

Advanced supporting anodes for Solid Oxide Fuel Cells





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Summary

Three different ceramic materials for nickel-cermet anodes have been used to prepare and characterise supporting anodes for Solid Oxide Fuel Cells. Symmetrical cells with nominally identical supporting anodes were prepared and electrochemically tested. The three different cermets were nickel/yttria stabilised zirconia (YSZ), nickel/gadolinium doped ceria (CGO) and nickel/titania and vttria doped zirconia (YZT). The Ni/YSZ anodes contained different ratios of fine and coarse YSZ. Their polarisation resistances varied from $2.0 - 7.4 \Omega \text{cm}^2$; the resistance increased with an increasing amount of coarse YSZ. The anodes suffered a lot from degradation, which makes a good analysis and comparison of the measurement data hard. Therefore it is hard to ascribe the impedances to certain electrochemical processes. The lowest polarisation resistance was found for the Ni/CGO anodes, with a polarisation resistance of 1.1 Ω cm². In the first place, the fine microstructure plays an important role for the relatively low impedance. Secondly, the stability of this anode in contrast to the other materials is thought to be due to the high purity powder that was used. From the electrochemical characterisation, it is believed that an adsorption process and oxidation/reduction of the ceria cause the main impedances. The last material, Ni/YZT, performed a bit worse than the Ni/YSZ anodes. The impedances of these Ni/YZT anodes were fitted with a Finite Length Fractal Gerischer, resulting in consistent fit data. This Gerischer describes a diffusion process coupled to a side reaction, which limits the amount of diffusing species. A proper electrochemical explanation has yet to be formulated, but the mixed ionic and electronic conductivity of YZT is almost certainly involved. In any case, the total polarisation impedances for this material amounted 5.9 – 10 Ω cm². Like the Ni/YSZ anodes, the impedance decreased with an increasing amount of fine YZT.

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1. Introduction

Fuel cells are of great interest nowadays for their high efficiencies of converting chemical energy into electrical energy. Like combustion engines, fuel cells use some sort of chemical fuel as its energy source. However, in the fuel cell the chemical energy is converted directly into electrical energy. In other words, the intrinsically inefficient conversion steps in the combustion process are surpassed. Efficiencies are hence not restricted by the Carnot cycle and could theoretically reach values approaching 100%. Besides the high efficiencies, fuel cells are of interest because of their low emissions and zero noise production.

A fuel cell primarily consists of three components: an anode, a cathode and an electrolyte. A schematic representation is depicted in Figure 1-1.



Figure 1-1: Schematic representation of a fuel cell with oxide ion conducting electrolyte.

The electrochemical reactions occur at the electrodes. The fuel is fed to the anode side, whereas the oxidant (often air or oxygen) is fed to the cathode. There exists an electrochemical potential for the chemicals to react; a driving force is thus created. However, the dense electrolyte prevents the fuel and the oxygen from reacting directly with each other. On the other hand, it does allow ion transport. Accordingly, half-cell reactions occur at the electrodes, producing ions that can migrate through the electrolyte. For example, when an electrolyte conducts oxide ions, oxygen will be reduced at the cathode to produce O^{2^-} ions, which in turn react with the fuel at the anode. The anode releases electrons that are consumed again at the cathode. The half-cell reactions that occur are the following:

Cathode:	$^{1}O_{+}2e^{-} \rightarrow O^{2-}$	(1 1)
Callioue.	$\frac{1}{2}O_2 + 2e \rightarrow O$	(1.1)

Anode:

$$H_2 + O^{2-} \rightarrow H_2O + 2e^- \tag{1.2}$$

Analogous electrode reactions occur for proton conducting electrolytes:

Cathode:	$\frac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$	(1.3)

Anode: $H_2 \rightarrow 2H^+ + 2e^-$ (1.4)

As the electrolyte should be a pure ion conducting material, the electron current that balances the ion flux, flows through an external circuit. This balance creates the electrical power.

Since the fabrication of the first fuel cell in 1839 by Sir Grove, a number of fuel cell types have been developed¹. The distinction of the different types of fuel cells is based on their electrolyte and the ion that is able to migrate through it. Table 1-1 lists the five most important types, along with their mobile

ion, temperature of operation, fuel and electrolyte. Since ion conduction is a thermally promoted process whose magnitude is strongly determined by the material used, operational temperatures vary strong from one fuel cell to the other².

Table 1-1: Fuel cel	I types and	selected	features
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Туре	Temperature (°C)	Fuel	Electrolyte	Mobile ion
PEM: polymer electrolyte membrane	70 – 110	H ₂ , CH ₃ OH	Sulfonated polymers	(H₂O) _n H⁺
AFC: alkali fuel cell	100 – 250	H ₂	Aqueous KOH	OH⁻
PAFC: phosphoric acid fuel cell	150 – 250	H ₂	H ₃ PO ₄	H⁺
MCFC: molten carbonate fuel cell	500 - 700	H ₂ , hydrocarbons, CO	(Na,K) ₂ CO ₃	CO32-
SOFC: solid oxide fuel cell	600 - 1000	H ₂ , hydrocarbons, CO	$(Zr,Y)O_{2\cdot\delta}$	O ²⁻

This work emphasises on the SOFC, one of the most promising fuel cell types. Its advantages are the solid electrolyte (instead of liquid, corrosive electrolyte materials), the possibility of using hydrocarbons as fuel and the good mechanical properties of the ceramic materials. A disadvantage is the high operating temperature, which restricts its use to stationary power production (i.e. power plants), since heating and cooling cycles take too long for the use in mobile applications (automotives, etc.).

1.1. Fuel cell characteristics

The performance of a fuel cell is measured as the voltage output as a function of current drawn from the cell. Figure 1-2 shows such an I-V curve along with a power density curve. The measured voltage, E, can be written as:

$$\boldsymbol{E} = \boldsymbol{E}_{eq} - \boldsymbol{E}_{L} - \boldsymbol{\eta}_{act} - \boldsymbol{\eta}_{iR} - \boldsymbol{\eta}_{conc} \tag{1.5}$$

In equation (1.5) E_{eq} is the equilibrium voltage as calculated from the Nernst equation, E_L is the voltage loss due to leaks in the electrolyte, η_{act} is the activation overpotential due to slow electrode reactions, η_{iR} is the overpotential due to ohmic losses in the entire cell and η_{conc} is the overpotential caused by slow gas diffusion processes in the electrodes. The Nernst equation for the half-cell reactions in (1.1) and (1.2) reads:

$$E_{eq} = E^{0} + \frac{RT}{nF} \ln \frac{p_{O_{2}}^{\frac{1}{2}} p_{H_{2}}}{p_{H_{2}O}}$$
(1.6)

 E^0 is the standard potential difference (T = 293 K) between the two half-cell reactions: $E^0 = E_2^0 - E_1^0 = -1.23$ V, where E^0 is related to the standard Gibbs energy by $E^0 = -\Delta G/nF$. Further, R is the gas constant, T the absolute temperature, n the amount of electrons involved (in this case n=2) and F is Faraday's constant³.

From equation (1.5) it becomes clear that apart from a dense electrolyte layer, three electrode processes play an important role in fuel cell performance. By choosing the right electrode materials and tailoring their microstructures, polarisation resistances due to slow electrochemical reactions, diffusion and low conductivity can be minimised.



Figure 1-2: Schematic I-V curve and power density curve

1.2. State-of-the-art SOFC

Basically, two SOFC designs are used: the electrolyte-supported and electrode supported cell. The first design consists of a thick electrolyte that has both sides coated with a thin electrode. The second uses an electrode as the support layer. State-of-the-art SOFCs use the latter design. Its advantage is the smaller ohmic resistance as compared to the electrolyte-supported design. The ohmic resistance in the electrolyte is caused by the low total conductivity, which is inherent in 'pure' ionic conductors. The ohmic loss can be reduced by decreasing the thickness of the electrolyte. Anode supported SOFCs have an electrolyte with a thickness of $10 - 30 \ \mu m$. On the other hand, in the electrode-supported design, attention must be paid to gas transport through the thick electrode. A porous microstructure is necessary to promote gas diffusion. Figure 1-3 shows both an electrolyte-supported cell and an electrode (anode) supported fuel cell⁴.



Figure 1-3: Design of an electrolyte supported SOFC (left) and an anode supported SOFC (right)

1.2.1. Electrolyte

The electrolyte material of the SOFC is in most cases 8 mol% yttria stabilised zirconia (8-YSZ). This material is preferred for its high oxygen ion conductivity, mechanical strength and stability. Doping ZrO_2 with Y_2O_3 has two functions. First, zirconia is transformed from the monoclinic phase into the otherwise only at elevated temperatures stable cubic phase (fluorite structure). And second, the doping with the Y^{3+} ions creates oxygen vacancies in the zirconia lattice, which is beneficial for the oxygen ion conductivity. The highest oxygen ion conductivity is obtained when doping with 8 – 10 mol% Y_2O_3 ; higher levels of dopant cause the positive oxygen vacancies and negative yttria ions to combine, lowering the concentration of free oxygen vacancies. Other dopants can be used instead of yttria as well. A good example is scandia (Sc_2O_3), which has a comparable stability compared to yttria stabilised zirconia, but higher ionic conductivity⁵.

Other materials with higher oxygen ion conductivity, such as $LaGaO_3$ or doped ceria (Gd, Y or Sm doped) have been proposed and investigated as electrolyte materials too. YSZ is however often preferred as electrolyte material. This is mainly because the alternative materials have some unsolved drawbacks. Doped ceria exhibits electrical conduction at low pO_2 and temperatures above 600°C, thus limiting its application temperature range⁶. LaGaO₃ is chemically unstable under reducing atmospheres.

1.2.2. Cathode

The cathode, or air electrode operates in oxidising environments at temperatures up to 1000°C. The next reaction (1.7) takes place, in which oxygen gas is converted into oxygen ions, consuming electrons.

$$\frac{1}{2}O_2 + 2e^- \to O^{2-}$$
 (1.7)

The cathode has to meet a number of requirements: high electronic conductivity, chemical and mechanical stability in an oxidising atmosphere, matching thermal expansion coefficient with other SOFC components and minimal reactivity with electrolyte and interconnect materials. Lanthanum manganites meet these requirements very well and are often used as cathode materials. By doping with strontium or calcium, the electronic conductivity is further improved. Although materials are present with higher activities towards the oxygen reduction, these are often quite reactive towards the YSZ electrolyte at higher temperatures⁴.

1.2.3. Anode

The requirements for a SOFC anode are good chemical and mechanical stability under SOFC operation conditions, high ionic and electronic conductivity over a wide pO_2 range, good chemical and thermal compatibility with the electrolyte and interconnect materials, high surface oxygen exchange kinetics and good catalytic properties for the anode reactions. In the anode supported SOFC design another requirement is present: sufficient porosity to promote gas transport through the thick electrode. The state-of-the-art SOFC uses a nickel-YSZ cermet as the anode. This material fulfils most requirements. The disadvantages of this material are the poor redox stability, low tolerance for sulphur and carbon deposition and the tendency of nickel agglomeration after prolonged operation. Especially the low tolerance for carbon deposition makes this material inappropriate for hydrocarbon fuels. Since nickel is an excellent catalyst for both steam reforming and hydrocarbon cracking, carbon deposition occurs rapidly when feeding hydrocarbons, unless excess steam is present to ensure steam reforming. The steam dilutes however the fuel flow, making the process less efficient. Equations (1.8) – (1.13) show the reactions that occur when methane is fed to a Ni-YSZ anode⁷.

$CH_{4} + H_{2}O \rightarrow CO + 3H_{2}$	(1.8)
	()

$$H_2 + O^{2-} \rightarrow H_2O + 2e^{-} \tag{1.9}$$

$$CO + O^{2-} \rightarrow CO_2 + 2e^{-} \tag{1.10}$$

Steam reforming is associated with the following gas shift reaction, in which carbon monoxide is converted into hydrogen and carbon dioxide:

$$CO + H_2O \rightarrow CO_2 + H_2 \tag{1.11}$$

If the steam content in the feed gas is insufficient for reaction (1.8) to occur, carbon will be deposited according to:

$CH_4 \rightarrow C + 2H_2$	(1.12)
$2CO \rightarrow C + CO_2$	(1.13)

The carbon deposition eventually causes a lot of mechanical stress in the cermet, resulting in cracks and the destruction of the cermet.

Coarsening and agglomeration of nickel particles result in a decrease of both the porosity and the amount of reaction zones (triple phase boundary, TPB) in the anode. This in turn affects the gas transport and reaction kinetics, leading to additional losses. Since reactions only can take place at sites where electrons, oxygen ions and fuel can interact, the so-called triple phase boundary (TPB), the microstructure is very important in order to prevent polarisations. Figure 1-4 shows a schematic representation of the TPB in a Ni-YSZ cermet.



Figure 1-4: The triple phase boundary region in a Ni-YSZ cermet. (a) YSZ particle does not contribute to the TPB, because is not connected to the YSZ electrolyte. (b) Ni is not active because the electrons cannot be removed.

On both cathodes and anodes extensive research is going on nowadays, to improve their performance in SOFC operation. This work will emphasise on the anode materials.

1.3. Objectives

This work investigates different anode materials in anode-supported cells. The anodes will be employed as thin functional layers on top of standard Ni/YSZ substrates. The anode materials in the functional layers are nickel cermets, containing either YSZ, titania doped YSZ (YZT) or gadolinium doped ceria. The latter two are promising new anode materials due to their mixed ionic and electronic conduction. Characterisation of these materials will be carried out with electrical impedance spectroscopy. In order to get reliable results with this technique, symmetrical cells will be prepared, consisting of two anodes separated by a thin electrolyte.

This report first describes some theoretical background in this project. This chapter contains a description of the electrochemical processes that are going on in SOFC anodes and some important things about impedance spectroscopy. Next, the general preparation of symmetrical anode-supported cells is discussed. The following three chapters describe the preparation and characterisation of the different anodes. The use of the Ni/YSZ anodes serves as an investigation of the effect of microstructure on anode performance. When clear trends are found, microstructural optimisation of the new anode materials might be possible as well. This would be interesting, since little is known yet about the microstructural effects in these materials.

2. Theoretical background

This chapter gives a brief introduction in the working principals of the anode and discusses some anodic processes that could contribute to a cell's impedance. Subsequently, some remarks are made about impedance spectroscopy as a tool in investigating anodic performance.

2.1. The anode

When optimising the anode build up, microstructure or material, one needs to understand the processes that are going on in the anode during operation. Among these processes are fuel gas diffusion, adsorption/desorption of fuel species, electrode reactions and charge transfer. All of these processes have their impedances, which can be found using impedance spectroscopy. As already mentioned in the introduction (paragraph 1.1), the polarisations occurring at the electrodes can be divided in the activation polarisation and concentration polarisation. The ohmic polarization mainly arises from the resistance in the electrolyte.

2.1.1. Hydrogen oxidation

De Boer⁸ proposed the following mechanism for the hydrogen oxidation on Ni/YSZ cermets:

Step 1	$H_2 + 2s_{Ni} \rightarrow 2H_{ads,Ni}$	(2.1)

Step 2 $H_{ads,Ni} + O_0^x \rightarrow OH_0^{\bullet} + e' + s_{Ni}$ (2.2)

Step 3
$$OH_{O}^{\bullet} + S_{YSZ} \rightarrow OH_{ads,YSZ}^{-} + V_{O}^{\bullet\bullet}$$
 (2.3)

Step 4
$$H_{ads,Ni} + OH_{ads,YSZ}^- \rightarrow H_2O_{ads,YSZ} + e' + s_{Ni}$$
 (2.4)

Step 5
$$H_2O_{ads,YSZ} \rightarrow H_2O(g) + s_{YSZ}$$
 (2.5)

From step 2 and 4 it becomes clear that the triple phase boundary (TPB) plays an important role in the hydrogen oxidation. Hydrogen atoms are adsorbed on the nickel surface and react with lattice oxygen or hydroxide ions adsorbed on the YSZ surface to form adsorbed water molecules. Electrons are released and have to be transported away from the reaction zone. Primdahl and Mogensen⁹ claimed that large polarisation resistances in the low frequency domain of impedance spectroscopy should be attributed to the adsorption/dissociation process of hydrogen. It is useful to work out the adsorption step a little bit further.

First of all, the rate equation for the adsorption/dissociation of hydrogen on the nickel surface (step 1) is described by equation (2.6).

$$r = k_1 (1 - \theta_H)^2 p H_2 - k_{-1} \theta_H^2$$
(2.6)

When Langmuir adsorption is assumed, this means that the equilibrium constant can be written as in equation (2.7), with θ_H being the fraction of occupied adsorption sites.

$$K_{ads} = \frac{k_1}{k_{-1}} = \frac{(\theta_H^{eq})^2}{(1 - \theta_H^{eq})^2 \rho H_2}$$
(2.7)

After rearrangement, θ_H can be written as a function of pH₂ and equations (2.8) and (2.9) are obtained.

Occupied sites

$$\theta_{H}^{eq} = \frac{\left(K_{ads}pH_{2}\right)^{\frac{1}{2}}}{1+\left(K_{ads}pH_{2}\right)^{\frac{1}{2}}}$$
(2.8)

(2.9)

Empty sites

$$(1 - \theta_{H}^{eq}) = \frac{1}{1 + (K_{ads} p H_{2})^{\frac{1}{2}}}$$

Two limiting situations are possible. At low temperature (i.e. θ_{H} is close to one) or high hydrogen partial pressure, $(K_{ads}pH_2)^{1/2} >> 1$, and the following dependency of θ_{H} with hydrogen partial pressure is valid:

$$\theta_{H}^{eq} \approx 1 \qquad \text{and} \ (1 - \theta_{H}^{eq}) \propto p H_{2}^{-\frac{1}{2}}$$
(2.10)

At high temperature (i.e. θ_{H} is close to zero) or low hydrogen partial pressure, $(K_{ads}pH_2)^{\frac{1}{2}} \ll 1$, giving:

$$(1-\theta_H^{eq}) \approx 1$$
 and $\theta_H^{eq} \propto p H_2^{\frac{1}{2}}$ (2.11)

When it is assumed that R \propto 1/r, it follows that for the resistance for hydrogen adsorption/dissociation one can write:

$$R \propto 1/r_{ads/diss} \propto pH_2^{-1}$$
 at high temperatures (2.12)

Mogensen and Skaarup¹⁰ showed however that the assumption that $\theta_H << 1$ at high temperatures, is often not valid for Ni/YSZ cermets. Especially at high hydrogen partial pressure (i.e. $pH_2 \sim 10 - 100$ kPa), the surface coverage may have a significant value. Moreover, the chemisorption of hydrogen on nickel is an activated process, making adsorption favourable at higher temperatures. Hence, the dependency in equation (2.12) is rarely found. Instead, a much smaller exponent is likely to be found. Primdahl¹¹ even found almost no dependency of the resistance with hydrogen partial pressure, indicating that the surface coverage of hydrogen on nickel approached one ($\theta_H \approx 1$). On the other hand, in cermets where the YSZ has been replaced by a mixed conducting material, the adsorption/dissociation may play a dominant role again. It would therefore be interesting to see which dependencies can be extracted from the impedance measurements.

