IMPROVED INITIAL STABILITY OF SOFC ANODE BY MICROSTRUCTURAL OPTIMIZATION

R. Wilkenhöner¹, Th. Kloidt², W. Malléner¹

Forschungszentrum Jülich GmbH, D-52425 Jülich, Germany
¹ Institut für Werkstoffe der Energietechnik
² Institut für Energieverfahrenstechnik

ABSTRACT

Previous SOFC anodes manufactured by Wet Powder Spraying showed a rapid degradation of their electrochemical performance due to the coarsening of nickel particles. By improved powder preparation anodes were realized with an increased electrochemical performance and a decreased initial overpotential degradation of about 2% in the first 300 hours at 0.2 A/cm² (950°C). In this paper results of microstructural observations and electrochemical tests for both types of anodes are presented.

INTRODUCTION

One of the major problems in the operation of Solid Oxide Fuel Cells (SOFC) as current generators is the deterioration of their performance in time. The deterioration may result from structural changes in the components or chemical interactions between the SOFC materials. Degradation of the anode due to structural changes, which leads to an increase of its resistivity, gives a substantial contribution to such deterioration.

There may be different reasons for the anode’s degradation. This work is focused on strong degradation in the first stage under electrochemical working conditions. Such strong initial degradation occurred in previous SOFC anodes manufactured by the Wet Powder Spraying process. To understand and avoid this degradation, structural investigations were performed and correlated to the results of electrochemical tests. The results were used to develop improved anodes.
EXPERIMENTAL

The SOFC anodes were manufactured by Wet Powder Spraying. This coating process has been successfully applied for several applications, e.g. manufacturing of SOFC cathodes (1). First a suspension of the initial powder, a binder and a solvent for the binder - generally water or ethanol - has to be mixed and homogenized. If a powder with less than 1 μm particle size is used as for these SOFC anodes, the powder has to be deagglomerated and stabilized to avoid reagglomeration in the spray suspension. Otherwise the required fine and homogeneous anode microstructure can not be realized. For that purpose the spray suspension consisting of the powder, the solvent and a suitable dispersant, which also acts as binder for the ‘green’ coating, were milled for at least 24 hours in a ball mill with 3 YSZ-balls (3 mol% Yttria Stabilized Zirconia). We used a high molecular weight polyelectrolyte as dispersant, which stabilizes the powder particles sterically and also electrostatically in hydrous solvents due to their dissociation. The suspension is sprayed on the substrate by means of a paint gun. Part of the carrier evaporates during the spraying process. Due to the remaining carrier present, the viscosity of the suspension remains low for a sufficient period of time so that local variations in the layer thickness can be compensated. After complete drying binder bridges are formed between the particles and towards the substrate ensuring sufficient green strength. Removal of the binder and sintering for consolidation of the layers may be performed in one step. Because of the higher viscosity and density of the powder suspensions compared to paints, the spray gun had to be modified so that the spray jet can be varied and reproducibly adjusted for each powder suspension. A computer-controlled X-Y system was installed to guide the gun during spraying ensuring high reproducibility. The required coating area is achieved by masks covering the uncoated areas of the substrate. Layer thickness can be varied by the spray parameters, and by superposing several layers. The minimum thickness depends on the powder particle size.

As initial powders for the anode mixtures of NiO (Nickel (II) Oxide green, J.T. Baker Inc., U.S.A.) and 8YSZ-powder (8 mol% Yttria Stabilized Zirconia, TZ-8Y, TOSOH Corporation, Japan) were used. The NiO was reduced to Ni in the fuel atmosphere during heating up to the SOFC’s working temperature. Different kinds of anodes have been manufactured, see Table 1 on the next page. For the anodes of type Ila and Ilib a finer powder particle size in the suspension was realized by a longer milling time (I24h, Ila and Ilib 48h) and a higher ball-to-powder ratio (10.4:1, Ila and Ilib 3:1). If only fine agglomerated 8YSZ-powder as received (d50=0.22 μm) is used, layers with more than 10 μm in thickness cannot be manufactured in one sintering step without cracks. Hence half the 8YSZ-amount in anode Ila was pre-calcined at 1300°C for 2h, so that a crack-free layer of about 40 μm thickness could be realized in one sintering step. Anode Ilib consisted of two different layers: The bottom layer was manufactured using only 8YSZ-powder as received, the top layer was manufactured like anode Ila. 8YSZ-foils fabricated
Table 1 Manufacturing characteristics for different kinds of anodes

| Type          | Composition [wt.%] | Particle Size * [μm] | Layer thickness [μm] |
|---------------|--------------------|----------------------|---------------------|
| I             | 65.5% NiO 34.5% YSZ | ≈ 1                  | 50                  |
| Ila           | 56% NiO 22% YSZ as received | 0.3                 | 32 - 40             |
|               | 22% YSZ pre-calcined | 0.22                |                     |
| IIb first layer | 56% NiO 44% YSZ as received | 0.3                 | 10                  |
|               | see type Ila       | 0.22                |                     |
| IIb second layer | see type IIa       |                      | 22 - 30             |

* after deagglomeration by milling of the spray suspension

by tape casting with a thickness between 150 and 400 μm were used as substrate for all kinds of anodes.

