FROM MODEL ANODES TO CERMET ANODES

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ABSTRACT

The electrochemical performance of different types of Ni-based SOFC anodes was studied. Model anodes made of a Ni gauze, of a Ni pattern, and of a Ni paste were compared with Ni-YSZ cermet anodes with three dimensionally connected Ni and YSZ phases. The Ni-YSZ anodes were deposited by screen-printing and by sputtering. Due to the different designs as well as due to the different ratios of Ni and YSZ, the anodes differ mainly in the extension of the electrochemically active reaction zone, i.e. the triple phase boundary (TPB) length. According to electrochemical impedance spectroscopy (EIS) measurements, two dispersions were found for most anode designs. The main impedance arc arises at two different relaxation frequencies depending on the anode design. In both cases, it decreases exponentially under anodic polarization and is thermally activated with an activation energy of 1 eV. The second impedance arc arises only under high anodic polarization. The impedance increases with increasing polarization and the activation energy is around 0.5 eV.

INTRODUCTION

State-of-the-art solid oxide fuel cell (SOFC) anodes consist of a Ni-YSZ cermet (1-5). While Ni plays the role of the catalytically active as well as of the electronically conducting phase, the YSZ is added in order to support the Ni particles, to inhibit coarsening of the Ni, and to provide a thermal expansion coefficient which is similar to that of the zirconia based electrolyte. Whether the YSZ itself influences the anode kinetics, is not exactly known, since the electrochemistry of SOFC anodes is not yet clearly understood (1,6-10). Electrochemical investigations of SOFC anodes from different research groups are inconsistent concerning the number of dispersion processes, their activation energies, as well as the rate limiting reaction steps (8,11-17). The disagreement is obvious, since the results from different research groups are based on rather different experimental conditions. In order to circumvent this problem, Brown et al. recently studied different
anode microstructures under the same experimental conditions [18]. One dominant arc was found for four different anode microstructures. While the anode thickness, the partial pressures of hydrogen and of water as well as the temperature were studied in detail, no polarization data was published.

In recent studies, we focused on the investigation of the reaction mechanisms of simplified model anodes, i.e. Ni pattern anodes (19,20). We found that these anodes are dominated by one main impedance arc under a wide range of experimental conditions. The aim of this paper is now to draw the line from these model anodes to the Ni-YSZ cermet anodes which are used in state-of-the-art systems. The anodes under investigation differ in terms of the materials selection (metallic Ni anodes and Ni-YSZ cermet anodes) and in terms of the preparation technique (sputtering, painting, screen-printing). The overpotential applied between the anode and the reference anode as well as the temperature were the main experimental parameters. The primary focus was attributed to the understanding of the electrochemistry of these anodes. It was studied whether similar effects can be observed for the different anodes so that general tendencies for the reaction mechanisms at SOFC anodes can be drawn from the results.

**EXPERIMENTAL**

All anodes prepared in this study have an area of 1 cm² and were prepared on a single crystal electrolyte of 9.5 mol% Y₂O₃-stabilized ZrO₂ (25 mm in diameter, 0.5 mm thick, (001) orientation, polished on both sides) (Zirmat Corp., Westford, MA, USA). The reference anodes covering an area of 4 mm² were prepared in parallel to the working anodes. The reference anodes were placed at a distance of 4 mm from the working anode. The geometrical design is described in detail in (20).

The Ni gauze anode consists of a 1 cm² Ni gauze (150 mesh, woven from 0.1 mm Ni wire, Paul GmbH, Metallgewebe und Filterfabrik, Steinau, D) which was fixed with a two component binder (type 1500, Firag, Ebmatingen, CH) between two pieces of single crystalline YSZ. The electrical contact was realized by spot-welding of Pt wires onto the Ni gauze. No paste was used for contacting.

