation regions are observed in the CVs, separated by a flattening of the current at intermediate polarizations. For the single crystal however, only one activation region is observed close to -1.4 V, which coincides with the reduction potential of ZrO$_2$. The cathodic current increase at polarizations between -0.6 V and -1.2 V could be due to reduction of silica because it fits with the reduction potential (-0.8 V) and it is not observed in the single crystal system. For the SiYSZ system a gradual cathodic current increase starts at lower polarizations than in the YSZ and YSZ100, and the flattening/inflection point is most pronounced in the system that contains the most silica and weakest in the purest system, indicating that there is a non-negligible contribution to the current of the reduction of the silicates. The second activation region is attributed to the reduction of zirconia and the expansion of the reaction zone related to the introduction of electronic conductivity in the reduced region. The normalized first derivatives of current with respect to potentials and the normalized in;verse $R_{x-L}$ are in good agreement for all the studies systems as shown Fig 4.21 c). The discrepancies observed are partly due to the fact that the time it takes to acquire the CV data is much shorter than the impedance series where the polarization is stepped down by 0.1 V or 0.2 V. Inflection points in the CV curves are indicated as local maxima and local minima in the derivative curves and clearly these inflection points shift towards higher polarizations for the single crystal, suggesting once more that the lack of grain boundaries causes a delaying effect. The doubling of the cathodic current with a 6-fold increases water partial pressure that is seen at -2 V in Fig 4.21 d) is related to the spreading of the contact area at strong polarizations, as the CVs were obtained with the same probe, and geometric effects therefore can be discarded. The reaction zone at such polarization spreads beyond the water diffusion-limited region due to the introduction of electronic conductivity in YSZ. If the active area around the Ni|YSZ interface is the same for both atmospheres, the current
increase should be the same as the increase in the water partial pressure. However, in the humidified environment, due to the higher concentration of water, more electrons are consumed at the gas|YSZ interface, resulting in a smaller effective reaction zone. The CVs for the Pt|YSZ (Fig. 4.22) and Pt|SiYSZ (Fig. 4.23) show the same behaviour, i.e. the increase of sweep rate decreased the cathodic current and the CVs show inductive behaviour. Therefore no indications of the influence of silica in the system can be pointed out from these curves. The CVs shown in Fig. 4.24 a) and its corresponding first derivative curve (Fig. 4.24 b) show similar behaviour as the curves of the Ni|YSZ system. However, the peaks in Fig. 4.24 b) are shifted towards lower potentials, confirming that Ni promotes the reduction of zirconia.

4.4.1 Chemistry, electrochemistry and electrical measurements.

The formation of both high and low conducting regions in the vicinity of the Ni|YSZ, Ni|YSZ100 and Pt|YSZ contact points as a result of the strong cathodic polarization, as shown by the conductance maps in Fig. 4.25, Fig. 4.28, Fig. 4.29 and Fig. 4.30 is in accordance with the $R_s$ not returning to their initial high values. The low conducting regions are probably due to accumulation of SiO$_2$, as this is observed by both EDS and ToF-SIMS to be associated with the contact region on the YSZ and on the Ni or Pt tip. SiO$_2$ originating from the impurities in the raw materials is normally found to segregate to YSZ surfaces at elevated temperatures and form an impurity film with other present impurities [66, 134, 135]. Conductance images of the YSZ before polarization show a uniform conductance. This, however, does not explain the low conductance areas or the proximity to the contact, since a film would have caused a lower conductance through the sample and not localized close to the polarization spot. Therefore, it is suggested here that the impurity film is modified upon polarization, resulting in a non-uniform distribution of impurities, where higher impurity content is accumulated around the tip resulting in lower conductance. The accumulation of the Si-based impurities close to the tip|YSZ contact as well as the creeping of the impurities up the surface of the Ni tip, can be explained by the Marangoni effect [136], if it is assumed that the silicates are in a liquid/glassy phase at the testing conditions. The fluid motion is driven by gradients of the surface tension as a result of temperature gradients (thermo-capillary convection) or concentration gradients. When the nickel tip comes in contact with the thin layer of glassy silicates on the surface of the YSZ, the impurities form a concave meniscus due to the surface tension of the glassy phase. The temperature gradient of the YSZ surface and the tip itself
causes a surface tension gradient in the impurity layer, where the highest surface tension is observed at the lowest temperature. The motion of the fluid will be towards the highest surface tension, i.e. towards the lowest temperature. Hence, the silicates would accumulate closer to the tip causing the low conductance region. The electrode applied potentials are well below the reduction potential for SiO$_2$. Additionally, thermodynamic calculations predict the Si from the SiO$_2$ to diffuse into the Ni, as well as the formation of Si-Ni intermetallic [119]. At a later stage, when the electrode potential is high enough the Si will be re-oxidized to SiO$_2$ as found by Tao et al. [28]. This oxidation might occur when the polarization is released. The presence of silica is observed both in the EDX analysis of the tips and the YSZ samples. In the case of the Ni|YSZ, the dissolution of metallic Si in Ni may be locally “purifying” the contact between Ni and YSZ. This is further supported by the ToF-SIMS images (Fig 4.35) where there is a region in the middle of the Ni contact area, which is depleted of Si and Ni but rich in Zr and Y. The applied potentials are also below the zirconia reduction potential. Additionally, thermodynamic calculations have shown that the stability of ZrO$_2$ decreases when in contact with Ni [29], thus allowing the reduction of ZrO$_2$ and the formation of intermetallic Ni-Zr to occur at higher $pO_2$ than expected for pure ZrO$_2$. This suggests that zirconia is reduced as well under the conditions of these experiments. Similiarly, Pt-Si-Zr intermetalics are also expected but at lower potentials. The roughening of the Ni|YSZ contact area, also observed at higher temperatures in macroscopic system [57], as shown in SEM images of the YSZ sample, suggests interaction between the Ni probe and the zirconia sample. These microstructural changes are present in the Pt|YSZ macroscopic systems, however the degree of modification is lower in the Pt|YSZ systems in comparison to Pt|YSZ.

4.5 Conclusions

The operando highly localized study of the Ni|YSZ and PtIr|YSZ microelectrode system under strong cathodic polarization reveals several important features related to the electrochemical reduction of YSZ as well as to the degradation mechanism of the Ni|YSZ cathode system in SOECs. Strong cathodic polarizations using Ni and PtIr microelectrodes result in substantial changes in the electrical, microstructural and chemical properties of the YSZ. EIS measurements indicate two rate determining processes where the low frequency process, associated with the reduction of H$_2$O at the gas|YSZ interface (and oscillation of this reaction zone) becomes more dominant at stronger cathodic polarizations. The high frequency
4.5. Conclusions

process is associated with the charge transfer reaction at the Ni|YSZ contact. One to three orders of magnitude decrease is observed in the high frequency resistance upon increasing cathodic polarization from 0 V to -2 V, indicating introduction of electronic conductivity in all the YSZ samples, which is supported by the presence of high conductance regions in the conductance scans. Additionally, a 3–6 orders of magnitude decrease in the $R_{x-L}$ suggests increase of the reaction zone from the triple phase boundary to the YSZ surface. The expansion of the reaction zone can be beneficial for the operation of the SOECs, since it yields higher gas conversion rates. The polarization, however, also caused roughening of the contact surface due to the interaction of the Ni or Pt with the YSZ. Additionally, impurities are accumulated around the tip|YSZ contact suggesting that the impurity film is modified upon polarization resulting in a non-uniform distribution of impurities. These results increase the understanding of the degradation mechanism of the Ni or Pt electrodes where impurity segregation at the Ni|YSZ or Ni|YSZ interface causes blocking of the triple phase boundaries and reduces the reaction rate. The comparison between polycrystalline YSZ, and SiYSZ and single crystal YSZ samples suggests that the reduction and reoxidation of the single crystal is retarded pinpointing the importance of the grain boundaries in the redox chemistry of YSZ. Additionally, the CVs suggested that the reduction of zirconia occur at lower potential for the PtIr than for the Ni microelectrode system, confirming that Ni promotes the reduction of zirconia.
Chapter 5

Strong cathodic polarization on macroscopic model electrodes

5.1 Introduction

In Chapter 4, the impact of strong cathodic polarization on YSZ using sub-micron to a couple of micron PtIr and Ni microelectrodes was investigated. There were a couple of challenges related with the set up used to perform these measurements:

1. Due to the small contact area, finding the contact spot for post-mortem analysis was not always possible.
2. Temperature gradients are unavoidable in the CAHT-SPM, therefore the temperature effect was unclear.
3. The small amount of material involved in the reaction caused small to no changes of current.

Therefore, a different system was used to investigate the reduction of YSZ where the contact area between the metal and YSZ was larger and the temperature gradients were negligible.

5.2 Experimental

The YSZ and SiYSZ samples used were prepared as described in Chapter 3. Platinum paste was applied to the unpolished side of the YSZ samples creating a porous Pt counter electrode. A Pt grid was used as current collector on the side
5.2. Experimental

Figure 5.1: Experimental set up a) using a Pt wire and b) a Ni wire as a point electrode.

Table 5.1: Summary table with all the sample used in this chapter. * indicates that the sample was cooled keeping the polarization. These data were collected in collaboration with Vignesh Balasubramanian

<table>
<thead>
<tr>
<th>Test Name</th>
<th>Electrode</th>
<th>Sample</th>
<th>Temperature</th>
<th>Experiment</th>
</tr>
</thead>
<tbody>
<tr>
<td>36t38-0</td>
<td>Pt</td>
<td>YSZ</td>
<td>650 °C</td>
<td>CV</td>
</tr>
<tr>
<td>36t38-2</td>
<td>Ni</td>
<td>YSZ</td>
<td>650 °C</td>
<td>-1.0 V *</td>
</tr>
<tr>
<td>36t38-3</td>
<td>Ni</td>
<td>SiYSZ</td>
<td>650 °C</td>
<td>CV</td>
</tr>
<tr>
<td>36t32-0</td>
<td>Ni</td>
<td>YSZ</td>
<td>650 °C</td>
<td>CV</td>
</tr>
<tr>
<td>36t33-0</td>
<td>Ni</td>
<td>YSZ</td>
<td>750 °C</td>
<td>CV</td>
</tr>
<tr>
<td>36t34-3</td>
<td>Ni</td>
<td>YSZ</td>
<td>650 °C</td>
<td>Staircase</td>
</tr>
</tbody>
</table>

of the counter electrode. The working electrodes were made of Ni or Pt wires. A diagram of the cells is shown in Fig.5.1. This setup is similar to the ones used in Ref.[58, 59, 97]. Since the working electrode contact area is much smaller than the area of the counter electrode (same as the area of the sample), the resistance of the counter electrode is negligible, therefore, serving as a reference electrode. The Ni wires had a diameter of 0.5 mm and a purity of 99.99%. They were bent in a "J" shape as shown in Fig.5.1 b). The Pt wire was melted at the end with a reducing torch flame which formed a spherical bulb tip [58] as shown in Fig.5.1 a). The wires were then annealed at 1000 °C for 72 hours in 3% H$_2$O, 9% H$_2$ in N$_2$ and electropolished. Finally, the wires were placed in alumina tubes.

The sample holder, which can hold four samples at a time, was carefully cleaned of any particles using compressed air. The alumina tubes with the wires were held in place by attaching copper rods of 300 g above the tube. Once the samples were secured in their proper positions, a routine check was made to make sure that there was no short circuit in the system. The sample holders were then carefully placed in a pot furnace. The temperature and the $pO_2$ were continuously monitored.
5.3. Results
during the experiment. A 1255 Solatron Frequency Response Analyser and a 127 electrochemical interface were used for the electrochemical measurements. All the measurements in the furnace were performed in humidified 9% H$_2$ in N$_2$ atmosphere. As shown in Table 5.1 different type of measurements were performed on different types of systems. The types of measurements performed were:

1. **Cyclic Voltammetry**: The samples were subjected to cyclic polarizations ranging from 0 V to -1.6 V vs. $E_{Ref}$ with sweep rates of 100, 50, 20, 10, 5, 2 and 1 mV/s. At each sweep rate, three different cycles were collected and in between each sweep rate an electrochemical impedance spectrum (EIS) was collected at open circuit voltage (OCV). The parameters for the EIS were: Vrms of 10 mV/s and a a frequency range of 1 MHz to 0.1 Hz.

2. **Chronoamperometry**: A DC polarization was applied across the sample and its current response was recorded. In Table 5.1 the chronoamperometry measurements are denoted as DC polarization. The '*' implies that the polarization was kept during the cooling.

3. **EIS under DC polarization**: Impedance spectroscopy was recorded when a DC potential was applied. In test 36t34-3 the DC polarization was stepped from 0 V to -1.6 V vs. $E_{Ref}$.

In addition to the electrochemical measurements the microstructure of the contact area was investigated by investigating both the YSZ samples and the wire.

5.3 Results

5.3.1 Electrochemical measurements

Cyclic voltammetry measurements were performed in three different systems at 650 °C, namely Pt|YSZ shown in Fig.5.2 a), Ni|YSZ shown in Fig.5.2 b), and Ni|SiYSZ shown in Fig.5.3. In all systems the sweep rate was changed from fastest to slowest. The current at -1.6 V vs. $E_{Ref}$ increases with decreasing sweep rate in all the systems. Additionally, in all systems almost no hysteresis is observed. Despite the similarities there are a couple of very obvious differences between the three systems. A peak is observed in the current when the potential was swept in the increasing direction in the Ni|YSZ system. This peak is observed at -0.5 V vs. $E_{Ref}$ for the scan rate of 100 mV/s and it shifts towards lower potentials for lower scan rates, ending up at -0.7 V for the 1 mV/s scan rate. In addition to this peak, another oxidation peak is observed at higher potentials (between -0.3 and 0.4 V.
5.3. Results

Figure 5.2: Cyclic voltammetry performed on a) Pt|YSZ (36t38-0) and b) Ni|YSZ (36t32-0). Both sets were collected at 650 °C in humidified 9% H₂ in N₂. The inset in b) shows details of the CVs in the -0.2 down to -1.2 V region.

Figure 5.3: Cyclic voltammetry on the Ni|SiYSZ system (36t38-3) a) with 100, 50 and 20 mV/s scan rates and b) with 10, 5, 2 and 1 mV/s. These sets were collected at 650 °C in humidified 9% H₂ in N₂. The inset shows details of the CVs where small peaks were observed.

vs. $E_{Ref}$) in the Ni|SiYSZ. This second peak also shifts towards lower potential with decreasing scan rates. Furthermore, its amplitude decreases with decreasing sweep rate as well. An additional CV set was collected on the Ni|YSZ system at 750 °C and the CVs have similar features as at 650 °C of the same system. The CVs at 750 °C exhibit higher current densities and the oxidation peak is more pronounced.

For easier comparison, the currents were normalized to the triple phase boundary lengths for each system which were calculated using the SEM images of the YSZ samples after the experiments. For comparison purposes, the 10 mV/s sweeps are shown in Fig.5.4. The line current density at the lowest polarization (-1.6 V vs. $E_{Ref}$) is the highest in absolute value in the Ni|YSZ, suggesting that the presence
5.3. Results

![Figure 5.4: Comparison of the line current densities for the Pt|YSZ, Ni|YSZ and Ni|SiYSZ with sweep rate of 10 mV/s.](image)

![Figure 5.5: Comparison between the impedance before the CV measurement and the impedance after three sweeps at 100 mV/S.](image)

of silica in the system limits the current. An additional feature of the Ni|YSZ current behavior is that at polarizations close to equilibrium a current decrease is observed, while for the other two systems, the current remains almost zero up to -0.8 V.

After each scan rate, EIS were collected at OCV. Fig.5.3 shows an EIS collected on the pristine Pt|YSZ (i.e before any measurement was performed) and after three CVs at 100 mV/s. The time to record these voltammograms was 94 s and only half of this time was at polarizations below -0.8 V vs. $E_{Ref}$. However, one order of magnitude decrease in the low frequency resistance is observed. The rest of the impedance spectra collected in between the cyclic voltammograms are shown in Fig.5.6 and Fig.5.7 for the Pt|YSZ and Ni|SiYSZ. For both systems, the low frequency resistance decreases by a factor of approximately four while the high frequency resistance remained unchanged as illustrated by the detailed plot.
5.3. Results

Figure 5.6: a) OCV EIS measurements after each CV on the Pt|YSZ system (36t38-0).

b) Detailed plot of the high frequency region.

Figure 5.7: a) OCV EIS measurements after each CV on the Ni|SiYSZ system (36t38-3).

b) Detailed plot of the high frequency region.

of the EIS in the high frequency region, shown in Fig. 5.6 b) and Fig. 5.7 b).

Impedance spectra acquired upon decreasing polarization from 0 V down to -1.6 V vs \( E_{\text{Ref}} \) with a step of 0.1 V are shown in Fig. 5.8. The EIS under polarization close to zero are noisy in the low frequency range. As the polarization decreases the low frequency resistance decrease about 3 orders of magnitude from -0.8 V down to -1.6V. Inductive loops are observed at low frequency for polarizations lower than -1.3 V. With decreasing polarization, the inductive loops become more pronounced. Indications of transitioning from single arc to two arcs are observed in the EIS under -1.1 V polarization. After the EIS were collected, the polarization was released, and the sample stayed at the same temperature for more than 12 hours.

Finally, with the purpose of investigating the microstructure without allowing the sample to reoxidize, a YSZ sample was polarized for 90 min at -1 V vs. \( E_{\text{Ref}} \) using a Ni wire, and the polarization was kept during cooling. EIS was collected every 10 min and the corresponding EIS are shown in Fig. 5.9. The EIS are almost identical, indicating that all the changes (microstructural, chemical) happened...
5.3. Results

Figure 5.8: Impedance spectra of the Ni|YSZ system (36t34-3) under different cathodic polarizations. The frequency range of these measurements was 82 kHz down to 0.1 Hz.

