Diplomarbeit

Electrochemical characterization of Ni pattern anodes in $H_2/H_2O$ and $H_2S$ containing atmospheres

ausgeführt am
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Preface

The world is ending, I hear them shout,
with letter so big to brag about,
terror, pest and that criminal,
the present seems so despicable.

But doomsday prophets, they all were wrong,
ext morning the world just went on.
Forever we’ve been at the ‘edge of doom’,
but there are some flowers that still bloom:

Literacy rates, just upwards they crawl,
Infant mortality is at an all time low,
the same record poverty numbers show,
and it’s the most peaceful time of all.

So maybe there’s light in all the black,
maybe the sky’s not falling on our head,
maybe if pessimism is just shred,
challenges of our present can be met.
— The author
The mere fact that these words are read by someone imbues me with gratitude since this means that the past months were not useless in a greater context. For this I want to thank you, dear reader, and I hope this thesis includes, but is not limited to what you are looking for.

I also want to thank everyone contributing to this thesis in one way or another. First of all my parents who, among other things, enabled studying for me. I want to thank Univ.-Prof. Dipl.-Phys. Dr. Jürgen Fleig for the opportunity to do research in this fascinating field with modern equipment and Alex for his valuable help with experiments and data interpretation. The rest of the research group – Lukas, Andi, Bernhard, Tschisi, Sandra, Tobi, Plüsch & Plausch, the other Alex, Peter, Steffi, Gregor and Georg – also deserves my gratitude for the great working atmosphere.

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Abstract

In this thesis the $H_2$ oxidation kinetics of micropatterned nickel electrodes on yttria stabilized zirconia (YSZ) was electrochemically characterized in $H_2/H_2O$ and $H_2/H_2O/H_2S$ atmosphere. As a prerequisite, a reliable procedure was established to manufacture microelectrodes, which remain dense during electrochemical experiments at 750°C. On these geometrically well-defined and morphologically stable model electrodes the polarization resistance, the electrode capacitance and the current-voltage characteristics were investigated using electrochemical impedance spectroscopy and DC methods, respectively. Analysis of impedance data reveals the existence of at least 2 independent factors causing scattering of electrode properties. Moreover, the effect of different YSZ substrate orientations on the polarization resistance and electrode capacitance of Ni/YSZ in $H_2/H_2O$ atmosphere was investigated and the effect of temperature gradients in the setup is discussed. For the interpretation of DC data a model is suggested explaining current-voltage curves of Ni pattern electrodes. Finally, sulfur poisoning effects on impedance spectroscopy data were characterized and the effect of bias voltage under poisoned conditions is discussed.
Chapter 1

Introduction

1.1 Motivation and field of study

Internal combustion engines for electrical energy production like diesel engines or gas turbines convert chemical energy into thermal energy, then the heat into mechanical energy and finally into electrical energy by using an alternator. It is apparent that this complexity further reduces the already low thermomechanic conversion efficiency. Fuel cells on the other hand directly convert chemical energy into electrical energy eliminating the need of multiple conversion stages. The focus of this work will lie on solid oxide fuel cells (SOFCs) which exhibit promising characteristics:[1]

- SOFCs are the most efficient fuel-to-electricity conversion system compared to other fuel cell types.
- SOFCs can convert a wide range of fuels like hydrogen, natural gas, biogas or higher hydrocarbons.
- SOFCs have no (internal) moving parts allowing indoor and outdoor operation with almost no noise pollution.
• High operating temperatures result in high quality heat as byproduct, which can be used for co-generation of electricity.

• High operating temperatures also limit the danger of CO emission due to conversion to CO$_2$.

The main advantage in this list is high efficiency. As described above, in traditional systems multiple steps are required to obtain electrical energy. The main source of losses is the conversion from thermal energy to mechanical energy. Its theoretical efficiency is described by Carnot’s theorem:[2]

$$\epsilon = \frac{W}{Q} = \frac{T_H - T_C}{T_H} \tag{1.1}$$

where

$\epsilon$ Thermal efficiency [ ]
$W$ Mechanical work [J]
$Q$ Heat [J]
$T_H$ Temperature of the hot junction [K]
$T_C$ Temperature of the cold junction [K]

In fuel cells, efficiency is limited by the thermodynamic driving force, namely the Gibbs free energy (See section 1.2.1 for a more detailed description). To ensure comparability to traditional engines thermal efficiency is used. Hence, assuming an isobaric and isothermal process, the theoretical efficiency can be written as:

$$\epsilon = \frac{\Delta R G}{Q} = \frac{\Delta R H - T \Delta R S}{\Delta R H} = 1 - T \frac{\Delta R S}{\Delta R H} \tag{1.2}$$

where

$\Delta R G$ Reaction free enthalpy [J/mol]
$\Delta R H$ Reaction enthalpy [J/mol]
$\Delta R S$ Reaction entropy [J/molK]
$T$ Temperature [K]
Differences in efficiency can best be illustrated by examples: KKI2, the biggest german nuclear reactor has a maximum hot reservoir temperature of 328°C and assuming a minimum cold reservoir temperature of 30°C a theoretical efficiency of 51% is yielded. As far as real values are concerned, electrical efficiency reaches only 36%. The newest generation of gas turbines by Siemens achieve 40% efficiency without steam coupling.

For comparison, at typical SOFC operating temperatures of 1000 K the direct electrochemical oxidation of methane \( (\Delta R H = -949 \text{KJ/mol}, \Delta R S = 0 \text{J/molK}^2) \) yields a theoretical thermal efficiency of 100%. For hydrogen as fuel the value is below 100%, higher hydrocarbons on the other hand yield >100%. A state of the art 200kW SOFC-stack suitable for distributed power generation using natural gas or biogas (main component methane) currently has an electric efficiency of 'only' >50%, which is already higher than common Carnot-based systems.

By now, it should be obvious to the reader that SOFCs have the potential to revolutionize electricity production since their electrical efficiency is already comparable or even higher than conventional Carnot-cycle based systems and there is still much room for improvement. This study aims to improve SOFCs by investigating effects that cause the gap between real and theoretical efficiency.

The main sources for lower efficiency in fuel cells are resistive losses in the electrolyte and kinetic losses at the anode and cathode. This study is going to focus on kinetic losses in the anode. Current state of the art anodes consist of a mixture, a so called cermet, of nickel and yttria stabilized zirconia (YSZ).

---

1. 328°C is the reactor output temperature, hence overestimated for the calculation due to design constraints, 30°C an assumed technically possible minimum temperature
2. Values calculated from thermochemical data from [5]
Such a cermet forms a network of interconnected grains, leading to a high three phase boundary (TBP) length where metal, ceramic and gas meet. The pore volume is perfused by fuel which can contain impurities that affect the performance of the electrode. This work particularly aims to investigate performance loss by \( H_2S \), a common contaminant in fuels like biogas and diesel (maximum S-content in diesel fuels: 10mg/kg\([7]\)).

Real porous cermet electrodes, which are designed to minimize gas diffusion, reaction and conductivity-losses pose significant challenges for basic research. Firstly, characteristic geometrical values like TBP-length are not known, making comparison of data obtained on different materials or differently processed anodes of the same material challenging. Secondly, charge and gas transport may interfere with electrochemical processes being investigated, thus the separation of relevant elementary steps is not straightforwardly possible. And thirdly, active regions deep inside the cermet are not easily accessible by microscopic or spectroscopic methods. To alleviate all the mentioned problems, model-type electrodes with defined geometry were employed in this study.

### 1.2 Theoretical background

#### 1.2.1 Introduction into electrochemistry

**Thermodynamic theory**

Electrochemistry is the study of chemical reactions that lead to or are driven by electric potential differences involving spatially separated charge transfer. Electric potentials are applied via electrodes and reactions take place in direct vicinity of them. The most basic electrochemical system therefore consists of an electrode and an electrolyte, commonly referred
to as electrochemical half cell. Since aqueous electrochemistry is most
illustrative, an example of a metal in water is presented in figure 1.1(a).
When the metal comes into contact with water, some of the atoms will
dissolve as ions, while electrons remain in the metal. This charge separation
causes an electric field which leads to re-deposition of the metal. When
both reactions proceed with the same rate the system is in a dynamic
equilibrium and no further net-dissolution occurs. Moreover, due to the
attraction of cations and the negatively charged metal a double layer is
formed. Integrating the electric field from the electrode to infinity yields
a characteristic voltage for a specific half cell, which is commonly refered
to as Galvanopotential difference. The same principle is applicable when
there already are metal ions in the solution, but the equilibrium will be
shifted, resulting in a different voltage. Introducing another half element
with its own Galvanopotential difference into the system gives a net voltage
at the electrodes, which is externally measurable and equates the sum
of all potential steps in the system. This is shown for a Daniell element
consisting of a $Cu|Cu^{2+}$ and a $Zn|Zn^{2+}$ half cell in figure 1.1(b). The salt
bridge in the illustration prevents $Cu^{2+}$ ions from directly reacting with
the $Zn$ electrode while closing the electric circuit by providing ion transport.

But why does this happen? To answer this question thermodynamic
considerations are necessary. The second law of thermodynamics states
that a process in an isolated system can only occur if the total entropy
increases. Unchanged entropy means equilibrium. For non-isolated systems
the entropy change $\Delta S$ of the surrounding also has to be taken into account:

$$\Delta S_{\text{internal}} + \Delta S_{\text{external}} \geq 0$$  

(1.3)
Assuming a reversible isothermal process, $\Delta S_{external} = -\frac{Q}{T}$ can be inserted leading to

$$\Delta S_{internal} - \frac{Q}{T} \geq 0 \quad (1.4)$$

respectively

$$T\Delta S_{internal} - Q \geq 0. \quad (1.5)$$

Assuming an isobaric process $Q$ is equal to the enthalpy change $\Delta H$ and multiplicating with $-1$ yields

$$\Delta H - T\Delta S_{internal} \leq 0. \quad (1.6)$$

This inequation can be transformed into an equation by defining a quantity:

[8]

$$\Delta G = \Delta H - T\Delta S_{internal} \quad (1.7)$$

with
\( \Delta G \) Free enthalpy change \([J]\)

Comparing equation (1.7) to (1.6) shows that processes with \( \Delta G < 0 \) are thermodynamically favorable and processes with \( \Delta G = 0 \) are equilibrium processes.

Deriving equation (1.7) by the extent of reaction \( \xi \) yields the fundamental equation already mentioned in section 1.1:

\[
\Delta R G = \Delta R H - T \Delta R S
\]

(1.8)

The reader should note that \( \Delta R \) is not a difference, but the operator \( \frac{\partial}{\partial \xi} \).

Free enthalpy is an extensive state variable, hence assuming \( G = G(p, T, n_i) \) an exact differential can be formed.

\[
dG = \left( \frac{\partial G}{\partial p} \right)_{T,n_i} dp + \left( \frac{\partial G}{\partial T} \right)_{p,n_i} dT + \sum_i \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j,j \neq i} dn_i
\]

(1.9)

with

- \( p \) Pressure \([Pa]\)
- \( n \) Amount of substance \([mol]\)

Assuming isobaric and isothermal processes \((dT = 0, dp = 0)\) the equation can be rewritten with \( \left( \frac{\partial G}{\partial n_i} \right)_{p,T,n_j,j \neq i} = \mu_i \) as

\[
dG = \sum_i \mu_i dn_i
\]

(1.10)

with

- \( \mu \) Chemical potential \([J/mol]\)

In chemical reactions \( dn_i \) can be described as follows:

\[
dn_i = n \nu_i d\xi
\]

(1.11)
with

\( n \) Reaction unit amount \([mol]\)
\( \nu \) Stoichiometric factor \([\text{]}\]
\( \xi \) Extent of reaction, \( 0 \leq \xi \leq 1 \), \([\text{]})\]

Dividing the equation by \( n \) and deriving by \( \xi \) yields an expression for the reaction free enthalpy:

\[
\Delta_R G = \sum_i \mu_i \nu_i \quad (1.12)
\]

Every system with suitable preconditions will tend to minimize its free enthalpy since any process with \( \Delta G < 0 \) is favorable. The chemical potential is defined as the difference in free enthalpy when the amount of a species is changed under otherwise equal conditions. Therefore, the chemical potential can loosely be interpreted as free enthalpy for a single species, so each species tends to minimize its own chemical potential. The reader should note that the only real physical law for ‘chemical potential minimization’ is stated in equation (1.12).

The concentration dependence of the chemical potential can be written for low concentrations as

\[
\mu_i = \mu_{i,0} + RT \ln(x_i) \quad (1.13)
\]

with

\( \mu_{i,0} \) Chemical potential at standard conditions \([J/mol]\)
\( R \) Universal gas constant \([J/molK]\)
\( x \) Normalized concentration \([\text{]}\]

Inserting equation (1.13) into (1.12) one gets

\[
\Delta_R G = \sum_i (\mu_i) + RT \ln \left( \prod_i x_i^{\nu_i} \right) \quad (1.14)
\]

respectively

\[
\Delta_R G = \Delta_R G_0 + RT \ln \left( \prod_i x_i^{\nu_i} \right) \quad (1.15)
\]

8
\[ \Delta R G_0 \text{ Free enthalpy at standard conditions } \left[ \frac{J}{mol} \right] \]

The reader should note that stoichiometric factors are defined to be \(< 0\) when the reactant is on the left side of the chemical equation. Under equilibrium conditions \(\Delta R G = 0\) holds and the term in the logarithm can be defined as an equilibrium constant.

\[
\Delta R G_0 = -RT \ln(K) \quad (1.16)
\]

with

\[ K \text{ Thermodynamic equilibrium constant } [ ] \]

Equilibrium constants can therefore easily be calculated from thermochemical data available e.g. at NIST [5].