2.1.2. Polarisation

The activation polarisation, which is caused by sluggish electrode kinetics, is described by the Tafel equation:

$$\eta_{act} = \frac{RT}{zF} \ln \frac{i}{i_0}$$
(2.13)

In this equation *R* is the gas constant, *T* the temperature, *z* is the number of electrons participating in the electrode reaction, *F* is the Faraday's constant and i_0 is the exchange current density. Adsorption/desorption processes, electrode reactions and charge transfer can all contribute to the activation polarisation³.

Virkar et al.¹² worked out some equations that describe the resistances for charge transfer. They state that the intrinsic charge transfer resistance of an electrocatalyst/electrolyte pair (for instance

nickel/YSZ) can be reduced when the electrode shows ionic conductivity. The intrinsic charge transfer, R_{ct} (in Ωcm^2) is defined as:

$$R_{ct} = \frac{RT}{zFi_0}$$
(2.14)

However, in an electrode that has some ionic conductivity the reaction zone is extended from the electrolyte/electrode interface. This causes an increase of the real surface area per geometric area. When it is assumed that the electronic conductivity of the electrode far exceeds the ionic conductivity and gas transport is not rate limiting, the effective charge transfer in a thick electrode approaches:

$$R_{ct}^{eff} \approx \sqrt{\frac{BR_{ct}}{\sigma_i (1 - V_v)}}$$
(2.15)

In this equation, *B* is the grain size of the ionic conductor in the electrode, σ_i the ionic conductivity and V_v the fractional porosity. So for small YSZ grains and a porosity not too high, the effective charge transfer resistance can be reduced significantly.

The concentration polarisation is caused by concentration gradients between the reaction interface and the bulk. Several processes may be responsible for the concentration polarisation, the major being gas diffusion through the electrode. The rate of electron transport (current density, *i*) follows Fick's first law of diffusion:

$$i = \frac{nFD(C_b - C_s)}{\delta}$$
(2.16)

In equation (2.16), *D* is the diffusion coefficient of the reacting species, C_b its bulk concentration, C_s its surface concentration and δ the thickness of the diffusion layer. The limiting current density, i_L , i.e. the maximum current density, occurring when the surface concentration is zero, is defined as:

$$i_L = \frac{nFDC_b}{\delta}$$
(2.17)

From equations (2.16) and (2.17) it then follows that:

$$\frac{C_s}{C_b} = 1 - \frac{i}{i_L} \tag{2.18}$$

When no current is flowing, i.e. the concentration at the electrolyte is the bulk concentration, the Nernst equation becomes:

$$\boldsymbol{E}_{i=0} = \boldsymbol{E}^0 + \frac{\boldsymbol{R}\boldsymbol{T}}{\boldsymbol{n}\boldsymbol{F}} \ln \boldsymbol{C}_b \tag{2.19}$$

When however current is flowing, a potential difference is created between the bulk and the electrolyte/electrode interface. This is the concentration polarisation.

$$\Delta E = \eta_{conc} = \frac{RT}{nF} \ln \frac{C_s}{C_b}$$
(2.20)

Or alternatively:

$$\eta_{conc} = \frac{RT}{nF} \ln \left(1 - \frac{i}{i_L} \right)$$
(2.21)

As can be seen from equation (2.17), the limiting current density, i_L , can be expressed in terms of the diffusion constant. The effective diffusion constant in turn depends on porosity (V_v) and tortuosity (τ):

$$D_{\rm eff} \propto rac{V_{
m v}}{ au}$$
 (2.22)

In effect, an open porous microstructure of the anode results in a decrease of the polarisation due to fuel gas diffusion. Virkar et al. showed that when both the concentration and activation polarisation contribute to the overall polarisation, the polarisation in an anode supported cell could be described by equation (2.23).

$$\eta = iR + \frac{RT}{2F} \ln \frac{i}{i_0} + \frac{RT}{2F} \ln (1 + \frac{p_{H_2}^0 i}{p_{H_0}^0 i_{as}}) - \frac{RT}{2F} \ln (1 - \frac{i}{i_{as}})$$
(2.23)

In this equation, pH_2O^0 and pH_2^0 are the water and hydrogen partial pressures outside the anode, *i* is the current density and *i*_{as} is the limiting anode current density (the maximum current density, occurring when the hydrogen partial pressure at the electrolyte/anode interface is nearly zero. Figure 2-1 shows the partial pressure gradient of water and hydrogen in an anode-supported cell¹². A gradient for hydrogen that drops very quickly at the outer surface of the anode indicates poor gas transport.



Figure 2-1: Concentration profile in the electrodes of an anode-supported cell

2.1.3. Anode structure

Because electrochemical reactions at the anode involve oxygen ions, electrons and fuel, these can only take place in the so-called triple phase boundary (TPB). In the TPB, a connection exists between an ion conducting, electron conducting and the fuel gas phase. The electrochemical reaction zone appears to

exist just within a distance of about 10 µm from the electrolyte¹³. From this point of view, it seems logical to create an interlayer between the bulk anode and the electrolyte that offers an increased amount of reaction sites. This interlayer and the bulk anode should differ in microstructure, regarding porosity and particle size¹⁴. Whereas the bulk layer is porous, promoting fuel gas diffusion, the interlayer has a finer structure in order to increase the TPB area. Even a graded structure can be made with multiple layers with decreasing particle size and pore sizes when approaching the electrolyte¹⁵. In effect, the thin anode interlayer near the electrolyte is the functional anode, whereas the substrate merely functions as a current collector and provides mechanical strength. In this work, the substrate is a standard Ni/YSZ cermet. This choice guarantees a chemical and thermal stable substrate under the reducing atmospheres used. The nickel in the substrate provides the substrate with electronic conductivity to minimise efficiency losses. The impedance measurements will be carried out in wet hydrogen, so there is no danger of carbon deposition on the anode. When hydrocarbons are used, especially the Ni/YSZ substrate will be affected by carbon deposition, as few oxygen ions will be present outside the reaction zone (i.e. beyond the functional anode layer) to oxidise the carbon precipitates. That's why researchers have already proposed to use the steel interconnect (Fe-30Cr) as the substrate, because the sole function of the substrate is to collect current¹⁶. Catalytic activity is not important; stability under reducing atmospheres is.

In a cermet, the TPB only exists on places where nickel and YSZ particles connect (see Figure 2-2). The YSZ electrolyte is actually extended into the anode by the YSZ matrix of the anode. The amount of extension defines the thickness of the electrochemical reaction zone, since the oxygen ions cannot diffuse any further when no ionic conducting path exists. The nickel particles serve to catalyse the fuel oxidation and to collect the current.



Figure 2-2: Representation of the triple phase boundary (TPB) where the electrochemical species can react with each other

2.1.4. Alternative materials: mixed ionic-electronic conductors (MIEC)

Clearly, an anode material that conducts both electrons and oxygen ions, a mixed ionic-electronic conductor (MIEC), seems to have advantages over the Ni/YSZ cermet. The TPB area would not anymore be restricted to places where different particles connect. In fact, the fuel oxidation could take place anywhere (see Figure 2-3). The MIEC both provides oxygen ions and removes the electrons that are formed during the oxidation.



Figure 2-3: The electrochemical reactions could theoretically take place over the whole surface of a MIEC

A number of MIEC materials has been investigated as potential anode material. Most research has been done on ceria (doped with gadolium, samarium or yttrium), mixed conducting perovskites (doped LaCrO₃ and SrTiO₃) and titania doped YSZ¹⁷. Some complications evolve however and unfortunately none of these materials can substitute the Ni/YSZ cermet on its own. First of all, the electronic conductivities of these materials are often too low to be an effective current collector. Hence the use of a second component is necessary to fulfil this requirement. The second problem is the catalytic activity. It seems that all of these materials have some catalytic activity towards the hydrogen oxidation^{18, 19, 20}, but it is very doubtful that any of these materials has catalytic activity towards hydrocarbon conversion^{21, 22, 23}. Most of the hydrocarbon conversion is thus performed via internal steam reforming, followed by oxidation of hydrogen and carbon monoxide (equation (1.8) - (1.10)). Although some exiting papers have been published, claiming that ceria catalyses hydrocarbon directly^{24, 25}, i.e. without steam reforming (see equation (2.24)), contradicting papers exist showing almost no catalytic activity for hydrocarbon conversion at all^{21, 26}. The sensational results probably arise from oxygen gas leaking through the electrolyte and partially oxidising the hydrocarbons. Even the electrocatalytic activity for hydrogen oxidation on ceria is proven to be low for temperatures below 1000°C. Furthermore, Primdahl and Mogensen⁹ showed that only small additions of nickel (~1w%) to anodes consisting of a mixed conductor (YZT, ceria, substituted lanthanum chromite), resulted in a large reduction of the polarisation resistance. They explained the existence of the polarisation resistance as a slow adsorption/dissociation step of hydrogen on the ceramic part of the cermet. This confirms that the catalytic activity of the mixed conductors is intrinsically low.

$$CH_4 + 4O^{2-} \rightarrow CO_2 + 2H_2O + 8e^-$$
 (2.24)

With other words, an anode consisting of one material still seems impossible. That's why the mixed conducting materials still have to be used in a composite (cermet) material. There are still some advantages, however. With the use of mixed conducting materials, the amount of nickel might be reduced. This might be beneficial for SOFCs operated with hydrocarbons. In the samples prepared in this project, the amount of nickel is 40 vol%. This is done to allow for proper comparison of the ceramic part of the anodes.

2.1.5. Coke formation

Since nickel is such a good catalyst for hydrocarbon cracking, it would be logical to look for alternative metals to replace the nickel. Copper may be a good candidate. Copper is, like nickel, an excellent electronic conductor, but is a poor catalyst towards hydrocarbon cracking. In experiments using a Cu-YSZ cermet, no carbon deposition was observed after operating the anodes for several hours in toluene at 800°C. However, the use of copper has some drawbacks. First, the melting points of CuO_x and Cu are low, making the fabrication of Cu-YSZ cermets tricky and limiting the operating temperature of SOFCs. Second, Cu is a poor catalyst towards hydrocarbon activation as well. So the same property that allows Cu to be used in direct hydrocarbon oxidation makes it inappropriate to be used for

hydrocarbon fuels. Another disadvantage of using copper in anodes is the precipitation of Cu-metal between the anode and electrolyte after prolonged SOFC operation. This precipitation decreases the performance of the anode¹³.

2.2. Impedance spectroscopy

Impedance spectroscopy is a powerful tool in the analysis of solid-state systems. The technique utilises an AC excitation voltage at different frequencies. This perturbation signal is applied to the sample under consideration and the current response is measured. The amplitude and phase shift change with the frequency of the signal and the combination of these two give the information of the impedance. Since different processes that are going on in the measured systems have different relaxation times, each of these processes will respond to signals at different frequencies. Hence, different processes can be identified by measuring the impedance over a range of frequencies. For a solid oxide fuel cell electrode, these include gas diffusion, electrochemical reactions, charge transfer, adsorption/dissociation, etc.

When a small ac-perturbation, $V_0 e^{i\omega t}$, is applied to an electrochemical system, the impedance is given by:

$$Z(\omega) = \frac{V(\omega)}{I(\omega)} = \frac{V_0 e^{j\omega t}}{I_0 e^{j(\omega t + \varphi)}} = \frac{V_0}{I_0} (\cos \varphi - j \sin \varphi)$$
(2.25)

In this equation, ω is the angular frequency (2 π f), *j* the imaginary unit and φ the phase shift. Another representation is the admittance Y(ω), which is basically the inverse of the impedance:

$$Y(\omega) = \frac{1}{Z(\omega)} = \frac{I_0 e^{j(\omega t + \varphi)}}{V_0 e^{j\omega t}} = \frac{I_0}{V_0} (\cos \varphi + j \sin \varphi)$$
(2.26)

In a graphical representation it is custom to plot the real and imaginary part against each other, with V_0/I_0 being the norm and $\cos(\varphi)$ gving the real and $i\sin(\varphi)$ the imaginary part, respectively.

Analysis of the impedance spectra occurs by fitting the data with a model. The system under consideration is regarded as an electrical circuit, consisting of a number of basic elements (resistances, capacitors, inductances, constant phase elements (CPE's) etc.). The electrical circuit that now represents the real time system can help to understand which processes are playing a dominant role in the impedance behaviour.

2.2.1. Cell design

Doing impedance measurements on SOFC electrodes normally requires the use of three electrodes: a work electrode (the measured electrode), a counter electrode and a reference electrode. Without the reference electrode it is impossible to ascribe the measured impedances to either of the two remaining electrodes. Therefore, most researchers put a reference electrode on the electrolyte, which is assumed to have a stabile, constant potential when far enough away from the active electrode. This is however often not the case, especially in thin electrolyte systems. Adler²⁷ describes that improper placement of the reference electrode can easily lead to false interpretation of impedance measurements. When a setup is used like in Figure 2-4, the counter and work electrode have to be aligned very well. If this is not the case, the reference potential can show frequency dependent displacements, leading to errors in the electrode resistances extracted from impedance spectra. In the extreme case, the reference electrode can almost have the same potential as the counter electrode (Figure 2-4)⁸. Even when properly aligned, a difference in resistance between the two active electrodes can cause distortion in the impedance.



Figure 2-4: Left) Set-up that is susceptible to errors due to misalignment of electrodes. Right) Extreme misalignment causes the reference potential to be close to the potential of the counter electrode

Some different cell designs have been developed to overcome these problems. Figure 2-5 shows two of these designs. The left design has the reference electrode as a ring around the thick electrolyte pellet. Current lines have been added in the figure⁸. The right design is utilised by Risø, Denmark²⁸. In this design a hole is drilled in the centre of the electrolyte pellet to allow the reference electrode to be positioned close to the work electrode. Due to the cavity, the reference electrode now shares an equipotential electrolyte surface.



Figure 2-5: Two cell designs with proper reference electrode placement. Left) Ring electrode around the electrolyte. Right) Risø pellet, with a drilled hole.

Another way to solve the problem of the positioning of the reference electrode is the use of symmetrical cells. Since there is no need for distinguishing the two electrodes in such a design, the use of a reference electrode is unnecessary. Especially in the case of electrode supported SOFCs, this way of measuring the impedance is advantageous, since the cells contain very thin electrolytes. Clearly, positioning of a reference electrode on such a thin electrolyte becomes even more difficult. So, the symmetrical cell design is used in this project, too. Two anodes (consisting of a support and a functional anode layer) are separated by a thin electrolyte (~40 µm). A schematic representation of such a cell is given in Figure 4-1, in chapter 3. A two-electrode configuration is thus used. The voltage and current are applied, respectively read using four leads. A drawback of using symmetrical cells is the fact that polarisation studies are impossible. Polarisation of one of the electrodes implies a non-symmetric test situation. A reference electrode would again be required. Polarisation studies are useful, because measuring impedance under polarisation gives a more realistic view of the anode's properties under SOFC operation. After all, a fuel cell isn't operated under open circuit voltage (OCV).

2.2.2. Equivalent circuits

Fitting of the measurement data is performed with the EQUIVCRT software. An equivalent circuit has to be found that fits the measured impedances and can provide a physical meaning of the system under investigation. For instance, processes that are expected to occur simultaneously or after each other appear as typical parallel or series circuit elements, respectively. The elements that can be used in the equivalent circuits are listed in Table 2-1, along with their impedances and admittances. *R* is a normal resistance and *C* is a standard capacitor. W is a Warburg element, which describes semi-infinite diffusion. *Q* is a constant phase element (CPE) and is in fact a phenomenological element. The exponent α can take any value between -1 and 1. For $\alpha = -1$ the CPE becomes an inductance, for $\alpha = 0$ a resistance, for $\alpha = 0.5$ a Warburg and for $\alpha = 1$ a capacitor. The deviation of α from these ideal values represents the non-ideal behaviour of the measured system. Finally, *G* is a Gerischer impedance. The Gerischer element describes an impedance that originates from an electrochemical process coupled with a chemical side reaction.

Element	Description	Impedance	Admittance
L	Inductance	jωL	1/(<i>j@</i> L)
R	Resistance	R	1/R
С	Capacitor	1/(<i>j</i> ∞C)	j∞C
W	Warburg	$Z_0 / \sqrt{j\omega}$	$Y_0 \sqrt{j\omega}$
Q	CPE	$Z_0 / (j\omega)^{\alpha}$	$Y_0(j\omega)^{\alpha}$
G	Gerischer	$Z_0 / \sqrt{k + j\omega}$	$Y_0\sqrt{k+j\omega}$

Table 2-1: Impedances and admittances of different circuit elements

3. General set-up considerations

A short overview is given of the set-up that was used for the electrochemical impedance measurements. Some strange observations were made, during the electrochemical characterisation and it is useful to discuss these first, to put all the following results in the right perspective.

