A new approach for the identification of reaction mechanisms at SOFC electrodes is used in this paper for the anodic SOFC system Ni, H$_2$-H$_2$O/YSZ. The approach is based on a combination of modeling, simulations, and experiments. Initial results on each part of the approach will be presented: The electrochemical model is derived from surface science literature and the relevant SOFC literature concerned with the kinetics of the anode. The model considers two desorption pathways for water from the triple phase boundary (tpb). The model is implemented into the computer and is the source for the simulations. A first simulated electrochemical impedance spectra (EIS) is shown. Experimental data are obtained from Ni pattern electrodes with tpb lengths varying by three orders of magnitude (0.4 - 4 m/cm$^2$). Experimental impedance spectra are measured as a function of the tpb length and of the overpotential. The match of the simulated and the experimental impedance spectra is satisfactory for a first approach and can be compared to literature data.

**INTRODUCTION**

The state-of-the-art Solid Oxide Fuel Cell (SOFC) anode is Ni-YSZ cermet. This material has been considered in many studies in the past with the aim to increase the performance of SOFCs. However, the losses at the anode are still a considerable part of the total losses in SOFC systems, especially at intermediate temperatures (500-800°C). It is therefore desirable to improve the understanding of the anodic processes. This demands a thorough understanding of the reaction mechanisms which are not well known so far.

Kinetic studies on SOFC anodes are mostly based on the interpretation of experimental impedance measurements of Ni-YSZ cerments (1,2). The electrochemical impedance spectra (EIS) are usually discussed in terms of equivalent circuits which give only little information about the electrochemical system and the reaction steps. In addition, Ni-YSZ cermet anodes are very complicated due to the three interpenetrating networks of Ni, YSZ, and the porosity with unspecified triple phase boundary (tpb) length. Only few studies have so far been concerned with simplified anodic systems with well-defined tpb length, like Ni pattern electrodes (3,4,5) or Ni point electrodes (6).
The following reaction mechanisms for SOFC anodes are proposed in literature: Mogensen et al. (1,2) postulate for Ni-YSZ cermet electrodes that hydrogen might exist on the surface of Ni and YSZ as well as in the bulk. The formation of interstitial hydrogen as well as the formation of water are supposed to be rate limiting. Impedance analyses would result in two impedance arcs in the Nyquist plot. Mizusaki et al. (2,3,4) suggest for Ni pattern electrodes that oxygen is removed from the electrolyte to the Ni surface where it reacts directly with the hydrogen from the gas atmosphere as rate limiting step. Water is formed on the Ni surface and desorbs into the gas atmosphere. Water might also be formed from two adsorbed hydrogen and oxygen from the electrolyte. This reaction mechanism accounts for a single arc in impedance measurements only. De Boer (5) postulates for Ni pattern electrodes a reaction mechanism with dissociative adsorption of hydrogen and the formation of hydroxyl from adsorbed hydrogen and oxygen from the electrolyte. The hydroxyl is formed in the bulk of the electrolyte and is then adsorbed on the surface where it reacts with adsorbed hydrogen to water. As alternative path the immediate formation of hydroxyl on the surface of the electrolyte from adsorbed hydrogen and oxygen is suggested. Three semicircles were found by EIS. Jiang (7) studied porous Ni layers prepared from NiO paste. The surface diffusion of hydrogen is supposed to be rate determining in dry fuel gas measurements. In wet fuel gas, it is proposed that both Ni and YSZ surfaces contribute to the reaction. The surface diffusion of hydrogen is not rate limiting anymore, as fast spill-over processes may take place in fuel gas saturated with water.

Even though several possible reaction mechanisms are discussed in literature, all experimental findings cannot be explained conclusively so far and it is still difficult to interpret the experimental EIS data. We are therefore following a new approach which correlates directly the chemical and the electrochemical reactions with the impedance spectra. In this paper, we will describe this approach shortly and we will focus on the initial results concerning modeling, simulation, and experiments. The study is exclusively based on the Ni, H₂-H₂O | YSZ system.