*How does this relate to electrochemical systems?* A reaction with \(\Delta R G = 0\) is in equilibrium and reactions with \(\Delta R G < 0\) are thermodynamically favorable. Any excess free enthalpy is therefore 'lost' after the reaction. It is imaginable to 'use' this excess free enthalpy (also called exergy) and bring the reaction back into equilibrium. In electrochemical systems this is done by charged particles and electric fields. Assuming all exergy is transformed into electrostatic energy one gets the electrochemical equilibrium condition[9]

\[
\Delta R G = -zF U_C \quad (1.17)
\]

with

\[ z \text{ Number of unit charges } [ ] \]

\[ F \text{ Faraday-constant, } F = 96485 \frac{C}{mol} \]

\[ U_C \text{ Open circuit voltage } [V] \]
Plugging equation (1.15) into equation (1.17) yields
\[ zF U_C = -\Delta_R G_0 - RT \ln \left( \prod_i x_i^{v_i} \right) \] (1.18)

Dividing this equation by \( zF \) and redefining \( \frac{-\Delta_R G_0}{zF} \) as a standard voltage (compare (1.17)) yields Nernst’s equation
\[ U_C = U_C^0 - \frac{RT}{zF} \ln \left( \prod_i x_i^{v_i} \right) \] (1.19)

Using this equation, the equilibrium voltage of every electrochemical reaction (also non-aqueous) can be calculated knowing one reference point and the concentrations of all reactants.

**Kinetic theory**

Above mentioned considerations are only valid for equilibrium conditions which do not allow (external) current to flow. To allow this, a thermodynamic driving force has to be provided. This driving force will be defined analogous to the Gibbs free energy as
\[ \Delta_R \tilde{G} = \Delta_R G + zF U \] (1.20)

with
- \( \Delta \tilde{G} \) Electrochemical free enthalpy \([\frac{J}{mol}]\)
- \( U \) Cell voltage \([V]\)

The cell voltages in current-carrying fuel cells will be lower than thermodynamically possible, in electrolysis cells a higher voltage has to be applied. This electrical driving force is defined as this missing/additional voltage:
\[ \eta = U - U_C \] (1.21)
with

\( \eta \) Overpotential of the entire cell [V]

The principle is illustrated for a SOFC and a Solid oxide electrolysis cell (SOEC) in figure 1.2. The figure also shows that anodic overpotentials are always \( > 0 \) while cathodic overpotentials are \( < 0 \). All resistances are in series, they can therefore be summed up to give the overall internal resistance of the system. It can be assumed that the electrolyte resistance is ohmic, while the electrode resistances are in general current dependent.[9]

For electrode reactions one can apply Faraday’s law:

\[
q = nzF = it
\]

\[
i = rzF
\]  \quad (1.22)

with

\( q \) Charge \([C] = [A \cdot s]\)
\( i \) Current \([A]\)
\( r \) Reaction rate \([\text{mol s}^{-1}]\)

This fundamental equation couples the electronic quantity current with a chemical reaction rate. Hence, chemical kinetic theories can be applied to the system. Several steps of the electrode reaction may be rate limiting and thus responsible for the main part of an electrode overpotential:[10]

- Charge transfer
- Chemical reactions
- Adsorption/Desorption
- Crystallization
Figure 1.2: Illustration of the concept of overpotential in SOFCs and SOECs. The cell is sketched with dark gray electrodes and a light gray electrolyte. In the graphs below, the potential distribution $\phi(x)$ under thermodynamic equilibrium is shown in dashed lines while the potential distribution under current flow is shown in solid lines. Adding the contact voltage of the terminals to $\Delta \phi_{I=0}$ and $\Delta \phi$ results in the open circuit voltage and the cell voltage, respectively.
Figure 1.3: Illustration of the activated complex theory. In order to react from A to B or B to A the electrochemical free enthalpy barrier has to be overcome. The state at the maximum of the curve is called activated complex. On the right hand side it is shown that applied voltages influence the barrier.

- Reactant transport to the electrode

In every electrochemical reaction at least one charge transfer process takes place. Therefore, a closer analysis of charge-transfer controlled reactions is valuable for many electrochemical reactions. Here, the theory of the activated complex will be used to model this process. This theory states that for a reaction to happen, a free enthalpy barrier has to be overcome, which is illustrated in figure 1.3. When the activated complex at the maximum of the free enthalpy curve is formed, it is assumed that it will decompose into both possible reactants with the same probability. When the activated complex is in equilibrium with the reactants one gets

\[
\frac{c^\#}{c_A} = K^\# = e^{-\frac{\Delta G_f^{0,*}}{RT}}
\]

\[
\frac{c^\#}{c_B} = K^\# = e^{-\frac{\Delta G_b^{0,*}}{RT}}
\]

\[\text{(1.23)}\]
Thermodynamic equilibrium constant \( K^\# \)

Concentration \( [\text{mol} / \ell] \)

The reaction rates therefore becomes

\[
\begin{align*}
r_+ &= k^\#_c^\# = k^+_c A e^{\frac{-\Delta G_{f}^{0,*}}{RT}} \\
r_- &= k^-_c c^\# = k^-_c B e^{\frac{-\Delta G_{b}^{0,*}}{RT}}
\end{align*}
\]

(1.24)

with

\( k \) Reaction rate coefficient

Since on the reaction ordinate the activated complex is located between the reactants, this is also the case when a potential difference is applied. This translates into the formula

\[
\begin{align*}
\Delta \tilde{G}_{f}^{0,*} &= \Delta G_{f}^{0,*} - zF\Delta \phi^* = \Delta G_{f}^{0,*} - \alpha zF\Delta \phi \\
\Delta \tilde{G}_{b}^{0,*} &= \Delta G_{b}^{0,*} + zF\Delta \phi^* = \Delta G_{b}^{0,*} + (1 - \alpha) zF\Delta \phi
\end{align*}
\]

(1.25)

with

\( \alpha \) Asymmetry coefficient \( 0 < \alpha < 1 \)

\( \Delta \phi \) Potential difference at the electrode \([\text{V}]\)

Combining (1.24) and (1.25) and forming the net reaction rate yields

\[
r = r_+ - r_- = k^+_c A e^{\frac{\Delta G_{f}^{0,*}}{RT}} e^{\frac{\alpha zF \Delta \phi}{RT}} - k^-_c B e^{\frac{\Delta G_{b}^{0,*}}{RT}} e^{\frac{(1-\alpha) zF \Delta \phi}{RT}}
\]

(1.26)

Condensing the constants gives

\[
r = k_f^0 c_A e^{\frac{\alpha zF \Delta \phi}{RT}} - k_b^0 c_B e^{\frac{(1-\alpha) zF \Delta \phi}{RT}}
\]

(1.27)

After taking a deep breath one can plug (1.27) and the local version of (1.21) for one electrode \( \eta = \Delta \phi - \Delta \phi_{I=0} \) into (1.22) which yields the kinetic version of Butler-Volmer’s equation

\[
i = zF \left( k_f^0 c_A e^{\frac{\alpha zF(\Delta \phi_{I=0} + \eta)}{RT}} - k_b^0 c_B e^{\frac{(1-\alpha) zF(\Delta \phi_{I=0} + \eta)}{RT}} \right)
\]

(1.28)
with

\[ \Delta \phi_{I=0} \] Potential difference at the electrode without current flow \([V]\)

We now define an equilibrium condition under which \(i = 0\) with \(c_A = c_{A,0}, c_B = c_{B,0}, \eta = 0\). This allows the definition of an exchange current:

\[
i_0 = zFk_f^0 c_{A,0} e^{\frac{\alpha zF \Delta \phi_{I=0}}{RT}} = k_f^0 c_{B,0} e^{-\frac{(1-\alpha)zF \Delta \phi_{I=0}}{RT}} \quad (1.29)
\]

Plugging (1.29) into (1.28) yields the well-known Butler-Volmer equation \([10]\)

\[
i = i_0 \left( \frac{c_A}{c_{A,0}} e^{\frac{\alpha zF \eta}{RT}} - \frac{c_B}{c_{B,0}} e^{-\frac{(1-\alpha)zF \eta}{RT}} \right) ; \quad (1.30)
\]

respectively for equilibrium concentrations

\[
i = i_0 \left( e^{\frac{\alpha zF \eta}{RT}} - e^{-\frac{(1-\alpha)zF \eta}{RT}} \right) . \quad (1.31)
\]

Equation (1.31) is plotted for some values of \(\alpha\) and \(z\) in figure 1.4(lhs). Butler-Volmer’s equation considers charge transfer as the only rate limiting step. On real electrodes, however, concentrations on the surface of the electrode (which are the relevant ones in equation (1.30)) might be different from bulk concentrations in the surrounding area of the electrode. Such deviations from the equilibrium concentration lead to voltage losses commonly referred to as concentration overpotentials.

Diffusion controlled reactions are a special form of a concentration overpotential and deserve a closer analysis in this thesis. For this case it will be assumed that all the other reaction steps (including charge transfer) are fast compared to reactant transport to the electrode. It is useful to define a length to characterize the gradient of the bulk solution concentration \(c_0\)
to the electrode surface concentration $c_s$ ($y = 0$ means at the surface of the electrode):

$$\delta_N = \frac{c_0 - c_s}{(\partial c/\partial y)_{y=0}}$$  \hspace{1cm} (1.32)

with

$\delta_N$ Nernst diffusion layer thickness [m]

$y$ Distance from the electrode surface [m]

This can then be inserted into Fick’s first law of diffusion:

$$i = -zFD \left( \frac{\partial c}{\partial x} \right)_{y=0} = -zFD \frac{c_0 - c_s}{\delta_N}$$  \hspace{1cm} (1.33)

with

$D$ Diffusion coefficient

With this equation it becomes obvious that there is a limit for the current when $c_s \to 0$. The limiting current then is $i_{lim} = -zFD \frac{c_0}{\delta_N}$. One can then write:

$$\frac{i}{i_{lim}} = \frac{c_0 - c_s}{c_0} = 1 - \frac{c_s}{c_0}$$  \hspace{1cm} (1.34)

The overpotential is also concentration dependent, its dependency is given by Nernst’s equation:

$$\eta_D = \frac{RT}{zF} \ln \frac{c_s}{c_0}$$  \hspace{1cm} (1.35)

respectively

$$\frac{c_s}{c_0} = e^{\frac{zF}{RT} \eta_D}.$$  \hspace{1cm} (1.36)

Inserting (1.36) into (1.34) yields[9]

$$i = i_{lim} \left( 1 - e^{\frac{zF}{RT} \eta_D} \right)$$  \hspace{1cm} (1.37)

respectively

$$\eta_D = \frac{zF}{RT} \ln \left( 1 - \frac{i}{i_{lim}} \right).$$  \hspace{1cm} (1.38)
Figure 1.4: Examples for UI curves of charge transfer- and diffusion-controlled reactions. On the left hand side Butler-Volmer’s equation is plotted for several values of $\alpha$ and $z$, on the right hand side a diffusion controlled reaction is compared to a charge transfer controlled reaction. Parameters are $i_0 = 2 \cdot 10^{-8} \text{A}, T = 300 \text{K}, i_{\text{lim}} = -2 \cdot 10^{-8} \text{A}$

If both diffusion and charge transfer are rate-limiting, the overpotentials cannot simply be added together since the concentration at the surface has to be taken into account in (1.30). The comparison of UI curves caused by charge transfer and diffusion limitation can be seen in figure 1.4(rhs).

1.2.2 Electrochemical impedance spectroscopy

Electrochemical impedance spectroscopy (EIS) is an important tool in electrochemistry due to its potential to separate and identify different processes in electrode reactions. This is done by recording the impedance (complex resistance) as a function of AC frequency and modeling the resulting spectrum with suitable equivalent circuits. Disadvantage of this method is possible ambiguity which can result in misinterpretation of results. The following chapter will examine the physical basis of impedance spectroscopy.

In EIS sinusoidal voltage waveforms are used, which can be described using trigonometric functions. The mathematics, however, becomes simpler when
a complex approach is used. The voltage waveform will therefore be defined as

\[ \tilde{U} = |U| e^{i\omega t} \] (1.39)

with

- \( \tilde{U} \) Time dependent voltage [V]
- \(|U|\) Voltage amplitude [V]
- \( \omega \) Angular frequency \([s^{-1}]\)
- \( t \) Time \([s]\)

Due to Euler’s identity \( e^{ix} = \cos x + i \sin x \) the periodicity of this function is obvious. As a consequence of this approach, current is also going to be a complex quantity. Now, analogously to DC a complex AC resistance (referred to as impedance) can be defined:

\[ Z = \frac{\tilde{U}}{\tilde{I}} \] (1.40)

with

- \( Z \) Impedance \([\Omega]\)
- \( \tilde{I} \) Time dependent current \([A]\)

The impedance will in general be dependent on the angular frequency, which is the basis for EIS. In the following, some basic components in an equivalent circuit will be discussed.