The microstructure of the anodes was evaluated by applying the line intersection method on photographs obtained by light-optical microscopy. For this purpose, the intercept lengths of at least 50 particles per phase were averaged for each specimen. The total number of three-phase-boundaries (TPB) [metal/(solid electrolyte)/pore], where the anode reaction takes place, was counted in such micrographs. Therefore micrographs with a sufficient high magnification of at least 2000x were used to increase the measurement accuracy. It is not possible to distinguish between ‘inactive’ and ‘active’ three-phase-boundaries, only the latter being accessible for all reactants (H₂, e⁻, O₂⁻).

A scheme of the experimental set-up for the electrochemical measurements on circular samples with ring-shaped electrodes is shown in Figure 1. The inner and the outer diameter of the electrodes are 4 mm and 12 mm, respectively. The current collectors have been made of platinum mesh. A nickel mesh has been placed between the anode and the current collector to improve the electrical contact. Two platinum points are used as reference electrodes. They are placed in the center of the ring shaped working or counter electrode. The current collectors and the reference electrodes are pressed on the electrodes or electrolyte by spring-loaded alumina tubes. Gold has been used as sealant. The characterization of square samples, 5 x 5 cm² electrolyte and 4 x 4 cm² electrodes, has been carried out in an experimental set-up without reference electrodes. Platinum and nickel mesh have been used as current collectors and gold as sealant. The galvanostatic current voltage measurements and the impedance measurements have been carried out with the apparatus listed in the Table below. The cathodes were manufactured by Wet Powder Spraying as described in (1) or they were made of platinum paste (DEMETRON 308A). The current-overpotential -curves have been calculated by subtracting the ohmic potential drop from the measured potential values. The ohmic potential drop is due to the
resistances of electrolyte and electrical contacts, determined by impedance measurements.

RESULTS AND DISCUSSION

Anodes of type I, sintered at 1300°C and 1400°C, respectively, reach a current density of about 0.3 A/cm² at 100 mV overpotential (1000°C), but a rapid deterioration of this performance occurs already during the first hours of electrochemical testing. In Figure 2 the decrease of the cell potential under a constant current density of 0.1 A/cm² is given for the first hours of electrochemical testing. The ohmic resistances of the electrolyte and the contacts as well as the non-ohmic losses of the Pt-cathode can be regarded as constant, so that the degradation results from an increase of the anodic losses.

The microstructure of type I anodes was examined in the initial state and after a certain time under working conditions at 1000°C. For this study we regarded the state after reduction of the NiO to Ni at 650°C as initial state. Micrographs of anodes in both states are given in Figure 3 and 4. It is clearly visible that the microstructure has coarsened in the first hours of electrochemical characterization. In Table 3 the results of structural evaluations for both anode states are given. The mean diameter of the nickel-particles and the pores has increased by a factor 2, the increase of the 8YSZ diameter is substantially lower. It can be assumed that the reduction of the nickel surface by particle coarsening is the driving force for the observed structural changes. At the SOFC operation temperatures the nickel metal exhibits already rather high plasticity, so that

| anode type | sintering (3h) °C | d_{YSZ} [μm] | d_{Ni} [μm] | d_{Pore} [μm] | Porosity [%] | TPB per area [1/μm²] | TPB per volume [1/μm³] |
|------------|-------------------|--------------|-------------|--------------|-------------|---------------------|------------------------|
| I, reduced at 650°C | 1300 | 5.7 | 1.9 | 3.1 | 49 | 4*10^{-2} | 8*10^{-2} |
| I, measured at 1000°C | 1300 | 7.4 | 3.9 | 6 | 53 | 1.5*10^{-2} | 1.9*10^{-2} |
| change | | +29% | +104% | +95% | | -62% | -76% |
| IIa | 1400 | 1.6 | 1.8 | 1.8 | 41 | 2.8*10^{1} | 1.5*10^{1} |
| IIb (first layer) | 1400 | 1.2 | 1.3 | 1.6 | 39 | | |
sintering of neighboring nickel particles can occur.

The coarsening of the microstructure diminishes the total number of active and inactive three-phase-boundaries (TPB), see Table 3. The number of TPB per area, which was estimated by the cross section analysis of both anode states, is reduced by about a factor 2.6. This corresponds to a reduction in the volume concentration by about a factor 4.5. This reduction must increase the resistance for the anodic reaction, which causes a deterioration of the current-potential-performance. Consequently the deterioration can be correlated with the coarsening of the microstructure.

