ADVANCES IN THE ANODE SUPPORTED PLANAR SOFC TECHNOLOGY

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ABSTRACT

The anode supported planar SOFC concept, with a 15 μm thin YSZ electrolyte layer has shown excellent performance operating on hydrogen and air at temperatures of 800 °C (0.26 W/cm²) without any noticeable degradation in the first 500 h. These low operating temperatures in combination with the higher value for the thermal expansion coefficient of the anode substrate allow the use of commercially available ferritic steel as metallic interconnect. A new design for the gas manifolding using metallic components was introduced in order to facilitate the assembly process and to reduce the cost of stack manufacturing. Test results from among others a 10-cell stack of 10x10 cm² cells operating on hydrogen and air and a 2-cell stack operating on methane are presented.

INTRODUCTION

Lowering the operating temperature of Solid Oxide Fuel Cells (SOFC) to below 800 °C potentially lowers production costs of a SOFC system because of a less expensive periphery and is able to guarantee sufficient life time of the stack. For SOFCs based on the oxygen-ion conductor yttria stabilized zirconia (YSZ) low temperature operation can only be achieved using thin film electrolyte concepts in order to minimize the ohmic losses in the electrolyte. The anode supported planar SOFC concept has been designed and tested at the Forschungszentrum Jülich (1-3). Thin electrolyte films of 15 to 20 μm are deposited on thick (1 - 2 mm) anode substrates. An additional advantage of the thick anode substrate, which offers sufficient mechanical stability, is the possibility to produce single cells with an effective electrode cross area of several hundred cm². Moreover, the thick anode substrate will allow for the SOFC to operate completely on internal reforming of methane. In the volume of the substrate the reforming process can be physically separated from the electrochemical processes occurring at the interface between anode and electrolyte. The larger part of the substrate can therefore be adapted for the reforming process in order to obtain an optimized balance between reforming and subsequent electrochemical processes.
MATERIALS AND COMPONENTS MANUFACTURING

Materials

In the anode supported planar SOFC concept 'state-of-the-art' materials are used, which are optimized for the planar self-supporting electrolyte concept operated at 950 °C. Up to now the starting powders are high purity materials to avoid uncontrolled chemical reactions and to reach reproducible results during the processing route of the components. Cost aspects are at this stage of development only of secondary importance except for the selection of the new interconnect material, which was done both from the technical specifications as well as from a cost viewpoint. Table I gives an overview of the materials used for each component.

Table I.
Materials and sources for the components used in the anode supported concept.

| component          | material                                           | vendor      |
|--------------------|----------------------------------------------------|-------------|
| (anode) substrate  | Ni (NiO) + 8 mol% Y2O3 stabilized ZrO2 (8YSZ)     | Baker, USA  |
|                    |                                                    | Unitec, UK  |
| anode functional layer | Ni (NiO) + 8 mol% Y2O3 stabilized ZrO2 (8YSZ)     | Baker, USA  |
|                    |                                                    | Tosoh, J    |
| electrolyte        | 8 mol% Y2O3 stabilized ZrO2 (8YSZ)                | Tosoh, J    |
| cathode            | La0.6Sr0.4MnO3 + 8 mol% Y2O3 stabilized ZrO2 (8YSZ) | FZ Jülich, D |
|                    |                                                    | Tosoh, J    |
| interconnect       | X 10 CrAl 18, 1.4742                               | KTN, D      |
| cathode contact layer | LaCoO3                                             | SSC, USA    |
| anode contact layer | Ni-mesh                                             | GKD, D      |

Substrate and anode functional layer

The supporting component of the concept is the Ni-8YSZ substrate with a standard composition of 44 at% Ni. This cermet is manufactured by the Coat Mix® process starting with a powder mixture of NiO and 8YSZ together with a resin binder. A more detailed description of this process is given elsewhere (1). By optimization of the manufacturing route the thickness could be lowered from 2.5 mm to 1.5-2.0 mm for substrates as large as 250x250 mm² preserving sufficient mechanical stability. Most experiments were performed on samples with the dimension of 100x100 mm². After a pre-sintering step at 1285 °C an anode functional layer is deposited by a modified slip
casting process (1) on one side of the substrate. Figure 1 shows a cross-section of the substrate with the additional anode functional layer. The latter is around 3 μm thick and has a much finer microstructure in comparison with the underlying substrate. The larger surface area and longer three phase boundary in the anode functional layer results in an increased performance of the substrate cells as reported previously (3). The anode functional layer, however, has not been optimized yet with respect to its microstructure and layer thickness.