**Capacitor**

A capacitance will store charge in some form (e.g. electrostatic double layer, redox reaction) when voltage is applied, which can be released when the voltage decreases again. The fundamental equation describing a capacitance is

\[ \tilde{I} = C \frac{d\tilde{U}}{dt} \] (1.41)
with

\[
C \text{ Capacitance } [F]
\]

Plugging (1.39) into (1.41) gives

\[
\tilde{I} = i\omega C|U|e^{i\omega t} = i\omega C\tilde{U}
\]  

(1.42)

The impedance can therefore be calculated as

\[
Z = \frac{\tilde{U}}{\tilde{I}} = \frac{1}{i\omega C}
\]  

(1.43)

Because \(i^{-1} = -i\) the complex part of the impedance is always negative. The impedance also lies on the imaginary axis in the complex plane, therefore the phase shift is \(-\frac{\pi}{2}\) radians (or -90°).

**Resistor**

Assuming an ohmic resistor one can use Ohms law

\[
\tilde{U} = R\tilde{I}
\]  

(1.44)

The impedance therefore simply is

\[
Z = R
\]  

(1.45)

The impedance lies on the real axis of the complex plane, therefore phase shift is 0 radians.

**Inductor**

The fundamental equation for inductors is

\[
\tilde{U} = L\frac{d\tilde{I}}{dt} \iff \tilde{I} = \frac{1}{L} \int \tilde{U} \, dt
\]  

(1.46)
with

\[ L \text{ Inductance } [H] \]

Insertion of (1.39) into (1.46) and integration over \( t \) gives

\[ \tilde{I} = \frac{1}{L} \left( \frac{1}{i \omega} e^{i \omega t} + K \right). \]  

(1.47)

Since \( \tilde{I} = 0 \) is expected for \( |U| = 0 \) the integration constant can be derived to be \( K = 0 \). One can therefore write

\[ \tilde{I} = \frac{1}{i \omega L} |U| e^{i \omega t} = \tilde{I} = \frac{1}{i \omega L} \tilde{U}. \]  

(1.48)

Hence the impedance is

\[ Z = i \omega L \]  

(1.49)

The impedance again lies on the imaginary axis of the complex plane, the phase shift in this case is \( +\frac{\pi}{2} \) radians (or \( +90^\circ \)).

**Phasor (Constant Phase Element)**

Capacitors are frequently used in equivalent circuits for electrochemical systems. Experimental spectra, however, often show a slightly deviant shape than expected—e.g. flatter semicircles in Nyquist-plots. This led to the use of a corrected element to describe the imperfect capacitance: The constant phase element. The concept was generalized to the Phasance (named for the phase shift) concept. The fundamental equation for a Phasor is a fractional differential equation:

\[ \ddot{\tilde{U}} = P^{\zeta} \dot{\tilde{I}} \]  

(1.50)

with

\[ \zeta \text{ Fractional derivation degree } [\ ] \]

\[ P \text{ Phasance} \]
The interested reader may want to refer to [11] for more information on the phasance concept and the mathematics behind it. The resulting impedance is

\[ Z = P(i\omega)^\zeta \]  

(1.51)

For \( \zeta = +1 \) the impedance is equivalent to the impedance of an inductor, for \( \zeta = 0 \) it is equivalent to the impedance of a resistor and for \( \zeta = -1 \) it is equivalent to the impedance of a capacitor. The phase shift is \( \frac{\zeta\pi}{2} \).

**Equivalent circuit example**

This section will show how impedance spectra can be calculated by hand for the example of a simple RC-circuit (a resistor and a capacitor in parallel). Since the components are wired in parallel, the overall impedance is

\[ \frac{1}{Z} = \frac{1}{R} + i\omega C \iff Z = \frac{R}{1 + i\omega CR} \]  

(1.52)

By expanding the fraction by the conjugated complex number of the denominator (i.e. multiplication with \( \frac{1-i\omega CR}{1-i\omega CR} \)) the real and imaginary part can be separated

\[ Z = \frac{R}{1 + \omega^2 C^2 R^2} - i\frac{\omega CR^2}{1 + \omega^2 C^2 R^2} \]  

(1.53)

The impedance can therefore be split into a real and an imaginary part \( Z_{Re} \) and \( Z_{Im} \) respectively:

\[ Z_{Re} = \frac{R}{1 + \omega^2 C^2 R^2} \]  

(1.54)

\[ Z_{Im} = -\frac{\omega CR^2}{1 + \omega^2 C^2 R^2} \]  

(1.55)

These equations can be visualized in different ways, two of which are discussed in the following.
Nyquist-plot  In the Nyquist-plot the real impedance is the independent variable and the imaginary impedance is the dependent one. Firstly, an expression for $\omega$ has to be found. For the example of the RC-circuit given above, equation (1.54) is rearranged (the positive square root is taken because only positive angular frequencies are physically meaningful).

$$Z_{Re}(1 + \omega^2 C^2 R^2) = R \Rightarrow \omega = \frac{\sqrt{R - Z_{Re}}}{CR\sqrt{Z_{Re}}} \quad (1.56)$$

Next the ratio of $Z_{Re}$ and $Z_{Im}$ is formed

$$\frac{Z_{Re}}{Z_{Im}} = -\frac{1}{\omega CR} \quad (1.57)$$

Plugging (1.57) into (1.56) gives

$$\frac{Z_{Re}}{Z_{Im}} = -\frac{1}{\sqrt{Z_{Re}} - 1} \quad (1.58)$$

Rearranging gives the equation of a semicircle with the diameter $R$.

$$-Z_{Im} = \sqrt{Z_{Re}R - Z_{Re}^2} \quad (1.59)$$

An example for this plot is shown in figure 1.5. It is worth noting that, by rearranging equation (1.57), the characteristic angular frequency (peak angular frequency) $\omega^*$ where $|Z_{Im}| = |Z_{Re}|$ can be calculated to be

$$\omega^* = \frac{1}{RC} \quad (1.60)$$

Bode-plot  The Bode-plot consists of two diagrams. In both the frequency is the independent variable and the phase shift as well as the impedance magnitude are the dependent one. First, the phase shift will be calculated.

$$\tan \delta = \frac{Z_{Im}}{Z_{Re}} = -\omega CR = -2\pi RC f \quad \iff \quad (1.61)$$

$$\delta = \arctan(-2\pi RC f) \quad (1.62)$$
Figure 1.5: Example of a Nyquist-plot (left hand side) and Bode-plots (right hand side). Assumed values: $R = 10^6 \Omega, C = 10^{-8} F$

with

$\delta$ Phase shift  
$f$ Frequency [$s^{-1}$]

For the modulus one can write

$$\sqrt{Z_{Re}^2 + Z_{Im}^2} = |Z| = \sqrt{R^2 + \omega^2 C^2 R^2} = \frac{R}{\sqrt{1 + \omega^2 C^2 R^2}} \quad (1.63)$$

$$= \frac{R}{\sqrt{1 + 4\pi^2 C^2 R^2 f^2}} \quad (1.64)$$

An example for a Bode-plot is shown in figure 1.5, rhs.

1.2.3 Statistical hypothesis testing

The statistical testing of hypotheses is an essential part of the data evaluation in this thesis. A closer inspection of this methodology therefore might be of interest to the reader.
Let \( x = \{x_1, x_2, \ldots, x_n\} \) be a random sample from a population. First step of testing is the formulation of a hypothesis \( H_0 \) for the population (e.g. the expected value \( \mu = 0 \)) and its alternative hypothesis \( H_1 \) (in this example \( \mu \neq 0 \)). By convention \( H_0 \) will be interpreted as ‘default’ hypothesis and only be rejected when there is sufficient evidence that it is wrong. Therefore the interest of the tester lies in the probability for the error of first kind, i.e. the probability of rejecting \( H_0 \) although it is true. This probability will be defined as the p-value: \( P(H_0\text{rejected}|H_0\text{true}) = p \). A conclusion can be made when a criterion for the p-value is defined, it will be referred to as significance level \( \alpha \). If the probability for incorrectly rejecting \( H_0 \) is lower than the significance level \( H_0 \) will be rejected, i.e. \( p < \alpha \Rightarrow H_0\text{rejected} \). The reader should note that the reversal (accepting \( H_0 \) means it is correct with a probability of \( 1 - p \)) is not true.

Conducting a statistical test can be broken down into the following steps:

- Collecting data, defining \( \alpha \) and stating \( H_0 \) and \( H_1 \)
- Considering prerequisites for possible tests
- Choosing an appropriate test
- Computing the p-value, comparing it to \( \alpha \) and accepting or rejecting \( H_0 \).

Statistical tests performed in this thesis include:

**Two-sample t-test**  In this test the mean values of two samples are tested for differences in the expected values \( \mu_1 \) and \( \mu_2 \). \( H_0: \mu_1 = \mu_2 \). Prerequisites: Two independent normally distributed samples, population variances are equal. When using the Welch-correction only normal distribution is required.
**F-test**  In this test the empirical variances of two samples $s_1^2$ and $s_2^2$ are tested for differences in the variance $\sigma_1^2$ and $\sigma_2^2$. $H_0 : \sigma_1^2 = \sigma_2^2$. Prerequisites: Normal distribution of the population.

**Shapiro-Wilk test**  In this test normal distribution of the sample is tested. $H_0$ : Population has normal distribution.

**Mann-Whitney test**  This test compares two samples with non-normal distribution. $H_0$ : Both samples are taken from the same population.

### 1.3 State of scientific knowledge

Ni/YSZ cermet electrodes are the most widely used anodes in SOFC applications and have hence been subject to extensive investigation. The following sections present a basic overview of research from the last 20 years, which is relevant for this thesis.

#### 1.3.1 Nickel pattern electrodes

In literature three types of nickel electrodes with defined geometry are described: Pattern electrodes, point electrodes and grid electrodes. The latter two are prepared by pressing a nickel wire or grid onto a YSZ substrate. Pattern electrodes, on the other hand, are prepared by photolithography, Ni deposition and subsequent lift-off or metal etching.[12]

Calculations by Utz et al. showed that cermet behaviour for hydrogen oxidation can accurately be simulated using experimental microelectrode data validating microelectrodes as model anodes for SOFCs.[13]
Microstructure  Having a melting point of 1728 K,[14] microstructural changes during testing of nickel anodes at elevated temperatures of typically 1000 K are expected. Grain growth, however, has an impact on geometrical properties, especially because the wetting angle of Ni on YSZ is above 90°.[15] It was reported that at 800 °C in wet hydrogen microstructural changes almost stopped after 20-25 h.[16, 17] Yao and Croiset found that high water partial pressures and high temperatures up to 800 °C lead to pore formation and thus to a significant increase in triple phase boundary (TPB)-length. Only 1000 nm thick electrodes were stable up to 800 °C in atmospheres with 3% water content. The authors also suggested that temporal increase in polarization resistance is caused by shortening of the TPB length due to filling of nanopores and edge rounding.[17] If films are too thin, porosity arises upon heating. The “inner TPB” of these pores was reported to exhibit different behavior for CO oxidation than the “outer TPB” of the electrode. H₂ oxidation, however, did not show different behaviour compared to dense electrodes.[18]

Characterization techniques  The most widely used electrochemical measurement technique for nickel electrodes found in literature is EIS. A direct comparison of EIS with galvanostatic current interruption (GCI), which analyzes processes in time domain, showed higher activation energies for the rate limiting process when using EIS in a 2-chamber setup on cermet electrodes. The authors explained this result with higher water content in the cermet when GCI is used compared to EIS measurements, since water is formed upon the inevitable anodic polarization.[19] Lower activation energies at higher water partial pressures is backed by findings of Sukeshini and co-workers.[20] This result might be applicable to microelectrodes because the effect of water partial pressure is most pronounced when no anodic bias

26
is applied to microelectrodes, thus no additional water being present at the electrode.[21]

Different equivalent circuits were used in literature to evaluate impedance spectra. Yao and Croiset found a spectrum consisting of 2 semicircles in the Nyquist plot[17] while Bieberle and Gauckler found 3 semicircles with one not scaling with TBP length.[22] The possibility that the non-scaling semicircle is an artifact of the counter electrode was not discussed. In a later publication a more complex equivalent circuit was used for fitting of the spectra.[21] Utz et al. also found 3 semicircles.[16]

Interestingly, absolute values of polarization resistance did not show good reproducibility, neither within a test series[23] nor from different authors.[12] The extend of scattering within a test series was, however, not quantified and the cause not discussed by Hansen and co-workers. A combination of different gas compositions, chemical & morphological integrity and degradation and relaxation effects was suggested as source for the scattering of polarization resistances between authors by Bessler and co-workers.[12]

**Geometry** The geometry dependence of the polarization resistance of Ni anodes in \(H_2/H_2O\) has been investigated in several articles. Bieberle and Gauckler used the following equation:

\[
R_P = \beta \frac{1}{l_{TPB}}
\]

with

- \(R_P\) Polarization resistance [Ω]
- \(\beta\) Normalized resistance [Ω]
- \(l_{TPB}\) Triple phase boundary length [m]
- \(\alpha\) Scaling factor [ ]

A value of \(\alpha = 0.80 \pm 0.04\) was reported and lead to the conclusion of an inverse proportionality of \(R_P\) and \(l_{TPB}\) although this means accepting a value
which is 5σ off the ideal value of \( \alpha = 1 \).[22] In a later article an inverse proportionality of \( R_P \) and \( l_{TPB} \) was reported for high values of \( l_{TPB} \).[21] Ehn et al. found a weak dependency between \( 1/R_P \) and \( l_{TPB} \) for hydrogen oxidation which reversibly vanished when switched to a CO/CO\(_2\) atmosphere.[18]

It should be noted that in this study bubbles formed beneath the thin film which may have influenced the measurements.