The Ni pattern anode was prepared from a dense, 1 μm thick, metallic Ni film which was deposited on the entire surface of the YSZ electrolyte by DC magnetron sputtering (Sulzer, Winterthur, CH). After deposition, the Ni layer was structured in two steps using the photolithography technique and wet chemical etching. First, a 1 cm² square electrode was etched. In a second step, the line pattern with equidistant lines of Ni and of YSZ with a line width of 20 μm was etched. The Ni pattern anode prepared in this study had a theoretical triple phase boundary (TPB) length of 3.7 m/cm². The anode and the reference anode were connected with Au wire, Au gauze, and Au paste at the edges of the Ni pattern. More detailed information about the preparation and about the design of Ni pattern anodes is given in (20).
The Ni paste anode is assigned to the metallic Ni anodes, even though it contains about 10 wt.% of YSZ. The Ni paste was obtained from S. Primdahl, Risø National Laboratory, Risø, Denmark. The preparation of the Ni paste is in detail described in (11). It was applied with a brush on top of the YSZ single crystal electrolyte. The electrical contact was realized with a Pt gauze pressed onto the wet Ni paste over the entire surface of the anode.

The screen-printed Ni-YSZ anode was prepared as described in (21). A screen-printing mask for a theoretical green film thickness of 50 μm was used. The anode was contacted with a Pt gauze and diluted Ni-YSZ paste over the entire surface of the anode. The anode was sintered at a maximum temperature of 1623 K for 2 h.

The sputtered Ni-YSZ anode was prepared by reactive magnetron sputtering (Sulzer Innotec, Winterthur, CH). After deposition, the anode was electrically contacted with a Pt gauze and Pt paste covering the entire surface of the anode.

The cathodes which were the same for all SOFCs were prepared by DC-sputtering (model SCD 040, Baltec, Balzers, FL) of a 30 nm thick Pt layer on the single crystalline YSZ electrolyte. The cathodes were placed symmetrically to the anode on the opposite side of the single crystal. They were connected with a Pt wire, Pt gauze, and Pt paste on the entire surface area of the cathode.

The electrochemical measurements were carried out in a single gas chamber measurement set-up using an IM6 ZAHNER® Impedance Analyzer, Kronach, D, in a three electrode, four lead configuration. The impedance was measured at anodic overpotentials, \( \eta \), between 0 mV and 400 mV and at temperatures between 673 K and 1173 K. The fuel gas consisted of a mixture of \( \text{H}_2 \) and \( \text{N}_2 \) equal to 1:3 (total gas pressure = 1 atm, total gas flow = 40 ml/min, purity of the gases > 99.5 %). The gas flow was adjusted with manual mass flow controls (Vögtlin Instruments AG, Aesch, CH).

RESULTS AND DISCUSSION

Microstructural Characterization

Due to the different anode designs and due to the different electrode preparation techniques, the anodes consist of rather different microstructures. Whereas the Ni pattern anode and the Ni gauze anode have a well-defined, two dimensional region for the chemical and the electrochemical reactions to take place, the other anodes have a three dimensional microstructure where Ni and YSZ are interconnected in a complicated manner. Hence, the TPB is not exactly known in the case of Ni-YSZ cermet anodes.
The microstructure of the Ni gauze anode is determined by the mesh size of the Ni gauze (Figure 1a). Due to the woven structure of the gauze, the anode touches the electrolyte only at the cross points of two wires. Hence, the Ni gauze anode is, in effect, a point electrode made of multiple single contacts. It does not degrade under the experimental conditions used in this study.

The Ni pattern anode consists of lines of Ni and YSZ with a width of 20 μm and a height of 1 μm (Figure 1b). This results in a TPB length of 3.7 m/cm². Due to the anode design, the fuel gas is in direct contact with the electrochemically active area. It is found that the anode microstructure is not destroyed by thermal treatment or by electrochemical measurements.

The Ni paste anode is 40 μm - 60 μm thick and has a porous microstructure (Figure 1c). The Ni paste anode is well adherent to the electrolyte even after thermal treatment and after the electrochemical measurements. According to Energy Dispersive X-ray (EDX) analyses, it consists mainly of Ni with very fine dispersed zirconia located on top of the Ni grains.

The screen-printed Ni-YSZ anode is porous as well (Figure 1d). The microstructure seems to be finer structured than the one of the Ni paste anode. The Ni and the YSZ grains could not be distinguished by EDX analyses. The average thickness of the anode layer is 10 μm to 30 μm. The anode is well adherent to the YSZ electrolyte. No degradation due to thermal treatment or due to electrochemical measurements was found according to SEM analyses.