**Electrolyte**

On the highly porous anode functional layer the thin electrolyte layer is applied also using the modified slip casting process. Layers can be deposited with thicknesses ranging from 5 to 50 μm. The particle size distribution and the solid content of the casting suspension were optimized in order to improve the gas tightness of the sintered layer. The better results with regard to gas tightness and cell performance were obtained for layers having a thickness of around 15 - 20 μm. Typical leak rates of these highly dense layers are between $10^{-5}$ and $10^{-4}$ mbar·l·s⁻¹·cm⁻².

**Cathode**

The Wet Powder Spraying® (WPS) process (4,5) is used to deposit a cathode on the sintered electrolyte layer. The cathode consists of a double layer structure with a fine grained 10 μm thick composite layer of 8YSZ and LSM (40 wt% 8YSZ) contacting the electrolyte and a coarser LSM top layer of around 30 μm. Using the WPS® process with a high degree of automation cathode layers with an geometrical area of 240x240 mm² can be manufactured with good reproducibility (4).

**Interconnect**

Measurements of the thermal expansion coefficient (TEC) of several stack components (see Fig. 2) have shown that the TEC of an anode supported cell is higher in comparison to the TEC of an self-supporting electrolyte cell (YSZ sheet). It can be postulated that cost effective planar SOFC stacks require a metallic interconnect (6). For self-supporting electrolyte cells it is difficult to find a metal with matching TEC to YSZ. Only few materials, e.g. a Cr5Fe1Y-ODS-alloy (Plansee, Austria) with high Cr-contents show a matching TEC for these self-supporting electrolyte cells (see Fig. 2). Due to the high Cr-contents the processing of these materials and the manufacturing of components is usually difficult. The anode supported cell has the advantage of a higher TEC. Moreover, the high power densities reached with these thin electrolyte film cells at temperatures below 800 °C (3) allows the use of a ferritic steel as interconnect material. The oxidation rates of heat resistant ferritic steels seem to be sufficiently low at these temperatures. The TEC of the heat resisting steel X10 CrAl 18 (mat.no. 1.4742, base Fe, 18% Cr, 1% Al; KTN, Germany) matches well the TEC of the anode supported cell (see...
Fig. 2). It has been tested successfully in several short-stacks for several hundred hours of operation at 800 °C. Detailed examinations regarding the adaptation of the TEC and the corrosion of ferritic steels in SOFC are published elsewhere (7). Other main advantages of ferritic steels in comparison to the aforementioned Cr-based alloys are the commercial availability in many forms from many vendors at lower prices and the lower costs for processing (standard manufacturing processes as forging, welding, etc.).

STACK INTEGRATION

Sealing and contact layers

For the sealing of the stack a glass ceramic material based on the MgO-Al₂O₃-SiO₂ system is being developed. The glass is free of alkaline metals, i.e. Li, Na, K, because reactions of these elements with the Cr from the metallic interconnect leads to higher degradation rates. The glass ceramic material offers a good matching TEC to YSZ and the formation of strong and gas tight bonds. As is shown schematically in Figure 3 the anode supported concept needs sealing of the side surfaces of the substrate as well. This is realized by dip coating the cells in a slurry made of the glass ceramic. The sealing process, i.e. sintering and crystallisation of the glass ceramic, takes place during the first heating of the completely assembled stack in its test bed at temperatures below 950 °C.

Figure 3 also shows the contact layers necessary for providing the low resistive electrical contacts between the interconnect and the electrodes in the stack. On the fuel side the contact layer is formed by a Ni-mesh which is spot-welded to the interconnect. On the oxidant side a LaCoO₃ paste is applied on the ribs of the interconnect. The reliability of the sealing process has still to be improved, especially the interaction between the sealing and contact layers during the sintering process.