**Activation energy** Published activation energy values of the dominating polarization resistance (i.e. the rate limiting step of the electrode reaction) vary by almost a factor of two. Bieberle et al. obtained a value of \( E_A = 0.88 \pm 0.04 \text{eV} \) in the range of 700-400 °C in \( 1.5 \cdot 10^4 \text{ Pa H}_2, 50 \text{ Pa H}_2\text{O} \).[21] Sukeshini et al. reported \( E_A = 1.15 \text{eV} \) in dry and \( E_A = 0.95 \text{eV} \) in wet hydrogen in a range of 750-850 °C pointing out oxygen ion transport has an similar activation energy.[20] Utz et al. found an activation energy of \( E_A = 1.15 \text{eV} \) for 700-800 °C and \( E_A = 1.37 \text{eV} \) for lower temperatures.[16]

**Partial pressure dependence** The polarization resistance as a function of partial pressures of \( H_2 \) and \( H_2\text{O} \) has been studied extensively. In literature a consensus about a catalytic effect of water was found.[15, 19, 21] Utz et al. also found a slight hysteresis upon fast (5 min per data point) partial pressure change.[16] Hydrogen partial pressure on the other hand showed only a weak effect on the polarization resistance. Only at high temperatures (850 °C) and low hydrogen partial pressures (<30 kPa) the polarization resistance was proportional to \( p^{1/2} \).[15, 21, 24] However, a strong hysteresis upon fast gas change was observed.[16] Bieberle et al. claimed that reaction orders for hydrogen vary due to design and microstructure of the electrode.[21] Upon partial pressure change a slow relaxation was found by Utz et al.[16] No hysteresis, however, was observed in cermet electrodes.[13]
**Effect of Polarization**  The effect of electrochemical polarization was also investigated in several studies. For anodic overpotentials an exponential current dependency was found. [21, 24] For high anodic overpotentials (400 mV) a co-limitation of adsorption and surface diffusion was stated to become rate-limiting.[21] Jensen et al. reported inconsistent results about the reversibility of polarization resistance after DC polarization. By applying cathodic or anodic overpotentials of 100 mV the polarization resistance decreased, but only some of the anodically polarized samples returned to resistances before polarization.[25] Hansen et al. concluded that the decreased polarization resistance after anodic voltages was caused by redistribution of an impurity film around the electrode.[23] In contrast to the studies mentioned above, Utz et al. found that the resistance change upon 350 mV cathodic and anodic polarization was reversible[16] and Jensen et al. found no structural changes upon polarization.[26]

**Impurities**  Contaminations at the TPB were investigated thoroughly on nickel point electrodes at 1000 °C. A rim of impurities and particles within the contact area were found[25, 26] with Si, Al, Ti and Na as main elements. A later investigation using time-of-flight secondary mass spectrometry (ToF-SIMS) revealed a different contaminant composition on differently oriented YSZ grains.[27] Even using 99.995 % pure Ni instead of 99.8 % pure one could not totally avoid an impurity rim.[23] It was also observed that in case of higher purity Ni electrodes the polarization resistance was an order of magnitude lower compared to impure Ni.[25] The authors proposed proton conduction in the rim as a mechanism to overcome the barrier.[23] The reader should note that later articles on pattern electrodes found no impurity rim in TEM images.[16] It seems that point electrodes are prone to contamination segregation due to their high volume to TPB-length ratio. Thus, comparison
of results between studies on point contact and thin film Ni electrodes might not be straightforwardly possible.

**Reaction mechanism** Many mechanisms have been proposed in literature like hydrogen spillover, oxygen spillover and hydrogen interstitial movement.[12] Hydrogen spillover as an example is sketched in figure 1.6. Spillover denotes the process when an adsorbed species on one phase (e.g. hydrogen on Ni) diffuses onto another phase (in this case YSZ). Vogler et al. analyzed data from Bieberle et al. and found that of seven proposed mechanisms hydrogen spillover showed the best correlation with experimental data.[28] Goodwin et al. analyzed data from Mizusaki et al. and also stated hydrogen spillover to be the best explanation for the experimental data.[29]
CO oxidation  Besides $H_2$ oxidation also studies on CO oxidation have been published and significantly different behavior compared to hydrogen oxidation was reported. Firstly, reaction rates were slower resulting in higher polarization resistances, which were, moreover, not correlated to the TPB-length.[18] The open circuit potential (OCP) of SOFCs dropped when introducing wet instead of dry CO indicating that water prevents reaching an equilibrium. Partially replacing hydrogen with CO resulted in similar performance compared to pure hydrogen fuel indicating that direct CO electro-oxidation was negligible.[20]

1.3.2  Sulfur poisoning

Sulfur poisoning of Ni electrodes has been studied extensively due to the high prevalence of sulfur in common hydrocarbon-based fuels. Studies have mostly been conducted in SOFC setups and, to the best of the author’s knowledge, only on cermet electrodes.

General poisoning & regeneration  Matsuzaki and Yasuda observed that depending on the temperature a minimal concentration of $H_2S$ is needed for poisoning of Ni/YSZ anodes. At 1000°C 2 ppm are needed, at 900°C 0.5 ppm and at 800°C only <0.05 ppm are enough to cause an effect. For lower temperatures the detrimental effect of $H_2S$ also increases.[30] In literature a consensus was found that the relative performance drop as a function of $H_2S$ concentration exhibits lower slopes at higher concentrations.[30–33] For the poisoning process Matsuzaki and Yasuda also reported a duration of $3 \frac{1}{3}$ h at 750°C to again get stable values after insertion of $H_2S$. Moreover, the performance loss was only depending on the total S concentration but
not on the equilibrium $S_2$ partial pressure and poisoning did not affect the shape of EIS-spectra.\cite{30}

Trembly et al. (as well as others) described $H_2S$ poisoning as a 2-step process: A fast performance drop followed by a slow degradation over many hours.\cite{34}

The root of this phenomenon has been theorized as Ni bulk diffusion leading to a change in surface chemistry or adsorption of S to surfaces that are more difficult to access or surface reconstruction.\cite{35} However, no experimental data to support any of the hypothesis was published yet.

Regeneration after sulfur degradation was also found to be temperature dependent but did not show any correlation with the concentration of $H_2S$ during the previous degradation. Matsuzaki and Yasunda reported complete regeneration after 1 h at 1000 °C, 25 h at 900 °C and 100 h at 750 °C.\cite{30}

Rasmussen and Hagen reported that $H_2S$ poisoning was fully reversible after stopping $H_2S$ supply with relaxation times of 50 h at 850 °C. Therefore, they concluded grain coarsening could not be the reason for degradation.\cite{31}

Sasaki et al. reported reversible poisoning with relaxation times of some hours at 1000 °C\cite{33} while Zhang et al. found irreversible poisoning at 800 °C.\cite{32} Xia and Birss reported 90% recovery of polarization resistance after treatment in $N_2$ or air and only 75% recovery in hydrogen at 800 °C.\cite{36}

Gong et al. concluded that at lower temperatures poisoning becomes irreversible.\cite{37}

**Current density** The effect of current density/cell voltage has been subject to debate in literature. Using the relative power output drop as an indicator of degradation, galvanostatic\cite{36} and potentiostatic\cite{38} measurements yielded contradictory trends. The contradiction, however, disappeared when the relative polarization resistance change was used as an indicator, as shown by Cheng et al. with a simple equivalent curcuit. In both cases the relative
polarization resistance change was lower for higher current densities/lower cell voltages.[39]

**Low temperature** Investigations of Deleebeeck et al. on sulfur poisoning at lower temperatures revealed an interesting contrary effect, namely activation of the electrode. This effect develops gradually in an atmosphere containing 5 ppm $H_2S$, which was shown by an intermediate temperature range of 550-600 °C where activation and deactivation occur co-existentially. An activated electrode was shown to be kinetically stable up to 650 °C for tens of hours. This catalytic effect also holds for the electrolysis reaction. DFT calculations showed that $Ni_3S_2$ exhibits higher activity towards $H_2$ oxidation than a pure Ni surface, but thermodynamically a monolayer of adsorbed $S$ was expected. The authors concluded that oxidation at the TPB hinders recombination of sulfur to $H_2S$ and consequently stabilizes a thin sulfide film at the TPB.[40] This, however, contradicts their observation that electrolysis is also catalyzed.

**Sulfide phase** The formation of sulfide phases in operational conditions has also been topic of research. Cheng an Liu found slow and reversible sulfide formation in 50 ppm $H_2S$ at 100-400 °C.[35] Due to its thermodynamic instability at higher temperatures (at 800 °C more than 1% $H_2S$ are needed to form Ni sulfide) Gong et al. concluded that $H_2S$ adsorption is the main cause of poisoning.[37] Thermodynamic calculations showed that at 1000 °C 8000 ppm $H_2S$[41] and at 800 °C 2000 ppm[35] are necessary to produce a stable sulfide phase. Kuhn et al. found no sulfide phase after treatment with 50 ppm $H_2S$ in $N_2$. However, additional Raman bands were observed and the $Ni2p_{3/2}$ XPS-peak was to higher binding energies indicating interaction of Ni with S.[42]
Catalytic studies  The effect of sulfur on Ni/YSZ cerments has also been evaluated in catalytic studies (i.e. no electrochemical setup). Kuhn et al. found reactions with participating water e.g. water gas shift (WGS) being more affected than oxidation reactions like CO or CH₄ oxidation.[42] Also, Lakshminarayanan and Ozkan[43] got similar results regarding water gas shift reaction and methane oxidation. In temperature programmed reaction (TPR) - experiments they also observed that poisoned catalysts show activity for the WGS reaction in the initial heating period, but irreversibly lose the activity for the reaction at 700 °C. This phenomenon was explained by further experiments showing significant adsorption/desorption of H₂S on pure YSZ and increased desorption in presence of water. It was concluded that this might cause the delayed response in the TPR experiment. In steady state stoichiometric methane oxidation experiments it was shown that water alone did not affect the activity at 700 °C, adding H₂S to this reaction feed, however, did. This poisoning was partially recovered by removing water from the feed and totally recovered by also removing H₂S. The authors concluded surface reconstruction as the reason for activity loss. Also, in contrast to non-poisoned catalysts no coking was observed during CO oxidation experiments on poisoned catalysts. This behaviour is in accordance with the above discussed blocking of catalytically active surface sites on Ni by H₂S.[43]

Other contaminants  The effect of other contaminants has also been investigated by Haga et al.. They reported that COS showed the same behaviour as H₂S indicating that equilibrium composition (low partial pressure of COS compared to H₂S) was reached. CH₃SH caused the same initial drop in cell voltage, but additionally a further continuous degradation which could be reversed by removing the contaminant from the feed at 1000 °C. Chlorine leads to the formation of Ni-nanoparticles by gas phase transport and an al-
most constant degradation rate and siloxanes caused continuous degradation until total cell failure due to $SiO_2$ formation.[41]

Sulfur-tolerant anodes  Due to the severe effect of sulfur poisoning on the performance of SOFC cells, significant effort has been made to develop more resilient anode materials. A detailed review on this topic has been written by Gong et al.[37] Completely new concepts like metal sulfide and thiospinell anodes (which might have a stability problem under operational conditions) and mixed ionic/electronic conductors are described as well as modifications to the existing Ni/YSZ cermet electrode. For cermet electrodes, replacement of Ni and/or the ceramic component have been proposed. On the metal side, partial or full replacement with Cu might be a viable way of reducing sulfur poisoning. On the ceramic side, replacing YSZ with scandium stabilized zirconia has been shown to improve resilience to $H_2S$ but also impregnating the cermet with certain elements such as $Ce$, $Y$, $La$, $Zr$ and $Ti$ also showed an improvement.[33] As an example of replacing the electrolyte, Zhang et al. showed that replacing YSZ with gadolinium doped ceria (GDC) significantly reduced the increase of polarization resistance upon sulfur poisoning up to a concentration of 700 ppm $H_2S$. Interestingly, contrary to YSZ GDC showed morphological changes after testing.[32]

1.4 Open questions

In section 1.3 it was shown that extensive research effort has been directed towards nickel electrodes in general. Yet, some questions have still to be answered/asked:
What causes the polarization resistance scattering between different samples? Bessler et al. provided some suggestions, but no conclusive answer.[12]

Does the orientation of YSZ have influence on microelectrode properties? In literature different substrates were used, yet only one study investigated this topic with few data points.[44]

What causes long-term degradation in cermet electrodes when $H_2S$ is present?

Do microelectrodes behave the same way as cermet electrodes when poisoned with $H_2S$?