Figure 5.9: EIS spectra under -1 V polarization (36t34-3). 1-5 indicate the order at which the impedances were collected.

the first 10 min of the polarization and steady state was achieved.

5.3.2 Post-mortem analysis

All tested samples were initially investigated optically followed by detailed SEM investigation to observe any changes in the microstructure of the samples. Additionally, the Ni and Pt wires were also investigated. All the samples described in this chapter had some coloration which could be seen in by naked eye. The following optical observations were noted:

1. **All the samples on which CV was performed:** A dark (black) small spot, which optical images showed that it was the wire-sample contact area,
5.3. Results

was surrounded by a light brownish/grayish circular area a few mm larger than the spot, as shown in top image in Fig.5.10. In the optical micrograph, the contact looks almost "metallic" as shown by the examples in the bottom image in Fig.5.10.

2. Ni|YSZ -1.0 V polarization during cooling: No black spot was observed but a large circular brownish/grayish was observed. It was not possible to find the contact area using the optical microscope.

3. Ni|YSZ stepwise polarization (36t34-3 CV set): A dark small spot surrounded by light brownish/grayish circular larger area.

Figure 5.10: Top: Optical image of a YSZ sample after cyclic voltammetry measurements using Ni as a working electrode at 650 °C (36t32-0). Bottom: Optical image of a contact area between the Ni wire and YSZ sample after cyclic voltammetry measurements at 650 °C (36t32-0).

SEM images of the samples on which CV was performed are shown in Fig.5.11.
5.3. Results

Fig. 5.12 and Fig. 5.14, which are images of the Pt|YSZ, Ni|YSZ and Ni|SiYSZ contact, respectively. The first of each image is a secondary ion (SE) image of the sample showing the general shape of the metal|sample contact. Detailed images of different regions, indicated by a coloured circle, were also taken using the SE detector. The corresponding images have the same color circle at the top right corner.

Figure 5.11: a) SEM image of the Pt|YSZ contact area after CV measurements at 650 °C. The rim of the contact region is outlined with a yellow dotted line. The red, green and blue circles indicate the positions where the images shown in b), c) and d) were taken. b) Detailed image close to the center of the contact, c) detailed image of the rim of the contact area and d) detailed image of a region where part of the YSZ was lifted off the surface.

After the CVs, the systems under investigation have undergone several redox cycles, resulting in very complex microstructural changes. The Pt|YSZ contact
5.3. Results

Figure 5.12: a) SEM image of the Ni\text/YSZ contact area after CV measurements at 650 °C. The green, red and yellow circles indicate the positions where the images shown in b), c) and d) were taken. b) Detailed image close to the center of the contact showing the presence of grain boundary phases, d) detailed image of a region where a YSZ grain was lifted off the surface and d) a detailed image of the rim of the contact area.

region exhibits a variety of microstructures. The center of the contact (Fig.5.11 b) is characterized by a very particular rough microstructure, were the usual grain structure of the YSZ is not visible. Close to center of the contact a part of the YSZ was removed, and SEM images of the Pt wire indicate that it stuck to the surface of Pt wire. An image of the rim of this region, marked by the blue dot in Fig.5.11 a), is shown in Fig.5.11 d). This image shows that the surface layer has a very different microstructure when compared to the bulk YSZ. This layer is very rough on the surface but it appears quite dense. It also does not follow the grain structure of the underlying YSZ. As one moves close to the edge of the contact region, the microstructure changes. An image of the outer edge of the contact is shown in Fig.5.11 c).

The microstructure of the YSZ contact area for the Ni\text/YSZ system shows some interesting microstructure changes. The inner part of the contact resembles a crater where the center is a highly uneven and grainy surface. Fig.5.12 b) shows a detailed image of a region in the inner surface of the crater. What is interesting about this image is that the grain boundaries are visible, pointing towards normal
5.3. Results

Figure 5.13: 3D AFM image of the rim of the contact area which resulted after CV measurements on the Ni|YSZ system

The microstructure of the grain is very different than the microstructure of a normal YSZ grain. Additionally, it appears that a thin grain boundary layer is formed. Another image, taken in the center of the crater which displays a region where a YSZ grain is pulled off the YSZ, is shown in Fig. 5.12 c). Fig. 5.12 d) shows a detailed image of the rim of the contact region. AFM measurements of the rim indicate that this region is elevated (approximately 500 nm) as shown in Fig. 5.13 and moving towards the inside of the contact a descending slope is observed where two distinct ledges/channels are observed. The SEM images of the Ni|SiYSZ contact after performing the CV measurements, have similar traits to the above described microstructural changes. A rough surface close to the rim (Fig. 5.14 b), a very textured, grainy and rough surface towards the center of the contact (Fig. 5.14 c), and regions where the YSZ grains were pulled off the surface (Fig. 5.14 d). Furthermore, in Fig. 5.14 d) some small inclusions of different (pointed by the green arrows) phases are observed in this redox layer. Even though this phase has different atomic mass, as indicated by the different shade in the SEM image, its texture seems to match the redox layer. Such inclusions were only observed on the Ni|SiYSZ system. Fig. 5.3 e) shows YSZ grains, the surface of which has been modified from the redox cycles, however the textured surface is observed along the grain boundaries, and it is not specific to a given depth.
5.3. Results

Figure 5.14: a) SEM image of the Ni|SiYSZ contact area after CV measurements at 650 °C. The blue, red, green, and yellow circles indicate the positions where the images shown in b), c), d) and e) were taken. b) Detailed image of the rim of the contact area, c) detailed image close to the center of the contact d) detailed image of a region where a YSZ grain was lifted off the surface and e) image of YSZ grains the surface of which were modified by the redox cycles.
5.4 Discussion

The cyclic voltammetry study of the three systems revealed some crucial differences. The Pt|YSZ is routinely considered very stable and considering the very low incorporation of the Pt into the YSZ crystal one would expect the formation of small amount to no Zr-Pt intermetallic compounds [137]. The cyclic voltammograms of Pt|YSZ system (Fig 5.2 a) show no indication of formation of Zr-Pt intermetallic compounds in the voltage range used to perform the CVs. When considering the Ni|YSZ, Ni-Zr intermetallic are expected at polarizations above the reduction of ZrO$_2$ [29] which according to thermodynamic calculations at 650 °C occurs at -2.4 vs. $E'_0(O_2)$ (or -1.34 vs. $E_{Ref}$). The peak observed in the CVs of the Ni|YSZ (Fig 5.2 b) when the voltage was swept upwards, reveals that certain species are oxidized at approximately -1.8 V vs. $E'_0(O_2)$ (or 0.74 V vs. $E_{Ref}$) this could be attributed to the oxidation of intermetallic species. This peak is present in the Ni|SiYSZ (Fig 5.3) as well. The charge transfer was calculated by integrating the peaks for both systems. The calculated charge transfer was not constant but it appeared to oscillate (maximum charge is about 2 or 3 times the minimum charge) for both systems. When normalized to the contact area these charges are very similar for both systems. Thus, the presence of a larger amount of silica impurities in the system did not influence the amount of Ni-Zr intermetallic compounds formed. The presence of silica impurities, however, influenced the current density at -1.6 V, which points to the fact that the increased amount of silica impurities prevents the spreading of the reaction zone. Thermodynamic calculations also predict the formation of Ni-Si intermetallic compounds as shown in Fig 5.15. Note that the phase diagram is calculated for 600°C. According to the Ellingham diagram shown in Fig 4.1 at 600 °C the SiO$_2$ is expected to reduce at a $pO_2$ of 1e-45 bar, while the phase diagram in Fig 5.15 suggests that intermetallic compounds start to form at $pO_2$ close to 1e-40. The five order of magnitude difference in the $pO_2$ translates to 0.2 V increase in the reduction potential. In other words, the formation of Ni-Si intermetallic compounds is expected to occur at approximately 0.2 V higher potential than the reduction of SiO$_2$. These are, of course, very rough estimates, and more data is needed to precisely determine these potentials. The presence of a second peak in the Ni|SiYSZ (Fig 5.3) at lower potentials, is an indication of the formation of the Ni-Si intermetallic. The formation of intermetallic is further supported by the microstructural changes observed in all systems. Even the Pt|YSZ interface was modified denoting some interaction between the YSZ and Pt. The absence of the reoxidation peak indicates that this layer might be too thin to have an impact on the current. The OCV impedance spectra obtained in between the CVs show no significant change in the
5.4. Discussion

Figure 5.15: The Ni-Si-O\textsubscript{2} phase diagram at 600\textdegree C. This diagram was provided by Ming Chen \cite{138}.

high frequency resistance, which indicates that as the polarization is released, the top layer of the contact is re-oxidised, thus creating the "same quality" contact. A significant decrease on the low frequency resistance occurs as the scan rate of the CVs decreases. After only three CVs at 100 mV/s (total time of 94 s) the low frequency resistance decrease by two orders of magnitude pointing towards a two orders of magnitude increase in the active area. Another four fold decrease is observed after the scan rate was decreased by a factor of 100 (i.e 100 times longer time to perform the CVs). Since it takes roughly 15 min to record a full EIS, the decrease in the low frequency resistance, indicates that the active area does not shrink to its initial value after the polarization is released. Such phenomenon is supported by the presence of the large brownish/grayish circular region around the contact region which according to literature is due to the trapping of electrons in the colour centers \cite{117}. A series of EIS where the polarization was stepped downwards was performed at 650 °C with the purpose of comparing it to the same data collected using the CAHT-SPM. The same trends are observed in in both cases, including the presence of low frequency inductive loops which become more prominent as the polarization decreases.

The behaviour of the EIS collected under different applied DC potential (the
5.5. **Conclusions and outlook**

Staircase series 36t34-3) shown in Fig.5.8 resembles the general behaviour observed on the Ni|YSZ impedance collected using the CAHT-SPM. These general features, such as the decrease of the low frequency resistance, the transition from one arc to two and the appearance of an inductive loop as the cathodic polarization is increased indicate that the reaction mechanism is very similar for the two different systems (micro-contact and macro-contact). Therefore, one can state that the inductive loop at high cathodic polarizations is associated with the modulation of the increased reaction area.

The SEM images reveal a possible mechanism related to the formation and oxidation of the intermetallic phases. The fact that YSZ grains were torn off the samples, points towards the fact that applied potentials and in a more pronounced manner the potential cycling weakens the grain boundary bonds. Such phenomenon, could be explained as follows: As the Ni migrates into the YSZ, it chooses the lowest energy path which could be along the grain boundaries where it encounters impurity phases. As the polarization is stepped downwards, Ni-Si and Ni-Zr phases are formed. These intermetallic phases are then re-oxidized as the polarization is stepped upwards. Therefore, morphological changes are observed on the top surface of the YSZ as well as along the grain boundaries, and as the Ni or Pt wire is pulled off, the YSZ breaks at its weakest points. It was noted from the SEM images of the cross-section of the Ni wires, that the contact surface of the Ni had a small concave curvature, which also indicates that Ni migrates towards the YSZ.

**5.5 Conclusions and outlook**

Electrochemical evidence of the formation of Ni-Si and Ni-Zr intermetallic compounds was provided using CV on point contact two electrode configuration. The post-mortem microstructure analysis of the samples further supports the fact that intermetallic compounds are created between Ni and YSZ resulting in a complex interface microstructure. The CV measurements show no indications of Zr-Pt intermetallic formation, however microstructural changes on the Pt|YSZ surface point towards interaction between the Pt and YSZ. The electrochemical impedance spectra reveal an expanding reaction zone which does not compress to its original size even after the polarization is released. Such phenomenon is attributed to the trapping of the electrons in the F-centers in the YSZ. The trapping of the electrons in the F-centers is associated with coloration of the YSZ which is optically observed in all the samples.

The detailed microstructural investigation of the three different system (Pt|YSZ,
5.5. Conclusions and outlook

Ni|YSZ and Ni|SiYSZ) reveal the following:

1. The most microstructural changes were observed on samples which were exposed to several redox cycles.

2. As the Ni migrates into the YSZ, it chooses the lowest energy path which could be along the grain boundaries, therefore the reduction and re-oxidation of the intermetallic phases starts at the Ni-YSZ interface and at the grain boundaries.

3. Si-Ni intermetallic are also created and impurity phases are observed at the grain boundaries. The re-oxidation of such intermetallic weakens the grain boundaries causing YSZ grains to be torn off the sample.

This study was mainly performed to supplement the results described in the previous chapter since there are various limitations related to using very small working electrodes, as mentioned in the introduction of this chapter. The EIS measurements under DC polarizations revealed similar behaviour to the EIS obtained in the CAHT, indicating that the processes in the micro- and macro-contact systems are similar. The CV measurements revealed some interesting features, which were not observed in the CAHT measurements, which in combination with chemical analysis can be used to support thermodynamic calculations in regard to the formation of Ni-Si-Zr intermetallic compounds. Therefore, obtaining CVs which have a better voltage resolution at the high sweep rates could reveal more information about these systems.
Chapter 6

Study of Sr-substituted lanthanum ferrite model electrodes

6.1 Introduction

The studies summarized in Section 1.4.2.2 have improved understanding of the oxygen reduction reaction mechanism. However, due to the large number of parameters which influence the oxygen exchange rate at the electrodes, a comprehensive understanding of the reaction mechanism has not been achieved yet. The experiments presented in this chapter were performed on dense circular LSF (La_{0.6}Sr_{0.4})_{0.99}FeO_{3-δ} microelectrodes. The work done here, in addition to the electrochemical measurements, investigates microstructural and chemical changes of the surface of the microelectrodes, which were exposed to different polarizations. The diameter of the used electrodes were 100, 50 and 20 µm and their thickness was in the range between 250 and 300 nm.

6.2 Oxygen electrode processes

This chapter has the aim of investigating the oxygen reduction reaction at the oxygen electrode which can be summarized by the following reaction:

\[ O_2(gas) + 4e^-(electrode) \leftrightarrow 2O^{2-} \]  \hspace{1cm} (6.2.1)

Even though this overall equation seems rudimentary, there are several intermediate complex steps which include: the diffusion of oxygen molecules in the gas phase, adsorption of the oxygen on the electrode surface, dissociation of the
6.3. LSF structure

oxygen molecules into atomic species, charge transfer between the electrode and the oxygen species, incorporation of the oxygen ions into the vacancies present in the electrode, bulk transport of the oxygen ions to the electrode/electrolyte interface and finally the crossing of the interface of the oxygen ions. Depending on the properties of the electrode, two different mechanisms might occur. For electrodes which have very low ionic conductivity, the adsorbed oxygen molecules diffuse on the surface of the electrode until they reach the active triple phase boundary (TPB) where the gas phase, the electrode and the electrolyte meet. When the electrode material is a mixed electronic and ionic conductor (MIEC), after the oxygen dissociation, the oxygen ions can travel through the bulk of the electrode, increasing this way the active region from only the TPB, to the electrode area. Since Eq.6.2.1 is a multistep reaction, the kinetics of the reaction is defined by the slow processes, which are otherwise referred to as the rate determining steps.

6.3 LSF structure

Different ABO$_3$ perovskite-type solid solutions, where the A-site cation is a rare and/or alkaline earth such as La and Sr, and the B-site cation is a reducible 3d transition metal such as Fe, Co, Cr etc., have been studied extensively due to their electronic and catalytic properties and their technological relevance. These perovskite materials are considered as possible candidates for air electrodes in SOFC/SOEC systems, chemical sensor elements, catalysts etc. Information about their defect chemistry [139, 140], thermodynamics as well as their electronic and ion transport properties are reported in literature. The high electronic conductivity of such materials results from the mixed valence state of the 3d transition metal, while the large oxygen nonstoichiometry is related to the high diffusivity of the oxide ions [140].

The ABO$_3$ crystal structure takes its name from the perovskite mineral CaTiO$_3$ after the Russian mineralogist L.A. Perovski, and it consists of a face centred cubic structure (FCC) where the A-cations occupy the cube corners while the oxygen ions occupy the face centred positions. The B-cation occupies the center of the cube as shown in Fig.6.1. The octahedral symmetry around the B transition metal cation, very often provides a metallic or semiconducting band structure at elevated temperatures which leads to high electronic conductivity [141]. Additionally, this structure can support a large number of oxygen vacancies, thus making these materials good ionic conductors. The bulk oxygen ion transport occurs by random hoping of the oxygen vacancies [141] and is illustrated in Fig.6.2.
6.3. LSF structure

Figure 6.1: Perovskite structure

Figure 6.2: Oxygen ion transport in the perovskite bulk by random hopping of the oxygen vacancies as described in Ref. [141]
6.4 Defect chemistry and oxygen stoichiometry of LSF

In this section, the defect chemistry and oxygen nonstoichiometry of $La_{1-x}Sr_xFeO_{3-\delta}$ will be described in terms of point defects, where the charge carriers are assumed to be localized on some Fe sites. In the $La_{1-x}Sr_xFeO_{3-\delta}$, the main defects are $V_O$, $Sr_La^\prime$, $Fe^\prime_Fe$ and $Fe_Fe^\prime$ [139, 140]. When the $La^{3+}$ in the lattice is substituted by $Sr^{2+}$, electroneutrality requires charge compensation, which is achieved either by the creation of a hole localized close to the B-site (i.e. valence change of Fe) or by the formation of oxygen vacancies [139]. This can be expressed as follows [140]:

$$[Sr_La^\prime] + [Fe_Fe^\prime] = 2[V_O] + [Fe_Fe^\prime]$$  \hspace{1cm} (6.4.1)

where

$$[Sr_La^\prime] = x$$ \hspace{1cm} (6.4.2)

$$[V_O] = \delta.$$ \hspace{1cm} (6.4.3)

Eq.6.4.3 holds true since the solid solution is oxygen deficient. Using Eq.6.4.2 and Eq.6.4.3, Eq.6.4.1 can be written as follows:

$$x + [Fe_Fe^\prime] = 2\delta + [Fe_Fe^\prime]$$ \hspace{1cm} (6.4.4)

Considering that in oxidizing conditions $Fe_Fe^\prime \ll Fe_Fe^\prime$, Eq.6.4.4 can be expressed as

$$x = 2\delta + [Fe_Fe^\prime].$$ \hspace{1cm} (6.4.5)

For sufficiently low $pO_2$, the $[Fe_Fe^\prime]$ approaches zero and $\delta = x/2$. While in reducing atmospheres the $Fe_Fe^\prime \gg Fe_Fe^\prime$ the following expression is valid

$$x + [Fe_Fe^\prime] = 2\delta$$ \hspace{1cm} (6.4.6)

The above equations indicate that the behaviour of non-stoichiometry with changing $pO_2$ can be classified in three different regions as shown in Fig.6.3. In the first region the non stoichiometry is described by Eq.6.4.5, in the second region the electronic charge carriers are equal to each other, i.e. $[Fe_Fe^\prime] = [Fe_Fe^\prime]$ and the $\delta = x/2$, while in the third region the non stoichiometry is described by Eq.6.4.6.