The sputtered Ni-YSZ anode is as-prepared 1 μm thick. During thermal treatment under reducing atmosphere, it degrades considerably so that distinct islands of Ni are formed. Hence, the electrical contact between the Ni islands is only realized by the Pt current collector. No close contact between the Pt gauze and the Pt paste on the one side and the Ni islands on the other side was found. The Pt gauze could be easily detached with the Pt paste from the Ni anode. According to EDX analysis, the Pt paste created no residue on the anode surface. A comparison to a separately prepared sample allows the conclusion that the contacting as well as the electrochemical measurements have not deteriorated the microstructure of the anode.
Figure 1: Scanning electron micrographs of Ni-based anodes (top view): a) Ni gauze anode, b) Ni pattern anode (20 μm line width), c) Ni paste anode, d) screen-printed Ni-YSZ anode.

Electrochemical Characterization

A summary of the main EIS results obtained at 973 K is given in Table 1. It is found that the all anodes considered in this study are dominated by one main impedance arc ($\omega_1$ and $\omega_2$, respectively). This result is in agreement with the findings in (18). We have found that a second arc develops at high anodic overpotentials in the low frequency domain ($\omega_3$). This low frequency impedance arc increases the higher the overpotential which is applied between the working and the reference anode. The main impedance arc, in contrast, decreases strongly the higher the overpotential.
Table 1: Comparison of different anode designs concerning their electrochemical behavior characterized by EIS.

| Anode design       | # of arcs at 0 mV | # of arcs at 200 mV | R_p at 0 mV [Ω] | ø₁ at 0 mV [Hz] | ø₂ at 0 mV [Hz] | ø₀ at 0 mV [Hz] | ø₀ slope | Warburg diffusion | Inductive behavior |
|---------------------|-------------------|---------------------|-----------------|----------------|----------------|----------------|---------|-------------------|-------------------|
| Ni pattern          | 1                 | 1                   | 400             | 14             | 0.5            | -              | -       | no                | no                |
| Ni gauze            | 2                 | 2                   | >1k             | -              | -              | -              | -       | yes               | -                 |
| Ni paste            | 1                 | 2                   | 7               | -              | -              | 5750           | 170     | <10               | -0.01             | yes yes           |
| Screen-printed Ni-YSZ | 1-2             | 1-2                 | 5               | -              | -              | 6350           | 135     | possible          | yes               |
| Sputtered Ni-YSZ    | 2                 | 2                   | 5               | -              | -              | 400            | 2       | 20                | -0.003            | no yes            |

The polarization resistances, R_p, are not only listed in Table 1 but are also illustrated in Figure 2 as a function of the overpotential. The Ni pattern anode has the highest R_p of all anodes. Note that the R_p of the Ni gauze anode could not be determined exactly from the impedance spectra, since the impedance arc was not closed under the experimental conditions used for the EIS measurements. However, a rather high R_p would result when the data will be extrapolated (R_p > 1000 Ω). The screen-printed, the sputtered, and the paste anode have all very similar polarization resistances. According to Table 1, it can be concluded that the polarization resistance is directly related to the TPB length of the anode: the Ni pattern and the Ni gauze anode have a high R_p and a low TPB length, the Ni paste and the screen-printed Ni-YSZ cermet anode have a low R_p and a high TPB length. The R_p of the main impedance arcs of all anodes depend exponentially on the overpotential (slopes in Figure 2, closed symbols). If the low frequency impedance arc which arises only under high overpotential is included, the total electrode impedance increases (open symbols in Figure 2).
Figure 2: Polarization resistance, $R_p$, as a function of the overpotential, $\eta$. Closed symbols: high frequency impedance arc, open symbols: total anode impedance ($T = 973$ K, total gas flow = 40 ml/min, $p(\text{H}_2) = 10^4$ Pa, $p(\text{H}_2\text{O}) = 5 \times 10^3$ Pa, $10^3$ Hz < $\omega$ < $10^4$ Hz).