1.4.1 Scope of this study

This study mainly aims to provide a reliable methodology in order to further investigate Ni microelectrodes and sulfur poisoning of such. Tackled topics include:

- Finding a method to produce dense Ni electrodes on YSZ substrates that remain dense under testing conditions.

- Optimizing the setup to remove measurement artifacts with special focus on the counter electrode influence.

- Establishing standard operation conditions for testing under which Ni electrodes remain morphologically stable and characterizing the electrode kinetics under these conditions.

- Investigating the effect of substrate orientation on polarization resistance and current-voltage dependency.
• Investigating the effect of $H_2S$ exposure on microelectrodes regarding polarization resistance, polarization behavior and microstructure.
Chapter 2
Experimental

2.1 Materials and devices

A list of materials used in this thesis is shown in table 2.1, commercial apparatuses are listed in table 2.2.

Electrochemical testing of cells was performed in 2 setups: A 'Micro' and a 'Micro-Macro'-setup. The Micro setup consists of a furnace where the sample is placed on, 2 micro-manipulators which enable precise positioning of contacting needles and wiring that connects the needles to external circuits. The setup is designed gas-tight to enable filling with a defined atmosphere. Contacting of microelectrodes is facilitated by a microscope (Mitutoyo, JAP). This setup allows fast switching between electrodes under testing conditions.

The temperature distribution, however, is inhomogeneous due to asymmetric heating, which also does not allow performing temperature cycles. The principle of the device is sketched in figure 2.1 and photographs are shown in figure 2.2. Figure 2.1 also shows a sketch cross-section of the samples. On the bottom side of the substrate (not polished) the counter electrode is deposited and the micro-structured electrodes are applied on the top side of the electrolyte.
**Table 2.1: List of materials used in this thesis.**

<table>
<thead>
<tr>
<th>Material</th>
<th>Detailed description</th>
</tr>
</thead>
<tbody>
<tr>
<td>Photoresist</td>
<td>ma-N 1420 Negativ Photoresist (Micro Resist Technology GmbH, GER)</td>
</tr>
<tr>
<td>Developer</td>
<td>ma-D 533S Developer for Photoresis (Micro Resist Technology GmbH, GER)</td>
</tr>
<tr>
<td>(100)YSZ</td>
<td>P3925 $ZrO_2 : Y(100)K$ (9.5 mol% $Y_2O_3$) single sided polished, 10x10x0.5mm (Crystec, GER)</td>
</tr>
<tr>
<td>(111)YSZ</td>
<td>P3526 $ZrO_2 : Y(111)K$ (9.5 mol% $Y_2O_3$) single sided polished, 10x10x0.5mm (Crystec, GER)</td>
</tr>
<tr>
<td>YSZ powder</td>
<td>TZ-8Y (TOSOH, JAP)</td>
</tr>
<tr>
<td>Pt-Paste</td>
<td>GWENT GROUP, UK</td>
</tr>
<tr>
<td>NiO/YSZ powder</td>
<td>Fuel cell materials, USA</td>
</tr>
<tr>
<td>NiO/YSZ binder</td>
<td>Fuel cell materials, USA</td>
</tr>
<tr>
<td>LSF powder</td>
<td>$La_{0.6}Sr_{0.4}FeO_{3-δ}$ (Sigma-Aldrich)</td>
</tr>
<tr>
<td>LSF binder</td>
<td>Terpineol (Sigma-Aldrich)</td>
</tr>
<tr>
<td>Ni-target</td>
<td>Goodfellow, UK</td>
</tr>
<tr>
<td>ARCAL</td>
<td>2.4 ± 0.5%$H_2$ in Ar (Air Liquide, AT)</td>
</tr>
<tr>
<td>$H_2S$-ARCAL</td>
<td>209.5ppm$H_2S$, 2.5%$H_2$ in Ar (Air Liquide, AT)</td>
</tr>
</tbody>
</table>

*Figure 2.1: Basic construction of a Micro-setup. 1 Furnace, 2 Sample, 3 Contacting needles*
Table 2.2: List of apparatuses used in this thesis.

<table>
<thead>
<tr>
<th>Device</th>
<th>Detailed description</th>
</tr>
</thead>
<tbody>
<tr>
<td>CIP</td>
<td>KIP-PK Ø25 (Paul-Otto Weber Maschinen- und Apparatebau GmbH, GER)</td>
</tr>
<tr>
<td>Sinter furnace</td>
<td>CWF1300 (Carbolite, GER)</td>
</tr>
<tr>
<td>Cut-off machine</td>
<td>Secotom-10 (Struers, AT)</td>
</tr>
<tr>
<td>Polishing machine</td>
<td>TegraPol-31 (Struers, AT)</td>
</tr>
<tr>
<td>Spincoater</td>
<td>Delta6RCTT (SUSS MicroTec, GER)</td>
</tr>
<tr>
<td>UV lamp</td>
<td>350W high pressure ( Hg ) lamp, maximum intensity 365nm (Ushio Inc., JAP)</td>
</tr>
<tr>
<td>Sputter machine</td>
<td>MED020 Coating system, QSG100 Quartz Film Thickness Monitor (BAL-TEC, now Leica Microsystems, AT)</td>
</tr>
<tr>
<td>EIS measurement device</td>
<td>Alpha-A High Performance Frequency Analyzer &amp; Electrochemical Test Station POT/GAL 30V/2A (Novocontrol Technologies, GER)</td>
</tr>
<tr>
<td>SMU</td>
<td>2611 System Source Meter (Keithley Instruments Inc., GER)</td>
</tr>
<tr>
<td>SEM</td>
<td>Quanta 200 FEG (FEI, USA)</td>
</tr>
<tr>
<td>Optical Microscope</td>
<td>Axio Imager M1m (Zeiss, AT)</td>
</tr>
<tr>
<td>Furnace (Micro-Macro setup)</td>
<td>SR 70-200/12SO (Gero GmbH, GER)</td>
</tr>
</tbody>
</table>

Figure 2.2: Practical realization of the Micro-principle. Left: Sample stage with contacting needles and sample, right: complete setup (without electrochemical testing kit and gas preparation)
A ‘Micro-Macro’ setup on the other hand consists of a free contacting arm with a needle attached to it and a current collector where the sample lies on. The needle is placed on the sample, the setup is sealed gas-tightly with a quartz tube, filled with a defined atmosphere and inserted into a furnace. Due to homogeneous heating of the cell this setup allows testing at well-defined temperatures. Conducting of temperature cycles is also possible, switching electrodes, however, can only be done ex-situ. A schematic drawing of a Micro-Macro setup is shown in figure 2.3, a photograph of the actual device is shown in figure 2.4.

Data acquisition of U-I-curves and recording of impedance spectra using a Novocontrol Alpha Mainframe with a POT/GAL was performed with the software WinCHEM 2.04 and Javalab (custom) respectively. Impedance spectra were measured with 10mV RMS stimulus in a frequency range of 1MHz to 50mHz and 0mV bias voltage unless otherwise noted. Analysis of impedance spectra was done using ZView 3.3e. Statistical tests were performed with OriginPro 9.0.0G(64 bit) SR2.
Figure 2.4: Practical realization of the Micro-Macro-principle. Left hand side: Whole setup (except gas treatment), right hand side: Contacted sample

In the following, x% wet ARCAL will denote the percentage of water saturated ARCAL (saturated at room temperature) of the whole gas filling in/flow through the sample chamber.

2.2 Substrate preparation

Single crystal substrates were used as delivered. Polycrystalline samples were prepared from YSZ-powder: The powder was filled in a silicon mold and pressed at 3 kbar for 10 s in the cold isostatic press (CIP). The green compact was sintered at 1550 °C for 5 h, cut into ~1 mm thick discs and polished on one side with the following plates:

- MD-Piano 220, 20 s
- MD-Piano 600, 30 s
- MD-Largo 9 µm, 6 min
- MD-Largo 3 µm, 3 min
The substrates were subsequently cleaned for 5 min in an ultrasonic bath in acetone.

### 2.3 Counter electrode

In order to use a 2-point setup (i.e. eliminating the need for a reference electrode) an unpolarizable counter electrode is inevitable. Therefore the polarization resistance of the counter electrode should be $< 5\%$ of the polarization resistance of the microelectrode. Since 250 $\mu$m circular Ni-microelectrodes have a polarization resistance of about 1 M$\Omega$ the counter-electrode should have $< 50 k\Omega$ which equals an ASR of $< 50 k\Omega cm^2$ (single crystal substrates have an area of 1 $cm^2$).

The best available counterelectrode was the porous LSF-electrode with Pt-current collector. For testing its performance, two electrodes were prepared by brushing LSF-paste (0.57 g $\alpha$-Terpineol per 1 g of LSF powder with 3 wt% ethyl cellulose) on both sides of a 5x5 mm (100)YSZ substrate and sintering at 850 $^\circ$C for 5 h in air. Subsequently, Pt-paste was brushed on the sample. Finally, the sample was electrochemically characterized in a Micro-Macro setup (the needle was replaced by a Pt-sheet to allow contact on the whole area) in 100 $\%$ wet ARCAL. A typical resulting spectrum at 750 $^\circ$C and the equivalent circuit used to parametrize it is shown in figure 2.5. All resistance parameters in the equivalent circuit were summed, normalized to the area and halfed (the symmetric cell has 2 electrodes in series that cause resistance) to compute the area specific resistance. The error caused by the resistance of the electrolyte is estimated to be 30 $\Omega$ (which translates to 3.75 $\Omega cm^2$); this resistance does, however, not affect the
direct comparison of these counter electrodes. The temporal progression of the ASR is shown in figure 2.6. It is shown that the electrode is relatively stable at 750°C with the ASR being more than 3 orders of magnitude below the benchmark of 50 kΩcm². At 800°C there seems to be faster degradation going on, but stabilization of microelectrodes at this temperature takes only some hours, hence no stability problem of the counter electrode is expected.

Ni/YSZ cermets were also tested as counter electrodes. Samples were prepared by brushing cermet-paste (83% NiO/YSZ powder in binder) on both sides of a 5x5 mm (100)YSZ substrate and sintering at 1250°C for 2 h (after removal of the binder at 300°C for 30 min). The sample was placed in the modified Micro-Macro setup and electrochemically measured. A typical resulting spectrum at 750°C with the equivalent circuit used for data
analysis is shown in figure 2.7. The ASR was calculated analogously to the LSF-sample; the evaluated measurement can be found in figure 2.8. It can be seen that besides a continuous degradation seemingly abrupt degradation can be observed. While still below the benchmark value, ASR-values for this electrode are about an order of magnitude higher than for LSF-Pt electrodes and degradation is significant. Hence, the cermet was not used for further investigations.

Porous Pt-electrodes were also subject to investigation. Samples were prepared by brushing Pt-paste onto both sides of a 5×5 mm (100)YSZ substrate and drying at 120°C. A typical impedance spectrum of such a sample is shown in figure 2.9. ASR-values were calculated analog to the LSF-electrode; the evaluated measurement can be found in figure 2.10. It can be seen that significant degradation takes place and that ASR-values are 2 orders of magnitude
higher than for LSF-Pt electrodes. Despite being below the benchmark value, this electrode type was not used in the standard sample preparation.

2.3.1 LSF-Pt counter-electrode under $H_2S$

An experiment analog to the LSF-Pt electrode measurement in the previous section was conducted to investigate the effect of $H_2S$ on the electrode. The evolution of the ASR upon $H_2S$ addition is shown in figure 2.11. The figure shows a delayed response to the sulfur introduction when the resistance increases by a factor of $\sim 25$. After removing $H_2S$ from the feed the poisoning effect partially regenerates. The ASR-value still remains well below the benchmark-value under all tested conditions, therefore the electrode is suitable to investigate sulfur poisoning of Ni microelectrodes.
Figure 2.8: Degradation experiment of a symmetric cell with Ni/YSZ electrodes. The temperature change at the end shows stability under microelectrode stabilization conditions.

Figure 2.9: Typical impedance spectrum and equivalent circuit of a symmetric cell with 2 porous Pt electrodes.
2.4 Ni microelectrode preparation

Since varying procedures and preparation parameters were tested until viable samples were obtained, the following subsections will show the general procedure for each step of the microelectrode manufacturing process. The effect of different procedures will be discussed afterwards.

2.4.1 Thin film deposition

Ni thin film deposition was done by sputtering at room temperature. The YSZ substrate was placed below the Ni-target, the chamber evacuated down to $1 \cdot 10^{-4}$ mbar and then Ar was leaked into the system to get a steady pressure of $3 \cdot 10^{-2}$ mbar. The sputtering process was started with closed shutter at a fixed current of 150 mA to remove any oxide layer on the target.
After 30 s of sputtering the shutter was opened and the sputtering process was continued for the time needed to deposit the desired layer thickness. Calibration measurements using a quartz crystal showed a deposition rate of 1 nm/s. After deposition, the sample was allowed to cool for 15 min. This was done to avoid oxidation of the hot target when finally venting the chamber.