In Kröger-Vink notation [142] the reaction between the defects of $La_{1-x}Sr_xFeO_{3-\delta}$ and the oxygen gas phase can be written as follows:

$$\frac{1}{2}O_2(gas) + V_O + 2Fe_Fe^\prime \rightarrow O_O^x + 2Fe_Fe^\prime$$ \hspace{1cm} (6.4.7)
6.5. Equivalent circuits and chemical capacitances

Interpretation of electrochemical impedance data are usually done by using equivalent circuits that can represent the system which is being studied. Therefore,

\[
2Fe_{Fe}^x \leftrightarrow Fe_{Fe}^e + Fe_{Fe}^{e'},
\]

the \([Fe_{Fe}^{e'}]\), equivalent to electron concentration, increases. The mobility of the \(Fe_{Fe}^{e'}\) is influenced by the amount of oxygen vacancies, because the electronic transfer occurs along the Fe-O-Fe chains \[143]. The increase in the oxygen vacancies, causes disturbance in these chains resulting in a decrease of hopping of the electronic charge carriers \[144]. Thus, LSF is less conductive in reducing conditions.

6.5 Equivalent circuits and chemical capacitances

Figure 6.3: A schematic of the oxygen non-stoichiometry and the other defect concentrations versus the Log \(pO_2\) for LSF. This diagram was reproduced from Ref.\[140\]
6.5. Equivalent circuits and chemical capacitances

In this section a widely used equivalent circuit, shown in Fig.6.4, proposed by Jamnik and Maier [78], is briefly described. This equivalent circuit represents the oxygen exchange and diffusion at a mixed electronic and ionic conductor electrode. As shown in Fig.6.4 a), it is a transmission line composed of three trails; the ionic, the electronic and the displacement current [77]. Chemical capacitances are used to connect the ionic and electronic trails. In the case of an electrode material which has a very high electronic conductivity, the electronic trail will short circuit as shown in Fig.6.4 b) and the contact resistance of the surface will be negligible. A further simplification is shown in Fig.6.4 c), where the ionic trail is also short circuited in the bulk due to the high ionic conductivity. Since the chemical capacitance \( C_{chem} \) is much larger than the parallel surface capacitance \( C_s \), \( C_s \) can be omitted, therefore the reaction occurring at the gas|LSF interface is described by the surface resistance \( R_s \) and the chemical capacitance \( C_{chem} \). This
further modification of the circuit gives a final, simple equivalent circuit shown in Fig. 6.4 d), in which the $R_i$ and $C_i$ are the resistance and capacitance associated with the transfer of the oxygen ions across LSF|CGO interface. To account for the ohmic resistance of the electrolyte, an additional element ($R_b$) was added. The capacitances were changed to constant phase elements, to account for non-perfect capacitive behaviour. This equivalent circuit has been used by several authors [49–51, 74, 77] and it seems to represent the system quite well. The chemical capacitance of an electrode is associated with the oxygen nonstoichiometry. By definition capacitance ($C$) is the change of charge ($dQ$) with changing potential ($dE$):

$$C = \frac{dQ}{dE} \quad (6.5.1)$$

One can calculate the charge associated with a stoichiometry change as follows [145]:

$$dQ = -\frac{2LAFd\delta}{V_m} \quad (6.5.2)$$

where $L$ and $A$ are the thickness and area of the film respectively, $V_m$ is the molar volume of the film material and $F$ is the Faraday’s constant. The change of the potential can be expressed in terms of $pO_2$ using Nernst equation:

$$dE = -\frac{RT}{4F} \ln pO_2. \quad (6.5.3)$$

Combining the above equations, the chemical capacitance can be calculated as follows [145]:

$$C_{chem} = -\frac{8F^2L}{RTV_m} \frac{d\delta}{d\ln pO_2}. \quad (6.5.4)$$

The chemical potential can be calculated using Eq. 6.5.4 only if one assumes that the change in oxygen chemical potential (represented by $d\ln pO_2$) is dependent only on changes in the applied potential [145].

6.6 Experimental

6.6.1 Microelectrode history

One can generally find a huge discrepancy in the literature when studying perovskite materials for SOFC/SOEC applications, and one reason that could explain these discrepancies could be the sample history, such as exposure to elevated temperatures, different atmospheres and high vacuum which might alter the surface
6.6. Experimental

chemistry and morphology. Therefore, a detailed history of the sample environments is describes in this section.

The thin films used to produce the microelectrodes were deposited at 600 °C and because the ablation rate of LSF was very low (approximately 0.03 Å/pulse), the time required to deposit a 300 nm LSF thin film was 2 hours and 45 min using a pulsing frequency of 10 Hz. Small amount of cation cross diffusion between LSF and CGO is expected during this time. During the argon ion etching, which was performed after photolithography, the exact temperature that the samples reached was unknown because the instrument used was not equipped with any temperature monitoring device for the sample. However, the sample was not exposed to temperatures higher than 200 °C, because the photoresist did not burn during the etching. Once the microelectrode samples were cleaned the sample were exposed to high vacuum several times as a result of the used characterization techniques which require high vacuum. Before testing the microelectrodes in the CAHT-SPM, they were heat treated at 750 °C for 16 hours. The heat treatment was performed to avoid any temperature effect during the electrochemical measurements.

6.6.2 Sample characterization

The microelectrode samples were fabricated using PLD to deposit the thin film layers and photolithography to pattern the microelectrodes, as described in Chapter 3. Different thickness LSF films were deposited and investigated to observe how thickness the crystallinity, growth type and surface quality of the film. Prior to photolithography, XRD was used to investigate the degree of crystallinity and preferential orientation of the thin film.

SEM was used to investigate the microstructure of the film surface, the interface between YSZ/GCO and CGO/LSF. The SEM images were obtained without any carbon coating with the purpose of not contaminating the surface of the film. Due to the low electronic conductivity of the YSZ (substrate) at room temperature, local charging of the sample was observed during the scanning. For this reason, most of the SEM images were taken using a very low accelerating voltage of 1.5-2.0 kV. The cross sections of some of the films were investigated using SEM, mainly to determine thickness and observe the quality of the film.

Once the microelectrodes were fabricated using photolithography, ToF-SIMS, SEM and AFM were used to gain the most information about the chemistry and microstructure of the microelectrodes. These techniques were used on the as deposited, heat treated and tested microelectrodes to observe changes after each
step so that temperature effects could be distinguished from electrochemical effects. ToF-SIMS high resolution images were taken using mainly positive ion mode. Negative ion mode was only used for some microelectrodes just to observe if any additional information could be obtained. Usually, when imaging microelectrode samples, a large scale ToF-SIMS image was taken first to observe the whole sample. Such images give a general idea if the sample was contaminated during handling. Then, individual electrodes were imaged, providing this way chemical information for the specific electrode. SIMS was the first characterization technique used, since electron scanning during SEM imaging has been shown to influence the ToF-SIMS images [146].

6.6.3 Electrochemical measurements

The heat treated microelectrode samples were carefully placed on the hotplate inside the CAHT-SPM and held in place by three alumina pins, as shown in Fig.6.5. One of the pins was used to press down the platinum wire to one of the macro-electrodes, which was used as a counter electrode. A PtIr tip was mounted on the probe holder and used to create contact with the microelectrodes. Note that the counter electrode and the microelectrodes were all on the same side of the sample (planar configuration). This configuration was used to avoid having large temperature difference between the working and counter electrodes. Even in the planar configuration, there is some temperature difference due to the size difference between the counter and working electrode [147].

For the data shown in this chapter, two different samples were used, and each one of them was tested in the CAHT-SPM only once. The electrochemical data include EIS, which were either at open circuit voltage (OCV) or at different DC polarizations. Before each impedance spectrum a 5 min conditioning period was applied. The DC current was recorded during this time period. The EIS measurements were recorded in the frequency range from 82 kHz to 0.082 Hz using 10 mV rms and 7 points per decade. EIS with a superimposed DC voltage of -250 mV, 0 V and +250 mV versus the reference potential were recorded at 500, 650, 600, 650 and 700 °C using the 100 μm microelectrodes as indicated in Table 6.1. OCV EIS were also recorded when the sample was cooled at 600 and 500 °C. Such measurements were mainly recorded to observe if the heat treatment during the electrochemical measurements had degraded the microelectrodes. OCV EIS measurements were collected on the 50 and 20 μm microelectrodes as well.

Anodic and cathodic series of impedances (referred to as staircases) were collected at 600 and 700 °C. The 100b2 microelectrode was used for the cathodic staircases which included EIS with applied DC potentials from 0 to -300 mV with a 50 mV
6.6. Experimental

step at 600 °C and a 100 mV step at 700 °C. Similarly, the anodic series was collected in the 100b3 microelectrode with DC polarizations from 0 to +300 mV. After each series, an OCV EIS was collected to observe if the polarizations had permanently modified the electrochemical performance of the microelectrode.

Figure 6.5: Top view of the sample placed on the furnace in the CAHT-SPM, showing the placement of a microelectrode sample on the CAHT-SPM furnace.

Table 6.1: Summary table of the measurements performed on each microelectrode with the corresponding temperatures at which the measurements were collected

<table>
<thead>
<tr>
<th>Microelectrode</th>
<th>Type of measurement</th>
<th>Temperature °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>100a1</td>
<td>ToF-SIMS depth profiling</td>
<td>As deposited</td>
</tr>
<tr>
<td>100a2</td>
<td>OCV EIS</td>
<td>500, 550, 600, 650, 700</td>
</tr>
<tr>
<td>100a3</td>
<td>-250 mV EIS</td>
<td>500, 550, 600, 650, 700</td>
</tr>
<tr>
<td>100a4</td>
<td>+250 mV EIS</td>
<td>500, 550, 600, 650, 700</td>
</tr>
<tr>
<td>100b1</td>
<td>ToF-SIMS depth profiling</td>
<td>600 and 700</td>
</tr>
<tr>
<td>100b2</td>
<td>Cathodic Staircase EIS</td>
<td>600 and 700</td>
</tr>
<tr>
<td>100b3</td>
<td>Anodic staircase EIS</td>
<td>600 and 700</td>
</tr>
<tr>
<td>100b4</td>
<td>Untouched</td>
<td>NA</td>
</tr>
<tr>
<td>50a1</td>
<td>CV</td>
<td>500</td>
</tr>
<tr>
<td>50a2</td>
<td>CV</td>
<td>600</td>
</tr>
<tr>
<td>50a3</td>
<td>CV</td>
<td>700</td>
</tr>
<tr>
<td>50b1</td>
<td>OCV EIS</td>
<td>500, 600, 700</td>
</tr>
<tr>
<td>50b9</td>
<td>Conductance scanning</td>
<td>500, 550, 600, 650, 700</td>
</tr>
<tr>
<td>20b21</td>
<td>OCV EIS</td>
<td>600, 700</td>
</tr>
</tbody>
</table>

CV measurement were performed at 500, 600 and 700 °C with sweep rates of 100, 50, 20, 10, 5, 2, 1 mV/s. The voltage range used was from 0 to -300 mV
and then to +300 mV and back to zero. Three sweeps were taken at each sweep rate, except in the case of 2 and 1 mV/s, where only two sweeps were recorded. Each set of cyclic voltammograms was recorded using different 50 µm electrodes, therefore three different 50 µm electrodes were used for CV measurements as shown in Table. 6.1.

Furthermore, one 50 µm electrode (50b9) was used to observe the changes in the surface conductance with temperature. Once the desired sample temperature was reached, a waiting period of 30 min was used to make sure that the system was in thermal equilibrium, and then a conductance scan of the 50b9 microelectrode was performed. The same microelectrode was scanned once more before the temperature was changed.
6.7 Results

6.7.1 XRD

Several different depositions were made on single crystals YSZ with different deposition parameters, which resulted in films with different thicknesses.

Figure 6.6: XRD diffractogram of a) YSZ single crystal b) a dense thin film containing 50 nm of CGO and 80 nm of LSF c) a dense thin film containing 50 nm of CGO and 180 nm of LSF and d) a dense thin film containing 50 nm of CGO and 250 nm of LSF. All thin films were grown in single crystal YSZ.

For all the depositions, the parameters for depositing the CGO barrier layer were
kept the same, resulting in approximately the same CGO film thickness (50 nm). The deposition time of the LSF film was varied. Cross-sections of the samples were investigated by SEM to approximate the film thickness. The diffractogram of a YSZ substrate and of the three different samples with LSF film thicknesses of 80, 180 and 250 µm are shown in Fig. 6.6. The XRD diffractogram of the YSZ substrate (Fig. 6.6 a) shows two main peaks corresponding to the (200) and (400) reflection of the cubic YSZ. The XRD spectra of the film containing 50 nm of CGO and 80 nm of LSF clearly show the (200) and (400) peak of CGO and the (100) and (200) of LSF, indicating that the LSF film exhibited epitaxial or columnar growth with the 100 preferential orientation. As the thickness of the film increased, the LSF peaks became more prominent. In the case of the 250 nm LSF film (shown in Fig. 6.6 d) an additional peak was observed. This peak corresponds to the LSF (111) reflection. The peak positions are indicated in Table 6.2. Using Bragg’s law one can deduce that the lattice parameters for the YSZ and CGO are 0.511 nm and 0.541 nm respectively, while for the LSF the lattice distance decreases from 0.396 nm to 0.392 nm with increased thickness.

<table>
<thead>
<tr>
<th></th>
<th>YSZ (200)</th>
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6.7.2 ToF-SIMS

ToF-SIMS analysis was performed on the as deposited (LSF6-AD) sample, as well as after the sample was heat treated (LSF6-HT), to observe the chemical changes of the bulk and surface of the microelectrodes due to the heat treatment. A 100 µm electrode was analysed in each case, 100a1 and 100b1, respectively, as shown in Table 6.1. The depth profiles before and after heat treatment are shown in Fig. 6.7. Note that since no calibration was performed to convert the sputtering time to film thickness, the depth profiles are shown in terms of sputtering time. The individual ion intensities were normalized to the highest intensity of that particular ion.

Fig. 6.7 a) indicates that the interfaces between the layers are relatively sharp.
6.7. Results

Figure 6.7: a) and b) Depth profiles performed on the as fabricated microelectrode sample. c) and d) Depth profiles performed on the heat treated microelectrode sample.

and small cross-diffusion of ions is observed. The bulk properties of the LSF film appear uniform and a small Fe and Sr enrichment of the surface is noticeable. Fig. 6.7 b) shows the ToF-SIMS depth profiles of impurity ions which are common in the raw materials (CGO, LSF and YSZ). The noisy Al$^+$ and Si$^+$ signals indicate that their concentration is close to the background chemical noise, thus very low. The Al$^+$ signal is higher in LSF than in CGO and YSZ. Potassium and sodium impurities seem to prefer the surface of the sample, while calcium impurities are concentrated at the LSF/CGO and CGO/YSZ surface.

The depth profile of the heat treated electrode was performed on 100b1 and shown in Fig. 6.7 c) and d). The surface of this microelectrode seems to have a much higher content of iron and lanthanum than the bulk. The bulk to surface ratio of the Fe$^+$ signal ($Fe^+_b/Fe^+_s$) is approximately 0.3 for the heat treated microelectrode compared to approximately 0.8 in pristine one. Similarly, the La$^+_b/La^+_s$ changes from approximately 1 to 0.8. The surface, however, shows lower content of strontium when compared to the bulk after the heat treatment. The heat treatment did not modify drastically the distribution of the impurities as
shown in Fig. 6.7 d). The Na⁺, K⁺, Al⁺ and Ca⁺ signals show the same behaviour as in Fig. 6.7 b). The Si⁺ signal on the other hand, indicates that Si is found mainly on the surface after the heat treatment. Moreover, the heat treatment of the sample seems to have modified the chemical composition of the LSF/CGO and CGO/YSZ interface as shown in Fig. 6.8. Fig. 6.8 a) shows a zoomed in region of the depth profiles of the as deposited microelectrode (100a1) close to the LSF/CGO and CGO/YSZ interfaces while Fig. 6.8 b) shows the same region of the heat treated microelectrode (100b1). The Sr⁺, La⁺ signal of the heat treated microelectrode extends deeper into the CGO, indicating that these cations have diffused into the CGO due to the heat treatment.

