DEPOSITION OF THIN ANODE AND ELECTROLYTE LAYERS FOR MEDIUM OPERATION TEMPERATURES OF SOLID OXIDE FUEL CELLS

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ABSTRACT

The planar solid oxide fuel cell (SOFC) developed at Jülich is characterized by large area supporting anode substrates with rather thin electrolyte and cathode layers. This type of SOFC is designed for internal methane reforming and medium operation temperature at sufficiently high specific power. The porous YSZ/Ni anode (YSZ = Yttrium-Stabilized Zirconia) is coated with 1-2 μm porous YSZ/NiO interlayer and with 15-20 μm gastight YSZ electrolyte layer. Both layers are made by using an advanced slip casting technique. The ceramic layers can be dried at room temperature without any cracking. Cofiring of the anode-electrolyte unit is done at 1400°C. By helium leak tests of the electrolyte layer leakage values of < 5x10^(-3) mbar l/s cm² were measured. At 700 mV cell voltage maximum current densities of more than 1000 mA/cm² at 950°C and about 400 mA/cm² at 800°C could be reached.

INTRODUCTION

One of the main advantages of the anode supported solid oxide fuel cell developed at Forschungszentrum Jülich (1) (2) is the rather thin YSZ electrolyte layer (YSZ = Yttrium-Stabilized Zirconia = Zr_{0.85}Y_{0.15}O_{1.96}). These 15-20 μm electrolyte layers allow to lower the SOFC operation temperature from 950°C to 750-800°C at sufficiently high power densities of the fuel cells (2). The aim of the work described in this paper was to develop a suitable process for the preparation of gastight YSZ layers with uniform thicknesses of 15-20 μm on the surface of highly porous anode substrates (40% porosity) with sizes of 100×100×2 mm³ and 250×250×2 mm³ which were manufactured by using the “coat mix® process“ based on warm pressing of resin binder-coated YSZ/NiO powders. The result of this development was an advanced slip casting process, called “VSG“ (Vakuum-Schlicker-Gießverfahren). The process uses the high porosity of the anode substrate to deposit thin YSZ layers on its surface from a suspension of very fine dispersed YSZ particles in ethanol.
EXPERIMENTAL

The equipment for coating of porous anode substrates with thin and gastight electrolyte layers is shown in Fig. 1. The presintered substrate (3h at 1285°C) is cleaned by ethanol and then put on the porous silicon carbide plate of the coating equipment. The edges of the substrate are carefully sealed by an elastic silicone rubber mask in order to avoid any loss of suspension at the edges. The apparatus is adjusted to an exact horizontal substrate surface. Then the calculated volume of suspension is poured on the substrate surface. Coating is done in two steps: first - closing the open surface pores of the substrate by 0.5-1.5 μm interlayer consisting of YSZ/NiO, and second - preparing 15-20 μm electrolyte layer by using a pure YSZ suspension. The calculated suspension volume for the electrolyte layer is

\[ V = \frac{10^{-4} \times A \times d}{c} \]

with
- \( V \) = Volume of YSZ suspension (ml),
- \( x \) = layer thickness after sintering (μm),
- \( A \) = area of the substrate (cm²),
- \( d \) = density of the layer after sintering (ρ = 5.97 g/cm³),
- \( c \) = YSZ concentration in the suspension (g/ml).

The efficiency of the coating process is further enhanced by using a slightly vacuum at the downstream side. After 10-15 minutes the ready coated substrate can be removed from the apparatus. The freshly deposited layers were dried in dust-free air at room temperature without any crack formation.

The YSZ suspension was prepared according to M. Hruschka (3) by using YSZ powder from TOSOH (Table 1).