APPROACH AND THEORY

Our approach for the identification of the reaction mechanisms at SOFC electrodes combines modeling, simulations, and experiments (Figure 1). The approach was already successfully used for the Pt, O₂ | YSZ system (8,9) and is described in detail in (8,9,10). A summary of the approach is given in the following paragraphs.
From surface science literature, we extract data to predict the main reaction steps that might take place at the tpb between electrode, electrolyte, and gas phase. The main problem here is to find reliable data for conditions similar to those used in SOFC application, i.e. atmospheric pressure and high temperatures of about 700°C. The surface science literature is also a source for kinetic data such as reaction rate constants of the electrochemical reactions and surface coverage of the adsorbed species, as well as sticking, adsorption, desorption, and surface diffusion coefficients.

Using the information from surface science literature, first an electrochemical model for the reaction mechanisms is established. It consists of chemical and electrochemical equations, such as

\[ A + B \overset{k_i}{\rightarrow} C + D \]  

where \( A, B, C, \) and \( D \) are gas phase elements, surface species, adsorption sites, or electrons, respectively; \( k_i \) and \( k_f \) are the reaction rate constants for the forward and the backward reaction, respectively.

The equations of the electrochemical model are formulated as mass and charge balances. This representation of the model is identified with the well-known state-space model.
which is often used in control theory for computer simulations of complicated systems characterized by a set of coupled differential equations.

\[
\begin{align*}
\dot{x}(t, p) &= \frac{dx(t, p)}{dt} = f[x(t, p), u(t), t, p] \\
y(t, p) &= g[x(t, p), p]
\end{align*}
\]

where \( x(t, p) \) represents the vector of the state-variables depending on the time \( t \) and the vector of unknown parameters \( p \); the vector \( u(t) \) signifies the input variables that can be varied during the experiment and \( y(t, p) \) denotes the observation function.

The variables in the general state-space model (Eq. 2 and 3) can be directly interpreted in terms of the chemical and electrochemical variables used in the electrochemical model: The vector of state-variables \( x(t, p) \) represents the surface concentrations of the different species adsorbed on the electrode surface. The concentration of the adsorbed species is a function of the time \( t \) and the vector of unknown parameters \( p \), i.e. the reaction rate constants. The vector \( u(t) \) represents the overpotential \( \eta \). The observation function, i.e. the model output, \( y(t, p) \) can be identified as the Faraday current \( I_F \).

After the state-space model is implemented into the computer and the simulation algorithm is programmed, the kinetic parameters which are only roughly known from literature, are determined by an optimization step using an experimental EIS measurement under standard conditions. The derived kinetic parameters are then kept constant and are used for simulations of impedance spectra as a function of the partial pressure, the temperature, the overpotential, and the tpb length. Experimental impedance spectra are measured under the same conditions as the simulations are done. The obtained impedance data consist of the electrochemical contribution \( Z_f \) as well as of a contribution from the electrolyte and the double layer capacitance. The simulated impedance contains only the information from the electrochemistry. This means that the experimental EIS data has to be reduced to the Faraday impedance; \( Z_{F, \text{exp}} \) and \( Z_{F, \text{sim}} \) can then be compared. If the simulated and the experimental results behave in a similar way, the assumed electrochemical model might describe the kinetics of the system sufficiently. If major differences are identified, a modified electrochemical model has to be established and one has to restart with the optimization and the simulation procedure.

**EXPERIMENTAL**

For the simulations, we have chosen MATLAB 5.2.0 and its graphical programming extension SIMULINK 2.2. as software tools. In SIMULINK, the dynamic system is represented in block diagrams which can be formulated in subsystems so that large systems can be built.