Figure 6.8: Zoom in of the depth profiles around the LSF/CGO and CGO/YSZ interfaces of a) the as deposited and b) of the heat treated microelectrode

Additionally, ToF-SIMS high resolution images of individual electrodes were acquired. The ion images of a typical 100 µm microelectrode after deposition is shown in Fig. 6.9. In addition to the signals of the host elements (Sr⁺, Fe⁺, LaO⁺, CeO⁺, GdO⁺ and Zr⁺) the signal of Na⁺, K⁺, Mg⁺, Si⁺, Ca⁺ and Cr⁺ were imaged as well, with the purpose of gaining information on the distribution impurities on the sample surface. The same microelectrode was imaged after the heat treatment and the ToF-SIMS images are shown in Fig. 6.10. The heat treatment caused several changes on the surface. Small particles with higher content of Sr have appeared in the center of the microelectrode (refer to the Sr⁺ image in Fig. 6.10). If one compares the Sr⁺ signal outside the microelectrode in Fig. 6.9 with its corresponding signal in Fig. 6.10, it is evident that in the as deposited microelectrode the Sr⁺ signal outside the microelectrode is almost zero, while in the heat treated it is higher. In the heat treated microelectrode the CeO⁺ and GdO⁺ signal outside of the microelectrode become lower. The Na⁺ and K⁺ signals become visible on the surface after heat treatment. Detailed images of the edge and center of the microelectrode are shown in Fig. 6.11 and Fig. 6.12.
6.7. Results

Figure 6.9: High resolution imaging of a typical 100 µm after cleaning (100a3) of LSF6-AD sample.
6.7. Results

Figure 6.10: High resolution imaging of a typical 100 µm after heat treatment (100a3) of LSF6-HT sample.
6.7. Results

Figure 6.11: High resolution imaging of the edge of a typical 100 µm after heat treatment (100a3) of LSFe-HT sample.
6.7. Results

Figure 6.12: High resolution imaging of the center of a typical 100 µm after heat treatment (100 hrs) of LSF6-HT sample.
respectively. Fig.6.11 indicates that there is a region, approximately 3 µm wide, close to the edge of the microelectrode which has lower content of Na and K and slightly higher content of Ca impurities. Fig.6.12 confirms that the small particles have higher content of Sr and lower content of La. These particles appear to have the same content of Fe. The impurity distribution is almost constant and is not affected by the presence of these impurities. The CeO⁺ signal is not zero in the center of the microelectrode as it should have. Similar behaviour was observed on the 50 µm and 20 µm electrodes.

6.7.3 LSF film microstructure

The microstructure of the deposited films and of the microelectrodes was thoroughly investigated using AFM and SEM. Two PLD depositions, containing both CGO and LSF, were performed to gain information about the laser ablation rate. The fracture cross-sections of these samples were investigated using SEM and the obtained images are shown in Fig.6.13. Fig.6.13 a) indicates that both layers were grown epitaxially while in the case of the 180 nm thick LSF film (Fig.6.13 b) there are indications that the LSF film might be columnarly grown.

Figure 6.13: SEM images of a) the cross-section of a thin film consisting of 50 nm of CGO and 80 nm of LSF. b) the cross-section of a thin film sample consisting of 50 nm of CGO and 180 nm of LSF.

An AFM image of a pristine 50 µm electrode is shown in Fig.6.14. The edge of the microelectrode slopes for only 3 µm, which is small compared to the diameter of the microelectrode. The thickness of this microelectrode was 242 nm as indicated by the profile (Fig.6.14). SEM images of four different sizes of microelectrodes are shown in Fig.6.15. The electrodes with diameter 100 µm and 50 µm appear to have a very regular circular shape while the electrodes with 20 and 10 µm diameter have more irregular shapes. Additionally, the 10 µm electrode has been etched in
the center, thus indicating that the photolithography and etching procedure was not optimized for small features.

![AFM image of the edge of a 50 µm electrode and its height profile shown with the blue line.](image1)

Figure 6.14: AFM image of the edge of a 50 µm electrode and its height profile shown with the blue line.

![Typical microelectrodes of different diameters.](image2)

Figure 6.15: Typical a) 100 µm, b) 50 µm, c) 20 µm, and d) 10 µm in diameter microelectrodes. A 1.5 kV acceleration voltage and the secondary electron detector were used to image all of the microelectrodes.

The smaller microelectrodes, images of which were not shown, have a donut shape. Therefore, the microelectrodes with diameter smaller than 20 µm were not used.
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Figure 6.16: a) SEM image of a typical 100 µm electrode in its pristine state. This particular image is of 100a3 microelectrode. b) and c) correspond to magnified regions in the edge and center of the microelectrode, respectively. Similarly, d), e) and f) are images of the same microelectrode after the heat treatment. The colorful dots match the color of the rectangles to approximately indicate the region where the magnified images were taken.

for any type of measurements. All images shown in Fig.6.15 were imaged using a 1.5 kV acceleration voltage and the secondary electron detector.

As mentioned previously, the microelectrodes were imaged before and after the heat treatment. Fig.6.16 a), b) and c) show a 100 µm electrode and details of the microelectrode edge as well as center, respectively. The same microelectrode was imaged after the heat treatment and shown in Fig.6.16 d), e) and f). The edge of the microelectrode after heat treatment (Fig.6.16 e) has a different microstructure, slightly more porous, than the edge prior to the heat treatment (Fig.6.16 b).

Additionally, the heat treatment caused the formation of nano- and micro-particles which were mainly concentrated close to the center of the microelectrodes. This is clearly observed by comparing Fig.6.16 a) with d). A higher magnification of these particles, which appear to be crystalline structures, is shown in Fig.6.16 f). The ToF-SIMS images shown previously (Fig.6.10 and Fig.6.12) indicate that these particles contain higher content of Sr and lower content of La when compared to the surface. An EDX line scan, shown in Fig.6.17 is in agreement with the SIMS results. Additionally, the EDX line scan indicates that the oxygen content of these particles is higher than the oxygen content of the surface. Prior to performing any electrochemical measurements, the microelectrode sample was cleaned using
6.7. Results

ultra sound in distilled water for 5 min. SEM images of the sample indicate that the ultrasound cleaning was able to remove these particles as shown in Fig. 6.18. Note that there is some small particles in Fig. 6.18 but they are different in shape and size than the particles in Fig. 6.16 d).

Figure 6.17: EDX line scan across a particle aquired using 15 kV accelerating voltage. The green line on the bottom SEM image indicates the line scan.

Figure 6.18: Secondary electron SEM image showing that the Sr rich particles were removed from the surface at the center of the microelectrodes.
6.7. Results

6.7.4 Electrochemical measurements

6.7.4.1 Electrochemical impedance spectroscopy

Electrochemical impedance spectra with and without DC polarization were recorded on 100 µm electrodes at different temperatures. Fig. 6.19 a) shows the EIS spectra where no DC polarization was applied. The spectra show that the electrode is blocking and its behaviour is purely capacitive. The corresponding log-log plots of $Z_{im}$ versus frequency are shown in Fig. 6.19 b).

![Figure 6.19: a) Nyquist and b) Log-log plots of $Z_{im}$ versus frequency of OCV electrochemical impedance recorded at different temperatures. The same 100 µm electrode (100a2) was used for all these measurements.](image)

Figure 6.19: a) Nyquist and b) Log-log plots of $Z_{im}$ versus frequency of OCV electrochemical impedance recorded at different temperatures. The same 100 µm electrode (100a2) was used for all these measurements.

![Figure 6.20: a) Nyquist and b) Log-log plots of $Z_{im}$ versus frequency of electrochemical impedance recorded under -250 mV DC polarization at different temperatures. The same 100 µm electrode (100a3) was used for all these measurements.](image)

Figure 6.20: a) Nyquist and b) Log-log plots of $Z_{im}$ versus frequency of electrochemical impedance recorded under -250 mV DC polarization at different temperatures. The same 100 µm electrode (100a3) was used for all these measurements.
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Figure 6.21: a) Nyquist and b) Log-log plots of $Z_{\text{im}}$ versus frequency of electrochemical impedance recorded under +250 mV DC polarization at different temperatures. The same 100 $\mu$m electrode (100a3) was used for all these measurements.

Figure 6.22: EIS recorded on 100 $\mu$m electrodes under a) -250 mV b) +250 mV DC applied potential at 500°C. EIS under c) -250 mV d) +250 mV DC applied potential at 600°C. Open circuit EIS were recorded before and after (noted as OCV and OCV after respectively) the impedance spectra which were recorded under polarization.

The temperature dependency of the impedance spectra at open circuit, under
cathodic and anodic polarizations is presented in Fig. 6.19, 6.20 and 6.21 respectively. For the EIS which were recorded under anodic or cathodic polarization, an OCV EIS was recorded before and after the polarized EIS as shown in Fig. 6.22. The OCV EIS were recorded with the purpose of observing if the polarization affected the performance of the micro electrode. In Fig. 6.19, 6.20 and 6.21 the high frequency intercept with the $Z_{\text{real}}$ axis does not show a particular trend with temperature. However, the log-log plots of $Z_{\text{im}}$ versus frequency show a dependency of the $Z_{\text{re}}$ with respect to sample temperature in the $10^1$ to $10^4$ Hz region in the case of EIS recorded under no polarization and anodic polarization. As the temperature increases, the $Z_{\text{real}}$ decreases in this region. In the case of the impedance spectra recorded under cathodic polarization, this trend was not observed.

In addition to the dominating low frequency capacitance, the impedance spectra have some additional features. There is a high frequency intercept with the $Z_{\text{re}}$ axis as well as a 45 degree straight line in the high to intermediate frequency range. In the case of impedance spectra recorded at open circuit, the 45 degree straight line is more visible at 500 °C, as shown in Fig. 6.19. Additionally, in the smaller electrodes this feature appears more pronounced, as shown in Fig. 6.23 and Fig. 6.24.

Figure 6.23: EIS from three microelectrodes with different sizes. The inset shows a magnification of the high frequency region of the same impedance spectra. These impedance data were recorded at 700 °C in air.
6.7. Results

Fig. 6.23 and Fig. 6.24 show the impedance spectra recorded at 700 °C using three different size electrodes (100, 50 and 20 µm) at open circuit and when a -200 mV DC polarization was applied. In both cases the high frequency intercept with the $Z_{\text{re}}$ decreases with the increase of the size of the microelectrodes. However, the increase is not proportional with the inverse diameter as one would expect from Newman’s formula \[125\].

![Graph showing impedance spectra](image)

Figure 6.24: EIS carried out while a -200 mV DC polarization was applied in three different size microelectrodes. The image to the right shows a magnification of the high frequency region of the same impedance spectra. These impedance data were recorded at 700 °C in air.

6.7.4.2 Potential dependence

In order to investigate the effect of polarization on the impedance of the LSF microelectrodes, EIS measurements were carried out in 100 µm microelectrodes under polarization at 600 and 700 °C, and the resulting EIS are shown in Fig. 6.25 and Fig. 6.26 respectively.

The increasing anodic polarization at 600°C (Fig. 6.25a) influences the impedance in the following manner:

1. The low frequency region starts to resemble the behaviour of an RQ circuit rather than the behaviour of a capacitor.
2. The high frequency intercept shifts towards lower $Z_{\text{re}}$ values.
3. The 45 degree straight line at the high/intermediate frequencies becomes more prominent at the higher anodic polarizations.

The increasing cathodic polarization at 600°C (Fig. 6.25b) on the other hand causes the following changes:

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6.7. Results

Figure 6.25: EIS spectra under varying a) anodic DC polarization (100b3) and b) cathodic polarization (100 b2) at 600 °C. Each set was collected from different 100 µm microelectrodes.
6.7. Results

Figure 6.26: EIS spectra under varying a) cathodic (100b2) and b) anodic (100b1) DC polarization at 700 °C. Each set was collected from different 100 μm microelectrodes.

1. The low frequency region starts to resemble the behaviour of an RQ circuit rather than the behaviour of a capacitor at -300 mV.

2. The high frequency intercept shifts towards higher $Z_{re}$ values.

3. The 45 degree straight line at the high/intermediate frequencies becomes more prominent at higher cathodic polarizations.

Figure 6.27: Log-log plots of a) $Z_{re}$ and b) $Z_{im}$ versus frequency for the series shown in Fig. 6.26 a).

The same features were also observed at the impedance spectra carried out under cathodic and anodic polarizations at 700 °C, as shown in Fig. 6.26. At 700 °C an open circuit EIS was recorded after the polarization, denoted as "0 V back" in
6.7. Results

Fig. 6.26. In both anodic and cathodic series, little to no change is observed on the before and after open circuit spectra. The log-log plots of $Z_{im}$ versus frequency for the cathodic and anodic series (Fig. 6.26) are shown in Fig. 6.27 and Fig. 6.28 respectively.

![Log-log plots of $Z_{im}$ versus frequency plots for the series shown in Fig. 6.26 b).](image)

The log-log plots of $Z_{im}$ versus frequency of the real impedance show clearly the shift of the $R_b$ towards higher values as the cathodic polarization increases, and its shift towards lower values as the anodic polarization increase. The log-log plot of $Z_{im}$ versus frequency of the imaginary impedance shows almost no change for polarizations from 0 V down to -200 mV.
6.7. Results

6.7.4.3 Cyclic voltammetry

In addition to the electrochemical impedance measurements, cyclic voltammograms were obtained using different scan rates at three different temperatures, 500, 600 and 700 °C.

![Cyclic voltammograms](image)

Figure 6.29: Cyclic voltammograms were obtained scan rates at a) and b) 500°C, c)-d) 600°C and e)-f) 700°C. The CVs were performed on three different 50 µm microelectrodes, one for each temperature.

The potential was swept from 0 V to -300 mV to +300 mV and back to 0 V. The
resulting voltammograms are shown in Fig. 6.29. Note that the x-axis values were not corrected for the ohmic drop of the electrolyte. At 500 °C (Fig. 6.29 a) and b), the prominent feature of the CVs recorded with high scanning rate, is a peak which starts at approximately 0.05 V and it shifts towards lower potentials as the sweep rate is lowered. The intensity of this peak decreases with decreasing scan rate, and it also shifts towards higher cathodic polarizations. The hysteresis of the CVs also decreases with decreasing scan rate. At 600 °C, the high scan rate CVs (6.29 c) appear to have been influenced by an oscillating signal which could have been due to bad tip-sample contact or due to temperature oscillations. At the low scan rates (6.29 d), the current-voltage curve shows hardly any hysteresis. At 700 °C the hysteresis is present at the high scan rates (6.29 e) but is hardly present at the low scan rate (6.29 f).

6.8 Discussion

6.8.1 The impact of heat treatment

The heat treatment at 750 °C for 16 hours of the LSF microelectrodes caused significant changes on the surface chemistry of the microelectrodes. Sr rich particles were observed on the surface by EDX and Tof-SIMS. This phenomenon is one of the major degradation mechanism in perovskite materials [148–152] since cation segregation or phase separation have a blocking effect for the charge transfer and the oxygen exchange at the surface [148]. Cation segregation is influenced by several factors including stress gradients, size miss-match between the dopant and the host and the electrostatic interactions [153], therefore the fact that the Sr rich particles were mainly found at the center of the microelectrode could be explained by one of the above mentioned factors. Most probably stress gradients are present in the microelectrodes, since the heat treatment of the sample was performed after the microelectrodes were patterned and due to the miss-match in the thermal expansion coefficient of the LSF, CGO and YSZ the stress on the thin film would be different at the edge (where there is plenty of space for stress relaxation) than at the center. In addition to the change in the chemistry of the surface, some cation interdiffusion is observed at the LSF/CGO interface. The Sr cations diffused the furthest into the CGO and even a bit in the YSZ. Such phenomenon has been previously observed [143].
6.8.2 Electrochemical measurements

6.8.2.1 Impedance spectroscopy

EIS measurements at OCV (Fig.6.19) from 500 to 700 °C reveal a very high (infinite) resistance at low frequencies. According to the simplified equivalent circuit shown in Fig.6.4 d) the low frequency resistance corresponds to the surface reaction resistance. Therefore, the infinite resistances at low frequencies (Fig.6.19) indicate that the tested electrodes are completely blocking even at 700 °C.

![Figure 6.30: The $R_b$ as a function of the applied potential for both cathodic (blue) and anodic (green) polarization. The data were fitted to exponential decay functions which are plotted as continuous lines. Both data sets were collected at 600 °C.](image)

The high frequency resistance ($R_h$), on the other hand, is attributed to the ohmic resistance of the electrolyte with minor contribution from the electron transport within the thin film [49]. The impedance spectra, which were collected under cathodic (Fig.6.20) and anodic (Fig.6.21) polarizations, show a decrease in the high frequency resistance as the polarization is increase. The plot of $R_h$ vs. the applied potential (Fig.6.30 and Fig.6.31) suggests that the high frequency resistance decreases exponentially with increasing potential. The exponential decay fits of the anodic and the cathodic $R_h$ reveal similar exponential decay coefficients of 1.49 $RT/F$ and 1.32 $RT/F$ at 600 °C. At 700 °C, the combined cathodic and anodic $R_h$ were fitted to an exponential decay function, the coefficient of which is 1.401 $RT/F$. If it is assumed that the behaviour of $R_h$ is mainly attributed
6.8. Discussion

to the behaviour of the electrolyte (YSZ), the exponential decay represents the introduction of electronic conductivity into the YSZ, as explained and derived in section 4.4. A coefficient of $-RT/F$ reflects that the electronic conductivity of the YSZ is proportional to $pO_2^{-1/4}$ as reported by Park and Blumenthal [131]. However, these polarizations are too low to introduce electronic conductivity in the YSZ, which indicates that there might be some contribution from the film itself. This behaviour could be indicative of p-type conductivity, since p-type conductors exhibit better electronic conductivity under oxidizing conditions, or in terms of resistivity and applied potential, lower resistivity at higher potentials. The p-type conductivity behaviour of LSF in these conditions has been observed previously [143, 154].