3.1. Electrochemical set-up

The samples are heated in a tubular quartz reactor inside a furnace. A schematic representation of the sample holder inside the quartz tube reactor is given in Figure 3-1. The cells are mounted into an alumina sample holder between two elements that promote a homogeneous gas distribution outside the sample. This is important to prevent additional impedances in the obtained results that shouldn't be attributed to electrode processes²⁸. Platinum and nickel meshes serve as current collectors. On top of the whole assembly a weight is put, to prevent contact problems (not shown in Figure 3-1).



Figure 3-1: Setup of single atmosphere reactor.

3.1.1. Gas tightness of the set-up/position of the sample in the furnace

During the electrochemical measurements it was observed that there might be a gas leak in the set-up. First of all, the temperature of the sample decreased upon decreasing the hydrogen partial pressure. Secondly, the oxygen partial pressure in a 100% nitrogen gas flow (100 ml/min) was ten times as high as expected from the gas composition (measured with an oxygen sensor). And on lowering the gas flow, the oxygen partial pressure in the gas flow increased. The latter two effects clearly indicate an oxygen inflow. The first effect however can hardly be ascribed to the combustion of hydrogen in the quartz furnace. Since the amount of oxygen is the limiting factor in the combustion reaction, changing the hydrogen partial pressure should have no effect on the reactor temperature.

So where does the change in reactor temperature come from? This can only be explained by the change of heat capacity when the composition of the gas changes. Nitrogen is used as a balance gas, so when the hydrogen partial pressure decreases, the nitrogen partial pressure increases and the heat capacity of the gas increases from 30.5 J/mol·K to 33.0 J/mol·K. Likewise the reactor temperature will decrease, when the furnace temperature is kept constant. This effect will be even larger if the sample is not placed in the middle of the furnace, since the effect will increase the temperature gradient in the tubular reactor.

So what effect might we expect from the oxygen leak? As during the measurements we have a gas flow of 100 ml/min, the oxygen partial pressure could reach a maximum value of 100 ppm. On the other hand, we use a mixture of hydrogen/water that serves as a buffer to set the oxygen partial pressure. Since these hydrogen and water partial pressures are at least a factor of 200 higher than the oxygen partial pressure resulting from the leak, we assume that the equilibrium remains at its expected value.

4. General cell preparation

This chapter discusses the general preparation of the symmetrical cells that are measured electrochemically. Several different samples were prepared; they contain identical anode substrates, but differ in the functional anode layer. The anodes are separated by a thin electrolyte layer. The preparation of the different functional anode layers is discussed in the following chapters, dealing with the different anode materials.

4.1. Experimental

4.1.1. Anode substrates

The anode substrates were prepared by hand pressing a NiO/YSZ powder at 100 MPa. The NiO/YSZ powder is a granulate resulting from spray drying a slurry with a composition listed in Table 4-1. The nickel oxide used is a powder from Auer Remy Seltene Erden GmbH. Both coarse and fine 8 mol% yttria stabilised zirconia (8-YSZ) are used for the substrates. The fine YSZ powder is a powder from Tosoh Japan (TZ8Y) with a mean particle size of 0.2 μ m, whereas the coarse powder is a molten granulate from GTV GmbH, with a particle size of 5 – 15 μ m. The spray drying slurry further contains a dispersant (Dolapix CE 64), binders and other additives (PEG 750, PEG 4000 and PEG 15000). Both the preparation and characterisation of the slurry and granulate are described elsewhere in detail^{15, 29}. The designation of the granulate is KO50_10. After reduction the anode substrates should contain 40 vol% nickel (with respect to the ceramic material).

Crude material number	Compound	Amount (w%)
966	Nickel oxide	
837	8-YSZ (coarse)	
112	8-YSZ (fine)	
	Water	
101	Dolapix CE 64	
431	PEG 750	
360	PEG 4000	
278	PVA 15000	

Table 4-1: Composition of slurry KO50_10

The pressed green samples have a diameter of 14 mm and thicknesses of about 0.8 mm.

4.1.2. Functional anode layers

Functional anode layers were deposited on top of the anode substrates using an air spraying technique. Slurries containing fine anode material were prepared for this purpose. In order to create different functional anode layers, the composition of the slurries was varied. The composition of the different slurries and the resulting microstructures are dealt with in the respective chapters discussing the different anode materials.

4.1.2.1. Air spray deposition

The as prepared slurries were deposited on the anode substrates by air spray deposition. With this technique, a slurry is forced through a narrow nozzle, under slight overpressure (~0.6 bar). To enhance reproducibility, the substrates move under the fixed nozzle using an automatically moving table (X-Y Tisch), controlled by a computer program (PC 2000). In this way, it is possible to create even layers of material onto the substrates with a reasonably constant thickness. All the deposited functional anode layers had a thickness of 20 – 35 μ m. The thicknesses of the layers were calculated by weighing the samples before and after spraying and using formula 2.1. In this formula, Δm is the weight difference, D the diameter of the substrate and ρ_{anode} the specific weight of anode material, assuming a certain porosity.

$$thickness = \frac{\Delta m}{\rho_{anode} \cdot \frac{1}{4} \cdot \pi \cdot D_{substrate}^2}$$
(4.1)

The nozzle system used is one from Spraying Systems Co. (system 1/8 JAC SS, liquid nozzle 1650 SS).

4.1.3. Electrolyte layers

Like the functional anode layers, the electrolytes were deposited by air spray deposition as well. For this purpose, slurries were prepared, containing 8 mol% yttria stabilised zirconia (8-YSZ) as the electrolyte material.

4.1.3.1. Slurry preparation

Three different YSZ powders were used in the electrolyte slurries. Two of the powders were from Tosoh, Japan; TZ8Y ($d_{50} \sim 0.2 \mu m$) and TZ8Y-S ($d_{50} \sim 0.3 \mu m$). The third is a powder from Unitec, UK (FYT13-002H) with a d_{50} particle size of 0.7 μm . It is expected that the amount of shrinkage of the electrolyte during sintering plays a dominant role in the preparation of symmetrical cells. Therefore, different particle sizes were used in the electrolyte slurries to manipulate this shrinkage behaviour. Furthermore, the slurries contain isopropyl alcohol and terpineol as solvents, polyvinyl pyrrolidone (PVP) as dispersant and binder, and ethyl cellulose as binder material. First the powder, solvents and PVP are ball milled for at least 48 hours. After this, the ethyl cellulose is stirred in by using a vertical mixer. The slurry compositions are listed in Table 4-2.

Table 4-2: Electrolyte slurry compositions

Compound	Slurry 8.1 ^ª	Slurry 8.2 ^ª	Slurry NE1
Powder	TZ8Y (Tosoh)	TZ8Y-S (Tosoh)	FYT13-002H (Unitec)
Isopropyl alcohol (w% of YSZ)			
Terpineol (w% of YSZ)			
PVP (w% of YSZ)			
Ethyl cellulose (w% of YSZ)			
	9		

^a) Slurries from a previous project²⁹

4.1.3.2. Air spray deposition

The electrolytes were deposited on top of the functional anode layers. The solid content of the electrolyte slurries during spray deposition, amounted \sim 0.5 g/ml. Using this concentration, a smooth, equal deposition was obtained within about 5 minutes. Before using the slurries for deposition, they

were first de-agglomerated using ultrasonic sound. The thickness of the electrolyte layers was calculated with formula (4.1) as well, with for ρ_{YSZ} the density of dense YSZ, being 5.9 g/cm³.

4.1.4. Symmetrical cells

Symmetrical cells were prepared by assembling two individual cells, containing at least an anode substrate and an electrolyte layer. The two individual cells were pressed together at 40 MPa, using a hand press. Consequently, the symmetrical cells are fire at 1430°C for 2 hours. For trial purpose, not all cells contained a functional anode layer. The cells that were prepared for electrochemical characterisation however, all contained functional anodes. These symmetrical cells all look like the one in Figure 4-1.



Figure 4-1: Schematic representation of a symmetrical anode supported cell

The preparation route of the symmetrical cells is given in Figure 4-2. Important to notice is the fact that after the application of the functional anodes, the cells are dried in a stove. However, after the application of the electrolytes, no special drying step takes place. This is done to promote the attachment of the individual electrolyte layers during pressing at 40 MPa. In this way, one dense electrolyte can be obtained after sintering, instead of two separated electrolyte layers. After sintering the symmetrical cells have a surface area of 1.27 cm².

4.1.4.1. Shrinkage difference during sintering

As already mentioned in paragraph 4.1.3.1, it is expected that the difference in amount of shrinkage between the anodes and electrolyte can lead to problems during sintering. Since the electrolyte has to be sintered to a dense layer, whereas the anodes need to remain porous, one expects the electrolyte to shrink more than the anodes. When co-sintering an individual cell with a thin electrolyte layer this could either lead to cracks in the electrolyte or to bending of the samples towards the electrolyte. In the symmetrical cell however, both anodes apply an equal tensile force on the electrolyte. This could probably lead to separation of the thin electrolyte layer into two layers, leaving a gap between the individual cells. Figure 4-3 makes this problem clear.

From previous studies^{30, 15} it is known that the anode only shrinks 9 - 13%, whereas a typical submicron YSZ powder from Tosoh shrinks more than 20%. By varying the particle size of the electrolyte material, it is tried to reduce the shrinkage of the electrolyte. Dilatometer tests were performed on three YSZ powders to observe the shrinkage behaviour. These powders are TZ8Y-S from Tosoh, FYT13-002H from Unitec and a mixture of TZ8Y-S (60%) and a molten granulate from GTV GmbH (40%). The powders were isostatically pressed at 200 bar. Of course the electrolyte still has to be dense after firing at 1430°C. Too little shrinkage may therefore cause too much porosity and a compromise has to be found. The results of this dilatometer tests will be discussed later on.



Figure 4-2: Preparation scheme for the symmetrical anode supported cells



Figure 4-3: Separation mechanism during sintering of a symmetrical cell. The arrows show the direction in which the anodes and electrolyte move

4.2. Results

This paragraph contains results obtained from dilatometer tests and microstructure observations. Results from the impedance spectroscopy measurements will be discussed in the following chapters.

4.2.1. Symmetrical cells – dilatometer tests

Dilatometer tests revealed quite a big difference in the shrinkage behaviour of the various YSZ powders. As Figure 4-5 makes clear, the Tosoh powder has the biggest shrinkage, as could be expected from the particle size. The shrinkage of the TZ8Y-S powder amounts ~22%, resulting in a relative density of 98%. Since the powder used in the electrolyte slurries is TZ8Y, with an even smaller particle size and the green density of as-sprayed layers is lower than that of isostatically pressed

samples, the shrinkage of Tosoh electrolytes might be even higher than 22%. The shrinkage difference between Tosoh electrolyte and anode is therefore too high and the effect in Figure 4-3 is actually observed. Figure 4-4 is a SEM image, showing the splitting of the electrolyte layer.



Figure 4-4: Splitting of the electrolyte due to the large shrinkage difference between electrolyte and electrode

Figure 4-5 also shows the shrinkage of FYT13-002H from Unitec and the 60/40 mixture Tosoh/GTV. The Unitec powder already has a reduced amount of shrinkage (~16%) and the mixture has an even lower shrinkage of ~8%. SEM observations however, reveal that the Tosoh/GTV mixture can't be sintered to a dense electrolyte at 1400°C (see Figure 4-6). A simple density determination according to the Archimedes principle gives a relative density of only 77%. The Unitec powder on the other hand looks quite dense, with some residual porosity. The relative density amounts 94%, which means that this powder could produce dense electrolytes when used in the symmetrical cell design. Especially because the symmetrical cells are uniaxially pressed after spray deposition, the green density of the electrolyte is further increased. This is beneficial to the density after sintering. Figure 4-7 show some SEM images taken of samples coated with Unitec powder. The surface of an individual cell still looks too porous to serve as an electrolyte layer. A cross-section of a symmetrical cell however, shows a reasonable dense electrolyte layer with some residual porosity. This confirms the hypothesis about increasing the green density by hand pressing, since the individual cells were not pressed after spray deposition.

Finally, mixing fine Tosoh powder (TZ8Y or TZ8Y-S) with a small amount of a coarser powder might be an effective way of reducing the shrinkage during sintering. Chen et al.³¹, obtained similar results after mixing some coarse YSZ with fine YSZ powder. Obviously, a smaller amount than 40% of the coarse fraction is needed, since dense electrolytes are preferred. Reducing the amount of shrinkage is not only required in the symmetrical cell design, but in the normal SOFC design as well. This reduced amount of shrinkage prevents serious bending of samples or even cracked electrolytes. This is again beneficial to the long-term stability of SOFCs. Additional studies are required to adjust the amount of electrolyte shrinkage to the amount of anode shrinkage and to optimise electrolyte density.



Figure 4-5: Shrinkage behaviour of three YSZ powders, measured with dilatometer





Figure 4-6: Upper) Microstructure of a pellet sintered at 1400°C with Unitec powder. Lower) Microstructure of a pellet sintered at 1400°C with a mixture of GTV and Tosoh powder



Figure 4-7: Upper) Surface of a single cell with a Unitec electrolyte is clearly porous. Lower) Polished cross-section of a symmetrical cell with functional anode layers and a Unitec electrolyte; the electrolyte is dense with some residual porosity

4.2.1.1. Combining functional anode layers and electrolyte

It appears that using the application of the functional anode layers has some additional effect on the sintering behaviour of the electrolyte. When no functional anode layers are deposited and the electrolytes are sprayed on the bare substrates, even dense electrolytes can be obtained using the fine Tosoh powder. However, when functional anodes are applied, the Tosoh electrolytes split during sintering due to the effect described in Figure 4-3.

4.2.2. Microstructure

From SEM images a clear difference can be observed between the microstructure of the anode support and the functional anode layer. The functional anode layer has a finer and denser structure. The nickel particle size in the functional anode layer is a little bit smaller $(1 - 2 \mu m in the functional layer, against 2 - 4 \mu m for the anode support)$. The particle size of the ceramic component varies according to the slurry composition. Slurry compositions of the different functional anodes can be found in the respective chapters. The pore size is also reduced in the functional layer. Figure 4-8 shows a SEM image of an anode support with a Ni/ceria functional anode. It shows the different microstructures best, since the ceramics of these functional anodes had the finest particle sizes.



Figure 4-8: Different microstructure between anode support and functional anode layer

5. Ni/YSZ functional anodes

This chapter concerns the properties of Ni/YSZ functional anode layers. Functional anode layers have been sprayed on top of the anode substrates and differ in microstructure from the substrates. Different microstructures have been used in the functional anode layers to observe their influence on the anodic performance. The effect of microstructure on electrochemical performance is both used as a comparison with literature data and as a starting point to optimise the microstructures of the Ni/YZT and Ni/CGO anodes.

5.1. Theoretical background

The Ni-YSZ cermet consists of an YSZ matrix in which nickel particles have been dispersed. Nickel and YSZ are not miscible, so no reactions occur between the anode and electrolyte, even at high temperatures. By dispersing the nickel in the YSZ framework, the nickel particles are avoided from agglomerating at higher temperatures. Agglomeration of nickel affects the microstructure of the cermet unfavourably (decrease in porosity and amount of triple phase boundary). Secondly, the presence of the YSZ lowers the thermal expansion coefficient of the anode compared to a Ni-anode, so that it almost matches the thermal expansion coefficient of the YSZ electrolyte. Finally, the mixing of YSZ with Ni creates a material with both high ionic and electronic conductivity, which is necessary to avoid polarisation effects in the electrode under operation. To ensure sufficient electronic conductivity, the amount of nickel in the anode has to be larger than 30 vol.%, the percolation threshold. At this concentration, the conduction mechanism changes from jonic to electronic. The influence of Ni-concentration on the total conductivity is shown in Figure 5-1⁷.



Figure 5-1: Conductivity of Ni-YSZ cermet with varying Ni amount⁷

Nickel doesn't just serve as an electronic conductor; it also serves as an electrocatalyst. It especially promotes steam reforming and hydrocarbon cracking, as described in paragraph 1.2.3.

The electronic conductivity is furthermore influenced by the microstructure of the cermet. Particle sizes of both nickel and YSZ affect the conductivity. For a fixed Ni amount, the electronic conductivity increases with an increasing ratio of (d_{YSZ}/d_{Ni}) . Further roles of coarse YSZ particles are:

- Adjusting the thermal expansion coefficient with other components, especially YSZ electrolyte;
- Inhibiting Ni-agglomeration;

• Providing enough porosity.

However, using just coarse YSZ particles has two major drawbacks: 1) the mechanical strength of the cermet decreases with increasing YSZ particle size and 2) the amount of TPB area decreases due to larger YSZ particles. Therefore the state-of-the-art Ni-YSZ cermets consist of fine and coarse YSZ particles and NiO, which is reduced during SOFC operation. Figure 5-2 shows the relation between conductivity and amount of coarse YSZ particles in the cermet. Clearly, an amount of ~60 – 70% coarse YSZ particles gives good values for the conductivity.



Figure 5-2: Influence of the amount of coarse YSZ particles on the conductivity⁷

The thin functional anode layer is the actual anode where the electrochemical reactions take place. In a Ni/YSZ cermet anode, the electrochemical reactions can only take place at the triple phase boundary (TPB). Therefore it seems logical to increase the amount of reaction sites in this layer by creating a fine microstructure. This increases the total surface area and thus the amount of sites available for fuel oxidation. Hence, the use of a small nickel and YSZ particle size seems to be favourable. De Boer⁸ showed that increasing the content of fine YSZ particles (with fixed Ni-content) resulted in an increase of electrolyte/electrode surface coverage, i.e. amount of TPB. However, at 50 % fine YSZ (percentage of the total YSZ amount) this surface coverage reaches a plateau. Furthermore, the conductivity is smallest for 50 % fine YSZ. The ratio fine/coarse YSZ of 1:2 (as used in the anode substrates and thin anodes of electrolyte supported designs) seems therefore to be a good choice in the functional anode layer as well. Increasing the ratio namely, wouldn't result in much more TPB area, but decreases the electrical conductivity. Whether this is really the case, has to become clear from impedance measurements on cells with different ratios of fine/coarse YSZ.