For the experimental part of the study, Ni anodes were prepared on single crystalline substrates of 9.5 mol\% Y_2O_3-stabilized ZrO_2 (25 mm in diameter, 0.5 mm thick, (001) orientation, polished on both sides) (Zirmat Corp., Westford, MA, USA). A dense, metallic Ni layer (1μm thick) was first deposited on the whole surface of the substrate by magnetron sputtering (Sulzer, Winterthur, CH). Three Ni anodes with tpb lengths varying by three orders of magnitude from 0.04 to 4 m/cm^2 were then fabricated by
photolithography (Table 1). The ideal tpb lengths are calculated from the pattern designed
on the photolithography mask. However, due to defects in the sputtered layer, the ideal
values have to be corrected individually for each electrode using light microscope
pictures (corrected tpb lengths). Anode 1 consists of a 1 cm² Ni square area of 1 μm
thickness. Two steps were necessary for the fabrication of Anodes 2 and 3: First, a 1 cm²
square electrode was produced. In a second step, the line pattern with equidistant line
spacing was etched in the 1 cm² anode structure. For all structures, the photoresist
(S1813, Shipley, Kempraten-Rapperswil, CH) was spin-coated with a rotation speed of
4000 rotations/s for 45 s (thickness about 1.3 μm) and was exposed using a halogen lamp
for 15 s. The photoresist was developed for about 15 s and the pattern was etched for
about 45-60 s in diluted nitric acid (1:19 = 65% nitric acid:deionized water). The
cathodes were prepared by DC-sputtering 30 nm Pt on the single crystalline substrate
(model SCD 040, Baltec, Balzers, FL). The cathode was placed symmetrically to the
anode and was not patterned.

The anodes and reference anodes were connected with Au wire (99.99%, 0.3 mm in
diameter), Au gauze (52 mesh, woven from 0.102 mm), and Au paste (type C5754B,
Heraeus GmbH, Hanau, D). The cathodes were connected with a Pt wire (0.35 mm in
diameter), Pt gauze (52 mesh, woven from 0.1 mm), and Pt paste (type C3605P, Heraeus
GmbH, Hanau, D) on the whole 1 cm² surface of the cathode. All precious metals were
obtained from Johnson Matthey & Brandenberger AG, Zürich, CH. The wires and gauzes
were fixed to the electrolyte with a ceramic two-component binder (type 1500, Firag,
Ebmatingen, CH).

The electrochemical measurements were conducted in a single gas-chamber set-up in an
alumina tube in H₂-N₂ atmosphere (H₂:N₂ = 1:3, total gas flow = 40 ml/min). The fuel
cells were heated to 973 K with a heating rate of 1 K/min. The electrochemical
measurements were done with an impedance bridge from IM6 Zahner, Kronach, D, in a
three electrode, four lead configuration. The frequency was varied between 100 mHz and
100 kH, the excitation voltage was fixed at 10 mV, and overpotentials between 0 mV and
200 mV were applied. Electrode microstructures were investigated using a light
microscope (Polyvar Met, Reichert-Jung, D) and a scanning electron microscope (SEM)
(JSM 6400, Jeol, Eching, D) before and after photolithography as well as after the
electrochemical measurements.

Table 1: Pattern Ni Anodes for Electrochemical Impedance Spectroscopy (EIS).

| Sample   | Design          | Line Width [μm] | Ni Coverage [cm²] | Ideal tpb Length [m/cm²] | Corrected tpb Length [m/cm²] |
|----------|----------------|-----------------|-------------------|--------------------------|-------------------------------|
| Anode 1  | square electrode| -               | -                 | 0.04                     | 0.04                          |
| Anode 2  | pattern electrode| 200             | 200               | 0.368                    | 0.422                         |
| Anode 3  | pattern electrode| 20              | 20                | 3.648                    | 3.998                         |

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RESULTS AND DISCUSSION

The Electrochemical Model

The first electrochemical model is derived from surface science literature dealing with the Ni, H₂-H₂O | YSZ system (11,12,13). However, as most of the data is valid for this system at low temperatures (about 300 K), the proposed reaction steps and electrochemical constants can only be taken as a first hint. At higher temperatures (500-800°C), some information about the system can be obtained from studies on Pt catalysts (14,15) as well as from SOFC literature reporting about reaction kinetics (1-7). Taking all this information into account, we are able to propose a model consisting of the following reaction steps:

Dissociative adsorption of hydrogen:

\[ \text{H}_2(g) + 2\text{ad} \leftrightarrow 2\text{Had} \]  \[4\]

Removal of oxygen from the electrolyte:

\[ O^e + \text{ad} \leftrightarrow \text{O}_d + V^e + e^- \]  \[5\]

Formation of hydroxyl:

\[ \text{O}_d + \text{Had} \leftrightarrow \text{OH}_d + \text{ad} \]  \[6\]

Dissociative adsorption of water/recombination of hydroxyl:

\[ \text{H}_2\text{O}(g) + \text{O}_d + \text{ad} + e^- \leftrightarrow 2\text{OH}_d + \text{ad} \]  \[7a\]

\[ \text{H}_2\text{O}(g) + 2\text{ad} + e^- \leftrightarrow \text{OH}_d^e + \text{H}_d \]  \[7b\]

where \( \text{ad} \) signifies free adsorption sites. We assume that hydrogen preferentially adsorbs on the Ni surface, whereas oxygen is adsorbed on Ni as well as on YSZ. In contrast to reaction mechanisms described in SOFC literature, we suggest two pathways for the desorption of water (Eq. 7a and 7b). In addition to the discussed chemical and electrochemical reactions, this model is based on the following assumptions:

a) Hydrogen, oxygen, and hydroxyl are considered as time depending surface species in the dynamic system.

b) Water is assumed to adsorb and to desorb from the Ni surface without any time-dependence.

c) The removal of oxygen from the YSZ electrolyte is the only charge transfer reaction.

d) Gas phase diffusion as well as surface diffusion is not included into this first model.

e) The electrochemical reactions take place at the tpb between Ni, YSZ, and gas phase; no bulk diffusion in Ni and YSZ is considered.

Simulation Results

The transformation of the electrochemical model into state-space form as well as the linearization, the transfer function calculation, and the impedance calculation are done similarly as described in (8,9). Electrochemical impedance spectra based directly on the chemical and electrochemical equations are calculated for a set of kinetic parameters (Figure 2). The impedance plot seems to consist only of one semicircle. However, this is due to the fact that the relaxation times of the single processes are very similar; hence, the single processes are not deconvoluted. The polarization resistance i.e. the low frequency intercept of the impedance spectrum with the real axis, is very high (about 17500 Ωcm²).
Figure 2: Simulated Electrochemical Impedance Spectrum 
\( p(H_2) = 10^4 \text{ Pa}, \ p(H_2O) = 10^3 \text{ Pa}, \ \text{tpb} = 30 \text{ m at Zero Overpotential} \).

**Experimental Results**

**Microstructural characterization:** Ni line pattern on single crystalline YSZ substrates were prepared with line widths of 200, 20, 10, and 5 μm. Figure 3 shows a light microscope picture of a Ni pattern with a line width of 5 μm. The lines are continuous and equidistant. A cross view of the pattern would show that the edges of the lines are perpendicular to the substrate. EDX analysis indicated no Ni on the YSZ single crystal stripes. Both these analyses reveal that no over- or underetching has taken place. However, the edges of the lines are frayed out, as shown in SEM micrographs. If the extra tpb length due to the frayed edges is determined by measuring the real tpb length with a string in at high resolution, an increase in the tpb length of about 40% has to be considered. This value might even drastically increase, if the edges of the stripes show a fractal structure meaning that at even higher resolution down to the atomic level the edges are frayed out in another order of magnitude. However, as the edges of all samples are prepared in the same way, this effect would be common to all samples in the same manner.

Microstructure analysis of the samples after thermal treatment and after the electrochemical measurements at 973 K shows no destructive coagulation or coarsening of the Ni stripes. Only on the surface of the Ni layers small coagulated spheres of Ni are observed. The Ni stripes itself are not damaged, as long as the electrodes are not exposed to overpotentials of much more than 200 mV.
Electrochemical characterization: Figure 4 shows the Nyquist plots of the three anodes with tpb lengths between 0.04 and 3.998 m/cm² measured at zero overpotential. The electrode resistance is the highest for the anode with the smallest tpb length (Anode 1, \( l_{tpb} = 0.04 \) m/cm²) and the lowest for the anode with the largest tpb length (Anode 3, \( l_{tpb} = 3.998 \) m/cm²). The Bode representation of the data would show more distinct that the spectra are composed of at least two semicircles. A similar result was found by de Boer (5), whereas Mizusaki et al. (3,4) described only one semicircle.