![Graph showing $R_b$ as a function of the applied potential for both cathodic (blue) and anodic (green) polarization. Both data sets were collected at 700 °C. The red dashed line is an exponential decay fit where both the anodic and cathodic polarization data were used.](image)

Figure 6.31: The $R_b$ as a function of the applied potential for both cathodic (blue) and anodic (green) polarization. Both data sets were collected at 700 °C. The red dashed line is an exponential decay fit where both the anodic and cathodic polarization data were used.

The discrepancy in the $R_b$ observed at 600 °C under no applied polarization could be due to the fact that the EIS series under cathodic or anodic polarizations were performed using two different 100 µm microelectrodes. Even though the microelectrodes are almost identical, the positioning of the tip is impossible to reproduce. The tip position on the microelectrode would be irrelevant if the lateral resistance of the LSF film is negligible. Additionally, since the cathodic series was collected first, the electrodes might have experienced some degradation due to the heat during the measurements.

If the high frequency resistance or $R_b$ was a reflection of only the ionic conductivity of the YSZ, a decrease of the $R_b$ is expected with increasing temperature since
6.8. Discussion

the YSZ becomes a better ionic conductor at elevated temperatures, however this is not the case for the EIS shown in Fig.6.19, Fig.6.20 and Fig.6.21. These results could be explained if the lateral film resistance is non-negligible. Even though all the measurements at a given polarization were performed on the same microelectrode, it is almost impossible to place the tip at the same exact position after having moved it, hence every time a measurement was performed the tip was placed at a different position on the microelectrode resulting in a different lateral resistance contribution.

![Image: A plot of the $R_b$ versus the inverse radius of the microelectrode. The blue scattered points represent the $R_b$ obtained from the impedance data collected on the 100, 50 and 20 µm electrodes. The red dashed line represents the Newmann relation.](image)

Figure 6.32: A plot of the $R_b$ versus the inverse radius of the microelectrode. The blue scattered points represent the $R_b$ obtained from the impedance data collected on the 100, 50 and 20 µm electrodes. The red dashed line represents the Newmann relation.

An additional evidence of the non-negligible influence of the lateral film resistance can be observed in the behaviour of the $R_b$ with changing electrode size (See Fig.6.32). The blue data points in Fig.6.32 are obtained from the impedance data collected at 700 °C on three different size (100, 50 and 20 µm in diameter) electrodes. Using the Newmann relation and a conductivity of $1.63 \times 10^{-2}$ S/cm$^2$ [130], the corresponding theoretical resistances were calculated and shown by the red data points in the same graph. The $R_b$ of the smallest electrode is very similar to the theoretical resistance and as the size of the microelectrode is increased, the difference between the measured and theoretical resistance becomes more pronounced. Such behaviour is consistent with a non-negligible lateral film resistance because the larger the microelectrode, the larger the contribution of the lateral resistance.

Fig.6.22 a) through d) show impedance spectra which were taken without moving the tip from the microelectrode. An initial OCV EIS was collected, then an
6.8. Discussion

EIS under either +250 or -250 V and finally another OCV EIS was collected both at 500 and 600 °C. The results obtained here are also in congruence with p-type microelectrodes which have non-negligible lateral resistance where the lateral resistance of the microelectrode decreases as the conditions become more oxidizing.

LSF is a perovskite material whose oxygen nonstoichiometry (δ) increases with decreasing oxygen partial pressure. The change in concentration of a species of the bulk is a capacitive process, electrically speaking. Such capacitance is commonly referred to as chemical capacitance (CChem) to point out its chemical nature. The process associated with the CChem occurs at long time scales (i.e. at low frequencies) [78]. The CChem is associated to the oxygen nonstoichiometry as described by Eq.6.5.4 [145], which indicates that the chemical capacitance is proportional to the slope of the stoichiometry versus log pO2:

\[ C_{Chem} \propto \frac{\partial \delta}{\partial \log pO_2} \]

Figure 6.33: a) Chemical capacitance versus log pO2 at 600 °C for both the anodic and cathodic polarizations. The pO2 was calculated from the DC polarization using the Nernst equation. b) Data obtained from Kuhn et al. [155] showing the behaviour of the nonstoichiometry change versus the oxygen partial pressure (red data points). The first derivative of 3-δ with respect to the log pO2 is also plotted (blue data points).

EIS measurements can reveal information about the chemical capacitance and oxygen nonstoichiometry; therefore impedance spectroscopy at varying potentials were used to estimate the CChem by fitting a simple RQ to the low frequency arc. At OCV the chemical capacitance obtained from the fit was 15 mF/cm², which is comparable with other perovskite such as LSCF [77]. The obtained CChem (normalized to the area of the microelectrode) versus the pO2, which was calculated using Nernst equation, are shown in Fig6.33 a). For comparison reasons, the behaviour of the \(-\frac{\partial \delta}{\partial \log pO_2}\) with varying pO2 of the data obtained from Kuhn et al. [155] are shown in Fig6.33 b). The results obtained using the
microelectrodes are consistent with the results of Kuhn et al. [155], who have measured the change in the oxygen stoichiometry using thermogravimetry and coulometric titration [155] on La$_{0.6}$Sr$_{0.4}$FeO$_{3-\delta}$ powders. The highest $C_{\text{Chem}}$ was obtained at the same $pO_2$ (2.5e-5 bar) as the $-\partial\delta/\partial\log(pO_2)$ maximum (Fig.6.33). This similarities indicate that the chemical capacitance depends only on the oxygen chemical potential of the LSF film, independent if the source affecting this potential is the oxygen pressure in the atmosphere or external DC potentials. This conclusion was also reached by a recent paper published by Schmid et al. [156].

6.8.2.2 Cyclic voltammetry

![Figure 6.34: The decreasing polarization part of the CVs shown in Fig.6.29 at different sweeping rates a) 50 mV/s b) 20 mV/s c) 10 mV/s and d)5 mV/s. The baseline curve was selected manually and it is shown in the red continuous line in each figure. The area between the CV curve and the base line was calculated and it was used to determine the charge transferred (Q) as the potential was swept.](image)
6.8. Discussion

The last set of electrochemical measurements involved cyclic voltammetry measurements at different temperatures with varying sweep rate. The peaks observed at low temperature CVs indicate a change in the oxygen stoichiometry occurs. Using the 50, 20, 10 and 5 mV/s CVs at 500 °C, the charge transfer was calculated using the peak area under the CV curves. The baseline for the peak was chosen manually and it is shown in red continuous line in Fig. 6.34. The calculated charge for each sweep rate is shown in the top left corner of each figure. Using the charge transfer, the stoichiometry change was estimated and the results are shown in the table below:

Table 6.3: Summary of the calculated charge and stoichiometry change as the sweep rate was varied.

<table>
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<th>Sweep rate (mV/s)</th>
<th>Charge (nC)</th>
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</tr>
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</tr>
<tr>
<td>10</td>
<td>77.7</td>
<td>0.024</td>
</tr>
<tr>
<td>5</td>
<td>10.5</td>
<td>0.003</td>
</tr>
</tbody>
</table>

Figure 6.35: Current density versus applied potential obtained from two different measurements are plotted in a semilog graph.

Note that the curves shown in Fig. 6.34 are the oxidation curves where the current was swept from -0.3 V to + 0.3 V and no peaks are observed during the reduction
process, as seen in Fig.6.29, which indicates that the obtained sweeps are not equilibrium curves. The nonstoichiometry changes obtained from the oxidation curves give values from 0.035 to 0.003, which are smaller than expected. The calculation of the nonstoichiometry was done assuming that the charge transfer occurs only due to the change in oxygen stoichiometry, therefore using the charge trasfered, the total number of oxygen leaving the lattice was calculated. Knowing the volume of the microelectrode (50 $\mu$m in diameter and approximately 300 nm thick), the total amount of oxygen atoms in the microelectrode was estimated using a cell volume of $355 \, \text{Å}^3$\cite{157}. The nonstoichiometry reported in Table 6.3 is the number of oxygen atoms leaving the lattice for every three oxygen atoms in the microelectrode. A factor that might have contributed in the fact that the calculated change in nonstoichiometry ($\Delta\delta$) is smaller than expected is the non-negligible lateral resistance of LSF film, which indicates that the microelectrode volume is a overestimation of the "active" volume.

As the temperature increases, the surface becomes less blocking and the oxygen evolution is observed in the CV curves. At the 5, 2 and 1 mV/s sweep rates, the current exhibits a Butler-Volmer type behaviour at 600 and 700 °C, which can be observed in Fig.6.35. The 2 mv/s CV curve is also compared with the DC currents obtained during the conditioning period before the EIS measurements, and as shown in Fig.6.35, the behaviour of the current density from these two types of measurements is identical. The current densities obtained from these CVs as well as from chronoamperometry are two orders of magnitude smaller than those obtained by \cite{158}. Schmid et al. also note that LSF films have one to two orders of magnitude higher conductivity than LSF microelectrodes. They attribute this conductivity decrease to the photolithography process \cite{158}.

### 6.8.3 Microstructure and conductance

The SEM and SIMS images performed after testing of the electrodes show no significant change in the microstructure and chemistry of the microelectrode and therefore are not shown.

### 6.9 Conclusion

Dense LSF microelectrodes were deposited on YSZ electrolyte with a CGO thin barrier layer and were used to perform EIS with varying DC polarizations at different temperatures. Additionally, CVs were collected at three different temperatures, 500, 600 and 700 °C.
6.9. Conclusion

The observations/conclusions made on this system are the following:

1. The heat treatment at 750 °C for 16 hours causes segregation of Sr rich phase to the surface of the microelectrodes. This is a phenomenon that has been observed previously on LSF, LSCF [151], LSC [74, 148] and LSM [159].

2. All the EIS data reveal that the lateral resistance is significant.

3. The microelectrodes have a blocking behaviour as shown by EIS at OCV and anodic and cathodic polarizations improve the oxygen surface exchange, as indicated by the decrease in the low frequency resistance.

4. EIS sets where the DC polarization was increased anodically and cathodically reveal that the LSF is a p-type conductor in the testing conditions (500-700 °C in air).

5. The oxygen surface exchange improves more when the electrode is polarized anodically.

6. The chemical capacitances obtained from the EIS were in agreement with the nonstoichiometry data obtained from [155] which were collected using thermogravimetry and coulometric titration on LSF powder. Therefore, I could conclude that the chemical capacitance depends only on the oxygen chemical potential of the LSF film, independent if the source affecting this potential is the oxygen pressure in the atmosphere or external DC potentials.

7. The increase in chemical capacitance with increasing anodic polarization reveals that interstitial oxygen defects are created.

8. Lastly, the CV indicate that at low temperatures a change in the oxygen stoichiometry occurs.

By no means this work is comprehensive and complete as it is reflected by the mainly qualitative results. A challenging aspect of this work was that the lateral resistance of the LSF microelectrodes was not negligible. Hence, to be able to perform more quantitative analysis, it is important to optimized the LSF microelectrode fabrication process. Additionally, the fact that the process of photolithography lowers the conductivity of the LSF film by a factor of 10 to 100, is a draw back for microelectrode studies on this material. This work, however, indicates to some extent the potential of the instrument. It shows that the chemical capacitance is a good way for investigating the defect chemistry of thin films. The cyclic voltammetry measurements are also a great way to investigate
6.9. Conclusion

the oxygen reduction reaction as well as changes in the stoichiometry of the material. It would be interesting to perform the same type of experiments on a wider range of polarizations as well as by varying the oxygen partial pressure in the atmosphere.
Chapter 7

Conclusions summary

Operando localized probing of model electrodes for SOC application were successfully carried out using the CAHT-SPM. The scope of this work was to study in detail the interfaces of electrodes used in SOCs, paying attention to electrochemistry, chemistry and microstructure, which allow the study of different degradation mechanisms associated with these interfaces. The CAHT-SPM was used for carrying out electrochemical measurements on point contact electrodes or circular microelectrodes. Such measurements can be challenging in different ways as shown in this work. For example the use of point contact electrodes offers poor sample-electrode geometrical contact, which makes quantitative analysis difficult. The use of the circular microelectrodes on the other hand resulted with challenges related to the lateral resistance of the microelectrodes, which also prevents quantitative analysis. The major results obtained in this work are summarized below.

In Chapter 4, the investigation of metal|YSZ micro-contact under strong cathodic polarization revealed features related to the electrochemical reduction of YSZ as well as to the degradation mechanism of the metal|YSZ cathode system in SOECs.

1. Strong cathodic polarizations using Ni and PtIr microelectrodes resulted in substantial changes in the electrical, microstructural and chemical properties of the YSZ.

2. EIS measurements on the Ni|YSZ indicate two rate determining processes where the low frequency process, associated with the reduction of H$_2$O at the gas|YSZ interface (and oscillation of this reaction zone) becomes more dominant at stronger cathodic polarizations. The high frequency process is associated with the charge transfer reaction at the Ni|YSZ contact.
3. Impedance under strong cathodic polarization on Pt|YSZ reveal inductive loops at high frequencies which have been attributed to the frequency dependency of the charge transfer close to the Pt|YSZ interface.

4. One to three orders of magnitude decrease is observed in the high frequency resistance upon increasing cathodic polarization from 0 V to -2 V, indicating introduction of electronic conductivity in all the YSZ samples, which is supported by the presence of high conductance regions in the conductance scans.

5. A 3–6 orders of magnitude decrease in the $R_x - L$ suggests increase of the reaction zone from the triple phase boundary to the YSZ surface. The expansion of the reaction zone can be beneficial for the operation of the SOECs, since it yields higher gas conversion rates.

6. The cathodic polarization caused roughening of the contact surface due to the interaction of the Ni or Pt with the YSZ.

7. Impurities were accumulated around the tip|YSZ contact suggesting that the impurity film was modified upon polarization resulting in a non-uniform distribution of impurities.

8. The comparison between polycrystalline YSZ, and SiYSZ and single crystal YSZ samples suggests that the reduction and reoxidation of the single crystal is retarded, pinpointing the importance of the grain boundaries in the redox chemistry of YSZ.

9. The CVs suggested that the reduction of zirconia occurs at lower potential for the PtIr than for the Ni microelectrode system, confirming that Ni promotes the reduction of zirconia.

To further support the conclusions enlisted above a macro-contact configuration was used to investigate the same systems (Chapter 5). The following observations/conclusions were obtained:

1. CV measurements provided electrochemical indications for the formation of Ni-Si-Zr intermetallic compounds.

2. The post-mortem microstructure analysis of the samples further supports the fact that intermetallic compounds are created between Ni and YSZ resulting in a complex interface microstructure.
3. The CV measurements show no indications of Zr-Pt intermetallic formation, however microstructural changes on the Pt|YSZ surface point towards interaction between the Pt and YSZ.

4. The electrochemical impedance spectra reveal an expanding reaction zone which does not compress to its original size even after the polarization is released. Such phenomenon was attributed to the trapping of the electrons in the F-centers in the YSZ. The trapping of the electrons in the F-centers is associated with colouration of the YSZ, which is optically observed in all the samples.

The detailed microstructural investigation of the three different system (Pt|YSZ, Ni|YSZ and Ni|SiYSZ) reveal the following:

1. The most microstructural changes were observed on samples which were exposed to several redox cycles.

2. As the Ni migrates into the YSZ, it chooses the lowest energy path which could be along the grain boundaries, therefore the reduction and re-oxidation of the intermetallic phases starts at the Ni-YSZ interface and at the grain boundaries.

3. Si-Zr intermetallic are also created and impurity phases are observed at the grain boundaries. The re-oxidation of such intermetallic weakens the grain boundaries causing YSZ grains to be torn off the sample.

The results obtained from this work are scientifically interesting on their own, but they can be used to advance our understanding of the degradation of the Ni|YSZ can be very useful for the improvement of SOEC. Here I would like to provide an example of how information obtained from such studies can be helpful to design better operating conditions for SOC. Reverse current treatment have shown to improve immensely the performance of the fuel electrode, however as explained by [30] such treatment causes weakening of the Ni-YSZ bond, therefore the optimization of the reverse current profile (i.e time and intensity) is crucial. Using one or both set-ups one can perform systematic studies by varying the strength of the polarization, its length, the atmosphere and even contact area by using wires/tips with different thickness, the result of which would greatly benefit the optimization of the reverse current profile.

In addition to the study of the metal|YSZ system, some exploratory work was performed on LSF microelectrodes (Chapter 6). The results/observations made on this system are the following:
1. All the EIS data reveal that the lateral resistance is significant.

2. The microelectrodes have a blocking behaviour as shown by EIS at OCV. Anodic and cathodic polarizations improve the oxygen surface exchange.

3. EIS sets where the DC polarization was increased anodically and cathodacally reveal that the LSF is a p-type conductor in the testing conditions (500-700 °C in air).

4. The chemical capacitance obtained from the EIS under different polarization is a good tool to investigate the changes in stoichiometry caused by applied potentials.

5. Lastly, the CV indicate that at low temperature temperatures a change in the oxygen stoichiometry occurs.

In conclusion, it has been shown that the use of the CAHT-SPM in synergy with other characterization techniques to investigate the interfaces of electrodes of SOFC/SOEC can be useful to obtain information about different degradation mechanisms associated with applied potentials, temperature and atmosphere. Additionally, the conductance maps gives insights into the performance of the sample surface. The direct measure of the surface conductance enriches the field, since it is ocommon in SOC studies to only monitor the microstructural changes.


