FABRICATION AND PERFORMANCE OF ANODE-SUPPORTED SOLID OXIDE FUEL CELLS

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ABSTRACT

This work addresses the development of anode-supported solid oxide fuel cells using alternative low-cost techniques such as cold die pressing of the anode substrates and spray deposition of electrolyte layers. The new techniques have been developed up to the fabrication of disc cells with a diameter of 120 mm consisting of a co-sintered anode support and the yttrium-stabilized zirconia electrolyte layer. The concept was demonstrated in a three-cell stack according to the Sulzer HEXIS design and operated successfully in steam-reformed natural gas at around 800°C. The cell performance reached 430 mW/cm². Electrical efficiencies of >60% at a fuel utilization of 90% represent excellent performance for the non-sealed HEXIS stack design.

INTRODUCTION

Anode-supported solid oxide fuel cells (SOFC) based on a metallic/ceramic composite of nickel and yttria-stabilized zirconia (Ni-YSZ cermet) have attracted significant interest among SOFC developers worldwide for stationary, residential, and automotive applications. The concept allows for operating temperatures of around 800°C and thus the use of ferritic steel interconnects to assemble the SOFC stack. This SOFC operating temperature, compatible with structural and balance-of-plant components, contributes to cost reduction and system simplicity.

In this work the development of alternative techniques for the fabrication of complete anode-supported SOFCs is addressed involving cold die pressing of the anode substrate and spray deposition of thin film electrolyte layers. Cold die pressing has previously been proposed as a cost-effective option for substrate fabrication (1). The method is
environmentally friendly due to the comparatively low number of harmless organic binders used and is up-scalable for mass production. No complex de-binding or drying procedure is needed prior to the firing step. For the electrolyte deposition on anode substrates, frequently used techniques are aerosol spraying and screen printing. A further option is the spray pyrolysis technique, which deposits a ceramic layer by spraying a precursor solution onto a heated substrate. Thus this method does not necessarily require a subsequent firing or sintering step. Dense layers with a thickness of one micron can be prepared. The spray pyrolysis deposition was applied to deposit thin (250 nm) buffer layers of yttria-doped ceria (CYO) on top of electrolytes made from zirconia with 8 mol% yttria (8YSZ) in order to prevent the solid-state reactions known for the cathodes made from lanthanum strontium cobaltite-ferrite (LSCF).

**EXPERIMENTAL**

**Cell Fabrication**

The sequential steps in cell fabrication are presented in Figure 1. Polymer-bonded NiO-YSZ granules with 50 wt% NiO and 50 wt% YSZ were prepared by spray drying an aqueous suspension of NiO (Cerac) and fine and coarse YSZ fractions (Tosoh and GTV, respectively). The NiO has been used as received or milled prior to slurry preparation. The compositions K, O, and Q consist of different proportions of fine and coarse powders in the NiO/YSZ slurries. The solid phase content ratios in the granulate after-spray drying of the slurries is given in Table 1.

The near-net shape forming of the anode substrates according to the dimensions of SULZER HEXIS cells [120 mm diameter, center bore 20 mm, active area 100 cm² (4)] was intended. Disc NiO/YSZ structures with and without center holes were fabricated by press forming. The powders were filled into the respective pressing molds and pressed in a single step with a load between 50 and 150 MPa.

Two different deposition procedures for the 8YSZ (Tosoh) electrolyte were evaluated: aerosol spraying (5) and screen printing (6). The substrates used for screen-print electrolytes were coated with an additional anode functional layer before electrolyte application.

The screen-printed and sprayed electrolyte half-cells were co-sintered in air at 1430°C for 2 h. Oversized anode supports having a diameter of 150 mm without a center hole were used for these cells. To match the short-stack design, the center bore (20 mm) and specified outer diameter (120 mm) were obtained by laser cutting the co-sintered half-cell.

| Slurry ID | Fine YSZ | Coarse YSZ | NiO |
|-----------|----------|------------|-----|
| K         | 1 (TZ8Y) | 5 (ZrO2 8Y) | 6 (no milling) |
| O         | 1 (TZ8Y) | 2 (FYT13)  | 3 (milled)   |
| Q         | 1 (TZ8YS)| 2 (FYT13)  | 3 (milled)   |
The half-cells were further coated with a 250-nm CYO buffer layer applied by spraying ethanol-based solutions from cerium nitrate and yttrium chloride onto sintered half-cells that were heated to 280°C. LSCF cathodes were applied by screen printing on all prepared half-cells before single-cell tests and short-stack assembly.