### Table 1: Preparation of the YSZ suspension

| Calcining the YSZ powder: | Al₂O₃ crucible with 2 kg YSZ powder: |
|---------------------------|-------------------------------------|
| Rolling: 100 hours:       | RT → 3K/min. → 1200°C/3h → RT (in air) |
| Adding dispersant:        | 200 g calcined YSZ powder            |
|                          | 600 g (765 ml) ethanol 96%           |
|                          | 600 g 3 mm spheres (TZ-3Y/TOSOH)     |
|                          | 600 g 5 mm spheres (TZ-3Y/TOSOH)     |
| Sedimentation:           | 4.0 g polyethyleneimine (PEI) solution|
|                          | ≈40 h (settling of the nondispersed fraction) |
After settling the suspension is separated from the nondispersed fraction which can be used again for preparing new suspensions. Although the mean particle size in the suspension is nearly 0.3 μm, a small fraction (3-5%) has larger particle sizes between 1 and 5 μm. This coarser particle fraction is necessary to close the surface pores of the substrate. The typical particle size distribution of a suitable YSZ suspension is shown in Fig 2. The YSZ concentration is in the range of 40-45 g YSZ/l.

The YSZ/NiO suspension for the anode interlayer was prepared from 60 vol% of the YSZ standard suspension (with 44 g YSZ/l), 10 vol% of a NiO suspension (with 333 g NiO/l) and 30 vol% ethanol resulting in 26 g YSZ/l and 33% NiO/l. For the deposition of 1 μm YSZ/NiO interlayer on a 100x100 mm² substrate 6 ml of this suspension is necessary.

RESULTS

Characterization

Optical microscopy of ceramographic sections of the anode interlayer resulted in smaller grains and pores compared with the substrate (Fig 3). The gas permeability of the reduced substrate with interlayer is only 6-19% lower compared with the uncoated substrate which is still sufficiently high for the gas transport in the anode. The helium leakage of the electrolyte layer could be reduced by nearly one order of magnitude reaching leakage values below 5x10⁻⁵ mbar l/s cm². This can be explained by the formation of a very smooth surface by the deposition of the anode interlayer. The electrical conductivity perpendicular to the substrate plane was found to be equal with and without anode interlayer.

Fuel cell operation results

The anode substrate/electrolyte units were coated with La₀.₆₅Sr₀.₃MnO₃/YSZ composite cathodes by using the wet powder spraying (WPS) technique (4) and then tested in “short stacks”. These stacks consist of only two fuel cells (50x50 mm² or 100x100 mm² substrate/electrolyte/cathode units). The ferritic steel 1.4742 was used for the metallic interconnector plate and the two endplates. The electrical contact between steel and cathode was enhanced by a layer of LaCoO₃, between steel and anode by a net of Ni wires. Ceramic gas manifolds were sealed to the stack by using a composite glass. The stack was supplied with humidified H₂ as fuel gas and with air as oxidizing gas at different temperatures ranging from 750 to 950°C. Due to the thin electrolyte layer and the high electrochemical activity of the fine grained anode interlayer rather high current densities were measured at 700 mV cell voltage. Table 2 summarizes the results of four tests at operation temperatures of 800 and 950°C.
Table 2: Results of testing four fuel cells in short stacks

| Fuel Cell Nr. | Layer Thickness / μm | Current Density / mA/cm² (at 700 mV cell voltage) |
|---------------|----------------------|---------------------------------------------------|
|               | Interlayer  | Electrolyte | 800°C | 950°C |
| 10Q359        | 1.0        | 17          | 464   | 1112  |
| 10Q393        | 0.5        | 17          | 411   | 1195  |
| 10Q422        | 1.2        | 18          | 436   | 970   |
| 10Q467        | 0.5        | 18          | 374   | 1140  |

The measured current densities at 950°C operation temperature and 700 mV cell voltage were found to be correlated with the helium leakage of the electrolyte layer. Higher current densities resulted at lower electrolyte leakage values: 800-1200 mA/cm² at 3×10⁻⁵-10⁻⁴ mbar l/s cm², 200-500 mA/cm² at 2×10⁻⁴-10⁻³ mbar l/s cm², and 0 mA/cm² above 3×10⁻³ mbar l/s cm² (Fig 4). The plot shows clearly the superiority of substrate fuel cells with an anode interlayer.

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Fig. 1: Equipment for coating of porous anode substrates with thin electrolyte layers

Fig. 2: Particle Size Distribution of the YSZ Suspension
Fig 3: Ceramographic Section of the Anode Interlayer

Fig. 4: Current density at 950°C /700 mV as a function of the electrolyte leakage