### 2.4.2 Photolithography

The sample was cleaned in ethanol. Then it was spincoated with photoresist (30 s, $f = 60 \text{s}^{-1}$, 100 µl photoresist) and baked at 100°C for 2 min on a hotplate. This “coat&bake” process can be repeated several times to obtain thicker coatings. Afterwards, the spin-coated sample was aligned with an appropriate mask (Cr on glass) and irradiated by the UV-lamp for 60 s. The microstructure was then developed in developing solution for $\sim 90 \text{s}$ until
the last interference fringe disappeared for 5s. The developing process was stopped by submerging the sample in deionized water.

2.4.3 Etching/Lift-off

If etching was employed, layer deposition had to be performed in advance to photolithography. The counter electrode of the structured sample was protected by applying photoresist on the backside of the sample. The sample then was submerged into aqua regia at room temperature. The etching process was continued until no residual Ni between the electrodes was left. Then the sample was washed three times in deionized water, then once in ethanol and finally twice in acetone to remove all residual photoresist. For lift-off, photolithographic structuring had to be performed prior to layer deposition. The sample was submerged into ethanol and the Ni between the microelectrodes was removed by brushing it off (if possible) or treatment in an ultrasonic bath. Finally, the sample was cleaned in fresh ethanol.

2.4.4 Microelectrode microstructure

A first attempt was made by

- performing lithography for lift-off (3 layers of photoresist),
- depositing 800 nm Ni and
- micropatterning by lift-off.

The resulting structures had sharp edges and were not porous (not shown). Annealing a sample prepared by this method in 5 % wet ARCAL for 14 h at 600 °C and 3 h at 650 °C resulted in dull electrodes (were reflective in the beginning), which was attributed to Ni recrystallization. After subsequent
114 h of electrochemical testing in the same atmosphere at 700 °C the sample was investigated microscopically. A resulting image of a non-contacted electrode is shown in figure 2.12. The figure shows pores that are assumed to be formed during the recrystallization process. These pores increase the TPB length by an unknown factor, which cannot be accurately measured by optical methods due to their small size. Therefore, the parameters of the preparation had to be modified.

An attempt to eradicate the porosity problem was to increase the sputtered layer thickness to 1200 nm. A microscopic image of a sample prepared by this
protocol is shown in figure 2.13. The image shows that there are brighter and darker regions in the electrode which indicates partial delamination during the lift-off process (most likely due to the thickness of the Ni film). Since delamination modifies the TPB length and might even cause unstable electrode structure during testing, another preparation method was investigated. In the next step lift-off was replaced by etching. For that, film deposition was done before lithography and only one photoresist layer was applied. After recrystallization inconsistent results regarding porosity were obtained. Figure 2.14 shows a sample that was broken into 2 pieces before
Figure 2.14: Transmitted-light bright-field image of a sample with 1200 nm thick Ni layer, structuring was done by etching, recrystallization was performed after structuring. The sample was split into 2 pieces which were recrystallized separately, one microelectrode of each sample is shown. Only one of the samples developed a porous structure (big holes are due to the etching process). Color curves were adjusted to improve visibility of pores.
recrystallization. The sample on the left was kept at 750 °C in 100% wet ARCAL for 18 h, the one on the right at 750 °C in 100% wet ARCAL for 43 h.

The final attempt was made by rearranging the preparation order:

- Sputter deposition of 1200 nm Ni
- Recrystallization at 750 °C over night in 100% wet ARCAL
- Lithography with one layer of photoresist
- Etching

A typical result of this preparation can be seen in figure 2.15. By employing this method the formation of porosity could successfully be suppressed. An explanation for the effect of different preparation order is beyond the scope of the present work and is thus not discussed in detail. Thin films that are deposited at low temperatures (compared to the melting point of the layer material) generally show tensile stress which explains the formation of pores during recrystallization due to creeping. This phenomenon, even so, cannot explain that recrystallization of unpatterned films does not also cause porosity.

Figure 2.15 also shows that the edges of the microelectrodes are not perfectly circular but show some waviness. To obtain more precise data for the surface area and TPB length optical microscope images were evaluated with a custom semi-automatic program in the software-package AxioVision 4.8. Data from 3 samples with 5 microelectrodes each (nominal diameter of 250 µm) were evaluated, the result is shown in table 5.1. The samples were measured after electrochemical testing and had stable polarization resistances (see section 3.3 and figure 3.18), which is assumed to be equivalent to a stable microstructure.
Figure 2.15: Transmitted-light and reflected-light bright-field image of sample 111YSZ-Ni9a prepared by the final protocol after \( \sim 45 \) h at 750 °C in 100% wet ARCAL. The brightness curve of transmitted-light image was adjusted to ensure comparability to previous images.

The calculated average of the correction factors \( f_{\text{perimeter}} = 1.103, f_{\text{area}} = 0.883 \) were used for all calculations of LSRs and area specific capacitances. Those quantities can therefore be calculated by the formulae

\[
\text{LSR} = R_P d \pi \cdot 10^{-6} \cdot f_{\text{perimeter}} \quad (2.1)
\]

\[
\frac{C}{A} = \frac{4C}{d^2 \pi f_{\text{area}}} 10^{12} \quad (2.2)
\]

with

\[ d \text{ diameter } [\mu m] \]

For constant phase elements (CPEs) as capacitance-replacement (see equation (1.51)) in RC-elements a modified formula for the area specific capacitance was used:

\[
\frac{C}{A} = \frac{4 \left( R^{1-\zeta} P \right)^{1/\zeta}}{d^2 \pi f_{\text{area}}} 10^{12} \quad (2.3)
\]
2.5 Summary of sample preparation and standard testing conditions

Unless otherwise noted, data for the following chapters were obtained on samples that were prepared by this method (details for each preparation step are discussed in section 2.4):

- LSF paste was brushed on the unpolished side of the substrate.
- The paste on the substrate was then sintered at 850°C for 5 hours and Pt paste was brushed on the LSF.
- 1200 nm Ni were sputtered on the polished side of the substrate.
- The sample was then recrystallized in 100% wet ARCAL at 750°C for ~ 16 h.
- The recrystallized sample was patterned by lithography with one layer of photoresist (positive mask) and etching in cold aqua regia.

The following conditions were defined as standard conditions, any deviation will be noted in the following chapters:

- Ni deposition on a (111) YSZ substrate.
- Temperature: The sample was pre-heated to 800°C until the polarization resistance stabilized as suggested by Yao and Croiset[17] and then tested at 750°C.
- Atmosphere: Ambient pressure with flow of 100% wet ARCAL through the chamber.
• Microelectrode shape: Circular electrode with nominal diameter of 250µm.

• Measurement in a Micro-Macro setup.
Chapter 3

Results & Discussion

Statistical significance for this thesis is set to $\alpha = 0.05$. If $p$-values from statistical tests fall below this value, the null-hypothesis $H_0$ will be rejected.

3.1 Equivalent circuit

Typical impedance spectra (Nyquist-plots) of Ni microelectrodes are shown in figure 3.2. The curves resemble slightly depressed semicircles with a high frequency-intercept at $\sim 1\,k\Omega$. This offset is modeled with a series resistor fits rather well to the expected spreading resistance of ion conduction in the electrolyte.[45] The best fitting quality was found for the equivalent circuit $R-(RQ)-(RQ)$ (see figure 3.1(a)). In figure 3.2 a fit of the spectrum ‘Experimental(3)’ to this circuit is shown ($\chi^2 = 0.00286$). Physical interpretability of this equivalent circuit is nevertheless doubtful since the resistances of the high and low peak-frequency semicircle behave seemingly random for spectra of the same sample (see figure 3.17). This equivalent circuit was therefore just used to extract accurate total polarization resistances from spectra. These resistances were calculated as the sum of the resistances of the RQ-elements (i.e. $R_{Pol1} + R_{Pol2} = R_{Pol,tot}$). 
The use of only one RQ-element (cf. figure 3.1(b)) to model the quasi- 
semicircle reveals a slight lateral asymmetry of the spectrum (see fit of 'Ex-
perimantal(1)' in 3.2, $\chi^2 = 0.00329$). This asymmetry could be caused by a 
more complicated ‘true’ equivalent circuit. Typical values of $\zeta$ for the CPE 
element are around 0.96, which is close to the value for an ideal capaci-
tance. A better resolution of additional elementary processes in the electrode 
impedance may be complicated due to the relatively big capacitance repre-
sented in the CPE. Therefore, this equivalent circuit in figure 3.1(b) was used 
to obtain capacitance data from impedance spectra of Ni-microelectrodes.

### 3.2 General properties

#### 3.2.1 Activation energy

To determine the activation energy of the rate determining step, resistances 
from impedance spectra and small signal DC-measurements were used. These 
small signal DC-measurements were carried out using a source measure unit 
(SMU) (see section 2.1) for measuring the current under potentiostatic condi-
tions at several voltage points in the range of $\pm 15 \text{ mV}$. An example measure-
ment is shown in figure 3.3. The data then were converted into a U-I-diagram 
by averaging the last 30 current points (1 point/second) of each voltage step;
Figure 3.2: Typical impedance spectra (Nyquist-plots) measured in a Micro-Macro setup of circular microelectrodes with nominal diameter of 250 µm. Fitting results of 2 equivalent circuits are shown.
the result for all measured temperatures is shown in figure 3.4. Polarization resistance data were calculated by means of linear regression. Polarization resistance data were evaluated in Arrhenius-type plots as shown in figure 3.5. Using the linearized Arrhenius formula

$$\ln(R_P) = \frac{E_A}{R} \frac{1}{T} + \ln R_0$$  \hspace{1cm} (3.1)

the activation energy can be calculated. In case of data obtained by small signal DC measurements (measured in 100\% wet ARCAL) the activation energy computed to $0.73\,eV = 70.3\,kJ/mol$. For data obtained by EIS the value was similarly $0.70\,eV = 67.6\,kJ/mol$ (measured in 10\% wet ARCAL). ‘EIS(2)’ was not evaluated due to thermal drift during the measurement series.
The value of the activation energy is lower than values previously reported in literature. Also, at temperatures below 700°C no deviation from a classical Arrhenius activation as reported by Utz et al. could be found.[16] Assuming that film porosity and the different measurement technique did not have influence on the resulting activation energy, the effect of lower water partial pressure according to Sukeshini et al. (higher activation energy in dry compared to wet hydrogen)[20] could not be reproduced; data, however, cannot be directly compared because the term ‘dry’ hydrogen was not specified.

The behavior of the capacitance as a function of temperature was also evaluated and is shown in figure 3.6. It shows an almost linear dependency on the temperature at temperatures below 700°C. This behavior is not expected from a classical double-layer capacitance[9] and therefore further
Figure 3.5: Arrhenius-type diagram of all activation energy measurements performed in this study (small signal DC method and EIS). Series ‘DC’ and ‘EIS(2)’ were measured in 100% wet ARCAL on a porous microelectrode, ‘EIS(1)’ in 10% wet ARCAL.
Figure 3.6: Temperature dependence of the area specific capacitance.

indicates non-classical interfacial capacitances or chemical capacitance contribution.

3.2.2 Bias voltage

The effect of potentiostatic bias voltage on impedance spectra was also investigated. Since the polarization resistance is closely tied to current-voltage curves, which are analyzed in section 3.2.3, the effect of DC voltage on the electrode resistance it will not be discussed here. Resulting area specific capacities of a sample is shown in figure 3.7. It can be seen that upon voltage change the capacitance is not immediately constant. Hence, only the last value of each voltage step was used to illustrate the relationship of bias voltage and the area specific capacitance in figure 3.8. It can be seen that higher bias voltages increase the capacitance. This finding, again, shows that the
Figure 3.7: Temporal dependence of the area specific capacitance when varying the bias voltage. The capacitance does not change instantly to a constant value.

model of a classical double layer capacitance does not fit the experimental data.

3.2.3 U-I curves

U-I curves were measured under potentiostatic conditions using a step voltage profile (instrument: Novocontrol Alpha with POT/GAL 30V/2A interface), see section 2.1) with 25 mV step size. The raw data of such a measurement in the voltage range of -300 mV to +250 mV are shown in figure 3.9. Between the first and last step voltage profile a period of maximum polarization was used to investigate if polarization in this voltage range leads to irreversible electrochemical changes in the electrode. For obtaining U-I curves from the raw data, the last 30 values of each step were averaged and the resulting U-I-curves are shown in figure 3.10. It can be seen that a small hysteresis can
Figure 3.8: Effect of the applied bias voltage on the area specific capacitance.

occur, but that the U-I curves are very similar. Hence, it can be concluded that no irreversible changes take place at the electrode in this voltage range. Two models to describe the U-I curves showed promising fitting quality: The classical charge-transfer controlled reaction (Butler-Volmer-equation (1.31), \( c_A = c_{A,0}, c_B = c_{B,0} \)) and a diffusion limited reaction with a parallel path of water splitting on the free YSZ surface enabled by enhanced electronic conductivity on YSZ (Wagner-Hebb-polarization, here the limiting case for high voltages is used)[46][47]. For the latter model the following equation holds:

\[
I = I_{\text{lim}} \left( 1 - e^{\frac{\varepsilon_d n_f^*}{kT} U} \right) - I_0 e^{-\frac{bW}{kT} U} \tag{3.2}
\]

with

\( b \) Wagner-Hebb factor (4N, for YSZ \( N = 1/4 \) and thus \( b = 1 \))

Since exponential functions lead to values ranging over many orders of magnitude and most fitting algorithms are based on the square sum of resid-
**Figure 3.9:** Measurement of U-I curves in the voltage range of -300 mV to +250 mV on a (111) YSZ substrate.