For the new anodes of type IIA and IIB, the following changes in anode manufacturing were made to reduce the microstructure coarsening:
1) The initial powders were deagglomerated more effectively. For that purpose the milling time and the ball-to-powder ratio was increased.
2) The spray suspensions were stabilized by a suitable dispersant to avoid reagglomeration of the deagglomerated particles in the spray suspensions.
3) The amount of nickel was reduced from 50 vol.% to 40 vol.%, disregarding the porosity.

The micrograph of such a new anode is given in Figure 5. The microstructure is significantly more homogeneous and finer compared to that of type I anodes. The size distribution of the nickel particles and the pores is narrow. This effect is caused by the improved powder preparation. Results of the structural evaluations of type IIA and IIB anodes are also given in Table 3. Due to the lower particle size of the finer deagglomerated powder (Table 1) the microstructure of this anode is significant finer than that of the type I anode. This is correlated with an enhanced total number of three-phase-boundaries TPB: The number of TPB per volume is a factor of 18 higher than in the type I anode after the reduction of NiO. Accordingly, anodes of the types IIA and IIB reach a higher current-overpotential-performance, see Figure 6. The comparison of the structural and electrochemical values of type IIA and IIB anodes shows how the electrochemical activity increases with increasing fineness of the microstructure.

In addition to the improved current-overpotential-performance the stability of the new anode is also improved. For example, the potential of a 5x5 cm² single cell with a type IIA anode, sintered at 1300°C, does not deteriorate in the first 120 hours at 0.25 mA/cm², but improves slightly, see Figure 7. In another galvanostatic test of two type IIA anodes at 950°C and 0.2 A/cm², an averaged overpotential degradation of about 2% for various current densities up to 0.3 A/cm² was observed in the first 300 hours of electrochemical testing.

This improved stability is caused by a fine and continuous 8YSZ-skeleton or framework in the anode, as we assume. This framework limits the space for the growth
of the nickel particles, so that the coarsening of the microstructure is prevented. In fact no clear structural changes as a function of the electrochemical testing were observed. The existence of such 8YSZ-framework could be demonstrated by dissolving the nickel amount of a type IIa anode in HNO₃. Even after the nickel dissolution the remaining amount of 8YSZ built a mechanically stable layer. The pore size distribution of the same anode was measured before and after nickel dissolution by means of standard porosimetry, which is described in (2). The results are given in Figure 8. The mean diameter of the 8YSZ-framework in this anode is about 1 μm.

SUMMARY

In this paper some aspects concerning the correlation between structural and electrochemical properties of SOFC anodes are presented. It was demonstrated that a rapid deterioration of the electrochemical performance, which occurs for the previous anodes of type I, is connected with coarsening of the microstructure, especially coarsening of nickel particles. Additionally, it was shown that the finer and more homogeneous microstructure of the new type II anodes, realized by improved preparation of the initial powder, enables both an improved current-potential-performance and an enhanced initial stability of the electrochemical performance. A fine 8YSZ-framework in the type II anodes, whose existence was demonstrated, limits the place for growth of the nickel particles, which may cause the improved initial stability.

ACKNOWLEDGMENTS

The authors thank Dr. J.M. Volfkovich (A.N. Frumkin Institute of Electrochemistry, Russian Academy of Sciences, Moscow) for the porosity measurements by standard porosimetry and Dr. L.G.J. de Haart (Institut für Energieverfahrenstechnik, Forschungszentrum Jülich GmbH) for critically reading of the manuscript.

REFERENCES

1. R. Wilkenhöner, Th. Hauber, U. Stimming, W. Malléner, H.P. Buchkremer, ‘Cathode Processing by Wet Powder Spraying’, Proc. of the 2nd European SOFC Forum, Oslo, Norway, 6.-10.5.1996, published by Dr. Ulf Bossel, 1996, ISBN 3-922 148-19-0, S. 279-288
2. J.M. Volfkovich et al., Sov. Electrochem., 16, Nr. 11 (1980), S. 1325ff
**Fig. 1** Experimental set-up for the electrochemical measurements on circular samples (schematic)

**Fig. 2** Cell voltage versus measuring time for a pen consisting of the type I anode, an 8YSZ-electrolyte and a Pt-cathode (circular sample)
Fig. 3  Type I anode, sintered at 1300°C/3h, NiO reduced to Ni at 650°C: white Ni, gray 8YSZ, black pores.

Fig. 4  Type I anode, sintered at 1300°C, electrochemical characterized at max. 1000°C for more than 10h: white Ni, gray 8YSZ, black pores.

Fig. 5  Type IIa anode, sintered at 1300°C and electrochemical characterized at 950°C: white Ni, gray 8YSZ, black pores.
Fig. 6 Initial current-overpotential-performance of type IIa and IIb anodes, sintered at 1400°C (circular samples)

Fig. 7 Cell voltage versus measuring time for a pen consisting of the type IIa anode (sintered at 1300°C), a 150 µm thin 8YSZ-electrolyte and the cathode described in (1) (square sample)
Fig. 8  Pore size distribution of a type IIa anode, sintered at 1400°C, before and after Nickel dissolution in HNO₃.