Furthermore, the chemical composition can be altered in the interlayer. Koide et al.³² report that the electrical losses in a Ni-YSZ cermet primarily stem from contact resistance and polarisation resistance. Contact resistance is determined by the contact area of nickel and electrolyte and decreases with increasing Ni-content. Polarisation resistance is related to the number of reaction sites and depends on the Ni/YSZ ratio, with a minimal resistance at a Ni-content of 40 vol.%. This would suggest that the interlayer should contain more nickel than the bulk anode. However, when the electrochemical reactions indeed take place within a layer of 10 μ m from the electrolyte, creating an interlayer with a thickness larger than 10 μ m with increased Ni-content might not be beneficial to the overall resistance. Figure 5-3 shows the influence of Ni-content on the polarisation and contact (internal) resistance. Other researchers have however already mentioned a reduced long-term stability when working with nickel gradients in the anode³³.



Figure 5-3: Effect of Ni-content on polarisation resistance and internal resistance³²

A possible way to prevent carbon deposition when feeding hydrocarbons on the anode side, is doping the Ni-YSZ with molybdenum or gold⁷. Doping with ruthenium or platinum reduces carbon deposition as well. Moreover, doping with Ru and Pt results in increased methane conversion at lower temperatures and promotes electrochemical activity of the anode. Finally, resistance due to gas diffusion is greatly reduced by these precious metals³⁴. Consequently, adding precious metals to the Ni-YSZ cermets is a way to reduce steam/carbon ratio in a hydrocarbon fuel feed. This makes the process more efficient, but still not ideal. In this project however, no hydrocarbons are fed to the anodes, so carbon precipitation doesn't play a role.

5.2. Experimental

Functional Ni/YSZ anode layers were deposited on top of the anode substrates using an air spraying technique. Slurries containing fine anode material were prepared for this purpose. In order to create different functional anode layers, the composition of the slurries was varied. This means that the particle size and amount of 8-YSZ in the anodes is varied.

5.2.1. Materials

The Ni/YSZ functional anodes were prepared by spraying slurries containing NiO powder and 8 mol% yttria stabilised zirconia (8-YSZ) powder. The nickel oxide was a powder from Cerac Specialty Inorganics, USA, with a mean particle size of ~2 μ m. Three different YSZ powders were used in the NiO/YSZ slurries: a submicron powder from Tosoh, TZ8Y with a d₅₀ particle size of 0.2 μ m, a powder from Unitec, UK with a d₅₀ value of ~0.8 μ m, and a molten granulate with a particle size of 1 – 12 μ m. By using three different YSZ powders, the microstructures of the resulting anode layers were tailored. Also the amount of coarse YSZ in the NiO/YSZ slurries was varied to see its influence on electrochemical performance of the anode layer. The Tosoh powder is always used as the fine fraction of the YSZ powder, whereas either the Unitec or the molten granulate is used as the coarse YSZ fraction. The amount of fine YSZ varied and amounted 15%, 33% and 70%. So both the particle size and the amount of coarse YSZ in the NiO/YSZ slurries are varied. After reduction the anodes contain 40% nickel (with respect to the ceramic material). Table 5-1 summarises the compositions of the different Ni/YSZ anode interlayer slurries.

Slurry designation	Amount of Ni (vol%)	Ceramic material	Fine : coarse ratio of ceramic material	Particle size of coarse 8-YSZ
AI2	40	8-YSZ	33% : 67 %	0.8 µm
AI3	40	8-YSZ	15% : 85 %	0.8 µm
Al4	40	8-YSZ	70% : 30 %	0.8 µm
AI5	40	8-YSZ	33% : 67 %	1 – 12 µm
AI6	40	8-YSZ	15% : 85 %	1 – 12 µm
AI7	40	8-YSZ	70% : 30 %	1 – 12 µm

Table 5-1: Compositions of the different functional anode layer slurries

5.2.2. Slurry preparation

The powders in the slurries were dispersed in water, using Dolapix CE 64 as the dispersant. For the NiO/YSZ slurries, first the fine YSZ was ball milled for at least 24h, using zirconia milling balls. After this the NiO was added and after at least another 24h, the coarse YSZ was added. The dispersion with coarse YSZ was only ball milled for one hour, after which the binders were added using a vertical stirrer. Optapix KG 1000, Chimcell VM 695 (both carboxy methyl cellulose compounds) and Optapix AC 95 were used as binder materials. A typical slurry composition is listed in Table 5-2.

Table 5-2: Typical composition of an anode interlayer slurry

Compound	Amount
NiO/YSZ	
Water	
Dispersant	
Optapix KG 100	
Optapix AC 95	

5.2.3. Impedance spectroscopy

Impedance spectroscopy was performed on the anodes AI5, AI6 and AI7. The cells were mounted in a quartz reactor, designed for a single-gas atmosphere. Platinum/nickel meshes served as current collectors. Wet hydrogen was fed to the symmetrical cells. The impedance was measured as function of the pH₂, pH₂O and the temperature. At standard conditions a gas flow of 100 ml/min H₂ (STP) was used, containing 2.3% water at a temperature of 800°C. The water content of the gas flow was controlled by passing the gas through two water bubblers. The water temperature in the water bubblers was controlled by thermostats and it is assumed that the gas flow is saturated with water. The tubes between the water bubblers and the reactor were heated to prevent condensation of water. The hydrogen partial pressure was further controlled by mixing in nitrogen as a balance gas. All gas flows were controlled using Brooks 5800E Mass Flow Controllers.

The impedance was measured in the frequency range from 50 kHz to 50 mHz using a Solartron 1255 Frequency Response analyser in combination with a Solartron 1287 Electrochemical Interface. As it concerns symmetrical cells, no reference electrode was used. An excitation voltage of 10 mV was applied to ensure that the measurements were carried out in the linear regime. The impedance data was analysed using the computer program 'Equivalent Circuit'.

After heating the samples to 800°C and reducing them under standard conditions, the following measurements were performed:

- Impedance measurements in the pH_2 range $9.90 \cdot 10^4$ Pa – $4.95 \cdot 10^3$ Pa, with fixed pH_2O of $2.3 \cdot 10^3$ Pa.

- Impedance measurements in the pH₂O range $1.23 \cdot 10^3 1.99 \cdot 10^4$ Pa, with fixed pH₂ of $8.1 \cdot 10^4$ Pa.
- Impedance measurements under standard conditions ($pH_2 = 9.9 \cdot 10^4$ Pa and $pH_2O = 2.3 \cdot 10^3$ Pa), but at different temperatures, i.e. between 800°C and 600°C.

5.3. Results & discussion

5.3.1. Microstructure

Figure 5-4 shows the microstructure in the functional anode layer before and after electrochemical testing. After electrochemical measurements, the samples have been operated at 800° C for 3 – 5 days (70 – 120 hours). It is hard to see clear differences between the two functional anodes. The difference between the nickel and YSZ phases is particularly unclear. The fact that the microstructures don't differ that much is a good indication that the anodes are still reasonably stable under operation temperature. From the mass and thickness of the functional anode layers, it is estimated that their porosity amounts about 25%.




Figure 5-4: Microstructure of an AI5 functional anode layer (70% fine YSZ) before (above) and after electrochemical testing (under)

5.3.2. Electrochemical characterisation

The validity of the measured impedance was evaluated with software performing the Kramers Kronig transformation. This test checks whether the measured data is linear and the system is in equilibrium³⁵. Fitting of the measurement data was performed with the software EQUIVCRT. The impedance data of the Ni/YSZ anodes were fitted with the following equivalent circuit:



Figure 5-5: Equivalent circuit used for fitting impedance measurements on Ni/YSZ anodes

The circuit description code (CDC) for this circuit is $LR_{el}(Q_1[R_1G])(R_2C_2)$, which is adopted from ref. [37]. In this notation, L is an inductive element, R_{el} the electrolyte resistance, Q a constant phase element (CPE), R_1 and R_2 two resistances, G a Gerischer element, and C is a capacitor.

5.3.2.1. Degradation

To put the coming results in the right perspective, it has to be said that all the Ni/YSZ samples exhibited serious degradation behaviour within the time they were electrochemically characterised. The total electrode polarisation increased $1.5 - 2.0 \Omega$ for all samples, within 3 - 6 days. This means an increase in polarisation resistance of 28 - 94%, with the biggest relative increase for higher amounts of fine YSZ. Partly, the degradation could be explained by ageing of the anode, i.e. Ni-agglomeration, leading to a decreased number of conduction paths and reduced porosity³⁸. However, this effect cannot clearly be seen with SEM, as Figure 5-4 shows. Another cause of the degradation could be minor re-oxidation of the samples when they were left overnight in low reducing gas flow rate. As described in paragraph 3.1.1, the oxygen partial pressure increased in lower gas flow rates. It is well known that Ni-cermets have poor redox stability, because of the dimensional changes taking place during oxidation/reduction

of Ni/NiO^{6,39}. Again, degradation was also found within one day, i.e. when working with high flow rates and it was already said that the hydrogen/water mixture basically sets the oxygen partial pressure. Reoxidation will hence not be the cause for degradation. Another cause could be impurities in the ceramic powders. Also during spray deposition, the anode material could have been contaminated additionally. Liu et al.⁴⁰ reported serious degradation of Ni/YSZ-YSZ half-cells, due to impurities in the NiO powder used. Especially sodium silicates deposit near the electrode-electrolyte interface and cause a marked increase in the polarisation resistance after several hours of operation. The fact that the degradation is larger for high amounts of YSZ seems logical, since coarse YSZ stronger adheres to Ni and prevents Ni-agglomeration more effectively than fine YSZ. A degradation of the substrate is not expected, since the Ni/CGO anode (with Ni/YSZ substrate as well) did not show an increase in impedance at all.

Figure 5-6 shows the change of the shape of the impedance spectra over prolonged operation time. It seems that especially the high frequency part is affected by the degradation mechanism. Partial CNLS fitting confirms that the low frequency arc remains quite constant. Likely, the high frequency part of the spectra contains processes like charge transfer and hydrogen oxidation reaction steps, which are dependent on the length of the TPB area. Due to nickel agglomeration, the amount of TPB area diminishes. In Figure 5-6 as well, the change in polarisation resistance is shown as function of the operation time. The most serious degradation takes place during the first 50 hours. Also, at 600°C the degradation rate is small. After cycling (from 800°C to 600°C and back to 800°C) the polarisation resistance returns to its last measured value at 800°C. This indicates that the polarisation resistance eventually adapts a constant value, even at 800°C.



Figure 5-6: Left: Impedance spectra at standard conditions after different hours of operation. Right: Degradation rate at both 800°C and 600°C.

5.3.2.2. Influence of polarisation

Normally, anodic performance is tested under both open circuit voltage (OCV) and polarisation. Polarisation of the electrodes generally results in a dramatic reduction of the electrode impedance (when polarised correctly). It was suggested that polarising the anodes in this project might have a positive irreversible effect on their performance, possibly by changing the microstructure on an infinitesimal small scale. So after polarising the anodes for a while, a reduction of the impedance under OCV might be seen. To test this hypothesis, one sample with anode interlayer 7 (AI7, with 70% fine YSZ) was polarised in steps of 25 mV, up to ±300 mV. The current was measured for each polarisation step, to check Tafel behaviour. After the polarisation the impedance was measured at OCV. It was found that the impedance indeed decreases after polarisation, but that this reduction is completely reversible. Already after 45 minutes, the impedance reaches its original value. The Kramers-Kronig test revealed that the reduced impedance was measured, while the system was in non-equilibrium. Figure 5-7 shows the Tafel behaviour of the Ni/YSZ anode and the impedance recorded directly after polarising the anodes. In conclusion, polarising the anodes won't have a beneficial effect on their impedances under OCV. So the impedances that we will find can directly be compared to literature values.



Figure 5-7: I-V-curve for anode AI7. Clear Tafel behaviour can be observed

5.3.2.3. Measurements under standard conditions

The total impedance is the sum of the electrolyte resistance and the electrode polarisation. The electrode polarisation in turn is the sum of two nominally identical electrode impedances, "2 R_{pol} ". Hence, the impedance of one single supporting anode can be found by dividing the electrode impedance by two. This is clarified in Figure 5-8.



Figure 5-8: Example of an impedance spectrum. " R_{Ω} " is the electrolyte resistance, "2 R_p " the electrode impedance of the two nominally identical electrodes. Impedance recorded under standard conditions (pH₂=0.99 bar, pH₂O=0.023 bar, T=800°C)

In Table 5-3 an overview is given of the total polarisation resistances (2 R_{pol}) at standard conditions of the different Ni/YSZ anodes. This is the polarisation resistance after ~5 days of electrochemical measurements; the total impedances at the beginning were much lower, but after 5 days the most serious degradation has already taken place (see Figure 5-6), making the comparison probably fairer. $R_{pol, av}$ is the average polarisation resistance of one single electrode, which is normalised for the surface area of the electrode (i.e. 1.27 cm²). The activation energy for the total polarisation is given as well. The anodes only differ in the ratio fine/coarse YSZ.

Anode	Amount of fine YSZ	2 R _{pol} (Ω)	R _{pol, av} (Ωcm ²)	E _{act} (kJ/mol)
Al6	15%	11.6	7.4	127
AI5	33%	5.0	3.2	129
AI7	70%	3.1	2.0	138

Table 5-3: Polarisation resistances in different Ni/YSZ anodes at 800° C, pH₂=0.99 bar, pH₂O=0.023 bar

From Table 5-3 it becomes immediately clear that there is a large difference between the total electrode resistances of the different anodes. Whether this difference should be attributed to the amount of fine YSZ only, is doubtful. De Boer⁸ found that increasing the amount of fine YSZ in a cermet anode resulted in a decreased Ni particle size as well. So the TPB area increases due to a smaller particle size of both YSZ and Ni when using fine YSZ. The total electrode resistance clearly dropped with an increasing amount of fine YSZ. According to the work of De Boer, little increase in TPB area is obtained when the amount of fine YSZ exceeds ~33%. Table 5-3 however, clearly shows that the electrode resistance is still significantly improved when increasing the amount of fine YSZ from 33% to 70%. Possibly, the availability of an increased amount of adsorption sites, improves the electrode performance. Figure 5-9 shows the impedance spectra for the different Ni/YSZ cermet anodes at standard conditions.



Figure 5-9: Impedance spectra for Ni/YSZ cermets with different amounts of fine YSZ; T=800°C, pH_2 =0.99 bar, pH_2 O=0.023 bar

5.3.2.4. pH₂ and pH₂O dependencies

The impedance was measured at various hydrogen and water partial pressures. Typical impedance spectra on AI7 (70% fine YSZ) are shown in Figure 5-10. Two limiting processes can be clearly identified in the impedance spectra for Ni/YSZ anodes. Their summit frequencies lie around 100 Hz and 1 Hz, respectively. The process at lower frequencies disappears with increasing water partial pressure and is small at high hydrogen partial pressure. The process at higher frequency shows less dependency on water and hydrogen partial pressure. Figure 5-11 and Figure 5-12 show the change of the different equivalent circuit elements in AI5 (33% fine YSZ) with changing atmosphere.



Figure 5-10: Impedance spectra on AI7 (70% fine YSZ) at 800°C. Left: pH₂O = 0.023 bar. Right: pH₂ = 0.81 bar



Figure 5-11: Hydrogen partial pressure dependencies of the different circuit elements



Figure 5-12: Water partial pressure dependencies of the different circuit elements

As expected, R_{el} , the electrolyte resistance is fairly independent on changing the hydrogen and water partial pressure. The measured electrolyte resistance was always between $0.4 - 0.7 \Omega$, which is near the expected value for a $30 - 40 \mu m$ thick YSZ electrolyte (one sample once showed an electrolyte resistance of ~2 Ω , which was back at ~0.7 Ω again the next day; this is very strange, but may have got something to do with contacting problems). Literature often reports values for the conductivity of 0.01 S/cm for 8 mol% YSZ at 800°C. This would mean an electrolyte resistance of $0.3 - 0.4 \Omega$ in our case. The slightly higher value can be explained by the small thickness of the electrolyte layer. Several authors noticed a decreased conductivity of 8-YSZ in thin electrolytes^{41, 42}. Wanzenberg et al.⁴² claims that the increased resistance is due to non-ideal contacting between the electrolyte and the electrodes. This current restriction becomes significant for thin electrolytes and this explains the deviation from bulk conductivity values. The fact that the electrolyte resistances normally match the expected values reasonably well, means that there were no serious contact problems during the measurements and that there is a homogeneous current distribution in the cell.

R1 is guite independent of pH₂ and pH₂O as well, which is observed for all Ni/YSZ functional anodes. Q1 always has a α value of ~0.6. This may indicate that it describes a diffusion limitation. After all, for α =0.5, the CPE is identical to a Warburg element, which describes semi-infinite diffusion. Q1 is rather pH_2 independent. It has however a negative slope in the pH_2O log/log chart, which is somewhat lower for the anode with 15% fine YSZ. The reaction rate consant, k, of the side reaction increases for all Ni/YSZ anodes when increasing the water partial pressure. Furthermore, the slope of this function is larger for larger amounts of fine YSZ in the functional anode (see Table 5-4). This is a good indication that the side reaction involves water species, like OH⁻ or H₂O, possibly adsorbed on the ceramic surface. When the amount of fine YSZ in the anode is increased, more reaction sites are created for this side reaction. The side reaction could very well be part of the hydrogen oxidation mechanism. It would agree with the suggested 'catalytic effect' of water on the oxidation reaction, as the reaction rate increases with increasing water partial pressure. And apparently, when an increased amount of reaction sites is offered, the anode can utilise the increased water partial pressure more effectively for the oxidation reaction. The low frequency part, which is described by the final RC parallel circuit, often shows difficulties in the fitting procedure. Hydrogen and water partial pressure dependencies were not consistent for the different Ni/YSZ anodes.

A remarkable fact is the decrease of total electrode resistance when the hydrogen partial pressure was reduced. This is observed for the anodes containing 15% and 33% fine YSZ. For the anode containing 70% fine YSZ the electrode resistance first increased, when lowering the partial pressure from 0.99 bar to 0.50 bar. However, it decreased again after further lowering the hydrogen partial pressure. This is very strange behaviour for cermet anodes and the cause of it is not clear, yet. On the other hand, de Boer found similar behaviour for cermet anodes and Brown et al.²⁸ found it for Ni-felt and Ni-paste electrodes. The latter could mean that the cermet structure is not optimised in the functional anode and that on the electrolyte-electrode interface relatively much nickel is present.