**Figure 3.10:** Consecutively measured U-I curves in the voltage range of -300 mV to +250 mV.
uals, a fit without weighting function tends to emphasize only the largest values. To obtain a good fit over the whole domain of definition (measurement range) the functions were analyzed in the Tafel plot as shown in figure 3.11. The recalculated fitting functions in the linear plot are depicted in figure 3.12. For the Butler-Volmer-equation the fitting parameter were computed to $\alpha = 0.746 \pm 0.012, I_0 = (6.63 \pm 0.30) \times 10^{-5} \, A/m$ with fixed values of $z = 2, T = 1023 \, K$. Using only the anodic part of the curve a value of $\alpha = 0.70 \pm 0.02$ was found. Interestingly, the $\alpha$-value of Sukeshini et al. ($\alpha = 0.27$ at 750 °C in 33.3% $H_2/4\% H_2O$ in Ar) differ substantially from the value found here.[20] Also, the shape of the Tafel-plot in the cathodic regime in this thesis is different than in the cited study. The difference in $\alpha$ may indicate a dependence of the asymmetry factor on the hydrogen partial pressure which, however, is not possible in the model of charge-transfer controlled reactions. Additionally, in the present study the function fails to accurately describe the cathodic part of the curve. Therefore the reaction here cannot be purely charge-transfer controlled.

The second model shows good agreement for cathodic polarization, however some deviation for anodic polarization. The fitting values of $z_{diff} = 1.56 \pm 0.11, b = 1.60 \pm 0.21, I_{lim} = (5.0 \pm 1.0) \times 10^{-5} \, A/m, I_0 = (3.3 \pm 1.9) \times 10^{-6} \, A/m$ with the fixed value of $T = 1023 \, K$ are only in moderate agreement with the ideal values of $z = 2, b = 1$. This model, however, uses the limit case for high Wagner-Hebb polarization which is not necessarily applicable to the experimental data. Opitz et al. found, using the same model for Pt electrode in air, good agreement with an opening of the electronic YSZ path at $\sim 1.2 \, V$.[46] Using Nernst’s equation to correct for the oxygen partial pressure (in 1:1 $H_2 : H_2O$ $p_O2 \sim 1.7 \cdot 10^{-17} \, bar^{-1}$) one gets a shift of $U_C = +0.963 \, V$.

1Values calculated from thermochemical data from [5]
which agrees well with experimental data. A correction of the model might therefore lead to improved fits but is beyond the scope of this thesis.

### 3.3 Variation of substrate orientation

In this thesis Ni microelectrodes were prepared on YSZ single crystals with the crystallographic orientation (111) and (100) as well as on polycrystalline substrates. One big difficulty for comparing these different samples is the significant temporal drift of the polarization resistance at elevated temperatures which, however, decreases with time (see polarization resistances in figure 3.18 in the range of 0-80,000 s). In order to minimize systemic errors the following prerequisites were defined for a measurement contributing to the comparison:
The sample was prepared by standard procedure and is measured under standard conditions.

- The sample was initially stabilized at 800°C until the polarization resistance did not change, then the temperature was decreased to 750°C.
- The sample was then held at 750°C for at least 18h (impedance measurements) respectively 12h (U-I curves)

### 3.3.1 EIS measurements

A list of all measurement data used for statistical testing is presented in table 5.2. Errors due to fitting are assumed to be negligible.

To evaluate whether there is a difference of the expected polarization resistance values a 2-sample t-test is aspired. A prerequisite for this test
is normal distribution of the sample, hence a Shapiro-Wilk-test was employed. Normal distribution was accepted for all orientations \((p_{111} = 0.195, p_{100} = 0.408, p_{poly} = 0.203)\). Consequently, a 2-sample t-test was conducted for all orientation combinations (i.e. 111 vs. 100; 111 vs. poly; 100 vs. poly). No significant difference could be found for all tested combinations (see table 5.3). It can therefore be concluded that the YSZ orientation does not have a (strong) influence on the polarization resistance of Ni electrodes here. As the Ni electrodes are still polycrystalline, a distinct behavior of specific Ni-YSZ orientation combinations cannot be ruled out with available data.

Area specific capacitances were investigated likewise (Shapiro-Wilk-test results: \(p_{111} = 0.821, p_{100} = 0.902, p_{poly} = 0.763\)); detailed t-test results are shown in table 5.4. The single crystalline samples showed significantly different area specific capacitances compared to the polycrystalline substrate – the latter ones were about a factor of two larger. However, no significant difference was found between the single crystalline substrates. A possible reason for this difference is topology. The single crystals were polished in another process as the polycrystalline ones, which leads to a different contact area. Another reason could be a dissimilar contaminant profile leading to a different chemical capacitance.

Correlation between area specific capacitance and LSR was investigated as well. A corresponding scatter plot is shown in figure 3.13. No obvious connectivity was identified in the graph, consequently linear correlation was investigated. The Pearson product-moment correlation coefficient for the 111-dataset was calculated \((\rho = -0.00294, \text{significance } p = 0.99316)\).
with $H_0 : \rho = 0$) and a linear correlation could therefore be rejected – the data present a textbook example for an uncorrelated sample. Consequently, scattering of the interface capacitance and polarization resistance does not have the same source.

These results contradict findings by Rao et al.. The authors stated that the polarization resistance for cells on (111)YSZ substrates is higher than for cells on (100)YSZ substrates.[44] The reader should, however, note that these conclusions were based on only two data points per orientation.

### 3.3.2 U-I curves

The U-I curves of Ni microelectrodes on different YSZ substrate orientations were measured in the voltage range of -200 mV to +200 mV, too. The re-
resulting curves (evaluated analog to section 3.2.3) are shown in figure 3.14. It can be seen that, besides one measurement on the polycrystalline sample, no obvious difference between the orientations can be found.

3.4 Comparison of Micro & Micro-Macro-Setup

A sample with 250µm circular microelectrodes was prepared by standard procedure was measured in standard atmosphere in a Micro-setup; typical impedance spectra is shown in figure 3.15. In this setup the temperature of the microelectrodes cannot be measured accurately due to the asymmetric heating but has to be estimated. This is done by using the resistance value of the high-frequency $Z_{Re}$ intercept in the Nyquist-plots which can be attributed to the electrolyte.[45] Data for this calibration were obtained from the corresponding fitting parameter obtained from measurements in a
Micro-Macro setup (cf. 'EIS(1)' in figure 3.5). Plotting the logarithmic electrolyte resistance obtained in this homogeneously heated setup as a function of the temperature yields an acceptable linear relationship as shown in figure 3.16. At the highest possible furnace temperature of 870 °C where Micro-measurements were performed the electrolyte resistance was 2445 Ω which thereby translates into 677 °C. The measured polarization resistances then were corrected with the activation energy data ('EIS(1)' in figure 3.5) to get the analog polarization resistance at 750 °C. The resulting time dependent resistance-curve of the measurement is presented in figure 3.17. It can be seen that during the measurement series a more or less constant degradation took place which, however, was small compared to the scattering of the polarization resistances of the individual electrodes.

For statistical analysis the last LSR-value from each electrode was bundled into a dataset (see table 5.5). The mean value of this Micro-dataset was com-
Figure 3.16: Temperature dependence of the high frequency x-intercept in Nyquist plots of spectra obtained in a Micro-Macro setup.

pared to the mean value of the combined dataset of all substrate orientations mentioned in section 3.3.1 (‘Micro-Macro-dataset’). A Shapiro-Wilk-test did not reject normal distribution for the Micro-dataset \((p = 0.385)\) and the Micro-Macro-dataset \((p = 0.123)\). Hence, a 2-sample t-test was employed for comparison of the mean values (for equal variance \(p = 3.49 \cdot 10^{-7}\), Welch-corrected \(p = 0.012\)). Since in both cases of equal and unequal variance \(H_0\) is rejected it can be concluded that there is a significant difference in polarization resistances measured in Micro- and Micro-Macro setups with higher polarization resistance values in the Micro setup. The systematic error of unfinished degradation in Micro-measurements further solidifies this conclusion.

The outstanding discrepancy of results in different setups might be explained by temperature gradients. The cooler surface of the substrate where microelectrodes are located may act as a ‘cold trap’ for impurities: A
Figure 3.17: Time-dependent polarization resistance (equivalent resistance at 750 °C) of a measurement series in a Micro setup. Vertical lines indicate contacting of a different electrode. The resistance of the high peak frequency and low peak frequency RQ-element are shown as lines.
combination of reduced mobility due to the lower temperature and smaller chemical potential at the substrate surface compared to the bulk is expected to concentrate contaminations around the microelectrodes, which has a detrimental effect on the polarization resistance. Further investigation of this hypothesis might be subject to future research.

An analog analysis was conducted for the capacitance values. Pooled Micro-Macro single crystal data were compared to the Micro-data (see tables 5.5 and 5.2). A Shapiro-Wilk-test did not reject normal distribution for the Micro-Macro-dataset ($p = 0.497$) but rejected normal distribution for the Micro-dataset ($p = 0.024$). Hence, a Mann-Whitney-test was employed to compare the datasets. $H_0$ (both populations are equivalent) was not rejected ($p = 0.547$). One can therefore conclude that there is little if any influence of temperature gradients on the capacitance of Ni microelectrodes. Yet the first 2 and the last 3 electrodes exhibit very different capacitances, a degradation effect of some sort can therefore not be ruled out completely.

### 3.5 Sulfur poisoning

#### 3.5.1 EIS

The effects of sulfur poisoning were investigated at a concentration of 10 ppm $H_2S$ in the feed and the polarization resistance and electrode capacitance of a 250 µm electrode was obtained by EIS experiments. (Please note: A small consistently appearing semicircle in the high frequency region comprising 1.6% of the total resistance at the start was not included for fitting; it is most likely attributed to an effect at the counter electrode.) A typical measurement to investigate the scale of the poisoning effect on the resistance and
Table 3.1: Summarized results of poisoning experiments without bias-voltage.

<table>
<thead>
<tr>
<th></th>
<th>Absolute value</th>
<th>Relative change to start [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Start</td>
<td>Poisoned</td>
</tr>
<tr>
<td>LSR [Ωm]</td>
<td>2613</td>
<td>+108</td>
</tr>
<tr>
<td>C/A [Fm(^{-2})]</td>
<td>1.806</td>
<td>-50.0</td>
</tr>
</tbody>
</table>

its reversibility is shown in figure 3.18. The figure shows 3 short poisoning periods which indicate an initial accumulative effect. Afterwards \(H_2S\) was added for 10 h, subsequently switched off and the sample was regenerated for 22 h. The results of this measurement are summarized in table 3.1. The demonstrated partial reversibility of the poisoning is in good agreement with findings on cermet electrodes.[37] The effect on the capacitance in the same measurement can be seen in figure 3.19. The capacitance significantly decreased under poisoned conditions and was also partially recovered after \(H_2S\) was removed from the feed. Since \(S\) readily adsorbs on the \(Ni\) surface and blocks adsorption sites[37], this finding indicates a contribution of adsorbed species on the \(Ni\) surface to the observed capacitance. This may also explain a temperature dependence of the capacitance due to adsorption equilibria (temperature dependence shown in section 3.2.1).

Another measurement yielded similar results for the resistance degradation (523.7Ωm at the start, +84.0\% poisoned, +18.7\% regenerated), evaluation of capacitances was, however, not possible due to artifacts.

A problem observed in all measurements using \(H_2S\) was occurrence of measurement artifacts rendering most measurements inevaluable. Artifacts in this context are defined as deviations from the usual shape of impedance spectra (as shown in figure 3.2) appearing and disappearing without correlation to any known parameter (sometimes even within a measurement). Examples of these artifacts are shown in figure 3.20. They can be characterized...
Figure 3.18: Measurement of the effect of $H_2S$ on the polarization resistance. During 1 the sample was polarized at $+200\, mV$ for 30 min, at 2 the sample was disconnected and reconnected.

by either appearance of additional semicircles (without or with minor change of the overall LSR compared to the previous measurement) or change in the high frequency x-intercept with lower onsetting slope of the main semicircle. They were also observed before $H_2S$ addition in a measurement was initiated but started appearing after the first $H_2S$ poisoning experiment, hence some effect of residual sulfur in the system may play a role. Changing the counter electrode to Pt-paste (by grinding off the LSF and applying the paste) did not prevent artifacts from occurring. More research has to be conducted to pin the source of the artifacts down.

Additionally, high levels of noise were often observed when $H_2S$ was present in the feed (also shown in figure 3.20). A similar observation was also reported for cermet electrodes[48]. Explanations for the source of noise, however, were not discussed in this study.
3.5.2 Effect of bias-voltage

To investigate the effect of electrochemical polarization on the sulfur poisoning behavior DC-measurements in H$_2$S containing atmosphere were employed. A U-I curve in the range of ±200 mV was measured before, during and after poisoning. Between the U-I measurements the differential resistance was tracked by applying repeatedly +10 mV for 90 min and -10 mV for 30 min. An observed voltage offset was corrected by averaging the last 30 values of each voltage in the last cycle and computing the offset voltage by the formula

$$U_{off} = \frac{U_2 I_1 - U_1 I_2}{I_1 - I_2}$$  \hspace{1cm} (3.3)

with $U_1 = +10 \text{ mV}$ and $I_1$ the corresponding current, $U_2 = -10 \text{ mV}$ and $I_2$ the related current. The resulting temporal LSR-curve is shown in figure 3.19: Measurement of the effect of H$_2$S on the capacitance. During 1 the sample was polarized at +200 mV for 30 min, at 2 the sample was disconnected and reconnected.
Figure 3.20: Measurement artifacts found in sulfur poisoning experiments. The ’Bistable’ spectrum shows disappearance of the artifact within a measurement.