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Appendix A

Counter electrode configuration

Several counter electrode (CE) configurations were considered with the purpose of investigating its influence on the electrochemical measurements. Electrochemical impedance spectroscopy was performed in the CAHT1 using several different configurations on the same polycrystalline YSZ sample. It is important to note that in these particular configurations there is no difference between the two electrodes, but for the purpose of distinguishing between the changing electrode and the one kept at the same configuration, the first is referred to as the counter electrode and the latter is referred to as the working electrode. The considered counter electrode configurations (CEC) were the following:

1. CEC1: A platinum wire pressed against the sample surface (CE) and a platinum wire pressed against the sample as a working electrode (WE) (Fig. A.1 a)

2. CEC2: A platinum painted spot on the top surface of the sample as a CE. Platinum paste was painted on the surface, creating a circular spot. The sample was then heat treated at 1050 °C for 30 min (Fig. A.1 b). The same WE as in CEC1 was used

3. CEC3: A platinum mesh placed under the sample (Fig. A.1 c). The same WE as in CEC1 was used.

4. CEC3.1: A platinum mesh placed (CE) under the sample where the WE was the platinum spot (Fig. A.1 d).

5. CEC4: A platinum painted alumina plate placed under the sample. The alumina plate was painted using a platinum paste and then heat treated at 1050 °C for 30 min (Fig. A.1 e). The same WE as in CEC1 was used.
6. CEC4.1: A platinum painted alumina plate placed under the sample. The alumina plate was painted using a platinum paste and then heat treated at 1050 °C for 30 min (Fig. A.1 e). The same WE as in CEC3.1 was used.

Note that the following configurations, CEC1, CEC2, CEC3 and CEC3.1 had an alumina disk and a Pt mesh between the hot plate and the sample, while CEC4 and CEC4.1 had only a Pt painted alumina in between the hot plate and the sample, resulting in two different sample temperatures, approximately 550 °C and 610 °C respectively.

As shown in Fig. A.1 a), b) and c), the YSZ sample is placed on top a Pt mesh and one of the electrodes (i.e a Pt wire pressed on the surface of the YSZ) is kept at the same spot for the first three configurations and only the other electrode was moved. Therefore, any change in the collected impedance spectra results from this change. The impedance spectra collected for each configuration are shown in Fig. A.2 and Fig. A.3. All the configurations give high frequency resistances from 5 kΩ up to 20 kΩ except CEC4.1 which resulted on a high frequency resistance of 500 Ω. For better comparison refer to Fig. A.4. All the high frequency resistances obtained by these configurations are relatively small when compared to the high frequency resistances obtained when using a SPM probe (in the order of 10 MΩ),
Figure A.2: EIS at OCV for a) CEC1, b) CEC2, c) CEC3 and d) CEC4. Note that multiple impedance spectra were collected to see if the results were reproducible.

Figure A.3: EIS at OCV a) CEC4.1 and b) CEC3.1
therefore the assumption that the counter electrode can be used as a reference electrode when using a sharp tip as a working electrode is valid for all counter electrode configurations. The configuration of choice for the work performed in this thesis was the platinum wire pressed against the surface of the sample (CEC1), since it introduces the least amount of impurities (no need to use any platinum paste) and it requires no sample sintering. The platinum mesh was discarded as an option since it offered a poor thermal contact of the sample with the hot plate resulting in a low surface temperature.
Optimization of YSZ pressing procedure

Surface analysis techniques impose several conditions in the sample quality such as:

1. High density
2. Good surfaces (well polished and pore free)
3. Impurity free surface.

All the above mentioned qualities make the sample fabrication challenging. Several trials were performed with the purpose of finding the optimum procedure to manufacture YSZ pellets. Since there are several factors that can influence in the density of the YSZ, the pressing procedure was considered. Three different forces were chosen to be used in the uniaxial press, namely 0.5, 1.0 and 1.5 ton and four pellets for each force were prepared. Two of each batch were pressed isostatically using a weight of 55 ton while the remaining two were not. The matrix for the samples is illustrated in the Table B.1. All pellets were sintered using the same sintering temperature profile, which employs a heating and cooling ramp of 100 °C/h and 4 hours of sintering at 1500 °C.

Table B.1: A matrix of the YSZ preparation

<table>
<thead>
<tr>
<th>Uniaxial Weight</th>
<th>With Isostatic Press</th>
<th>Without Isostatic Press</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.5 T</td>
<td>2 Samples (Set 1)</td>
<td>2 Samples (Set 4)</td>
</tr>
<tr>
<td>1.0 T</td>
<td>2 Samples (Set 2)</td>
<td>2 Samples (Set 5)</td>
</tr>
<tr>
<td>1.5 T</td>
<td>2 Samples (Set 3)</td>
<td>2 Samples (Set 6)</td>
</tr>
</tbody>
</table>
The density of the pellets was measured as follows: Eight measurements of the
diameter at different spots were obtained and 8 measurements of the thickness
as well. An average and standard error were calculated for each data set and
the following formulas were used to calculate the density and its error (Gaussian
propagation error);
\[
Density = \frac{m}{\pi R^2 h} \quad (B.0.1)
\]
\[
\sigma f(x_i) = \sqrt{\sum_i \left( \frac{\partial f}{\partial x_i} \right)^2 \cdot \sigma_i^2} \quad (B.0.2)
\]
Where the \( f(x_i) = Density(m, R, h) \).
The samples in set 1 were produced using 0.5 T in the uniaxial press and 55 T in
the isostatic press. SEM images from two different samples are shown in B.1

![Figure B.1: SEM of two samples from Set 1. The respective measured densities are: 5.906 (0.04) g/cm³ and 5.91 (0.04) g/cm³](image)

Notes: The results for this pressing procedure are very reproducible. The measured
densities are very close to each other and the porosity is not so bad. The quality
of the polishing needed to be improved. The porosity at the edge of the sample
was much higher, however most of the measurements have to be performed close
to the center. Average diameters: 9.77 and 9.79 mm.
The samples in set 2 were produced using 1.0 T in the uniaxial press and 55 T in
the isostatic press. SEM images from two different samples are shown in B.2
From the SEM images, there is not a lot of difference between the first and the
second set. I would say maybe, the first set (with 0.5 Ton in the uniaxial press)
has slightly lower porosity; however the second (1.0 ton) has a higher measured
density. Both pellets which were prepared using 1.0 T uniaxial weight have similar
density, which, once more, indicates reproducibility. However, the shrinkage of
the pellet is the higher for set 1 since the average final diameters of the samples
in set 2 are 10.53 and 10.49 mm compared to 9.77 and 9.79 mm for the samples
in set 1.

When using no isostatic press, there is an improvement with the increase of the
uniaxial pressure. However, from the porosity, it is clear that when using the
isostatic press denser pellets were obtained. Since the same polishing procedure
was used for all the pellets, one can observe scratches in all of them. I have
polished them down to 0.1 µm particle size. Conclusion: The highest density was
obtained using 1.0 ton in the uniaxial press, and 55 ton in the isostatic press. The
isostatic pressing improves the density of the samples.
Figure B.4: SEM of two samples from Set 4.

Figure B.5: SEM of two samples from Set 5.

Figure B.6: SEM of two samples from Set 6.
Appendix C

Paper I
The Impact of Strong Cathodic Polarization on Ni|YSZ Microelectrodes

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This work is a study of the impact of short-term strong cathodic polarization in a Ni|YSZ model system using Ni probes as working microelectrodes in a high temperature scanning probe microscope at 650 °C in humidified 9% H2 in N2. Impedance spectroscopy revealed one to three orders of magnitude decrease in the high frequency resistance and four to five orders of magnitude decrease in the low frequency impedance with polarization from −1.06 V to −3.06 V vs E°(O2), indicating introduction of electronic conductivity and expansion of the reaction zone around the Ni micro electrode. The effect on the Ni|YSZ interface included formation of electronic conductance, reaction between Ni and YSZ and accumulation of impurities around the Ni|YSZ contact as verified by conductance scans of the polarized area. Cyclic voltammetry was used to compare three systems with different impurity levels and showed that the presence of silicates reduces the current, i.e. lowers the performance of the electrode reaction.

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Solid oxide fuel/electrolysis cells (SOFC/SOEC, collectively termed SOC) are currently one of the most promising reversible energy conversion and storage technologies. A critical challenge for such devices to become economically viable is their long term durability, and therefore a considerable amount of work has been done on understanding their degradation mechanisms. When using a SOC in electrolysis mode, it is economically beneficial to operate the cell at high current density, because it increases the fuel production rate.

Several long-term studies have been performed on SOEC operating at high current densities.1–3 They have revealed different degradation mechanisms on the fuel electrode. Tao et al.4 report silica nanoprecipitates inside Ni grains in SOEC which had been operating at current densities higher than 1.5 A/cm2. Chen et al.5 have performed post mortem analysis on cells operated for more than 300 hours at high current density. They observed the formation of ZrO2 nanoparticles on Ni surfaces in cells which were operated at current densities higher than 1 A/cm2 at 850 °C.2 The formation of the nanoparticles was strongly correlated to the cell polarization and lowered the electrode performance due to loss of Ni percolation. The degradation mechanism on highly polarized Ni-YSZ electrodes was also discussed by Mogensen et al.,3 and they observed that part of the Ni particles lose their electrical contact to the electrode. It was noted that the region close to the electrolyte after testing had lower Ni content and higher porosity.

In contrast to the long-term testing of SOEC at high current density, short-term tests with very high current densities1–3 and also reverse current treatment,7 have shown to improve the performance of the cell. Klotz et al.2 and Szasz et al.9 observe that a nanostructured interlayer between Ni and YSZ, which improves the performance of the SOFC, was formed after operating a SOEC at a current density of 2 A/cm2 for 10 s.

When an SOEC is operated at high current densities the Ni-YSZ cathode is strongly polarized and electronic conductivity is increased in the YSZ. Electronic conductivity in YSZ is associated with a partial reduction of zirconia which takes place in two steps. The first occurs at low temperatures where electrons are trapped by impurities (e.g. Fe), resulting in a yellow or gray color, and the second happens at higher temperatures where the electrons are trapped in the oxygen vacancies, resulting in blackening of the zirconia.8 The reduction of zirconia has been studied extensively and coloration has been observed by several authors.6–11

Electrochemical reduction of ZrO2 in Ni-YSZ systems has been studied by several groups and they find that as the cathodic polarization increases, the ZrO2 will become reduced resulting in formation of Zr dissolved in Ni and intermetallic Ni-Zr phases.6,12–15 Thermodynamic calculations show that at 650 °C a potential below −2.4 V vs. E(PO2 = 1 bar) is required for the reduction of ZrO2 into pure Zr13,15 whereas solid solution of Zr-Ni and intermetallic phases are formed at lower cathodic polarizations than the ZrO2 reduction. Thus, YSZ is reduced at higher electrode potentials when in contact with Ni. Additionally, under cathodic polarizations, Ni interacts with silicate impurities. According to the Ni-Si-O phase diagram Si forms intermetallic phases with Ni for ρO2 below 10−37 bar. Thus, under cathodic polarizations to potentials below −1.8 V vs. E(PO2 = 1 bar) silica may be reduced.

SOC electrodes possess a complex microstructure which includes a multicomponent porous structure with various particle sizes. Traditional studies of SOC using current-voltage curves (IV) and electrochemical impedance spectroscopy (EIS), provide invaluable information about the overall performance of the cell, but do not reveal the highly inhomogeneous spatial distribution of the potential losses. At present time we still have a limited understanding of the implications of the spatial heterogeneities of the potential losses in the SOC durability. Therefore, in this study an in situ localized probing approach is implemented to investigate the Ni-YSZ electrode under cathodic polarizations. Electrochemical measurements are carried out using Ni probes with small radii of curvature in contact with polished YSZ surfaces in a Controlled Atmosphere High Temperature Scanning Probe Microscope (CAHT-SPM). The CAHT-SPM offers the opportunity to perform highly localized in situ studies of the Ni|YSZ cathode system due to only applied cathodic polarizations without the influence of microstructure (porosity, particle size, size distribution etc.). The measurements are supplemented with Scanning Electron Microscopy (SEM) and Time of Flight Secondary Ion Mass Spectrometry (ToF-SIMS) performed before and after the electrochemical measurements to reveal microstructural or chemical changes caused by the polarization. As silicate impurities are17–19 the measurements are carried out on YSZ samples with different concentrations of silica. The high temperature in situ localized probing in synergy with surface chemical and microstructural investigation represents an important advancement in the characterization of the Ni|YSZ electrodes in SOECs.
Experimental

Nickel probe and sample preparation.—The nickel probes were produced in-house, using 250 \( \mu \text{m} \) (99.98% purity, Alfa Aesar) or 100 \( \mu \text{m} \) diameter Ni wires (99.994% Ni, Alfa Aesar). The 250 \( \mu \text{m} \) wire contains less than 10 ppm of Al, Si, Co, Mg, Cr, Fe and 23 ppm of C. The impurities in the 100 \( \mu \text{m} \) thick Ni wire consist of 12 ppm of Fe, 10 ppm of C, 5 ppm of O, 2 ppm of Cr and S, and 1 ppm of Co. The impurity data for both types of wires were provided by the manufacturer. The Ni wires were cut in pieces of 3 cm in length and one end was bent in a \( \approx \) shape so that the wire could be handled easily. The sharpening of the tip was done by electrochemical etching of the Ni using 2 M KCl as electrolyte and Pt wire as cathode.\(^{20}\) The Ni wire itself was the anode. A DC potential of 2.5 to 3 V was applied across the Ni and the Pt wire. After obtaining a sharp tip, the wire was pressed to create a flat surface, which serves as a reflecting surface for the laser beam in the scanning probe microscope (SPM). The end of the tip was then bent so that it formed roughly a 75 degree angle from the cantilever’s body. The other 15 degree inclination was offered by the tip was thus perpendicular to the surface of the sample. The tip geometry was verified before the experiments using scanning electron microscopy (SEM).

8 mol\% yttria-stabilized zirconia (8YSZ) powder (TZ8Y, Tosoh) was pressed uniaxially and isostatically using 87 and 275 MPa pressure, respectively, and then sintered in air at 1550 \( ^\circ \text{C} \) for 2 hours. The final pellets were 10 mm in diameter and 1 mm in thickness. They were polished on one side, finishing with 0.1 \( \mu \text{m} \) diamond suspension. Additionally, YSZ samples with 1000 ppm of Si were produced following the same procedure. The Si was introduced in the sample by mixing 8YSZ powder with 0.2 wt\% SiO\(_2\) (Alfa Aesar) (0.43 mol%). The powder mix was diluted in ethanol to ensure a uniform mixture and was dried while being mixed on a hot plate at 60 \( ^\circ \text{C} \) for 24 hours. After sintering and polishing, all the pellets were cleaned using 37% hydrochloric acid in ultrasonic bath for 2 min, then milli-Q water and later ethanol in ultrasonic bath for 5 min each, and finally they were dried using a nitrogen gun.

8 mol\% YSZ single crystals were purchased from MTI Corporation with the size 10 \( \times \) 10 \( \times \) 1 mm\(^3\). The polished surface had the (100) orientation. A zigzag scratch was applied to the sample using a diamond tip with the purpose of tracking the polarization spots. The crystals were cleaned in ethanol in ultrasonic bath for 5 min and dried using a nitrogen gun.

Experimental set-up.—The electrochemical characterization, the surface conductance and topography measurements were carried out in a controlled atmosphere high temperature scanning probe microscope (CAHT-SPM)\(^{21,22}\), a diagram of which is shown in Figure 1. The samples were placed on the heating plate and held down by three alumina pins, which were held in place by steel springs. A platinum wire, used as a macroscopic counter and reference electrode, was attached at the edge of the samples and held in place by one of the alumina pins. The conductance images were acquired in scanning mode, where each pixel of the image represents a single frequency impedance measurement. The AC voltage with a 10 kHz frequency and 0.5 V amplitude was generated by a Stanford RS830 lock-in amplifier and was applied across the Pt counter electrode and the Ni tip. The current response was measured by the lock-in amplifier through a 1 M\( \Omega \) resistor connected in series with the tip. The resistor protects the lock-in amplifier from any overload.\(^{23}\) Since these measurements were conducted in contact mode the resolution of the technique was determined by the electrical probe-sample contact area. Surface conductance and topography images were obtained simultaneously.

Additionally, the set-up has the capability of performing electrochemical measurements where the SPM tip is used as a working electrode, and it is pressed against the surface of the sample for the duration of the measurements. Since the Ni tips were fabricated in-house their dimensions vary slightly. On the basis of the force constant calculated from the dimensions of the cantilever,\(^{24}\) the force applied to the probe was estimated to be between 0.2 and 2 \( \mu \text{N} \). However, within each data set the force was kept constant unless noted differently. For the electrochemical measurements, such as electrochemical impedance spectroscopy (EIS), cyclic voltammetry (CV) and chronoamperometry, a Gamry Instruments FAS2 Femtostat was used. The surface temperature of the sample was determined utilizing a thermocouple placed at the surface of the sample in a separate calibration experiment. The temperature of the sample/tip contact was most likely underestimated due to the fact that the thermocouple/sample contact is larger than the sample/tip contact, therefore the cooling effect is more pronounced. Most measurements were carried out at 650 \( ^\circ \text{C} \) in a 9% H\(_2\)/N\(_2\) mixture humidified at room temperature by bubbling the gas through water. The electrochemical measurements were carried out using a two-electrode set up. Due to the large size difference between the working electrode (Ni tip-sample macro-contact) and counter electrode (Pt wire-sample macro-contact), the polarization of the counter electrode was negligible. Thus, the counter electrode also acted as reference electrode, and the reference potential was the equilibrium potential of the H\(_2\)/H\(_2\)O electrode reaction in the atmosphere applied, at the same temperature (650 \( ^\circ \text{C} \)). The oxygen partial pressure, \( pO_2 \), of the exhaust gas was continuously monitored with a YSZ-based oxygen sensor operating at 1000 \( ^\circ \text{C} \). Once the desired experimental temperature was reached, a waiting time of a minimum 30 min was applied for the temperature and the \( pO_2 \) to stabilize. When the \( pO_2 \) is stabilized a small decrease in the reference potential of roughly 5–10 mV is observed in a time period of five hours.