Anode	Amount of fine YSZ	R _{el}	Q1	R1	G	К	R2	C2
			pi	H ₂ dependency	V			
Al6	15	0 (-0.02)	0.08	0 (0.05)	0.06	-0.01	0.50	-0.59
AI5	33	0 (-0.04)	-0.03	0 (0.02)	-0.07	-0.36	-0.45	0.26
AI7	70	0 (-0.01)	0.14	0 (0.09)	0.44	0.26	0.53	-0.57
			рH	I₂O dependend	<i>y</i>			
Al6	15	0.18	-0.38	-0.09	0.33	0.08	-1.20	0.71
AI5	33	0 (-0.02)	-0.13	-0.10	0.07	0.21	-0.76	0.35
AI7	70	0 (0.01)	-0.15	-0.13	0.25	0.73	0.12	-0.24
A16 A15 A17 A16 A15 A17	15 33 70 15 33 70	0 (-0.02) 0 (-0.04) 0 (-0.01) 0.18 0 (-0.02) 0 (0.01)	0.08 -0.03 0.14 <i>pH</i> -0.38 -0.13 -0.15	0 (0.05) 0 (0.02) 0 (0.09) 4 ₂ O dependence -0.09 -0.10 -0.13	0.06 -0.07 0.44 5y 0.33 0.07 0.25	-0.01 -0.36 0.26 0.08 0.21 0.73	0.50 -0.45 0.53 -1.20 -0.76 0.12	-0.{ 0.2 -0.{ 0.7 0.3 -0.:

Table 5-4: Powers of th	e different circuit	elements with	changing pH	₂ and pH₂O
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5.3.2.5. Temperature dependency

For determining the temperature dependency of Al5 and Al7, not the equivalent circuit in Figure 5-5 was used, but a circuit with CDC $LR_{el}(Q1[R1G])$. So this is the same circuit, however with the final RC element omitted. This circuit gave better fitting results and clearer trends for determining the activation energy.

The activation of the electrolyte resistance was $70 - 99 \pm 9$ kJ/mol. This is close around a value reported by Mogensen and Skaarup, who found 92 kJ/mol for the oxygen ionic conductivity of YSZ¹⁰. The activation energy for the reaction rate constant, *k*, varies quite a lot for the different microstructures. Its value lies between 116 - 167 kJ/mol and increases with increasing amount of fine YSZ. The error for the lowest value is on the other hand ~20 kJ/mol, so the difference might not be so large after all. The increase in activation energy is unexpected, since most reactions benefit from an increased amount of reaction sites.



Figure 5-13: Temperature dependencies of different circuit elements. Functional anode AI5 (33% fine YSZ).

Furthermore, the main electrode impedance has an activation energy of ~125 – 140 ± 1 kJ/mol. This is rather a large value and should probably not be attributed to adsorption of hydrogen or diffusion/gas conversion processes. The latter two have very small energies^{43, 44, 45}, along with very small impedances, typical 0.1 Ω cm². Hydrogen adsorption on Ni has a activation energy of about 90 – 100 kJ/mol, which is too small for the process observed in the current anodes⁴⁵. Bieberle et al.⁴⁵ proposed the release of oxygen ions from the electrolyte as a possible limiting process in the anode. This reaction is the inverse reaction that takes place at the cathode, where oxygen ions are incorporated into the YSZ lattice. For this situation the process is better understood. The following reaction is assumed:

$$O_0^x + ad \rightleftharpoons O_{ad} + V_0^{\bullet \bullet} + 2e^{i}$$
 (5.1)

This process has an activation energy of 125 - 135 kJ/mol, which is the same energy as found for our main electrode impedance. Together with the fact that the pH₂ dependency resembles that of a Nipattern electrode, it may mean that the YSZ in the functional anode layer does not connect well to the electrolyte and the reaction zone isn't extended into the anode. The limited amount of TPB area then causes a smaller possibility for oxygen ions to be released from the electrolyte. Another possibility is a charge transfer limitation, which controls the hydrogen oxidation at low temperatures, as reported by Holtappels et al.⁴⁶. A charge transfer limitation could originate from a poor nickel dispersion in the YSZ matrix, as well. A typical charge transfer resistance with this activation energy can't however be found back in the equivalent circuit analysis.

Table 5-5 gives an overview of the values for the different elements at standard conditions for the different anodes.

Table 5-5: Values of the different equivalent circuit elements for different Ni/YSZ anodes at 800°C, pH_2 =0.99 bar, pH_2 O=0.023 bar

Anode	% fine YSZ	R _{el} (Ω)	Q1 (Ω ⁻¹ s ⁿ)	R1 (Ω)	G (Ω ⁻¹ s ^½)	k (s ⁻¹)	R2 (Ω)	C2 (F)
Al6	15	5.71E-01	3.74E-03	4.64E+00	8.06E-03	3.23E+02	4.31E-01	4.09E-02
AI5	33	6.40E-01	5.33E-03	2.06E+00	1.53E-02	4.45E+02	-	-
AI7	70	3.90E-01	6.37E-03	1.48E+00	2.53E-02	7.46E+02	3.02E-01	6.74E-02

5.4. Concluding remarks

The electrochemically measured cells have relatively high impedances. The value of $3.2 \ \Omega \text{cm}^2$ for the anode with 33% fine YSZ is however in fair agreement with results on Ni/YSZ cermets reported by Holtappels⁴⁶. The activation energies are comparable as well. On the other hand, it turned out to be

impossible to fit the current results with the equivalent circuit used by Holtappels, making the comparison between the data somewhat more tricky again.

5.4.1. Effect of microstructure on electrochemical performance

The decrease of polarisation resistance with an increasing amount of fine YSZ in the cermets is in agreement with the work of De Boer⁸. Measurements were done on a second sample with an AI7 anode and almost identical impedance spectra were obtained for both samples. These findings indicate that the functional anodes were reproducibly prepared by spray deposition and that different microstructures could be incorporated.

Two limiting processes can be clearly identified in the impedance spectra for Ni/YSZ anodes. Their summit frequencies lie around 100 Hz and 1 Hz, respectively. The process at lower frequencies disappears with increasing water partial pressure. This process is dependent on hydrogen partial pressure and might therefore be related to charge transfer related. The process at higher frequencies apparently involves a chemical side reaction, as described by the Gerischer impedance in the equivalent circuit.

Upon changing the microstructure of the Ni/YSZ anodes, the impedance spectra change a lot. Even more change occurs in the different powers with respect to pH_2 and pH_2O (and even temperature). This could relate to the equivalent circuit that was chosen for fitting the data. More important is, that it disturbs the analysis of the anode kinetics significantly. Ascribing real physical processes to the equivalent circuit elements remains therefore speculative. Suggesting a model for the hydrogen oxidation in these anodes would be even more risky.

5.4.1.1. Degradation

Another factor that probably seriously affected the measured data is the degradation of the samples. The degradation clearly affected the shape of the impedance spectra, thereby possibly affecting the fitting results with EQUIVCRT. The very inconsistent data in Table 5-4 might be explained partly by this behaviour. This effect makes it very difficult to create or check an electrochemical reaction mechanism, with clear meanings for the different equivalent circuit elements (including a proposed side reaction, resulting in a Gerischer impedance).

The preparation of anodes that are 'free' of degradation during the electrochemical measurements would mean a big improvement. Only when it is known that the anodes are stable, one can consider the electrochemical results seriously and try to think of modelling them. It would be recommendable to check the NiO on purity and on possible contaminants.

6. Ni/CGO anodes

Doped ceria has become a lot of interest, lately as a possible anode material. Ceria exhibits mixed ionic and electronic conductivity in reducing atmospheres. Doping with rare earth metals, like gadolinium, increases its stability and conductivity. This makes the material a good alternative for YSZ in nickel cermets. This chapter describes the preparation and electrochemical characterization of such a nickel/doped ceria anode.

6.1. Ceria

At low oxygen partial pressure, ceria exhibits mixed ionic and electronic conductivity⁷. Especially the ionic contribution is high up to a temperature of 800°C. That is actually the reason why ceria is considered as an interesting electrolyte material for intermediate temperature SOFCs. For temperatures higher than 800°C the electronic contribution to the conductivity increases rapidly (at low pO_2). Equation (6.1) describes the ionic conductivity based upon the migration via oxygen vacancies.

$$\sigma T = \sigma_0 \exp\left(-\frac{\Delta E}{kT}\right) \tag{6.1}$$

In this equation ΔE , the activation energy, involves both ΔH_m and ΔH_a , which are the enthalpy for migration of oxygen and the association enthalpy of defect complexes, respectively. Doping the ceria with certain rare earth oxides can markedly reduce the enthalpy of association. These rare earth oxides are Gd₂O₃, Sm₂O₃ and Y₂O₃. When properly doped, ceria can have an ionic conductivity one order of magnitude larger than YSZ.

In low pO₂ the ceria becomes reduced according to the following process:

$$O_{_{O}} + 2Ce_{Ce}^{\times} \rightarrow V_{_{O}}^{\bullet\bullet} + 2Ce_{Ce}^{+} + \frac{1}{2}O_{_{2}}(g)$$
 (6.2)

$$O_{O} + 2Ce_{Ce}^{x} + H_{2}(g) \rightarrow V_{O}^{\bullet\bullet} + 2Ce_{Ce}^{\bullet} + H_{2}O(g) \text{ in hydrogen gas}$$

$$(6.3)$$

When ceria is doped with oxides of lower valences, the oxygen vacancy concentration is mainly determined by the concentration of dopant.

$$Gd_2O_3 \xrightarrow{CeO_2} 2Gd'_{Ce} + V_O^{\bullet\bullet} + 2O_O^x$$
(6.4)

In doped ceria equation (6.2) still takes place. Doping affects however the equilibrium of this reaction, by changing the oxygen vacancy concentration and the concentration of Ce_{ce} . For undoped ceria, the oxygen vacancy concentration is determined by the concentration of Ce_{ce} , i.e. $Ce_{ce} = 2[V_0^{\bullet\bullet}]$. In doped ceria, $[V_0^{\bullet\bullet}]$ can be assumed to be constant. For undoped and doped ceria the concentration of Ce_{ce} is given by equation (6.5) and (6.6), respectively.

$$\left[Ce_{Ce}^{\prime}\right] = \frac{1}{2}K_{R} \cdot \rho O_{2}^{-1/2} \text{ for undoped ceria}$$
(6.5)

$$\begin{bmatrix} Ce'_{Ce} \end{bmatrix} = \frac{1}{2}K_R \cdot pO_2^{-\frac{1}{4}} \text{ for doped ceria}$$
(6.6)

Like in YZT, the electronic conductivity is caused by polaron hopping. So σ_e is determined by the concentration of the electron carrier, Ce_{c_e} (see equation (7.7)). Eventually the electronic conductivity can be described by equation (6.7), which has the Arrhenius form, as the electron mobility is temperature dependent.

$$\sigma_n T = \sigma_n^0 \exp\left(-\frac{\Delta H_n}{kT}\right) \rho O_2^{-\frac{1}{4}}$$
(6.7)

As becomes clear from this equation, the electronic conductivity increases with increasing temperature and decreasing oxygen partial pressure. The electronic conductivity remains, however too low at high temperatures (about 0.16 S/cm at 800°C). This means that combining the ceria with a metal component (like the Ni-YSZ cermet) is necessary in order to create a useful anode. The metal component can be either Ni or Cu. As already mentioned in paragraph 2.1.4, ceria is reported to be a catalyst for hydrocarbon reforming. In that case, the use of Ni might be avoided and hence carbon deposition can be prevented when using hydrocarbon fuel. However, the catalytic activity of ceria remains controversial.

A substantial doping (40 – 50mol%) of ceria with Gd, Y or Sm is required to guarantee long-term stability of the material under SOFC operation conditions. Without doping, the ceria degrades due to lattice expansion, which is caused by Ce^{4+} - Ce^{3+} transition at low pO_2 . Cracks in the anode or delamination from the electrolyte could be the result of this lattice expansion. Table 6-1 shows the lattice expansion due to reduction of $CeO_{2-\delta}$ for different doping levels of Gd_2O_3 at 1000°C.

Table 6-1: Expansion of ceria lattice (CeO _{2.5}) upon reduction for different Gd ₂ O ₃ doping levels at 1000°C (adapted from	n
Ref. 21)	

mol% GdO _{1.5}	δ	% expansion
0	0.105	1.14
0	0.200	2.10
18	0.060	0.77
18	0.120	1.49
40	0.022	0.28
40	0.045	0.67

6.2. Experimental

6.2.1. Materials

Ni/CGO functional anodes were prepared by spraying slurries containing a mixture of NiO powder and CGO powder (20 mol% gadolinium doped ceria). The powder for the NiO/CGO ($Ce_{0.8}Gd_{0.2}O_{1.90}$) slurries was an already prepared mixture from Praxair Specialty Ceramics, USA, containing 70 w% NiO (60 vol% Ni). Extra $Ce_{0.8}Gd_{0.2}O_{1.90}$ from Rhône Poulenc, France, was added to create a slurry with the normal amount of NiO (giving 40 vol% Ni in the reduced state, with respect to the ceramic material). The compositions of the different Ni/CGO slurries are listed in Table 6-2.

Slurry designation	Amount of Ni (vol%)	Ceramic material	Fine : coarse ratio of ceramic material	Particle size of coarse ceramic
Al8	40	CGO	_a _	_a
AI9	60	CGO	_a _	_a

Table 6-2: Compositions of	the different functional	anode layer slurries
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^a) The ceramic material consists of only one (fine) powder with a monomodal particle size distribution

6.2.2. Slurry preparation

The NiO/CGO slurries were prepared by ball milling the already prepared powder mixtures in water and Dolapix CE 64. After at least 24 hours, the binders (Optapix KG 1000 or Chimcell VM 695 and Optapix AC 95) were added as described previously in paragraph 5.2.2. In Table 6-3 a typical composition of a NiO/CGO slurry is given. The particle size of the components in the slurry is monomodal with a d_{50} value of 0.2 μ m.

Table 6-3: Typical composition of an anode interlayer slurry

Compound	Amount
NiO/CGO	
Water	
Dispersant	
Optapix KG 100	
Optapix AC 95	

6.2.3. Impedance spectroscopy

Only one cell containing the functional anode Al8 was electrochemically characterised in the same setup as described in paragraph 5.2.3. For this cell the impedance was measured in the frequency range from 500 Hz to 5 mHz. After heating the samples to 800°C and reducing them under standard conditions, the following measurements were performed (identical to Ni/YSZ and Ni/YZT anodes):

- Impedance measurements in the pH_2 range $9.90 \cdot 10^4$ Pa $4.95 \cdot 10^3$ Pa, with fixed pH_2O of $2.3 \cdot 10^3$ Pa.
- Impedance measurements in the pH₂O range $1.23 \cdot 10^3 1.99 \cdot 10^4$ Pa, with fixed pH₂ of $8.1 \cdot 10^4$ Pa.
- Impedance measurements under standard conditions ($pH_2 = 9.9 \cdot 10^4$ Pa and $pH_2O = 2.3 \cdot 10^3$ Pa), but at different temperatures, i.e. between 800°C and 600°C.

6.3. Results

6.3.1. Microstructure

In Figure 6-1 a SEM image of the Ni/ceria functional anode layer can be seen. Remarkable is the very fine microstructure compared to the Ni/YSZ support. As a matter of fact, the microstructure is much finer than those of the Ni/YSZ and Ni/YZT functional anodes as well. This could be expected, since both the nickel oxide and ceria powders in the spray deposition slurry had particle sizes that were much smaller than those in the NiO/YSZ and NiO/YZT slurries. Still, the anode looks quite porous, which is beneficial for the amount of TPB area (like for the Ni/YSZ and Ni/YZT anodes, the porosity is roughly

estimated on ~25%). The connection of the functional anode with the electrolyte and support doesn't seem to be too close. In the first place, this could pose a problem for the oxygen ions, which have to diffuse into the Ni/CGO anode. Secondly, the bad connection between anode and support could create problems in the current collection, when too few conducting paths exist.



Figure 6-1: Ni/ceria functional anode layer (AI8) with a very fine microstructure

6.3.2. Electrochemical measurements

The validity of the measured impedance was evaluated with software performing the Kramers Kronig transformation. This test checks whether the measured data is linear and the system is in equilibrium^{35,36}. The measurement data were fitted with the equivalent circuit shown in Figure 6-2. The circuit description code (CDC) is $R_{el}(Q1[R1(R2Q2)(R3Q3))$, which is adopted from Ref. 37. Figure 6-3 shows the impedance spectra at different hydrogen and water partial pressure. Three arcs can be observed in the spectra, when closely observed. The arc at high frequency has a summit frequency of ~100 Hz and is small compared to those at mid and low frequency (with summit frequencies of 1 Hz and 0.05 Hz, respectively). The constant phase elements are all capacitive in their behaviour, as their exponents are all close to 1.



Figure 6-2: Equivalent circuit, used to fit measurement data from Al8 (Ni/ceria functional anode)

The total electrode polarisation under standard conditions amounted to 1.8 Ω , which means that the average polarisation for one electrode amounted 1.1 Ω cm². The electrodes were stable under operation conditions, i.e. no degradation took place, as observed for the Ni/YSZ and Ni/YZT anodes. The total

electrode polarisation even decreased a little bit by 0.5 Ω . The activation energy for the electrode polarisation amounts 103 ± 3 kJ/mol.



Figure 6-3: Impedance spectra of Al8 at 800°C in different pH_2 and pH_2O atmospheres. Left: $pH_2O=0.023$ bar. Right: $pH_2=0.81$ bar.