The relaxation frequency is defined as the frequency with the maximum imaginary part of the impedance. The relaxation frequencies of the different anodes are characterized in Table 1 in form of their absolute values at $\eta = 0$ mV and in form of the slopes determined from the $\omega$ vs. $\eta$ diagrams. Even though two main arcs were found in the impedance spectra, three groups were defined for the relaxation frequencies in Table 1: the processes symbolized by $\omega_1$ and $\omega_2$ behave rather similar as a function of the overpotential and as a function of the temperature, while the relaxation frequencies are rather different. Hence, two different processes might be responsible for the main impedance arcs of the different anodes. The so-called low frequency impedance arc ($\omega_3$) has a very similar relaxation frequency as $\omega_1$. The relaxation frequency decreases with increasing overpotential (small negative slope). This result indicates that the two impedance arcs which are characterized by $\omega_1$ and $\omega_3$ should belong to two different effects, even though their relaxation frequencies are rather similar.

Concerning diffusion effects, very close relations between the appearance of a 45° tangent to the high frequency data and the microstructure are found: for the Ni pattern anode as well as for the sputtered Ni-YSZ anode, no 45° tangents were observed. Hence, diffusion should not be limiting. The Ni gauze anode owes most probably the Warburg behavior to the diffusion barrier in form of the YSZ cover on the anode which is necessary to ensure a
suitable contact of the Ni gauze onto the electrolyte. The Ni paste and the screen-printed Ni-YSZ anodes have both a porous microstructure. The fuel gas seems to be hindered in reaching the reaction zone and the water seems to be hindered in leaving the reaction zone. Both cells might be limited by diffusion.

With regard to the inductive behavior which was found for several anodes, it should be noted that an inductive behavior was never found for a Ni pattern anode (20), whereas it is always found for anodes with low electrode impedance. In the literature, low frequency inductive loops are also found for different types of SOFC electrodes (22-26). However, so far, the nature of the inductivities is not well understood and only some rough explanations exist. For instance, in (23), the inductive behavior in the low frequency region is attributed to intermediate adsorbates. In (24), the adsorption of several species at the same site seems to be responsible for the inductive loops. It is also suggested that electronic defects in the electrolyte or partial reduction of the electrolyte or the electrode at the counter electrode interface contribute to inductivities in the low frequency region (25). According to (26), the inductive behavior is caused by a bad cathode performance.

The temperature dependence of the different anodes yielded in the following results:
- In the case of the porous Ni anodes, i.e. the Ni paste and the screen-printed Ni-YSZ anodes, the impedance spectra change from two distinct arcs at low temperature \((T = 773 \text{ K})\) to only one impedance arc at high temperature \((T = 1173 \text{ K})\). In contrast to this, the impedance spectra of the Ni pattern anode consist always of one arc which merely becomes depressed at higher temperature.
- The relaxation frequencies of the main impedance arcs \((\omega_1, \omega_2)\) increase with increasing temperature.
- The activation energy for the main impedance arcs \((\omega_1, \omega_2)\) is around 1 eV, whereas the activation energy for the low frequency impedance arc \((\omega_3)\) is around 0.5 eV.

**CONCLUSIONS**

The study of the different anode designs in this paper starting from multiple-point Ni anodes, i.e. Ni gauze anode, to three dimensionally connected Ni-YSZ cermet anodes turned out to be a suitable way to investigate the electrochemistry of SOFC anodes. It is found that Ni-YSZ based anodes are dominated by two impedance arcs. The main impedance arcs decreased exponentially with increasing overpotential and were thermally activated with an activation energy around 1 eV. Considering also more detailed studies on Ni pattern anodes (19,20,27), the main process \((\omega_1)\) can most probably be attributed to the adsorption / desorption of hydrogen or the removal of oxygen from the electrolyte. The process characterized by \(\omega_2\) could be related to a diffusion effect. The low frequency impedance arc \((\omega_3)\) might be related to the desorption of water, since the impedance increases with increasing overpotential and since the activation energy is rather low with only 0.5 eV.
Depending on the microstructures of the anodes, diffusion and inductive effects were observed in the impedance spectra. The TPB length is a very important parameter which determines the performance of the anodes.

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