For the humidified 9% H\(_2\)/N\(_2\) atmosphere, the measured oxygen potential of \(-940 \text{ mV vs. air at } 1000^\circ \text{C}\) corresponds to \( pH_2O/pH_2 \) ratio of 0.309 at the outlet. In the case where the temperature of the water used to humidify the atmosphere was 25 \( ^\circ \text{C} \) and the gas was saturated, an experimental environment of 3% H\(_2\), 8.7% H\(_2\) and 88.3% N\(_2\) (i.e. a \( pH_2O/pH_2 \) ratio of 0.34) was expected. The difference between the measured and the theoretical \( pH_2O/pH_2 \) was small and corresponds to a change of less than 5 mV in the reference potential.
Table I. Samples types and impedance series acquired for each sample. i and d refer to increasing and decreasing potentials. F1 and F2 refer to two different contact forces applied on the tip.

<table>
<thead>
<tr>
<th>Type of Sample</th>
<th>Tip/Sample couple</th>
<th>EIS series name</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ</td>
<td>A</td>
<td>YSZ-A</td>
</tr>
<tr>
<td></td>
<td>B</td>
<td>YSZ-B F1</td>
</tr>
<tr>
<td></td>
<td>C</td>
<td>YSZ-C</td>
</tr>
<tr>
<td></td>
<td>D</td>
<td>SiYSZ-Di</td>
</tr>
<tr>
<td></td>
<td>E</td>
<td>SiYSZ-E</td>
</tr>
<tr>
<td></td>
<td>F</td>
<td>YSZ100-F1,d</td>
</tr>
<tr>
<td></td>
<td>G</td>
<td>YSZ-G</td>
</tr>
</tbody>
</table>

which is insignificant for the purpose of the experiments. From the pH2O/pH2 ratio determined by the pO2 monitor the reference electrode potential at 650°C was calculated to be −1.066 V vs. E’(O2). From one experiment to another, variations of the water temperature were observed, which result in a reference potential fluctuation of less than 20 mV. For dry 9% H2/N2, the measured oxygen potential of −1035 mV at 1000°C corresponds to a pH2O/pH2 of 0.055 at the outlet, which corresponds to a reference potential of −1.135 V vs. E’(O2) at 650°C.

DC polarizations starting from 0 V down to −2 V versus the reference potential with a step size of −0.1 V or −0.2 V were carried out. The current response, later referred to as chronoaunometry or conditioning period, of each applied polarization was recorded for 120–300 s before recording the EIS response under continued constant DC polarization. EIS measurements were recorded in the frequency range from 82 kHz to 0.082 or 0.0082 Hz using 10 mV rms with 7 points per decade.

A list of the samples used for electrochemical measurements is reported in Table I.

A fresh tip and sample was used for each experiment. The sample-tip couples are indicated by the letters A through G. With YSZ-A, SiYSZ-D and YSZ100-F, two data sets were collected, one with increasing (from −2 V up to 0 V vs. Eref) and one with decreasing (from 0 V down to −2 V vs. Eref) potentials, noted with i and d subscripts, respectively. With YSZ-B, two series of decreasing potentials (i.e. increasing polarizations) were acquired with two different contact forces, where the F2 series has a 50% higher force than F1. Additional experiments with decreasing polarizations were performed with probe C, E and G on YSZ, SiYSZ and YSZ100 respectively.

To obtain post-mortem information about the surface chemistry and morphology of the contact region in the YSZ sample time of flight secondary ion mass spectrometry (ToF-SIMS) imaging and SEM were performed. Additionally, the contact surface of the nickel tip was investigated using SEM and energy dispersive X-ray spectroscopy (EDS) (Zeiss Supra or Zeiss Merlin). The ToF-SIMS analysis was performed using a ToF-SIMS IV (ION-TOF GmbH, Munster, Germany). The ion beam used for imaging was a 25 keV Bi+ pulsed beam, with a 10 kHz frequency and a pulse length of 100 ns. Prior to imaging, a larger area (750 × 750 μm2) was sputtered using 30 nA of 3 keV Xe+ for 45 s to remove any hydrocarbon species adsorbed on the surface. The surface was flushed with 20 eV electrons to reduce surface charging.

Figure 2. Time dependence of the current during different polarizations at a) low cathodic polarization, b) intermediate polarization and c) high cathodic polarization for the YSZ-A sample. At low cathodic polarization the relaxation shows RC behavior while at high cathodic polarization RL behavior is observed.

Results

Electrochemical measurements on Ni/YSZ.—A series of impedance measurements were performed at polarizations stepped from 0 to −2 V and back to 0 V in steps of 0.1 V or 0.2 V and with a conditioning period of 300 s before each spectrum was recorded. Figure 2 shows conditioning currents as a function of time at selected polarizations. The behavior of the current evolves from capacitive to inductive with increasing polarization. In other words, under low cathodic polarization (Figure 2a), the cathodic current decreases with time, like the response of a resistor - capacitor (RC) in parallel, while at high cathodic polarization an increasing cathodic current is observed (Figure 2c), i.e. like that of a parallel resistor-inductor (RL) behavior.

Impedance spectra acquired upon increasing cathodic polarizations are shown in Figure 3. The impedance spectra evolve significantly with increasing polarization. From 0 V to −0.8 V, only one suppressed arc is present in the impedance spectra. A new arc becomes visible in the low frequency regime at −0.9 V. Furthermore, at low frequency an inductive loop is present at polarizations between −1.1 V and −1.5 V. Other series of impedance measurements with frequencies as low as 0.0082 Hz, reveal inductive loops from −1 V to −2 V, as illustrated in Figure 4.

As the results obtained with frequency range from 82 kHz to 0.082 Hz did not allow a reasonable extrapolation of the inductive loops to DC, the width of the spectra was used as a describing parameter instead of the DC polarization resistance. It is referred to as the intercept resistance (Ri), and is determined as the distance from the high frequency extrapolation (Rf) to the low frequency intersection of
the real axis. In the $R_{\text{L}}$, notation, $x$-L stands for real axis intercept at low frequency. Figure 5 shows the $R_s$ and $R_{\text{L}}$ values corresponding to the impedance spectra shown in Figure 3 are shown in Figures 5a and 5b respectively (YSZ-A). The $R_s$ values were obtained by fitting an equivalent circuit with a $\text{RQ}$ parallel combination to the high frequency data, whereas the $R_{\text{L}}$ values were read from the graphs. When determining $R_{\text{L}}$ by fitting was not possible, the $R_s$ values were read from the graphs. While the cathodic polarization increases from 0 V to −1 V, $R_s$ stays constant. For cathodic polarizations stronger than −1 V, $R_s$ decreases. This decrease varies from a factor of two to almost two orders of magnitude from one polarization series if lower frequencies are probed. Almost one order of magnitude decrease of the $R_{\text{L}}$ is observed upon increasing polarization down to −0.7 V. A steeper decrease of roughly three orders of magnitude of the $R_{\text{L}}$ follows for polarizations down to −1.4 V. For polarizations between −1.4 V and −1.7 V the $R_{\text{L}}$ displays an increase followed by a decrease down to −2 V. For an overall increase of the cathodic polarization of two volts, $R_{\text{L}}$ decreases by 4–5 orders of magnitude.

The $R_s$ and $R_{\text{L}}$ for the decreasing cathodic polarization series are also shown in Figure 5 (YSZ-A) and they show a similar behavior. It was not possible to extract values of the $R_{\text{L}}$ between −0.3 V and 0 V because the summit frequency was too far below the frequency range used for the measurements to obtain a valid extrapolation. However, the extracted $R_{\text{L}}$ points follow the same trend as for the increasing cathodic polarization. The $R_s$ during the increasing cathodic polarization deviates from the decreasing cathodic polarization, especially at low cathodic polarizations.

**Electrochemical measurements on Ni|SiYSZ**—A similar study was performed for the Ni|SiYSZ interphase, and Figure 6 shows a series of impedance spectra obtained upon increasing cathodic polarization. The chronoamperometry measurements during the conditioning time show similar behavior as that for Ni|YSZ shown in Figure 2. Similar to the Ni|YSZ system, the impedance spectra show the presence of one arc from 0 V to −0.9 V. At −1 V a clear emergence of a second arc is observed at low frequencies. Contrary to the Ni|YSZ impedance spectra, the two arcs are clearly separated in the Ni|SiYSZ system. As the low frequency arc becomes more prominent, the two arcs do not merge but remain very well separated. Additionally, the beginning of the low frequency arc shows a straight line behavior (~45 degree slope) at −1.1 and −1.2 V. The inductive behavior in the Ni|SiYSZ sample is only observed from −1.8 V to −2 V for frequencies down to 0.1 Hz. The inductive loops may be visible at lower cathodic polarizations if lower frequencies are probed.

The values of the high frequency resistance ($R_s$) and intercept resistance ($R_{\text{L}}$) for several series are obtained in the same manner as for the Ni|YSZ system and are shown in Figures 7a and 7b, respectively. In addition to the $R_s$ and $R_{\text{L}}$ extracted from the series shown in Figure 6 (SiYSZ-E) an additional series with 0.2 V step in both increasing (SiYSZ-D$_2$) and decreasing (SiYSZ-D$_3$) cathodic polarizations is shown in Figure 7. The $R_{\text{L}}$ and $R_s$ of the Ni|YSZ and the Ni|SiYSZ system show generally similar behaviors with some minor differences. The $R_s$ vs. potential curve of Ni|SiYSZ does not show a plateau at low cathodic polarization, and a steeper decrease...
Figure 5. a) The semi-log plot of $R_s$ and b) $R_{x-L}$ of Ni|YSZ as a function of the applied potential versus the reference potential (bottom x-axis). The A, B and C indicate the tip used for the series. The corresponding potential versus oxygen is shown in the top x-axis. The Si/SiO$_2$, Zr/ZrO$_2$ and Y/Y$_2$O$_3$ equilibrium potentials are indicated with red, black and blue dashed lines, respectively. The green triangle in a) indicates the equilibrium relation between potential and $R_s$ when electronic conductivity is introduced in YSZ.

is observed at cathodic polarizations stronger than $-1.6$ V. The $R_{x-L}$ activation behavior of the NiSiYSZ shows three different activations, a slow decrease of $R_{x-L}$ at low polarizations (0 V down to $-0.5$ V), followed by a steeper decrease at intermediate ($-0.6$ V down to $-1.4$ V) and at high polarization ($-1.6$ V down to $-2$ V), where the last two sections are separated by a small increase or a plateau ($-1.4$ V down to $-1.6$ V). The $R_{x-L}$ decreases by four to five orders of magnitude for both systems.

Electrochemical measurements on Ni|YSZ100.—Impedance spectra obtained with single crystal YSZ electrolyte show similar behavior to the previous two systems. The $R_s$ and $R_{x-L}$ of two different series are shown in Figures 8a and 8b, respectively. The YSZ100-D series shows the $R_s$ and $R_{x-L}$ in both increasing ($-0.1$ V steps) and decreasing ($0.2$ V steps) cathodic polarizations. The $R_s$ show an overall decrease of approximately one order of magnitude in the increasing cathodic polarization series, where the steepest decrease is observed from $-1.4$ V down to $-1.8$ V. The $R_{x-L}$ values at low cathodic polarizations do not return to the same value when the electrode potential is increased. At $-0.6$ V, the $R_s$ is a factor of two smaller in the decreasing series compared to the same electrode potential in the increasing series. In the decreasing direction the series finishes at $-0.4$ V due to loss of contact between the tip and the sample. The second series shows an increase in the $R_s$ at low cathodic polarizations, followed by a small decrease from $-0.8$ V to $-1.4$ V. The steepest decrease is observed from $-1.4$ V to $-1.8$ V. The $R_{x-L}$ for both series show very similar behavior, where an overall 4–5 orders of magnitude decrease is observed. A small decrease was observed from 0 V to $-0.7$ V followed by a steep decrease down to $-1.6$ V. Finally, the $R_{x-L}$ increases by approximately a factor of two from $-1.6$ V to $-2$ V. When increasing the electrode potential, $R_{x-L}$ remains suppressed and up to two orders of magnitude difference is observed compared to the starting value.

Cyclic voltammetry.—Figure 9a shows voltammograms recorded for the three systems. In Figure 9b they are shown normalized to their highest cathodic current for better comparison. The voltammograms follow similar trends in all the studied systems, namely in all the CVs inductive hysteresis is observed.

With increasing cathodic polarization in the Ni|YSZ100 system a strong increase in the cathodic current starts at $-1.4$ V. This increase starts at lower polarizations ($-1.2$ V) for the Ni|YSZ while the NiSiYSZ system shows a more gradual increase that starts at $-0.6$ V to $-0.8$ V followed by a steeper increase down to $-1.6$ V. CVs for both Ni|YSZ and NiSiYSZ have an inflection point at $-1.4$ V. Indications of an inflection point in Ni|YSZ100 are observed between $-1.6$ and $-1.8$ V. In Figure 9c the inverse $R_{x-L}$ values and the first derivative of the current with respect to polarization are compared to better illustrate this behavior. All data are individually normalized unless CC License in place (see abstract).
to their highest numerical value. The \( R_{x,L} \) values are calculated from the impedance spectra obtained after polarizations of 300 s, while the CVs are obtained with a sweep rate of 10 mV/s.

The difference observed between the current values at high cathodic polarizations could be due to the different contact areas. The contact radii are calculated using the Newman formula:

\[
R_s = \frac{1}{4\sigma r} \tag{1}
\]

where \( R_s \) is the high frequency resistance, \( \sigma \) is the bulk conductivity of YSZ in air and \( r \) is the radius of the contact. This formula is valid for a circular contact area, a homogeneous electrolyte conductivity and negligible contact resistance contribution to the serial resistance, i.e. \( R_s \) originates solely from the electrolyte resistance. Thus, using this formula for this system is a crude approximation. The radii are given together with the normalization factors in Figure 9b. The current densities at \(-2\) V (currents used to perform the normalization) are normalized to the tip circumference and to the tip area using the estimated Newman radius and shown in Table II. The normalized current densities increase with sample purity.

The water partial pressure during the measurements has a substantial impact on the cathodic current, as shown in Figure 9d. The voltammograms were acquired using the same sample and the same tip during the same day, but at two different positions on the sample. The general behavior is quite similar but in the wet 9% H\(_2\)/N\(_2\) (pH\(_2\)/pH\(_2\) of 0.306) the cathodic current at \(-2\) V is almost twice the value of the current in the dry 9% H\(_2\)/N\(_2\) (pH\(_2\)/pH\(_2\) of 0.055).

Conductance mapping.—Figure 10 shows a conductance map of a polarization spot on a single crystal YSZ100-G obtained at 650 °C after applying a polarization of \(-2\) V versus the reference for 40 min. The image is somewhat blurry due to the bold tip after prolonged contact at a large contact force. However, a low conductance region and a high conductance region can be observed. The difference in conductance between them is more than one order of magnitude.

Chemical and microstructural investigation of the Ni|YSZ contact region.—For additional chemical analysis, ToF-SIMS was performed on a YSZ sample polarized from 0 V to \(-2\) V with \(-0.2\) V step size. Conductance scanning was avoided to exclude any artifacts on the ToF-SIMS images due to possible spreading of impurities\( ^{23} \) while scanning in contact mode, since the ToF-SIMS is extremely sensitive to surface contamination. A large surface area of the YSZ was mapped by ToF-SIMS, and the Ni signal was used as indicator of the Ni|YSZ contact area. Figure 11a through f show ToF-SIMS ion images of the contact area between the Ni probe and YSZ. In addition to the Zr, Y and Ni maps, Si, Na and Ca maps are shown. A lateral distribution of Ni is shown in both Figure 11a, which indicates the shape and size of the contact area. Si is enriched in a roughly circular area with a diameter of 50 \( \mu \)m around the contact area, i.e. approximately four times the diameter of the Ni tip. A SEM image of the Ni-tip used in this experiment is shown in Figure 11h and reveals a contact area with approx. 12 \( \mu \)m in diameter. Figure 11g shows a SEM image of
the contact area on YSZ. From this SEM image it is obvious that the surface of the YSZ contacted by the Ni tip is substantially roughened. Despite the presence of Ni and Si, both Y and Zr are also observed in the region. Further investigations, such as SEM and EDS of the tips used for the strong polarizations revealed the presence of Si and Al oxide species in the contact region as well as on the walls of the tip.

Discussion

The chronoamperometry measurements at different potentials on the Ni|YSZ system, as shown in Figure 2, indicate that the current evolves from capacitive to inductive with increasing polarization. This behavior is further supported by the appearance of inductive loops at low frequencies in the impedance spectra seen in Figures 3 and 4. Inductive loops have been previously observed in metal|YSZ systems, and they have been attributed to either the potential dependency of the concentration of adsorbed intermediate species or to the increase of the reaction zone by the injection of electrons in the YSZ.

At low cathodic polarizations, the water splitting reaction does not extend far from the tip. Due to the high electrode overpotential and concentration of electrons close to the electrolyte/tip contact, we suggest that the reaction rate in the region close to the Ni|YSZ contact is limited by the steam diffusion rate. This region is indicated with

<table>
<thead>
<tr>
<th>Sample</th>
<th>Estimated radius (nm)</th>
<th>Current at -2 V (A)</th>
<th>Line current density (A/cm)</th>
<th>Area current density (A/cm²)</th>
</tr>
</thead>
<tbody>
<tr>
<td>YSZ 100</td>
<td>235</td>
<td>-1.38 · 10⁻⁶</td>
<td>-9.35 · 10⁻³</td>
<td>-795</td>
</tr>
<tr>
<td>YSZ</td>
<td>832</td>
<td>-1.65 · 10⁻⁶</td>
<td>-3.16 · 10⁻³</td>
<td>-76</td>
</tr>
<tr>
<td>SiYSZ</td>
<td>515</td>
<td>-4.11 · 10⁻⁷</td>
<td>-1.27 · 10⁻³</td>
<td>-49</td>
</tr>
</tbody>
</table>
Figure 10. Conductance map of a polarization spot recorded at 650°C after applying a polarization of $-2\, V$ vs. $E_{ref}$ for 40 min.