6.3.2.1. pH₂ and pH₂O dependencies

Figure 6-4 and Figure 6-5 show the dependencies of the different circuit elements with varying pH₂ and pH₂O. It becomes clear that the resistances are relatively independent of pH₂. R2 and R3 have only a slight dependence with n = 0.10 and n = -0.07, respectively. The capacitances show a bit more dependence: Q2 has an *n*-value of -0.13 and Q3 has n = 0.36. The story is the other way around for the pH₂O dependency. Now the capacitances are relatively independent of pH₂O, whereas the resistances show a bigger dependency. For R2 and R3 the powers in pH₂O are n = -0.24 and n = -0.52, respectively. R1 on the other hand is quite independent of pH₂O. The electrolyte resistance, R_{el}, is independent of both pH₂ and pH₂O, as expected. The strong dependency of R3 on the water partial pressure also becomes clear when the different impedance spectra are observed. The low frequency arc slowly disappears when the water partial pressure is increased.



Figure 6-4: Circuit elements as function of pH₂ for a Ni/CGO anode (Al8)



Figure 6-5: Circuit elements as a function of pH₂O for Al8

6.3.2.2. pO₂ dependency

CGO is like YZT a mixed ionic and electronic conducting material, which electronic conductivity is highly affected by the oxygen partial pressure (see equation (6.7)). So when a circuit element exhibits a clear trend as function of this oxygen partial pressure, its origin might well be related to the electronic conductivity of CGO. Only the arc in the mid-frequency range has a dependency on pO₂, with n = -0.08 for R2 and n = 0.04 for Q2. This trend is very weak, so it is not clear at the moment if it really relates to the electronic conductivity of CGO.

6.3.2.3. Temperature dependency

The temperature dependencies for the different equivalent circuit elements are shown in Figure 6-6. The electrolyte resistance R_{el} has an activation energy of 99 kJ/mol, which is a good match with literature data. The other activation energies are listed in Table 6-4. R2 doesn't exhibit arrhenius behaviour over the whole temperature range (600 – 800°C). It looks like its activation energy changes between 650°C and 700°C. Above this temperature the activation energy for R2 amounts 92 ± 2 kJ/mol, whereas below ~650°C the activation energy increases to 134 ± 9 kJ/mol. The CPE's are only weakly thermally activated. When the activation energies of the individual elements are compared to the activation energy of the total electrode polarisation (103 ± 3 kJ/mol), it is likely that both processes at mid and low frequency contribute equally to the electrode polarisation.

Circuit element	Activation ene (kJ/mol)	ergy
R _{el}		99
R1		124
R2	<650°C,	134
	>650°C,	92
R3		47
Q1		15
Q2		-4.3
Q3		29

Table 6-4: Activation energy for the different equivalent circuit elements



Figure 6-6: Arrhenius plots for the different circuit elements of a Ni/CGO anode

6.4. Discussion

6.4.1. Microstructure

The total electrode polarisation is still significantly larger than values for state-of-the-art Ni/CGO anodes, as reported in literature. Xia and Liu⁴⁷ found impedances of ~0.4 Ω cm² for Ni/Ce_{0.9}Gd_{0.1}O₂ anodes already at 500°C. They tested complete cells however in a three-electrode set-up and the attribution of the anodic and cathodic contribution to the total cell impedance is always questionable. Zha et al.⁴⁸ measured similar impedances for Ni/ Ce_{0.9}Gd_{0.1}O₂ anodes, but they determined the cathodic contribution of the total cell impedance, using symmetrical cells. In both researches the Ni content was relatively high (50 vol%) and the microstructures were optimised, with a Ni particle size of ~0.3 µm (like the nickel we use), but an even smaller CGO particle size of ~0.02 µm. Furthermore, they sintered their anodes at 1250°C and found a dramatic decrease of anodic performance when the sinter temperature was increased to 1350°C and 1450°C. So, with reduced sinter temperatures, the porosity can be kept high in the anode, resulting in a maximal TPB area. Reduced sinter temperatures would however require a different electrolyte material, since YSZ will not be sintered to a dense material at 1250°C. Gadolinium doped ceria could probably replace the YSZ as electrolyte material, thereby decreasing the possible operation temperature for the SOFC. Improvement of the connection between functional anode and electrolyte/anode support would be another improvement.

6.4.2. Electrochemical measurements

Between the first and second day of the electrochemical measurements, a remarkable change in electrolyte resistance and R1 took place. R_{el} increased from ~0.4 Ω to ~0.7 Ω , whereas R1 increased from ~0.03 Ω to ~0.07 Ω . After the second day the values seemed to remain constant. The reason for these increases is not clear, but it might very well relate to the poor connection between functional anode and anode support. This could create a kind of contacting problem, since it causes a worsening of the current collection. Why this is first seen after one day, is not clear. Especially the determination of the pO₂ dependency for R_{el} and R1 is difficult due to these changes. The results obtained from the pH₂ and pH₂O measurements don't agree, so they can only be analysed independently.

The shape, time constants and magnitude of the impedance spectra are very similar to those found by Rösch et al.⁴⁹, although they tested Ni/Ce_{0.9}Gd_{0.1}O_{2- δ} anodes at 850°C. Unfortunately, they didn't explain any origin of the arcs.

In the equivalent circuit in Figure 6-2, the constant phase element Q1 has an exponent, α , very close to 1. This means that it is mainly capacitive in its behaviour. In such an equivalent circuit, this capacitor is often a double layer capacitance. In our case however Q1 has values in the order of 20 – 60 mF, which is very large for a double layer capacitance, which normally has values of 0.1 – 10 μ F. On the other

hand, in very fine distributed systems, the surface area becomes large and the capacity can have larger values. Moreover, the activation energy of Q1, being $15 \pm 9 \text{ kJ/mol}$ agrees well with a typical double layer capacity.

The arc in the mid-frequency range (R2Q2 at 1 Hz, with $\alpha_{Q2} \sim 0.8$) has a large capacity of $\sim 100 - 300$ mF. The activation energy of R2 amounts 92 kJ/mol. Capacitances with this magnitude could relate to concentration polarisation. Primdahl⁴³ found comparable capacitances in Ni/YSZ anodes and attributed them to gas conversion, which is caused by current flowing through the cell and causing local atmosphere changes. These atmosphere changes give rise to shifting of the Nernst potential. Gas conversion is however not expected to play a role in symmetrical cells. Furthermore, the resistance in the gas conversion arc has an activation of ~0 kJ/mol. Another possibility is the occurrence of gas phase capacitance, which occurs in porous structures that are not entirely open. Using equation (6.8) (*i*, is the diffusing species, *n* is the amount of electrons involved, *P_i* is the partial pressure of the diffusing species and *V* is the control volume), a gas phase capacity for hydrogen of ~50 mF can be calculated, which comes near the values that were really found. Since R2 has a dependency of *n* = -0.24 on the water partial pressure, water would be the trapped gas.

$$C_{i} = \left(\frac{nF}{RT}\right)^{2} P_{i}V$$
(6.8)

However, the activation energy of this arc is quite high for a gas phase process. Normally, gas phase processes are hardly thermally activated. Another process that could be observed at low frequencies and high capacitances is the oxidation/reduction of the bulk: a redox couple. In this case that would be $Ce_{Ce}^{x} + e \rightleftharpoons Ce_{Ce}^{x}$. As this is a bulk process, it should be dependent on the oxygen partial pressure (electronic conductivity). This is what we actually saw: both R2 and Q2 have small dependencies on pO₂. So this is the most probable origin of the mid-frequency arc.

The last arc in the low frequency range $(0.1 - 0.05 \text{ Hz}, \text{ with } \alpha_{Q3} \sim 1)$, R3Q3 has a very high capacitance, 1 - 3 F. The activation energy of R3 amounts 47 ± 7 kJ/mol, which is quite small. The origin of this semicircle could be adsorption of an electrochemical species on the CGO surface. Primdahl⁵⁰ attributed impedances in the same frequency range on Ce_{0.6}Gd_{0.4}O_{1.80} anodes to hydrogen adsorption. Hydrogen adsorption is however in our case not a plausible possibility, since R3 is only weakly dependent on the hydrogen partial pressure. Furthermore, Primdahl found that adding only very small amounts of Ni (0.8 – 2.5 w%) to his CGO anodes, made the arc almost disappear. As in our case we have 40 vol% Ni, hydrogen adsorption shouldn't pose a problem and no impedance from this process is expected. Adsorption of water, on the other hand, could be a cause for the appearance of the arc. Since R3 has a clear dependency of n = -0.52 on the water partial pressure, the process is believed to involve H₂O or OH species that adsorb/desorb on the CGO surface. The activation energy is quite small, compared to what literature reports for water adsorption on ceria: 70 kJ/mol⁵¹. However, this value was determined between 300°C and 600°C.

6.4.2.1. Stable anode

It is quite remarkable that the Ni/CGO anode was stable over the whole characterisation period. A large difference between this anode and the Ni/YSZ (and later on Ni/YZT) anodes is the nickel oxide used. Therefore it would be advisable to check both NiO powder on their purities and contaminants, since these can seriously affect the degradation behaviour of SOFC anodes. The characterisations would become much more reliable, when it is known that only very little degradation takes place during the measurements.

7. Ni/YZT anodes

Titania doped YSZ (YZT) is a mixed conductor in reducing atmospheres and therefore an interesting candidate for use as an anode material. This chapter describes the preparation of different Ni/YZT functional anode layers and their electrochemical performance. Like the Ni/YSZ anodes, different microstructures of the Ni/YZT anodes were obtained by changing the ratio fine/coarse YZT.

7.1. TiO₂ doped YSZ – YZT

Some research has already been done to test the applicability of titania doped YSZ as an anode material. TiO₂ doped YSZ (YZT) is a mixed conductor at high temperature and low pO₂ (i.e. below 10⁻¹³ atm). The electronic conductivity is caused by a valence change of Ti^{4+} to Ti^{3+} resulting in n-type conduction^{52, 53}. Reduction of Ti^{4+} is related to the release of lattice oxygen at low pO₂:

$$O_0^{\mathsf{x}} \xrightarrow{\kappa_0} V_0^{\bullet\bullet} + 2e^{\mathsf{y}} + \frac{y_2}{2}O_2(g) \tag{7.1}$$

$$Ti_{Zr}^{x} + e^{i} \xrightarrow{\kappa_{R}} Ti_{Zr}^{i}$$

$$(7.2)$$

The corresponding equilibrium equations are:

$$K_{o} = \left[V_{o}^{\bullet\bullet}\right] n^{2} p O_{2}^{\frac{1}{2}}$$
(7.3)

$$K_{R} = \frac{\left[Ti_{Zr}^{*}\right]}{\left[Ti_{Zr}^{*}\right]n}$$
(7.4)

When it is assumed that only a very small amount of the titanium ions are reduced, i.e. $Ti_{Zr} \ll Ti_{Zr}^{x}$ and that the amount of oxygen vacancies is mainly determined by the yttria doping, i.e. $[Y'_{Zr}] = 2[V_{0}^{\bullet\bullet}]$, the concentration of reduced titanium ions can be described by:

$$Ti_{Zr} = K_{R} \left[Ti_{Zr}^{x} \right] \cdot \left(2K_{O} \right)^{\frac{1}{2}} \cdot \left[Y_{Zr}^{z} \right]^{-\frac{1}{2}} pO_{2}^{-\frac{1}{2}}$$
(7.5)

And with $\left[Ti_{z_r}^{x}\right]$ being constant, the pO₂ dependency for reduced titanium ions becomes:

$$\left[Ti_{Zr}\right] \propto \rho O_2^{-\gamma_4} \tag{7.6}$$

Electronic conduction is now presumed to take place by a polaronic mechanism, in which electrons hop from Y_{Zr} to the titanium ions⁵⁴. The electronic conductivity is proportional to the concentration of charge carriers, i.e. electrons, according to equation (7.7), in which *e* is the elementary charge of an electron and μ_e is the electron mobility.

 $\sigma_{\rm e} = \textit{ne}\mu_{\rm e}$

(7.7)

The electron concentration is in turn proportional to $\left[T_{Zr}\right]$ (equation (7.4)). So eventually it is deduced

that
$$\sigma_e \propto n \propto [Ti'_{Zr}] \propto pO_2^{-\frac{1}{4}}$$
.

The maximal solubility of TiO_2 lies however between 18 mol% and 20 mol%, which is not enough to create sufficient electronic conductivity for SOFC anodes. Therefore Ni or Cu should be used to create cermets that do exhibit enough electronic conductivity. The doping of titania is useful to reduce the amount of nickel in the cermets. Furthermore, doping with titania gives more mechanical strength to the cermets and Ni-agglomeration in Ni-YZT cermets is reduced, because of the better bonding between YZT and Ni-particles⁵⁵.

The best electronic conductivity is reported for $Y_{0.20}$ Ti_{0.18}Zr_{0.62}O_{1.90} (18 mol% TiO₂). Although the ionic conductivity decreases with increasing TiO₂ doping (due to decrease in oxygen vacancies), electronic conductivity rises with higher TiO₂ content⁵⁶. Moreover, higher titania contents show better stabilisation of the nickel dispersion in the YZT framework at high termperatures⁵³. Finally, higher titania contents result in lower values for the thermal expansion coefficients in Ni-YZT cermets, so that it better matches the thermal expansion coefficient of the YSZ electrolyte.

The anodic performance of YZT anodes was described by Kelaidopoulou et al.^{18,23}. Not optimised cells gave maximum power densities of 37 mW/cm² in wet hydrogen (3% H₂O) at 932°C. The polarisation resistance was large at OCV, but could be reduced significantly when applying a positive overpotential of about 0.14V (from about 13 Ω cm² to 2 Ω cm²). The anodes exhibited excellent redox and thermomechanical stability, as no change in the electrochemical behaviour was observed after 500h of operation. Similar tests were performed for methane as fuel. The maximum power densities were 2 mW/cm². Similar results were obtained for the polarisation resistance, which was even 160 Ω cm² under OCV, but dropped again after applying a positive overpotential. The polarisation could be reduced as well by lowering the methane/steam ratio. This again affects the system's efficiency negatively. The anode proved to be stable under methane operation as well; no decay in the electrochemical behaviour was observed after 700h and after rapid changes in anodic atmosphere.

The power densities obtained for this type of anode weren't that high. They are however not too bad for an anode with an inherent low electronic conductivity. Furthermore, the cells weren't optimised (YSZ-alumina electrolyte and non-optimised counter electrode). Optimising the electronic conduction of the material would probably be a good improvement.

7.1.1. YZT-cermets

Like in the YSZ-based cermets, Cu could be a candidate for the metal component in an YZT-based cermet. The use of copper results in good electronic conductivity of the anode and for temperatures not too high, it helps lowering the serial resistance in the anode. However, at higher temperatures (900°C) the copper becomes mobile and moves to the electrolyte-electrode interface⁵². The electrode becomes a pure copper electrode. This change in microstructure affects the anode performance negatively. It was proven again, that Cu acts as a catalyst for hydrogen oxidation. Ruiz-Morales et al.⁵⁷, who observed the same migration of Cu towards the electrolyte, confirm this behaviour.

Some researchers have already studied Ni-YZT cermet anodes. These anodes show some improvements compared to the standard Ni-YSZ anodes. First, anodic polarisation is decreased in Ni-YZT anodes. This might be caused by an extension of the reaction zone, since this is not restricted anymore to the TPB (YZT is a mixed conductor, after all)⁵⁶. Second, the mechanical strength is somewhat higher for Ni-YZT cermet, although this difference becomes very small at high temperatures⁵⁶ (Figure 7-1). Third, Ni agglomeration is more reduced in Ni-YZT cermets⁵³. The higher the TiO₂ content, the better these properties are. Skarmoutsos et al.⁵⁸ studied the electrochemical performance of Ni/YZT anodes too and found a decrease in activity, compared to standard Ni/YSZ anodes. They recognised some problems in the anodes: first some delamination occurred between the anode and electrolyte, decreasing the reaction surface area. Second, they suggested that the decrease in ionic conductivity (about one order in magnitude, due to TiO₂ doping) resulted in a reduced anodic activity. And third, some titanium diffused into the electrolyte layer during sintering. This might have caused some electronic conductivity in the electrolyte, shortcutting the SOFC. Proper processing is thus required to obtain satisfactory results with Ni/YZT anodes.



Figure 7-1: Three point bending strength of 40 vol.% Ni-xTi-YSZ cermets as function of temperature⁵⁶

Gonzalez Cuenca⁵⁹ found that the total electrode resistance for Ni-YZT anodes was in same order of magnitude compared to state-of-the-art Ni-YSZ anodes. However, the electrode polarisation decreased with time, a phenomenon not observed before with Ni-YSZ anodes. What causes this decrease is not known, yet, but it would be beneficial for SOFC operation. Anyway, the results are far more promising than those from the Cu-YZT anodes, which showed large polarisation resistances. Moreover, optimisation of the microstructure of Ni-YZT anodes (like in state-of-the-art Ni-YSZ anodes) could be a further improvement. Again, the nickel in these anodes is susceptible to coke formation when feeding hydrocarbons.

7.2. Experimental

Functional Ni/YZT anode layers were deposited on top of the anode substrates using an air spraying technique. Slurries containing fine anode material were prepared for this purpose. In order to create different functional anode layers, the composition of the slurries was varied.

7.2.1. Materials

The Ni/YZT functional anodes were prepared by spraying slurries containing a mixture of NiO powder and titania doped YSZ ($Y_{0.2}Ti_{0.18}Zr_{0.62}O_{1.90}$) powder. The nickel oxide powder in NiO/YZT slurries was a powder from Cerac Specialty Inorganics, USA, with a mean particle size of ~2 µm. Titania doped YSZ was prepared by a solid-state reaction of high purity titania, yttria and zirconia. The three powders were first dispersed in water by ball milling (zirconia milling balls), using dolapix CE 64 as dispersant. After drying the dispersion, the powder was calcined at 1450°C for 2000 min. The fluorite structure of the powder was confirmed by XRD (see Figure 7-2). The composition of the powder is $Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$, which is reported to have the maximal electronic conductivity.⁵²



7-2: XRD diagram of $Y_{0.20}Ti_{0.18}Zr_{0.62}O_{1.90}$, confirming the fluorite structure

After reduction, Ni/YZT anodes contain 40 vol% Ni (with respect to the ceramic material). Table 7-1 lists the compositions of the different Ni/YZT functional anode layers. Like for the Ni/YSZ functional anodes, the ratio fine/coarse ceramics was varied. The different Ni/YZT anodes have 0%, 100%, 50% and 30% fine YZT, respectively. The particle sizes of fine and coarse YZT can be found in Table 7-1 as well.