Manifold design, casing of the stack

In the previously reported tests of anode supported stacks (2,3) use was made of a ceramic gas manifold (so-called A-design) from partially stabilized zirconia (PSZ; Friatec, Germany). The lowering of the operating temperature to below 800 °C made a redesign of manifold and casing possible (B-design). Its main requirement was to allow for thermal cycling. For low temperature operation a full metal casing is much more convenient, since a metallic material for the interconnect already existed. In addition the B-design allows also for an easy assembly and fixing of the stack into the test bed. Figure 4 shows the assembly of a stack (first five cells) with the B-design manifold. The stack is placed on a base plate made of steel and fixed through four bars at the edges, which are joined (high temperature brazed) to the base plate. Layers for the necessary electrical insulation and sealing between the metallic parts of the manifold are made of
a glass ceramic, developed for this application. This glass ceramic devitrifies very fast, so that the amount of vitreous phase is minimised after crystallisation and the high temperature electrical insulation capabilities are sufficient. After assembling the stack an end-plate, similar to the base-plate, is fixed on top with excentrical pins. In this way the casing contributes to the mechanical integrity of the stack. The gas chambers are closed by a thin (50 μm) metallic foil (AluChromY (Fe22Cr5Al); Krupp-VDM, Germany), which is fixed by external rings (see Fig. 4).

CELL AND STACK PERFORMANCE

Cells and stacks were tested using humidified hydrogen as fuel gas and dry air as the oxidant. All cells were manufactured including the anode functional layer and the ferritic steel mentioned above was used in all stacks as interconnect. Leads were attached to the interconnect in the stacks, so that the performance of each cell could be monitored separately. Most investigations were performed using small 2-cell stacks, the cells having the dimensions of either 50x50 mm² (effective electrode area 16 cm²) or 100x100 mm² (eff. electr. area 81 cm²). These 2-cell stacks have ceramic gas manifolds (A-design). Figure 5 shows the current-voltage characteristics of a 2-cell stack as function of the operating temperature. We defined as realistic a working point for the cells/stacks a voltage of 0.7 V per cell. From Figure 5 it can be seen that the current density reaches 1.11 A/cm² (0.7 V) at 950 °C, corresponding to a power density of 0.78 W/cm². At an operating temperature as low as 750 °C the current density still reaches 0.32 A/cm² (0.22 W/cm²). Table II summarizes the average best results obtained for the performance of the cells from all stack tests. Included in Table II are also the values for the maximum power densities which can be reached with the anode supported cells. At the voltage of 0.7 V per cell the power densities are in the range of 80 to 85% of the maximum power density.

It should be mentioned that not for all cells the in Table II given average best performance was registered. The analysis of the temperature dependence of the stack and individual cell performances showed that these poor performing cells suffered from a higher contact resistance. Post-mortem investigations of the stacks revealed in these cases the contact layer between interconnect and cathode to be very brittle, which could account for this higher contact resistance.

One of the 2-cell stacks with 100x100 mm² cells was operated at 800 °C with humidified hydrogen as fuel gas under a galvanostatic load of 0.31 A/cm² for more than 550 h. The stack voltage was around 1.52 V, i.e. the power density around 0.24 W/cm². Only one of the two cells reached the performance data given in Table II, which accounts for the lower stack voltage measured under these operating conditions. After this period the fuel gas was changed to a mixture of CH₄/H₂O (volume ratio 1 to 2). Figure 6 shows the current-voltage characteristic of the stack for operation on
methane/water in comparison with hydrogen. The attainable power density decreases by a factor of two under the operation conditions given. The stack was subsequently operated at 800 °C with methane/water as fuel gas under a galvanostatic load of 0.15 A/cm² for another 100 h. The stack voltage was around 1.43 V, i.e. the power density around 0.11 W/cm². Figure 7 shows the section of the time dependence of the stack operation from 500 to 700 hours. It shows that there is hardly any difference in the rate of degradation of the cell performance in this period, whether the stack is operated on hydrogen or methane.