3.21. The U-I curves of the measurement series are shown in figure 3.22. It can be seen that in the beginning resistance jumps occur which can be attributed to a time dependence of the voltage offset; resistance degradation is more pronounced in this measurement and a smaller part of the resistance is recovered. The U-I curve under poisoned and recovered conditions show minute differences indicating irreversible changes that do not occur when no bias voltage is applied. This irreversibility might be caused by cathodic conditions under poisoned conditions since anodic polarization has been shown to decrease the effect of sulfur poisoning (see section 1.3.2). More data are needed, however, to confirm this hypothesis.
Figure 3.21: DC-differential resistance measurement with sulfur poisoning. $t = 0$ is defined at the start of the first U-I curve, missing data in the middle are due to a U-I measurement. Outliers are caused by switching of polarity.

Figure 3.22: U-I curves of a sulfur poisoning experiment.
3.6 Microstructure

Samples were examined in a SEM after electrochemical testing. In figure 3.23 an image of the TPB of an electrode, which was used to determine an U-I curve is shown. It can be seen that small particles are located on the larger electrode grains below and the electrode thus appears rather rough. These particles may be remains of the Ni oxide layer that formed between sputter deposition and recrystallization; formation by gas phase transport also seems possible. No apparent differences between polarized and non-contacted electrodes was found (images not shown).

An image of an electrode used in a S-poisoning experiment is shown in figure 3.24. Interestingly, the image shows (almost) no small particles on top of the electrode. This may be explained by a reduction of the surface energy of Ni when S is adsorbed on the surface. It is then expected that loose Ni particles merge more readily with the large grains.

The images also show no fractal structure of the TPB below the resolution limit of an optical microscope, therefore it can be assumed that microscopic geometric data from table 5.1 are reliable estimates for the actual TPB-length. To decide whether scattering of LSR-values can be explained by variations in microstructure, variances were compared. To do that, perimeter data from table 5.1 and pooled LSR-data from table 5.2 were normed on their average value. A Shapiro-Wilk-test for the perimeter-dataset did not reject normal distribution ($p = 0.33$), hence a F-test was employed. It resulted in a significant difference in variances ($p = 1.17 \cdot 10^{-11}$), microstructural variations can therefore not be the main source of LSR-value-scattering.

An analog test for area and C/A-values (pooled from single-crystal data in table 5.2) could not be done because normal distribution was rejected for area-values ($p = 0.028$). The relative standard deviations of both populations
Figure 3.23: SEM image of the TPB of an electrode after U-I measurement.

Figure 3.24: SEM image of the TPB of an electrode after sulfur poisoning and regeneration.
(area values $s/\varnothing = 0.053$, C/A-values $s/\varnothing = 0.182$) seem to be too deviant leading to the conclusion that other factors have to contribute to capacitance scattering.

Bessler et al. suggested 4 explanations for the scattering of LSR-data in literature over 1-2 orders of magnitude at the same temperature: Differences in water concentration, structural integrity (real/ideal TPB-length), chemical integrity (impurity ridge) and temporal drift.[12] In this study all factors have been controlled respectively held constant by equal sample preparation (or even measuring different electrodes on the same sample) but LSR-value-scattering still amounted to almost 1 order of magnitude. The reader should note that a local variation of impurity concentration can, however, not be ruled out completely. One of the main sources of scattering therefore remains unknown.
Chapter 4

Conclusion

The main three findings of this thesis are as follows (the reader may refer to section 3.1 for the exact meaning of polarization resistance and capacitance; statistical significance $\alpha = 0.05$ for hypothesis testing):

- YSZ substrate orientation does not have a significant influence on the polarization resistance of Ni microelectrodes. There is no significant difference in area specific capacitance values for (111) and (100)YSZ substrates. A differently prepared polycrystalline substrate, however, showed significantly different values. Current-voltage curves also did not show differences for any substrate orientation.

- Sulfur poisoning with 10 ppm $H_2S$ in the feed under standard conditions approximately doubles the polarization resistance ($+108\%$ compared to the start) while the capacitance halves ($-50.0\%$). After removing $H_2S$ from the feed the values partially return to the starting values (LSR: $+21\%$ and C/A: $-13\%$ relative to the start). Negative polarization under poisoned conditions might lead to increased irreversibility of poisoning.
There are at least 2 independent factors interfering with the reproducibility of Ni microelectrode properties. Geometric variances of individual electrodes cannot account for the scattering, neither can variables suggested by Bessler et al.\[12\] (Local impurity concentration variation can, however, not be ruled out completely). Values found at standard conditions for 250µm circular electrodes (capacitances of polycrystalline samples excluded): $LSR = 1.26 \pm 0.77 \, k\Omega m$, $C/A = 1.59 \pm 0.29 \frac{F}{m^2}$. The source of the extreme scattering remains unknown.

Additional findings include:

- Measurements in an inhomogeneously heated setup lead to significantly increased polarization resistances, possibly caused by impurity segregation. The effect on the capacitance is inconclusive.

- Exposure of microelectrodes to $H_2S$ leads to microstructural changes of the electrode. It can be assumed that adsorbed $S$ decreases the surface energy of $Ni$, which in turn could ultimately lead to delamination of the electrode after long-term exposure.

- The current-voltage curve was found not to be of Butler-Volmer-type. Instead a model of a diffusion limitation pathway in parallel to a path with electrochemical reaction on the free YSZ substrate is suggested.

- The capacitance was found to be non-classical due to its dependencies on temperature, bias voltage and sulfur presence. A contribution of adsorbed hydrogen to the capacitance therefore may be the case.

- The activation energy of the dominating rate-limiting process was found to be 0.70 eV at standard conditions. This value therefore is lower than
reported in any article to date. Contrary to the conclusion of Bessler et al., only one process seems to be dominant in the temperature range of 500-750 °C.\cite{12}

These results will form the base for future research on this topic. Poisoning data, for instance, will have to be reproduced without artifacts in order to solidify claims made in this thesis. The model used to describe the voltage-current curve can be tested by varying the oxygen partial pressure, which should directly influence the cathodic part of the curve. The role of impurities might be investigated by means of TEM analysis.
Glossary

$E_A$ Activation energy [eV] or $[\frac{J}{mol}]$. 28

$n$ amount of substance [mol]. 7, 8

$\omega$ angular frequency [s$^{-1}$]. 18

**ASR** area specific resistance [$\Omega cm^2$]. 43–46

$\alpha$ asymmetry coefficient $0 < \alpha < 1$, []. 14

$C$ capacitance [F]. 19

$U$ Cell voltage [V]. 10

$q$ charge [C] = [A · s]. 11

$\mu$ chemical potential $[\frac{J}{mol}]$. 7, 8

$c$ concentration $[\frac{mol}{L}]$. 14

$L$ Inductance [H]. 20

$i$ current [A]. 11

$r$ reaction rate $[\frac{mol}{s}]$. 11

$\tilde{I}$ time dependent current [A]. 18
$d$ diameter [$\mu m$]. 55

$D$ diffusion coefficient. 16

$\Delta \tilde{G}$ Electrochemical free enthalpy [$\frac{J}{mol}$]. 10

$U_C$ open circuit voltage [$V$]. 9

$\Delta S$ Entropy change [$\frac{J}{K}$]. 5

$K$ thermodynamic equilibrium constant [ ]. 9, 14

$\xi$ extent of reaction, $0 \leq \xi \leq 1$, [ ]. 7, 8

$z$ number of unit charges [ ]. 9

$F$ faraday-constant, $F = 96485 \frac{C}{mol}$. 9

$\zeta$ fractional derivation degree [ ]. 20

$P$ phasance. 20

$\Delta G$ Free enthalpy change [$J$]. 7

$f$ frequency [$s^{-1}$]. 23

$R$ universal gas constant [$\frac{J}{mol K}$]. 8

$Q$ heat [$J$]. 2

$Z$ impedance [$\Omega$]. 18

**LSR** line serial resistance [$\Omega m$]. 55, 71, 72, 74, 79, 80, 83, 85, 86, 92, 94, 104
\( \delta_N \) Nernst diffusion layer thickness \([m]\). 16

\( y \) distance \([m]\). 16

\( x \) normalized concentration \([\cdot]\). 8

\( \beta \) normalized resistance \([\Omega]\). 27

\( \eta \) overpotential of the entire cell \([V]\). 11

\( \delta \) phase shift. 23

\( R \) resistance \([\Omega]\). 27

\( \phi \) potential \([V]\). 14, 15

\( p \) pressure \([Pa]\). 7

\( \Delta_R G \) reaction free enthalpy \([\frac{J}{mol}]\). 2, 9

\( l_{TPB} \) triple phase boundary length \([m]\). 27, 28

\( \Delta_R H \) reaction enthalpy \([\frac{J}{mol}]\). 2, 3

\( k \) reaction rate coefficient. 14

\( \Delta_R S \) reaction entropy \([\frac{J}{molK}]\). 2, 3

\( \alpha \) scaling factor \([\cdot]\). 27

\( \nu \) stoichiometric factor \([\cdot]\). 8

\( T \) temperature \([K]\). 2

\( T_C \) temperature of the cold junction \([K]\). 2
$T_H$ Temperature of the hot junction [K]. 2

$\epsilon$ thermal efficiency [ ]. 2

$W$ mechanical work [J]. 2

$t$ time [s]. 18

$U$ voltage [V]. 18

$\tilde{U}$ time dependent voltage [V]. 18
Acronyms

CIP  cold isostatic press.  40, 42

CPE  constant phase element.  55, 59

EIS  electrochemical impedance spectroscopy.  17, 18, 26, 32, 40, 61, 77, 94, 104, 105

GCI  galvanostatic current interruption.  26

GDC  gadolinium doped ceria.  35

MFC  mass flow controller.  41

OCP  open circuit potential.  31

SMU  source measure unit.  40, 59

SOEC  solid oxide electrolysis cell.  11, 12

SOFC  solid oxide fuel cell.  1, 3, 11, 12, 25, 31, 35

ToF-SIMS  time-of-flight secondary mass spectrometry.  29

TPB  triple phase boundary.  26, 29, 31, 33, 51, 52, 54, 83–85, 93
TPR temperature programmed reaction. 34

WGS water gas shift. 34

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Chapter 5

Appendix
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<table>
<thead>
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<th>Sample identifier</th>
<th>Perimeter [μm]</th>
<th>Area [μm²]</th>
<th>f_{perimeter}</th>
<th>f_{area}</th>
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Table 5.2: EIS data used for orientation comparison.

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<td>822.18421</td>
<td>0.31724</td>
<td>407.46464</td>
<td>0.06352</td>
<td>977.67342</td>
</tr>
</tbody>
</table>

Table 5.3: 2-sample t-tests for mean value difference of LSR using data from table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>111</th>
<th></th>
<th>100</th>
<th></th>
<th>poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>p(σ² equal)</td>
<td>0.53151</td>
<td>0.45087</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p(Welch-corrected)</td>
<td>0.37599</td>
<td>0.5372</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>p(σ² equal)</td>
<td>-</td>
<td>0.86731</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p(Welch-corrected)</td>
<td>-</td>
<td>0.87127</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 5.4: 2-sample t-tests for mean value difference of area specific capacities using data from table 5.2.

<table>
<thead>
<tr>
<th></th>
<th>111</th>
<th></th>
<th>100</th>
<th></th>
<th>poly</th>
</tr>
</thead>
<tbody>
<tr>
<td>111</td>
<td>p(σ² equal)</td>
<td>0.35599</td>
<td>9.83619E-6</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p(Welch-corrected)</td>
<td>0.10155</td>
<td>0.00322</td>
<td></td>
<td></td>
</tr>
<tr>
<td>100</td>
<td>p(σ² equal)</td>
<td>-</td>
<td>0.00177</td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>p(Welch-corrected)</td>
<td>-</td>
<td>0.01387</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Table 5.5: EIS data for microelectrodes measured in a Micro-setup.

<table>
<thead>
<tr>
<th>LSR [Ωm]</th>
<th>C/A [Fm⁻²]</th>
</tr>
</thead>
<tbody>
<tr>
<td>2078.77185</td>
<td>0.75774</td>
</tr>
<tr>
<td>7476.21127</td>
<td>0.89505</td>
</tr>
<tr>
<td>8833.12435</td>
<td>3.77568</td>
</tr>
<tr>
<td>9747.54865</td>
<td>3.57304</td>
</tr>
<tr>
<td>6587.74872</td>
<td>3.55285</td>
</tr>
<tr>
<td>Ø 6944.68</td>
<td>2.511</td>
</tr>
<tr>
<td>s 2979.48</td>
<td>1.541</td>
</tr>
</tbody>
</table>