The three impedance spectra were fitted with the equivalent circuit based on a general model which was already used for other electrodes (8,9,16) (Figure 5). The whole electrochemistry is included in the box \( Z_f \) which consists in this model of three R-CPE units and the charge transfer resistance \( R_t \). As this equivalent circuit fitted well to the
measured data, it should represent the electrode behavior appropriately. It is found that $R_e$ and $R_t$ are not much influenced by a variation of the tpb length. However, $C_{dl}$ decreases significantly for long tpb lengths most probable due to scattering effects at the edges of the Ni stripes. Concerning the three R-CPE units, it is found that one resistance ($R_1$) decreases drastically with increasing tpb length, whereas the other two resistances ($R_2$, $R_3$) do not change significantly. One of the three processes represented by the three R-CPE units, i.e. $R_3$ - CPE$_3$, is very fast, whereas the other two processes, $R_1$ - CPE$_1$ and $R_2$ - CPE$_2$, are slower, but in the same frequency range.

![Figure 5: Scheme of the Equivalent Circuit Used for Fitting the Electrochemical Impedance Spectra of Anode 1, Anode 2, and Anode 3.](image)

Although the impedance spectra can be analyzed using equivalent circuits, it is not possible to interpret the R-CPE units in a physical way. We therefore calculate the Faraday impedance $Z_f$ by subtracting $R_e$ and $C_{dl}$ and can then be compare the simulated and the experimental impedances. It is found that the shape of the spectra is not changed significantly in case of Anode 2 and 3; however, the frequency behavior of Anode 1 was shifted.

The polarization resistances $R_p$ for the anodes with different tpb lengths are shown as a function of the overpotentials in Figure 6. It is found that the polarization resistance decreases with increasing overpotential as well as with increasing tpb length (from Anode 1 to Anode 3). Also, the saturation of the fuel gas with water (3% water) decreases the polarization resistance. The relation between $R_p$ and the overpotential is the same for all tpb lengths and fuel gas compositions (dry and wet fuel gas):

$$R_p = a \cdot e^{-m\eta}$$

where $m = (4.01 \pm 7.16) V^{-1}$ and $a$ is a characteristic constant for each curve.
CONCLUSIONS

The approach for the identification of the reaction mechanisms at SOFC electrodes was briefly described and initial results of each part of the approach were shown: The electrochemical model was derived from literature. Two pathways for the formation of water are proposed to take place. This was so far not considered in SOFC literature concerned with the reaction mechanisms at the anode. The model is based on many assumptions due to the complexity of the simulations. However, even though a simplified model is used, it is possible to simulate an impedance spectrum directly from the chemical and electrochemical equations. Concerning the experimental part, it is shown that Ni pattern electrodes with line widths down to 5 μm are continuous and stable with no significant coagulation and coarsening due to thermal treatment or electrochemical measurement. The increase in tpb length as well as the saturation of the fuel gas with water decreases the total electrode resistance. A deconvolution of the single contribution to the whole impedance can be done with equivalent circuit fits. However, the physical interpretation of the single elements is only partly possible. The elements $R_{p}$, $R_{s}$, and $C_{dl}$ can be identified in a physical sense, whereas the physical meaning of the $R - CPE$ units is not clear. Comparing simulations and experiments, it is found that the polarization resistance is much higher for the simulated data. The frequency behavior is similar to the frequency regime of the experimental impedance spectra. These results are very promising concerning the feasibility of the new approach.

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Figure 6: The Polarization Resistance $R_p$ as a Function of the Overpotential for the Three Anodes with Dry and Wet (i.e. 3% Water) Fuel Gas (slope = $(4.01 \pm 7.16)$ 1/V).
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