Table II.
Average best performance of anode supported planar SOFC with hydrogen/air.

| temperature / °C | current density / A/cm² | power density / W/cm² | area spec. resistance / Ω·cm² | cell voltage / V | current density / A/cm² | maximum power density / W/cm² |
|-----------------|--------------------------|------------------------|-----------------------------|-----------------|--------------------------|-----------------------------|
| 950             | 1.15                     | 0.80                   | 0.25                        | 0.495           | 1.97                     | 0.98                        |
| 900             | 0.969                    | 0.68                   | 0.32                        | 0.510           | 1.57                     | 0.80                        |
| 850             | 0.739                    | 0.52                   | 0.45                        | 0.515           | 1.15                     | 0.59                        |
| 800             | 0.500                    | 0.35                   | 0.66                        | 0.520           | 0.77                     | 0.40                        |
| 750             | 0.332                    | 0.23                   | 0.91                        | 0.502           | 0.55                     | 0.28                        |
| 700             | 0.179                    | 0.125                  | 1.40                        | 0.490           | 0.33                     | 0.16                        |

(a) obtained by linear regression of linear section of current-voltage curves around 0.7 V
(b) obtained by linear extrapolation of current-voltage curve using area spec. resistance

Figure 8 shows the initially recorded current-voltage characteristics of the 10-cell stack (B-design) with 100x100 mm² cells for humidified hydrogen as fuel gas. The initial performance of the stack was rather poor compared to the cell data given in Table II. Through prolonged galvanostatic operation at 800 °C with stepwise increase of current density and/or decrease of fuel utilization (through an increase of hydrogen supply) over a period of more than 400 hours the performance could be improved continuously, until finally under a load of 0.31 A/cm² and a fuel utilization of 22% a stack voltage of around 7.70 V could be attained (0.24 W/cm²). After a total operation time of 19 days the stack was subjected to three thermal cycles. Three subsequent nights the current was set to zero and the stack was cooled down and heated again to the operating temperature of 800 °C. Figure 9 shows the relevant section of the stack.
operation history as the time dependence of stack temperature, voltage and current density. The stack reached a lowest temperature of around 350 °C each thermal cycle. After the three subsequent cycles the stack voltage had decreased with 0.08 V, i.e. a performance loss of around 1%.

CONCLUSIONS

Cells and stacks based on the anode supported planar SOFC concept with a thin (15 μm) electrolyte layer, an additional anode functional layer between substrate and electrolyte and a ferritic steel as interconnect material yield power densities of 0.23 W/cm² (0.33 A/cm² at 0.7 V) operating on hydrogen and air at a temperature of 750 °C. Operation on methane/steam (ratio 1 to 2) decreased the power density by a factor of two, but showed no remarkable influence on the rate of degradation. A new design for the manifold using metallic components facilitates the assembly process and allows thermal cycling of the stack without a drop in performance occurring.

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Figure 1. Cross-section of a Ni/YSZ cermet substrate with an anode functional layer.

Figure 2. Thermal expansion behaviour of stack materials.

Figure 3. Schematic drawing of sealing and contact layers within the stack: CA = contact layer anode (Ni-mesh); E = electrolyte; C = cathode; CC = contact layer cathode (LaCoO3).
Figure 4. A 10-cell (100x100 mm$^2$) stack with metallic manifold/casing (B-design) during (left) and after complete assembling (right).

Figure 5. Current-voltage characteristics of a 2-cell (50x50 mm$^2$) stack for humidified hydrogen and air as function of the operating temperature. Fuel utilization is 7% at a current density of 0.31 A/cm$^2$. 

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Figure 6. Current-voltage characteristics of a 2-cell (100x100 mm²) stack at 760 °C for H₂/H₂O/Ar (2000/14/1000 / ml/min) and CH₄/H₂O/Ar (500/1092/500 / ml/min) as fuel.

Figure 7. Section of the time dependence of the performance of the 2-cell stack from Fig. 6 at 800 °C with H₂/H₂O (4000/14 / ml/min) under constant load of 0.31 A/cm² changing to CH₄/H₂O/Ar (500/1092/500 / ml/min) under constant load of 0.15 A/cm².
Figure 8. Current-voltage characteristics of a 10-cell (100x100 mm²) stack for humidified hydrogen and air as function of the operating temperature. Fuel utilization is 45% at a current density of 0.31 A/cm².

Figure 9. Section of the time dependence of the performance of the 10-cell stack at 800 °C with humidified hydrogen and air under constant load of 0.31 A/cm² (fuel utilization is 22%) and three consecutive thermal cycles (800 - 350 - 800 °C)