A continuous black line in Figure 12. As the cathodic polarization is increased, the reaction zone extends further away from the tip due to introduction of electronic conductivity in the YSZ. This is represented with the dashed line at the gas|YSZ interface in Figure 12. When an AC signal is superimposed on the steady state polarization, a damped electron concentration wave is created as indicated by the red line in Figure 12. At high frequencies, this concentration wave does not extend beyond the steam diffusion-limited area (shown in Figure 12). Therefore, the high frequency process in the EIS is attributed to the charge transfer reaction at the tip|YSZ interface while the low frequency arc, which appears at higher cathodic polarizations, is attributed to the YSZ|gas surface reaction. The impedance measurements for both Ni|YSZ and Ni|SiYSZ shown in Figure 3, Figure 4 and Figure 6 consistently show a splitting of one arc into two arcs at potentials below $-0.8\, V$ and $-1.0\, V$ reflecting two serial processes as explained above. YSZ100 exhibits a similar behavior.

Figure 12. Schematic of the electron concentration (red line) close to the Ni|YSZ contact when an AC signal is applied a) the high frequency case and b) the low frequency case. The gas|YSZ interface is represented using continues line for the surface where the water diffusion is limiting the surface reaction rate and by a dashed line for the surface where there is no water diffusion limitation. Note that the electron concentration variation is only illustrative and is drawn out of scale.

At very low frequencies, the electron concentration wave extends outside of the diffusion limited region, and thus a modulation on the reaction zone is observed. Such modulation causes an inductive loop at low frequencies as seen in Figure 4.

In the series shown in Figure 4 (YSZ-B $F_2$), however, there is no splitting of the capacitive arcs. The estimated contact radius for the

Figure 11. a)-f) ToF-SIMS images ($50 \times 50\, \mu m^2$) of the Ni|YSZ contact area g) SEM image of the YSZ at the contact where the dashed line indicates the border of the modified region and h) SEM image of the Ni tip after the polarization measurement.
YSZ-B $F_2$ is 5 times larger than the contact radius for the YSZ-A$_2$. Therefore, the details from the YSZ/gas interface impedance may be overshadowed by a relative increase of the parallel Ni/YSZ admittance.

Figure 5, Figure 7 and Figure 8a show that the behavior of $R_s$ is semi-quantitatively similar for the three systems. At low cathodic polarizations (lower than $-0.8$ V) the uncertainty on the $R_s$ values can be up to $30\%$. The standard deviation of the $R_s$ from the fits in the low polarization region varies from $20\%$ to $30\%$, even when only the high frequency region is fitted. For the spectra where the uncertainty was higher than $30\%$ the intercept was estimated from the graphs, instead of fitting the EIS. Due to the large spreading of the impedance spectra of more than 2 orders of magnitude, the uncertainty of the $R_s$ obtained from the estimation of the intercept is also estimated to be $30\%$. It should be noted that in this region with high frequency impedances in the MΩ range, the values obtained are likely to be influenced by stray capacitances. The stray capacitance of the system was measured to be $0.6$ pF, which would give rise to a shunting resistance of $2.65$ MΩ at $100$ kHz. Therefore, absolute values should be interpreted with care, whereas changes of the $R_s$ with polarization are significant. The extrapolations at higher polarizations are more accurate ($<5\%$ uncertainty at $-2$ V polarization), except for the SiYSZ samples where the uncertainty obtained from the fit was $15\%$ at $-2$ V.

The ionic conductivity of YSZ, which can be deduced from the $R_s$ at low cathodic polarizations, is here assumed to be independent of the oxygen partial pressure, while the electronic conductivity depends on the local Fermi potential of the YSZ. When a cathodic polarization lower than $-1$ V vs. $E_{eq}$ is applied, the $R_s$, which is inversely proportional to the ionic conductivity of YSZ, decreases slowly, corresponding to a region where the ionic conductivity is dominant. The cathodic polarization is equivalent to a change in the oxygen partial pressure at the Ni/YSZ interface, and as it increases, an exponential decrease of the $R_s$ is observed, indicating that the electronic conductivity begins dominating.

Interpolating from the data of Appel et al., the ionic conductivity of 8 mol% YSZ at $650$ °C is $9.7 \times 10^{-3}$ S cm$^{-1}$. Using Eq. 1, the high frequency resistance ($R_s$) at low polarizations and the ionic conductivity, the contact radius is estimated to be $0.8 \mu$m for the series YSZ-A$_2$ in Figure 5. SEM images of the tip show that the geometric radius of the contact area is approximately $7 \mu$m. The discrepancy on the measured versus calculated contact radius is not surprising because, in addition to the irregular and changing shape of the contact area due to modification of the tip during the experiment, the uncertainty of the $R_s$ at low cathodic polarization is the largest. Additionally, SEM images give the final physical contact after the experiment was performed, and the physical area does not necessarily indicate an electrical contact.

Therefore, both estimates of the contact area have large uncertainties, and only a semi-quantitative description of the experimental results is possible.

For low $pO_2$, in equilibrium conditions, the electronic conductivity of YSZ has a $pO_2$ dependency as reported by Park and Blumenthal. The linear behavior with a slope of $-1/4$ of the log $pO_2$ vs. log $\sigma$ corresponds to a linear behavior in the log $R_s$ versus applied potential with a slope of

$$\frac{\partial \log (R_s)}{\partial E} = \left(\frac{2.3026}{F}\right)^{-1} = 5.4$$

where $R_s$ is the gas constant, $T$ is the sample temperature in Kelvin and $F$ is the Faraday constant. This derivation of the slope assumes that the YSZ conductivity is constant throughout the sample, and that it is purely electronic. Additionally it does not take into account any changes in the electronic conductivity due to the change of the oxide vacancy concentration or the change in the area of the active zone around the tip when the potential is changed. The obtained slopes are $2$ to $6$ times lower than the equilibrium slope. Thus, as expected the above mentioned assumptions do not hold for our system under polarization. A factor that contributes to the flattening of the $R_s$ vs. applied potential is attributed to the decrease of the electronic conductivity away from the Ni/YSZ interface as a result of the potential distribution in a point contact configuration, as shown in Figure 13a. Additionally, due to the water splitting reaction, the electron concentration near the YSZ surface close to the contact is reduced, thus causing the current lines to loop up to the surface (Figure 13b).

This lowers the volume in which electronic conductivity is introduced in the YSZ, hence causing a decrease of the slope of the $R_s$ versus potential. The current and the equipotential lines in Figure 13b are qualitatively drawn but similar behavior was simulated by Ciucci et al. In the case of ceria ($\text{CeO}_2$)$_{0.95}(\text{Y}_2\text{O}_3)_{0.05}$, studies of the variation of conductivity at different temperatures as a function of $pO_2$ have shown that its conductivity flattens out at very low polarizations, which shows that the proportionality of the conductivity of ceria with $pO_2^{-1/4}$ breaks for very low $pO_2$. As the oxygen vacancy concentration is expected to increase upon reduction of YSZ the slope is expected to decrease similar to the case of ceria. Since we use potentials well below the reduction of $\text{ZrO}_2$, partial or full reduction of YSZ is expected; therefore the above relation is not expected to be valid for the entire polarization range.

The $R_s$ for all three systems shows similar behavior. For the YSZ100 and YSZ there is a low activation region from 0 V to $-0.7$ V followed by a steeper activation at stronger polarizations. For the SiYSZ system the second more pronounced activation region starts below the reduction of $\text{ZrO}_2$, partial or full reduction of YSZ is expected; therefore the above relation is not expected to be valid for the entire polarization range.

Figure 13. Qualitative sketch of the electron flux (in dashed lines) and the equipotential lines (continuous lines) near the point contact between YSZ and Ni where a) no surface reaction is present b) surface reaction is present.
SiYSZ and the YSZ and $-1.8$ V for the YSZ100). The shift in this local maximum toward more negative potentials for the single crystal indicates that the reaction responsible for the increase in the $R_\text{s}$ is delayed by the slower reducibility of the single crystal in comparison to the polycrystalline samples.

The $R_\text{s}$ and $R_{\text{cat}}$ for the decreasing cathodic polarization series performed in the same spot, immediately after the increasing polarization series to ensure that the probe/YSZ contact conditions were not changed, are shown in Figure 5, Figure 6 and Figure 8. For the Ni/YSZ100 (Figure 8) and the Ni/SiYSZ system (Figure 6), the $R_\text{s}$ and the $R_{\text{cat}}$ do not return to the initial high values indicating a permanent or at least a slowly decaying modification of the YSZ close to the probe contact. For the YSZ system the coincidence of the $R_{\text{cat}}$ between the anodic and cathodic direction does not suggest any irreversible changes. Notice that the biggest hysteresis is observed in the YSZ100 case, which indicates that the re-oxidation process proceeds slower for the single crystal. Luerssen et al.\textsuperscript{10} have observed that it is more difficult to induce electronic conductivity in single crystal YSZ than in polycrystalline samples, which is in line with our findings. This is attributed to the morphology and higher defect density in the polycrystalline sample in comparison to the single crystal.\textsuperscript{11} However, previous studies have also shown the fully reversible character of the reduction-oxidation in single crystal YSZ,\textsuperscript{60} therefore we attribute the hysteresis in the $R_\text{s}$ and $R_{\text{cat}}$ to the slow re-oxidation rather than to permanent conductivity changes of the YSZ. We explain the slower reoxidation rate of bulk YSZ by the fast “passivation” of the surface region when this is re-oxidized. The oxidized YSZ surface will impede the electronic conduction necessary to oxidize the reduced bulk YSZ below the surface region. Further, the polycrystalline YSZ will have higher electronic conductivity due to impurities concentrated in the grain boundaries and therefore reoxidize faster than the single crystal YSZ.

The CV measurements for all systems (Figure 9) show inductive hysteresis, and their current densities decrease in absolute value with increasing silica content. This behavior indicates that the quantity of silica in the YSZ impedes the H$_2$O splitting reaction and limits the current. For the SiYSZ and YSZ systems, two different activation regions are observed in the CVs, separated by a flattening of the current at intermediate polarizations. For the single crystal however, only one activation region is observed close to $-1.4$ V, which coincides with the reduction potential of ZrO$_2$.\textsuperscript{61}

The cathodic current increase at polarizations between $-0.6$ V and $-1.2$ V is attributed to the reduction of silicates as it fits with the reduction potential of SiO$_2$ ($-0.8$ V) and it is not observed in the single crystal system. For the Ni/SiYSZ system a gradual cathodic current increase starts at lower polarizations than in the Ni/YSZ and Ni/YSZ100, and the flattening/inflection point is most pronounced in the system that contains the most silica and weakest in the purest system, indicating that there is a substantial contribution to the current from the reduction of the silicates in the intermediate polarization region. The second activation region is attributed to the partial reduction of zirconia and the expansion of the reaction zone due to the introduction of electronic conductivity in the reduced region.

The normalized first derivatives of current with respect to polarization and the normalized inverse $R_{\text{cat}}$ are in good agreement for all the studied systems as shown Figure 9c. The discrepancies observed are partly due to the fact that the time it takes to acquire the CV data is much shorter than the impedance series where the polarization is stepped down by 0.1 V or 0.2 V. Inflection points in the CV curves are indicated as local maxima and local minima in the derivative curves and clearly these inflection points shift toward higher polarizations for the single crystal, suggesting once more that the lack of grain boundaries delays its reduction.

The doubling of the cathodic current with a 6-fold increase of the steam partial pressure that is seen at $-2$ V in Figure 9d is related to the spreading of the contact area at strong polarizations, as the CVs were obtained with the same probe, and geometric effects can be excluded. The reaction zone at such polarization spreads beyond the steam diffusion-limited region due to the introduction of electronic conductivity in the YSZ. If the active area around the Ni/YSZ interface is the same at the same pO$_2$ for both wet and dry atmospheres, the current increase should be the same as the increase in the water vapor pressure. However, in the wet environment due to the higher concentration of steam, more electrons are consumed at the gas/YSZ interface, resulting in a smaller effective reaction zone.

**Correlation between surface chemistry, electrochemistry and electrical measurements.**—The formation of both high and low conducting regions in the vicinity of the Ni/YSZ contact point as a result of the strong cathodic polarization, as shown by the conductance map in Figure 10, is in accordance with the $R_\text{s}$ and $R_{\text{cat}}$ not returning to their initial high values. Both the $R_\text{s}$ behavior and the conductance maps are similar to what was found in the Pt/YSZ system.\textsuperscript{38} The low conducting regions are probably due to accumulation of SiO$_2$, as this is observed by both EDS and ToF-SIMS to be associated with the contact region on the YSZ and on the Ni tip. This is also similar to the Pt-YSZ system.\textsuperscript{36} SiO$_2$ originating from the impurities in the raw materials is normally found to segregate to YSZ surfaces at elevated temperatures and form an impurity film with other present impurities.\textsuperscript{46-48} Conductance images of the YSZ before polarization show a uniform conductance. This, however, does not explain the low conductance areas. From the proximity to the contact, since a film would have caused a lower conductance through the sample and not localized close to the polarization spot.

The accumulation of the Si-based impurities close to the Ni/YSZ contact as well as the creeping of the impurities up the surface of the Ni tip, may be explained by the Marangoni effect,\textsuperscript{44} if it is assumed that the silicates are in a liquid/glassy phase at the testing conditions. The fluid motion is driven by gradients of the surface tension as a result of temperature gradients (thermo-capillary convection) or concentration gradients. When the nickel tip comes in contact with the thin layer of glassy silicates on the surface of the YSZ, the impurities form a concave meniscus due to the surface tension of the glassy phase. The temperature gradient of the YSZ surface and the tip itself causes a surface tension gradient in the impurity layer, where the highest surface tension is observed at the lowest temperature. The motion of the fluid will be toward the highest surface tension, i.e. toward the lowest temperature. Hence, the silicates would accumulate closer to the tip causing the low conductance region. We have observed that the SEM/EDX images of the tip after being held in contact with a SiYSZ sample without applying any polarization indicate that silica impurities creep up the tip, which support the impact of the Marangoni effect. However, investigations of strong cathodic polarizations on a SiYSZ sample using a bend Ni wire placed inside a furnace where the temperature gradients are negligible indicate that there are regions close to or within the contact region which contain higher concentration of silica impurities supporting the idea that the applied potentials modify the impurity films. Thus the accumulation of the silica impurities close to the NiYSZ contact is most likely caused by the combined effect of the polarization as well as the cooling of the probe.

The electrode applied potentials are well below the reduction potential for SiO$_2$. Additionally thermodynamic calculations predict the Si from the SiO$_2$ to diffuse into the Ni, as well as the formation of Si-Ni intermetallic.\textsuperscript{10} At a later stage, when the electrode potential is high enough the Si will be re-oxidized to SiO$_2$ as found by Tao et al.\textsuperscript{4} This oxidation might occur when the polarization is released. The presence of silica is observed both in the EDX analysis of the Ni-tips and the YSZ samples. The dissolution of metallic Si in Ni may be locally “purifying” the contact between Ni and YSZ. This is further supported by the ToF-SIMS images (Figure 11) where there is a region in the middle of the Ni contact area, which is depleted of Si and Ni but rich in Zr and Y.

The applied potentials are also below the zirconia reduction potential. Additionally, thermodynamic calculations have shown that the stability of ZrO$_2$ decreases when in contact with Ni,\textsuperscript{13} thus allowing the reduction of ZrO$_2$ and the formation of intermetallic Ni-Zr to occur at higher pO$_2$ than expected for pure ZrO$_2$, suggesting that we reduce the zirconia as well. The roughening of the Ni/YSZ contact area, also...
observed at higher temperatures in macroscopic system, as shown in SEM images of the YSZ sample, suggests interaction between the Ni probe and the zirconia sample.

Conclusions

The in situ highly localized study of the Ni/YSZ microelectrode system under strong cathodic polarization presented in this work reveals several important features related to the electrochemical reduction of YSZ as well as to the degradation mechanism of the Ni/YSZ cathode system in SOECs. Strong cathodic polarizations using Ni microelectrodes result in substantial changes in the electrical, microstructural, and chemical properties of the YSZ. EIS measurements indicate two rate determining processes where the low frequency process, associated with the reduction of H2O at the gas/YSZ interface (and oscillation of this reaction zone) becomes more dominant at stronger cathodic polarizations. The high frequency process is associated with the charge transfer reaction at the Ni/YSZ contact. One to three orders of magnitude decrease is observed in the high frequency resistance upon increasing cathodic polarization form 0 V to −2 V, indicating introduction of electronic conductivity in all the YSZ samples, which is supported by the presence of high conductance regions in the conductance scans. Additionally, a 4−5 orders of magnitude decrease in the R∞,L suggests increase of the reaction zone from the triple phase boundary to the YSZ surface. The expansion of the reaction zone can be beneficial for the operation of the SOECs, since it yields higher gas conversion rates. The polarization however, also causes blocking of the contact surface due to the interaction of the Ni with the YSZ. Additionally, impurities are accumulated around the Ni/YSZ contact suggesting that the impurity film is modified upon polarization resulting in a non-uniform distribution of impurities. These results increase our understanding of the degradation mechanism of the Ni electrodes where impurity segregation at the Ni/YSZ interface causes blocking of the triple phase boundaries and reduces the reaction rate. The comparison between polycrystalline YSZ, and SiYSZ and single crystal YSZ samples suggests that the reduction and re-oxidation of the single crystal is retarded pinpointing the importance of the grain boundaries in the redox chemistry of YSZ.

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