**Single-Cell Tests**

The single cells prepared with a sprayed 8YSZ electrolyte layer and an LSFC cathode in direct contact with the 8YSZ electrolyte (Ni-YSZ//YSZ//LSCF) were mounted between two current collector plates. The fuel and air flow was supplied from the center of the cell similar to the HEXIS cell design (4). As usual for this design, the outer rim of the disc cells remained unsealed. The cell performance and impedance response were tested at 750°C in dry hydrogen with flow rates of 1.7 and 4.5 g/h.
Short-Stack Tests

The cells consisting of an additional anode functional layer and CYO buffer layer (Ni-bidisperse YSZ)/YSZ/CYO/LSCF) were tested in a three-cell short-stack configuration (4) using test-grade metallic interconnects. For intimate electrode-interconnect contacts, as is usual practice, contacting interlayers were applied during assembly. The tests were performed at 800°C after heating at 100°C/h. The fuel was steam-reformed natural gas with a steam-to-carbon ratio of 2. The testing procedure first determined the stack performance dependence on fuel and air fluxes, then monitored degradation over 200 h. During this period the stack operated at constant current (400 A/cm²) while fuel and air feed rates for the whole stack were 20 and 1000 g/h, respectively. As a final step in the short-stack characterization, the sample was oxidized by switching off the fuel flow, and reduced again (redox cycle) while keeping the temperature at 800°C.

RESULTS AND DISCUSSION

Co-Sintering

For co-sintering the substrate shrinkage had to be adapted to the shrinkage of the YSZ electrolyte layer. In Figure 2 the shrinkage of compositions K, O, and Q is compared with that of a reference electrolyte slurry. Increasing the amount of fine YSZ and NiO and further decreasing the load during pressing increases substrate shrinkage, although electrolyte shrinkage, because it is higher than that of the substrate gastight electrolyte layers, could be obtained on co-sintering of the electrolyte onto anode substrates produced from composition O and having shrinkage of 12–13%. A cross section of an anode-supported cell (Ni-bidisperse YSZ)/YSZ/CYO/LSCF type is shown in Figure 3. The co-sintered cells were sufficiently flat to be mounted in either a single-cell testing rig or to be assembled as a short stack.

![Figure 2. Shrinkage of NiO/YSZ powder mixtures K, O, Q (see Table 1) compared with YSZ: lines and symbols: dilatometer measurements on pressed powders, symbols only: anode substrates pressed with various loads and sintered for 2 h at 1430°C.](image-url)
Figure 3. Cross section of anode-supported (Ni-bidisperse YSZ)/YSZ/CYO/LSCF) cell after 330 h in steam-reformed natural gas (steam-to-carbon ratio = 2).

Single-Cell Performance

The performance of single cells with a sprayed electrolyte layer in dry hydrogen at 750°C is shown in Figure 4. The open-circuit potential is around 930 mV, and, even with the unsealed test configuration, this value is lower than could be expected for dry hydrogen (>1100 mV), an indication of residual porosity in the electrolyte layer. Accounting for the cell size, impact on cell operating performance (temperature, gas flows) is considered small and acceptable at this stage of development. A limitation in cell performance is observed for low hydrogen flow rates at maximum power of 180 mW/cm². With higher hydrogen flow rates the power output increased to 250 mW/cm².

The full cell impedance is shown in Figure 5. It is obvious that the limiting processes are in the low-frequency part of the impedance. At low fuel flux the anode readily polarizes; this may indicate a mass transport limitation, probably inside the anode substrate.

Figure 4. Single-cell performance of an anode-supported Ni/YSZ/YSZ/LSCF cell at 750°C and various hydrogen flow rates.