Slurry designation	Amount of Ni (vol%)	Ceramic material	Fine : coarse ratio of ceramic material	Particle size of fine ceramic	Particle size of coarse ceramic
AI11	40	YZT	0 : 100 ^a	1.8 µm ^ª	1.8 µm ^a
Al11a	40	YZT	100 : 0 ^a	0.8 µm ^a	0.8 µm ^a
AI12	40	YZT	50 : 50	0.8 µm	2.2 µm
AI13	40	YZT	30 : 70	0.8 µm	2.2 µm

Table 7-1: Compositions of the different functional anode layer slurries

^a) The ceramic material consists of only one powder with a monomodal particle size distribution

7.2.1.1. Anode supports containing pore former

Porosity in the anode is important for fuel gas transport. Therefore, two more substrates were used, with an increased amount of porosity. The extra porosity was incorporated by adding pore former (spherical graphite particles) to the anode substrate slurry given in Table 4-1. Either 20 vol% or 30 vol% was added to the anode slurry (vol% of the ceramic mass). In a previous work, anodes with this amount of pore former showed better anodic performance than anodes without pore former²⁹. The graphite has a particle size of ~5.6 µm. The preparation route for anode supports containing graphite pore former can be found elsewhere⁶⁰. The anodes having a support containing 20 vol% and 30 vol% pore former are called A20 and A30, respectively.

7.2.2. Slurry preparation

The NiO/YZT slurry was prepared by first dispersing the YZT in water and Dolapix CE 64 in a planetary mill for six hours. Afterwards the NiO was added and dispersed for another six hours. Finally the binders (Optapix KG 1000 and Optapix AC 95) were stirred in as described in paragraph 5.2.2. A typical NiO/YZT slurry is given in Table 7-2.

Table 7-2: Typical composition of an anode interlayer slurry

Compound	Amount
NiO/YZT	
Water	
Dispersant	
Optapix KG 100	
Optapix AC 95	

7.2.3. Impedance spectroscopy

The cells were measured in the same set-up as the cells with Ni/YSZ anodes. A detailed description can be found in paragraph 5.2.3. For the Ni/YZT anodes the frequency range was 50 kHz – 10 mHz. After heating the samples to 800° C and reducing them under standard conditions, the following measurements were performed (identical to the Ni/YSZ cells):

- Impedance measurements in the pH_2 range $9.90 \cdot 10^4$ Pa $4.95 \cdot 10^3$ Pa, with fixed pH_2O of $2.3 \cdot 10^3$ Pa.
- Impedance measurements in the pH₂O range $1.23 \cdot 10^3 1.99 \cdot 10^4$ Pa, with fixed pH₂ of $8.1 \cdot 10^4$ Pa.
- Impedance measurements under standard conditions (pH₂ = $9.9 \cdot 10^4$ Pa and pH₂O = $2.3 \cdot 10^3$ Pa), but at different temperatures, i.e. between 800°C and 600°C.

7.3. Results

7.3.1. Microstructure

Figure 7-3 shows the different microstructures of a Ni/YZT anode before and after electrochemical testing. Both pictures show a quite dense structure. This could be expected, since the anodes were fired at 1430°C. Gonzalez Cuenca⁵⁹ already found that the anodic performance is better when YZT is fired at 1300°C instead of 1400°C, because of loss of porosity. Unfortunately, the anode-supported cells in this project can't be sintered at lower temperatures, as the YSZ electrolyte wouldn't become dense at these temperatures. However, from the layer thickness and mass, still a porosity of ~25% was calculated.

The shape of the nickel phase is remarkably different in both anodes. In the tested anode, the nickel has adapted a porous, fluffy structure, whereas the nickel in the untested anode doesn't exhibit this shape. The cause for this reshaping is not clear, but is probably beneficial to the anode performance, as it seems to enlarge the nickel surface. This in turn means an increase in the surface area for the electrochemical reactions. No clear differences can be observed, regarding the nickel dispersion in the tested and untested anodes. This is in a way expected, since YZT is reported to bond stronger to nickel than YSZ and should hence prevent serious nickel agglomeration at 800°C. However, the Ni/YZT sample that was electrochemically measured exhibited a serious increase in impedance, like the Ni/YSZ anodes. So a change must have taken place, but apparently on a too small scale to be noticeable.



Figure 7-3: Microstructure of an Al11 functional anode before (above) and after electrochemical testing (under).

7.3.2. Electrochemical characterisation

The validity of the measured impedance was evaluated with software performing the Kramers Kronig transformation. This test checks whether the measured data is linear and the system is in equilibrium^{35,36}.

7.3.2.1. Fitting

The measurement data obtained from the Ni/YZT anodes were fitted with a tangent hyperbolic function. Figure 7-4 shows the impedance spectrum recorded at standard conditions. It obviously has strong similarity with a spectrum for Finite Length Warburg diffusion. On the other hand, when the small arc at high frequencies is subtracted, a Gerischer-like spectrum is obtained. Such a spectrum is given too in Figure 7-4.



Figure 7-4: Upper left: Measurements data. Upper right: Measurement data with the high frequency arc subtracted. Lower left: Spectrum for a Gerischer impedance. Lower right: Impedance spectrum for a Finite Length Warburg

However, the spectrum (after subtraction of the high frequency arc) cannot be fitted with a normal Gerischer element or Finite Length Warburg impedance in series with a resistance (for the electrolyte). The mathematical representation of a Gerischer element is as follows:

$$Z(\omega) = \frac{Z_0}{\sqrt{(k+j\omega)}}$$
(7.8)

In formula (7.8), *k* is the reaction rate constant of the chemical side reaction that takes place parallel to the electrochemical reaction at the electrode. Boukamp and Bouwmeester⁶¹ derived a more general formula for the electrochemical behaviour of mixed conducting materials and showed it could be reduced to this formula (7.8) in a special limiting case. This formula takes the change of oxygen activity in account, which takes place when a current flows through such a material. The redox process that takes place due to this change in oxygen activity is now the chemical side reaction, with reaction rate constant *k*.

$$Z(\omega) = \frac{RTW}{4F^2 c^0 \sqrt{\tilde{D}}} \frac{\tanh\left[L\sqrt{(k+j\omega)/\tilde{D}}\right]}{\sqrt{(k+j\omega)}}$$
(7.9)

In equation (7.9), *W* is the thermodynamic enhancement factor, c^0 the concentration of the reacting species in the bulk, \tilde{D} the chemical diffusion coefficient and *L* the length of the reaction zone. Equation (7.9) describes in fact a process that combines Finite Length Warburg diffusion (FLW) and a chemical side reaction. So at high frequencies, Warburg diffusion can be seen, whereas at low frequency the impedance is limited by a finite dc-value. This is the so-called Finite Length Warburg impedance. And in this special case, the chemical side reaction is assumed to cause the finite dc-value, by creating a 'sink' for the electrochemically active species. In the case that $\tilde{D} \ll L^2 k$ this formula reduces to equation (7.8). Apparently this condition does not hold in the case of the Ni/YZT anodes, as their spectra can

only be fit properly using equation (7.9). To be precisely, another adaptation has been applied to equation (7.9) to make the fit even better: a double fractal.

$$Z(\omega) = Z_0 \frac{\tanh\left[L\left((k + (j\omega)^{\alpha})/\tilde{D}\right)^n\right]}{(k + (j\omega)^{\alpha})^n}$$
(7.10)

In this formula α is close to 1 and *n* is close to 0.5. The double fractal makes the physical interpretation difficult, but is in analogy with the empirical Havriliak-Negami dielectric response function, equation $(7.11)^{62}$. Gonzalez-Cuenca et al.⁶³ used a similar double fractal formula to fit impedance data on mixed conducting chromite titanate materials.

$$\varepsilon(\omega) = \varepsilon_0 + \frac{\varepsilon_0 - \varepsilon_\infty}{\left(1 + (j\omega\tau)^{1-\beta}\right)^{\alpha}}$$
(7.11)

The big advantage of fitting with this tangent hyperbolic function is that in this way the number of equivalent circuit elements is reduced to the electrolyte resistance, an (RQ) circuit at high frequencies and the tangent hyperbolic (with characteristic parameters Z_0 , L and k). So despite the complex fitting procedure, in the end we will be left with two electrode processes, describing the electrode impedance. Finally, the equivalent circuit can be described by the one in Figure 7-5, with *TG* being the finite Warburg diffusion element with a chemical side reaction (alternatively, Finite Length Fractal Gerischer).



Figure 7-5: Equivalent circuit for the Ni/YZT anodes

7.3.2.2. Anode model

Adler et al.⁶⁴ developed a model to describe the electrode kinetics in mixed conducting oxygen electrodes (cathodes). The model both involves electrochemical and chemical contributions in the electrode kinetics. In this way they were able to resolve two parallel processes in their impedance spectra that didn't contribute additively to the cell impedance. In other words, the processes couldn't be resolved by simply using a set of equivalent circuits in series. The processes were oxygen reduction at the mixed conductor surface (electrochemical) and solid-state diffusion inside the mixed conductor (chemical). Due to the oxygen reduction, a concentration profile develops. This concentration profile in turn affects the oxygen concentration in the mixed conductor lattice, giving rise to solid-state diffusion.



Figure 7-6: Competitive solid-state diffusion and surface exchange of oxygen ions in YZT

In our situation, the concentration profile is upside down, since oxygen ions are built out from the electrolyte and mixed conducting material. However, there's still the same competition between oxygen diffusion inside the YZT lattice, away from the electrolyte and oxygen exchange with the gas phase. This is also shown in Figure 7-6. In any case, the oxygen partial pressure plays a dominant role in the behaviour of mixed conducting SOFC electrodes. That might as well be the reason why the presence of water in the fuel gas is so important: it sets the oxygen partial pressure on the anode side. And for mixed conducting materials, the oxygen partial pressure also determines the electronic conductivity of the material.

The model of Adler is probably not applicable to our anodes, because Adler's model seems to break down for materials with low ionic conductivity. This is probably exactly the reason for the poor performance of the YZT material. Due to the high doping with titania, the ionic conductivity decreases with almost one order of magnitude, compared to 8 mol% YSZ⁵⁸. Holtappels et al.⁶⁵ modelled the competitive oxygen exchange/diffusion in YZT anodes with a Gerischer impedance as well. Gonzalez-Cuenca et al.⁶³ found typical Gerischer behaviour too in mixed conducting lanthanum chromite/titanate materials for SOFC anodes. They specifically found this impedance in thin electrodes and suggested that the poor electronic conductivity limited the electrode performance. In the Ni/YZT anodes electronic conductivity shouldn't be the limiting process. Low ionic conductivity on the other hand, can seriously limit the extent to which the oxygen ions are able to diffuse into the anode material.

7.3.2.3. Measurements under standard conditions

The total electrode polarisation is quite high for all Ni/YZT anodes and amounts $9.3 - 16 \Omega$ as can be seen in (this is the polarisation resistance after some days of testing, i.e. after the most serious degradation). The activation energies of the electrode polarisation are slightly lower than those obtained for the Ni/YSZ anodes, $102 - 113 \pm 1$ kJ/mol. This is close to the activation energy for oxygen ion conduction in YZT^{58, 66}. This supports the suggestion that the low ionic conductivity in YZT seriously limits the anodic performance. The amount of fine YZT has a positive effect on the electrode impedance. Upon adding some fine YZT, the impedance drops significantly. As expected, the lowest impedance is measured for Al11a, with 100% fine YZT. The difference between Al12 and Al13 is not so clear, however, although they should contain different amounts of fine YZT (as a matter of fact, Al13 with 30% fine YZT has a slightly smaller impedance than Al12, with 50% fine YZT). Possibly, some of the coarse YZT was milled to finer ceramic powder during the preparation of the bimodal slurries.

Anode	Amount of fine YZT	2 R _{pol} (Ω)	R _{pol. av} (Ωcm ²)	E _{act} (kJ/mol)
AI11	0%	16	10	102
AI13	30%	11	7.1	113
AI12	50%	13	7.9	113
Al11a	100%	9.3	5.9	113

Table 7-3: Polarisation resistance and activation energies for the different Ni/YZT anodes

The impedance measurements under standard conditions for the different Ni/YZT anodes with standard anode supports are shown in Figure 7-7. Notice that these spectra are the first that were recorded, so little degradation has taken place, yet. The values for the different circuit elements at standard conditions are given as well, in Table 7-4. From this table, it seems that the impedance in the low frequency regime is not caused by one of the three parameters, L, Z_0 and k, separately. Their values are quite correlated and changing the amount of fine YZT affects all three of the elements in such a way, that the total impedance decreases for an increasing amount of fine YZT.



Figure 7-7: Impedance spectra of different Ni/YZT anodes at standard conditions (T=800°C, pH_2 =0.99 bar, pH_2 O=0.023 bar)

Anode	Amount fine YZT	R _{el} (Ω)	R1 (Ω)	Q1 (Ω ⁻¹ s ⁿ)	n1	L	Ζ ₀ (Ω)	k (s⁻¹)
AI11	0%	0.437	0.209	2.13·10 ⁻²	0.62	1.39	9.39	0.33
AI13	30%	0.386	0.271	2.06·10 ⁻²	0.58	1.15	8.63	1.37
AI12	50%	0.489	0.254	1.78·10 ⁻²	0.60	1.51	11.19	1.71
Al11a	100%	0.435	0.193	1.85·10 ⁻²	0.60	1.10	5.31	0.98

Table 7-4: Values for the equivalent circuit elements at standard conditions (T=800°C, pH₂=0.99 bar, pH₂O=0.023 bar)

7.3.2.4. pH_2 and pH_2O dependency

The impedance spectra of AI11a (100% fine YZT) in different hydrogen and water atmospheres are shown in Figure 7-8. In Table 7-5 the dependencies on water and hydrogen partial pressure are listed. It becomes clear that the finite length L is only weakly dependent on pH_2 but more on pH_2O (notice that *L* contains the square root of the diffusion coefficient, \tilde{D} , as well). Z_0 has a negative dependency on pH₂, which can be explained by the presence of a bulk concentration c^0 in Z_0 (see equation (7.9)). When the hydrogen bulk concentration is lowered, equation (7.9) predicts an increase in Z_0 . Furthermore, Z_0 is independent of pH₂O, which may mean that c^0 mainly involves the bulk concentration of hydrogen as a diffusing species. This is a fair assumption, in respect with the slow surface diffusion of water, compared to the fast diffusion of hydrogen in the bulk. The reaction constant, k, is dependent both on the water and hydrogen partial pressure. Its large dependency on pH₂O suggests that water is involved in the chemical side reaction. There is also a very clear increase in its power with respect to pH₂O, with increasing amount of fine ceramics, i.e. amount of reaction sites. This is a good indication too, that the fitting model is valid. In the high frequency part we see that R1 has a dependency of -0.25 -0.30 with the pH₂ and a value of ~0.20 with regard to the water partial pressure. The high frequency arc probably relates to a diffusion process, since the α -value of the CPE (Q1) lies between 0.60 and 0.65, which is close to $\alpha=1/2$. The electrolyte resistance is almost independent on pH₂ and pH₂O, as expected. All dependencies are very consistent with each other, which is a good indication that the microstructures are similar (apart from the ratio coarse : fine YZT), resulting in similar electrochemical mechanisms. The variation of the different circuit element in changing pH₂ and pH₂O are shown in Figure 7-9 and Figure 7-10 for Al11a (100% fine YZT).



Figure 7-8: Impedance spectra of Al11a (100% fine YZT)

Anode	Amount of fine YZT (%)	R el'lyte	R1	Q1	L	Z 0	k
		pH ₂ c	lepende	ncy			
Al11a	100	0.01	-0.25	0.32	0.01	-0.32	-0.21
AI12	50	0.01	-0.26	0.24	0.06	-0.21	-0.11
AI13	30	0.00	-0.25	0.38	0.04	-0.24	-0.16
AI11	0	-0.05	-0.31	0.32	0.08	-0.18	-0.29
pH ₂ O dependency							
Al11a	100	0.01	0.14	-0.32	-0.16	-0.01	1.4
AI12	50	0.00	0.21	-0.10	-0.19	-0.01	1.1
AI13	30	0.02	0.21	-0.20	-0.16	0.02	0.77
AI11	0	0.01	0.21	-0.24	-0.19	-0.04	0.43

Table 7-5: Powers in pH₂ and pH₂O dependency



Figure 7-9: pH₂ dependencies for Al11a (100% fine YZT)



Figure 7-10: pH₂O dependencies for Al11a (100% fine YZT)

7.3.2.5. pO₂ dependency

For mixed ionic and electronic conducting materials it is interesting to see what the dependency of the different circuit elements is on pO_2 . Since the pO_2 has a large influence on the electronic conductivity of YZT, changes of circuit elements as a function of pO_2 probably relate to this electronic conductivity. The

pO₂ can be calculated from the pH₂, pH₂O and equilibrium constant for the water formation reaction, using equation (7.12). At 800°C, K_{eq} has a value of 9.83·10⁸.

$$pO_2 = \left(\frac{pH_2O}{pH_2 \cdot K_{eq}}\right)^2$$
(7.12)

A short investigation learns that only four circuit elements show a consistent change as function of pO₂. Those are R_{el} , R1, Q1 and L. An example of a graph that plots these circuit elements against pO₂ is Figure 7-11. Table 7-6 lists all powers for the different anodes. As expected, the electrolyte resistance, R_{el} is almost independent of pO₂. R1 and Q1 both have a relatively large dependency on the pO₂, with powers of 0.10 - 0.13 and -0.06 - -0.16, respectively. The possible origin of the high frequency arc and its relation to pO₂ is discussed later on. Finally, L has a dependency of -0.04 - -0.08 with respect to the pO₂.