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Figure 5. Full-cell impedance of anode-supported Ni/YSZ//YSZ//LSCF cell at 750°C and various hydrogen flow rates.

Short-Stack Performance

Figure 6 shows the performance of the three-cell short stack in reformed natural gas. The OCV is around 980 mV per cell. Given the absence of outer rim sealing and the steam content in the fuel mixture, the OCV value confirms adequate electrolyte specifications. With 200-g/h cell air and 4-g/h cell fuel flows, a power output of 32 W/cell (320 mW/cm²) with an electrical efficiency of 61% and a fuel utilization of 90% was attained. The highest power output (43 W/cell, 430 mW/cm²) was achieved with an electrical efficiency of 32% and a fuel utilization of 45%.

Considering the different experimental conditions (higher hydrogen/water content, higher cell temperature) the initial short-stack performance is compatible with the single-cell tests. The high power output at high electrical efficiency and fuel utilization is attributed to the match of porosity and thickness of the anode substrate.

Figure 6. Performance of three-cell short stack and individual cells at ~800°C; natural gas flow 4 g/h, air flow 200 g/h per cell [(Ni-bidisperse YSZ)//YSZ/CYO//LSCF].

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Short-Stack Durability and Redox Stability

The overview of the three cell short-stack test is reported in Figure 7. The small irregularities in the curves between 25 h and 90 h are attributed to air and fuel flow variations associated with electrochemical characterization (see discussion above).

From 90 to 285 h an average degradation of 6.7% can be observed in the operating voltage. This corresponds to an increase in the average area specific resistance (ASR) from 0.43 to 0.65 Ωcm². The cathode composition used is known to be relatively unstable above 800°C with a degradation rate of approximately 3.6%. Therefore, the observed degradation is partly due to the cathode aging. The remaining 3% degradation of the cells may arise from substrate microstructural changes. The irregular profile ("wave-like") of cell 1 between 175 and 250 h is also related to some intrinsic cell defect because the other two cells performed regularly. The spike at 165 h is due to a current interrupt in the test lab that caused a fuel supply cut with transfer to nitrogen gas to prevent a redox cycle. The incident had no notable effect on stack performance.

After 290 h, a redox cycle was conducted while keeping the stack at 800°C. For cell 1 a stable OCV was maintained. Moreover, its ASR had decreased from 0.78 before to 0.67 Ωcm² after the cycle, indicating a slight improvement of this cell. The OCV of cells 2 and 3, which were performing well before cycling, was strongly decreased to ~750 mV. This decrease in the cell voltage indicates that cracks had developed in the electrolyte layers, most likely due to structural changes in the anode support. This result, in line with the initial cell performance, is attributed to differences in the microstructure of the nominally identically fabricated cells.

It is well known that a coarse YSZ support structure in the Ni-YSZ cermet is advantageous for the redox stability of Ni/YSZ cerments. On the contrary, a fine porous structure leads to higher electrochemical activity, in line with the results that the lowest

Figure 7. Time dependence of the three-cell short-stack test; numbers indicate cells.
performing cell shows the best redox stability in the stack. Because well known materials and processes have been applied for the electrolyte and cathode deposition, the observed differences in cell performance are attributed to a coarser structure in the anode/anode support of cell 1 than in cells 2 and 3. Further post-mortem characterization of the short stack will be performed to verify this interpretation.

**SUMMARY**

The fabrication of anode-supported disc SOFCs with a diameter of 120 mm by using cold die pressing and spray pyrolysis has been proven. The concept was demonstrated in a three-cell stack operated successfully in reformed natural gas at Sulzer Hexis at around 800°C. With reformed natural gas the cell performance reached 430 mW/cm². Electrical efficiencies (>60%) at high fuel utilization (90%) were achieved, an excellent performance for the non-sealed HEXIS stack design. However, further optimization of the anode substrate fabrication with respect to reproducibility and redox stability of the cells is clearly needed. Further automation of the fabrication procedure is promising for reproducibility and low-cost mass production of anode-supported cells.

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