Table 7-6: pO2 dependence of some circuit elements in Ni/YZT anodes

Anode	Amount of fine YZT (%)	R el'lyte	R1	Q1	L
Al11a	100	-0.01	0.10	-0.16	-0.04
AI12	50	-0.01	0.12	-0.06	-0.06
AI13	30	0.00	0.12	-0.13	-0.05
AI11	0	0.01	0.13	-0.11	-0.08



Figure 7-11: pO₂ dependencies of some circuit elements for Al13 (30% fine YZT)

7.3.2.6. Temperature dependency

The electrolyte resistance has an activation energy of $81 - 92 \pm 5$ kJ/mol, which agrees well with the activation energy for oxygen ion conductivity in 8-YSZ. All the values for the activation energies can be found in Table 7-7. The activation energies are very consistent with each other, like the dependencies

in the water and hydrogen partial pressures. Again, notice that *L* stands for $L/\sqrt{\tilde{D}}$. So the negative activation energy is actually a positive one for the diffusion coefficient. Similar to the dependency of *k* in the water partial pressure, the activation energy of *k* seems to increase with decreasing amount of fine YZT in the anode. This might indicate that *k* involves an adsorption step or that the YZT catalyses the side reaction somehow. However, the errors in these particular activation energies are quite high (± 11 kJ/mol), so they might as well be quite comparable. Figure 7-12 shows the arrhenius plots for the different circuit elements.

Anode	Amount of fine YZT (%)	σ el'lyte	σ1	Q1	L	Z0	k
Al11a	100	92	117	63	-34	-112	47
AI12	50	81	122	35	-35	-110	57
AI13	30	88	117	62	-39	-112	65
AI11	0	89	123	50	-31	-105	72

Table 7-7: Activation energies of different circuit elements



Figure 7-12: Arrhenius plots for equivalent circuit elements of AI13 (30% fine YZT)

7.3.2.7. Anode supports with increased porosity

Cells were tested with anode supports with an increased amount of porosity to check whether gas diffusion plays a role in the impedance measurements. Two cells were tested with 20 vol% and 30 vol% graphite in the anode substrate green bodies. Their functional anode layers are anodes with 100% fine YZT, i.e. identical to Al11a. They were designated A20 and A30 (for 20 vol% and 30 vol% graphite, respectively). Mercury intrusion measurements in a previous work revealed that the porosity in the oxidised samples increased from 18% in standard supports to 34% and 40% in the anode supports with 20 vol% and 30 vol% graphite, respectively. This would mean an increase of porosity in the reduced state from 32% to 45% and 50%, respectively. Actually it is not really expected that gas diffusion plays a dominant role in the impedance, since these impedances are small (~ 0.1Ω cm²) and the process itself is hardly thermally activated. Such impedances were not found in our spectra, but nevertheless it is good to check the effect of the anode support on the impedance measurements.

A20 has a very similar electrode polarisation under standard conditions as compared to anode Al11a $(2.97 \ \Omega \text{cm}^2 \text{ for A20} \text{ against } 2.60 \ \Omega \text{cm}^2 \text{ for Al11a}$, measured during the first day). This is as expected, since both anodes contain 'identical' functional anodes. And apparently, the anode support doesn't play an important role in the anode's impedance. However, this cell (A20) is stable during the days of electrochemical testing and doesn't show any form of degradation. The cell's impedance even decreases within three days (see Figure 7-13). The reason why this particular anode doesn't show the degradation that was observed in all other anodes is not very clear. It has to be said that the sample tube was replaced, before the measurements on these anodes, but how this could have affected the measurement is unclear. Also if the problem of the gas leak has disappeared, this gives no explanation (see 3.1.1). Electrochemically, there is no clear explanation as well, why the different anode support could have an effect on the degradation. So it might as well be related to a step in the preparation process. Perhaps burning out the graphite during sintering has affected the Ni/YZT anode as well. Microstructural analysis might reveal differences between the different anodes. The activation energy of this anode is somewhat larger than those of the other Ni/YZT anodes: 124 kJ/mol.



Figure 7-13: Improvement of anodic performance. 1^{st} and 3^{rd} day under standard conditions; 2^{nd} day: T=800°C, pH₂=0.81 bar, pH₂O=0.023 bar.

A30 showed some odd behaviour. It exhibited a quick increase in the electrode polarisation, which was already noticeable during the first day. After this day the electrode polarisation remained constant again. During the first day the electrode polarisation was 3.35 Ω cm², which is still comparable to the polarisation of Al11a. The second day it was 4.92 Ω cm². Very peculiar was the very large dependency on the hydrogen partial pressure and the worsening of anodic performance when increasing the water partial pressure. The first effect can be explained by the instability of the anode during the first day, i.e. the day that the hydrogen partial pressure dependency was measured. The second effect has not been seen earlier for Ni/YZT anodes; actually, no literature was found that reports this kind of behaviour. The presence of water is basically always beneficial to the anodic performance. Whether this behaviour should be attributed to the functional anode layer or to the anode support is not sure. The thermal activation of the electrode polarisation is similar to the other Ni/YZT anodes: 110 kJ/mol. More remarkable is that the shape of the impedance spectrum has changed a little when compared to the other Ni/YZT anodes. This can be seen when the mathematical model is used to fit the low frequency arc. It doesn't fit anymore and the value for the reaction rate constant for the chemical side reaction, k. is constantly set to zero by the model. The spectrum now resembles more a typical finite length Warburg impedance, i.e. without the chemical side reaction.

Table 7-8 shows the hydrogen and water partial pressure dependencies that were found for the anodes A20 and Al11a. Another Al11a sample (with a normal anode support) was tested as well in the new setup for proper comparison. Since anode A30 couldn't be fitted with the finite length fractal Gerischer function, this anode is left out from the comparison. There are some clear differences between the two other anodes. Again, the reaction rate constant, *k*, seems to behave most differently. It is worth noting that in the case of A20, for high hydrogen partial pressure, *k* was set to zero as well by the mathematical model. This may imply that the chemical side reaction may be strongly dependent on the supply of hydrogen and might disappear in excess of hydrogen (i.e. for high pH₂ and improved gas transport in the anode support). The most remarkable observation however, was that Al11a's impedance was almost independent of pH₂O, which is hard to explain.

Anode	Pore former in anode support (vol%)	R el'lyte	R1	Q1	L	20	k
			pH₂ dep	endency			
A20	20	-0.07	-0.27	0.60	0.13	-0.16	-1.2
A30	30	-0.02	-0.25	0.64	а	а	а
Al11a	0	0.01	-0.25	0.32	0.06	-0.21	0.22
pH ₂ O dependency							
A20	20	0.00	0.14	-0.18	-0.05	0.03	0.71
A30	30	0.01	0.27	-0.06	а	а	а
Al11a	0	0.00	0.08	-0.07	-0.09	0.00	0.02

Table 7-8: Powers for hydrogen and water partial pressure	e dependencies in anodes with alternative anode supports
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^a Not determined

7.4. Discussion

The limiting process in the Ni/YZT anodes is found in the low frequency range. At 800°C its summit frequency is ~0.3 Hz, whereas it shifts to 0.03 Hz when the temperature is decreased to 600° C.

From the dependencies on pH₂, pH₂O and pO₂ a rough mechanism can be proposed for the hydrogen oxidation in the Ni/YZT anodes. In the high frequency arc we see a clear and consistent dependency on all partial pressures. Especially the fact that both *R1* and *Q1* have a dependency on the pO₂ indicates a process that relates to the electronic conductivity in YZT. Moreover, the activation energy of *R1* is similar to the activation energy for polaron hopping, the electronic conduction mechanism (110 kJ/mol⁶⁷). Furthermore, the constant phase element in this arc has an α -value of ~0.6. As this value is near α =½, which would be identical to a Warburg element, the process describes some sort of diffusion.

A finite length Warburg combined with a Gerischer impedance describes the large low frequency part. The reaction constant of the chemical reaction exhibits a strong dependency on the water partial pressure and moreover, the dependency is stronger with an increasing amount of fine YZT. So H_2O or OH^- species could play a dominant role in the electrode impedance. Combining this information, leads to the following model, in which hydrogen adsorption and dissociation preferentially takes place on the Ni metal. The adsorbed hydrogen atom subsequently diffuses towards and over the YZT surface. Then two reaction paths are possible. In the first path, the adsorbed hydrogen atom reacts with an oxygen ion from the YZT lattice (equation (7.14)). Next, the OH⁻ ion diffuses from the lattice to the surface. There it can react with another hydrogen atom, upon releasing a second electron (equation (7.16)). In the second reaction path, adsorbed water plays an important role. It could react with the oxygen ions from the lattice, forming two OH⁻ ions. These hydroxide ions subsequently react with adsorbed hydrogen atoms again. This gives an explanation for the 'catalytic' role of water. It serves as an alternative reaction species for the lattice oxygen. Hence, only the second reaction ((7.16)) in the hydrogen oxidation depends on the presence of adsorbed hydrogen.

Possible reactions occurring on the Ni/YZT anode:

$H_2(g) + 2s_{_{Ni}} ightarrow 2H_{_{ads,Ni}}$	(7.13)
$H_{ads} + O_0^x \rightarrow OH_0^{\bullet} + e^{i}$	(7.14)
$OH_{O}^{\bullet} \rightarrow OH_{ads}^{-} + V_{O}^{\bullet\bullet}$	(7.15)
$H_{ads} + OH_{ads}^{-} \rightarrow H_2O_{ads} + e^{-1}$	(7.16)
$O_{O}^{x} + H_{2}O_{ads} \rightarrow OH_{O}^{\bullet} + OH_{ads}^{-}$	(7.17)

In general, the Ni/YZT anodes perform somewhat worse than the Ni/YSZ anodes. The smallest impedance (in the old set-up), was $5.9 \ \Omega \text{cm}^2$, which is even lower than the impedance for the Ni/YSZ cermet with 15% fine YSZ. Increasing the amount of fine YZT in the anodes results in a clear decrease of the anode's impedance. Further decreasing the YZT particle size will probably improve its performance even further. Another way to improve these anodes, is to lower the sintering temperature to 1300° C, to avoid coarsening of the anode structure. However, this will be complicated in electrolyte-supported cell designs, since the YSZ electrolyte will not be dense if fired at such a low temperature. Sintering aids that inhibit the YZT grain growth might help in optimising the YZT microstructure. Furthermore, a way to prevent the quick degradation has to be found. The anode with the improved anode support, A20, didn't exhibit degradation and its performance even improved over time. Whether this was caused by its anode support is unclear at the moment, but it proves that Ni/YZT is an interesting anode material. This anode eventually had a polarisation resistance of 2.1 Ωcm^2 , which is comparable to the polarisation resistance of the Ni/YSZ anodes.

Another way to improve the Ni/YZT anodes is to replace 75% of the yttrium by scandium (i.e. $Y_{0.05}Sc_{0.15}Ti_{0.18}Zr_{0.62}$), which gives an increased ionic and electronic conductivity⁶⁸. Especially the electronic conductivity increases markedly when replacing some of the yttrium, but the small increase in

ionic conductivity may be more important, since this could be one of the critical limitations for YZT as anode material.

In order to get more insight in the mechanism for hydrogen oxidation in Ni/YZT anodes, it would be useful to investigate anodes with a more defined microstructure, like pattern electrodes. This will be a more complex preparation than the preparation of Ni-pattern electrodes, since three phases come into play, instead of the two in Ni/YSZ anodes. However, knowing the length of the TPB is critical for understanding the processes that take place in this cermet with a mixed conducting material. For a start, the nickel could be left out of the anodes. Already then it can be verified, whether hydrogen adsorbs on the ceramic material instead of on the nickel, which is assumed for Ni/YSZ anodes.

7.4.1. Increased porosity in the anode supports

The increased porosity in the anode supports led to results that did not really agree with the measurements on the anodes with standard supports. The presence/absence of degradation in the anodes had quite an effect on the trends that are found as a function of water and hydrogen partial pressure. Anode A30 showed some very peculiar behaviour. Some quick degradation seemed to take place. Furthermore, the worsening of anodic performance upon increasing the water partial pressure is contradictory. The fact that this anode performs worse than A20 and Al11a (with 'identical' functional anodes) may be explained by a decreased conductivity in the anode support. The large amount of pore former may have reduced the number of percolating nickel pathways. How this could lead to the other behaviour observed is still unclear.

A20 showed an improvement in performance over the days, just like Gonzalez Cuenca observed on her Ni/YZT anodes⁵⁹. The reason for the improvement in anodic performance may be found in the microstructural change that was observed. The nickel phase undergoes a shape change, which increases the surface area for the electrochemical reactions.

Finally, the use of different anode supports has some effect on the impedance measurements, but it doesn't seem fair to compare them directly to the anodes with standard anode supports. Although the supports with increased porosity are not expected to affect the electrochemical performance, they might have had an effect on the processing of the samples.

7.4.2. Set-up change

Another reason for not comparing the results of A20 and A30 directly with the Ni/YZT anodes containing standard supports, is that the set-up was changed before doing these last measurements. By this change of set-up probably just the position of the sample in the furnace was optimised. This shouldn't have an effect, but it would be recommendable to perform some more measurements in this set-up to try to reproduce the data.

The fact that Al11a's impedance was almost independent of pH_2O in the new set-up is quite confusing. Whether this result is reliable is questionable. A whole series of measurements with different anodes in this set-up would again be required to verify this behaviour.

8. Conclusions

The work describes the preparation and electrochemical characterisation of three different anode materials for Solid Oxide Fuel Cells. The anodes were tested in symmetrical anode supporting cells. The first material was a standard nickel/YSZ cermet, with varying ratios of fine and coarse YSZ. The results were partly consistent with earlier findings on Ni/YSZ anodes. The total electrode impedance $(2.0 - 7.4 \ \Omega cm^2)$ was certainly not comparable with those obtained for state-of-the-art Ni/YSZ anodes, but agree well with finding by other researchers. Furthermore, the electrode impedance decreased with an increasing ratio of fine to coarse YSZ. Problematic was the quick degradation of the anodes under operating conditions. The impedance increased within four days dramatically. For one anode the increase amounted almost 100%. The extent of degradation cannot be assumed to have no effect on the impedance measurements. To be more precise, they probably did affect the results, since the various data obtained on the different Ni/YSZ anodes was inconsistent. So it is difficult to come up with clear mechanisms and models for the hydrogen oxidation on these anodes. The effect of microstructure stays uncertain as well, apart from the fact that it influences the total electrode polarisation. The preparation of stable anodes would therefore be a first issue. To achieve this, the first recommendation would be to check whether purer nickel oxide powders could be used.

The Ni/CGO anode showed the best performance of the three tested materials, with a polarisation resistance of 1.1 Ω cm². This is in the first place due to the fine microstructure of the anode, compared to the Ni/YSZ and Ni/YZT anodes. This is also the only anode material that didn't suffer from degradation during the electrochemical testing. As this is the only anode material that was prepared from an already prepared powder mixture, powder morphology and purity probably play an important role in the eventual performance and stability of an anode. The main impedance in the Ni/CGO anode is caused by two processes: an adsorption process, which involves water species, and probably bulk oxidation/reduction of cerium ions.

Since the results on the Ni/YSZ anodes seemed to reveal that different microstructures could indeed be incorporated in the anodes, using the simple spray deposition technique, different microstructures were made for a third anode material: a Ni/YZT cermet. In contrast to the Ni/YSZ anodes, these Ni/YZT anodes gave very consistent impedance measurement data. It was believed that in the mixed ionic and electronic conducting YZT a competition takes place between solid-state diffusion and surface exchange of oxygen. Therefore the impedance data on this anode material was modelled with a Finite Length Fractal Gerischer, a combination between Finite Length Warburg diffusion and a Gerischer impedance. The impedance for Warburg diffusion is finite at low frequencies, as the process of oxygen release creates a sink for the oxygen ions. A more detailed study on the results is required to present a valid model and mechanism for the hydrogen oxidation reaction on Ni/YZT anodes. A further recommendation would be to synthesise anodes with a known Triple Phase Boundary area (like pattern electrodes) or just single-phase anodes. The highly dispersed cermet structure always makes it hard to model impedance results.

The overall performance of the Ni/YZT anodes is a little bit worse than the Ni/YSZ anodes. Especially for coarse microstructures, total electrode polarisations up to 10 Ω cm² were measured (for one single electrode). This value decreases however significantly when the microstructure is made finer. These anodes exhibited degradation as well. There was however one sample that didn't degrade and even showed an improvement in performance over time. Knowing what exactly causes the degradation is necessary to benefit from this improving behaviour.

9. Danke, danke,

Dan is er nog een moment om verschillende mensen te bedanken. Zonder hen was het werk van de afgelopen tien maanden niet mogelijk geweest en waren de maanden zelf bovendien zeer saai geweest. In de eerste plaats is er natuurlijk de commissie: Barbara, het was best wel weer eens goed, om wat basisbegrippen uit de katalyse naar boven te halen. Hoe snel je die toch kunt vergeten... Dave, nogmaals bedankt voor de avond racletten. Zo kon ik meteen weer eens iets aan mijn Zwitserse kaasverslaving doen. Henny, het is toch altijd weer leuk om de oogjes van de echte wetenschapper te zien glunderen, bij het zien van een aantal interessante resultaten. Hopelijk komen er nog een paar interessante dingen uit de komende discussies. Nog iemand wiens hart sneller gaat kloppen, wanneer er een mooi impedantie-spectrum op zijn beeldscherm verschijnt: Bernard. Ik hoop dat ik je weer een beetje op weg geholpen heb bij je queeste naar de heilige Gerischer. Maar vooral, bedankt voor alle discussies over polarisatie, diffusie en triple phase boundaries. Zum Schluss: Peter, danke für all deine Kommentare und Hinweise. Wie Bernard, hattest du immer wenig Zeit, aber das gab mir dann oft die Gelegenheit auf deinem Rechner zu arbeiten. Manchmal habe ich mir auch gedacht: wir haben vielleicht mehr telefonisch diskutiert als bei dir am Schreibtisch. Aber gut, so waren sie auch am sinnvollsten. Oh ja, die Schweizer Polkamusik soll ich immer noch an meinem Repertoire hinzufügen.

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10. Literature

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