Fuel Cells

Preparation of Porosity–Graded SOFC Anode Substrates

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Abstract

Porosity graded anode substrates for solid oxide fuel cells are considered to optimise the gas transport through the substrate by maintaining a high electrochemical activity for fuel oxidation at the anode/solid electrolyte interface. In this work, the fabrication of porosity graded anode substrates, made from nickel oxide and yttria-modified zirconia and produced by dry uni-axial pressing, are described. Using carbon as pore formers and adjusting the particle size distribution in the ceramic NiO-YSZ masses, samples with gradu-ally changing porosity are built up. The sintering behaviour of the individual layers is analysed and partly adjusted so the multi-layer support can be co-fired together with the YSZ electrolyte layer. In the oxidized state, four-layer, porosity graded anode supported half-cells with a dense YSZ electrolyte are demonstrated.

Keywords: Anodes, Graded Porosity, Solid Oxide Fuel Cells, Substrates

1 Introduction

Anode supported electrolyte cells have attracted much interest in recent years, mainly with the aim of enabling efficient operation of the solid oxide fuel cell at temperatures around 800 °C, using yttria stabilized zirconia as the electrolyte material and Ni-YSZ cermets as the anode substrate. The anode substrates are fabricated using various processes: Jülich demonstrated the feasibility of the anode supported electrolyte design with substrates of 1–2 mm thickness, prepared by the so called Coat Mix process and warm pressing [1], while others developed tape cast substrates with a lower thickness of several hundred micrometers [2].

Previous investigations of Ni-YSZ cermet anodes indicated that two processes can significantly contribute to the losses of the fuel oxidation reaction; (i) the electrochemical reaction in the vicinity of the so called Triple Phase Boundary (TPB) and (ii) the change of the gas atmosphere due to gas transport and fuel utilization (gas conversion) from and to the TPB [3–5]. The performance of the anode supported cells can easily reach up to 1 W cm^{-2} from 750 to 850 °C (0.5 W cm^{-2} at 0.7 V) in hydrogen fuels [6]. In order to optimise the anode substrate further, a graded structure with increasing porosity and pore size from the anode/solid electrolyte interface towards the gas supply channels is envisaged, to allow for high electrochemical activity at the interface towards the solid electrolyte and less hindered gas transport to and from the gas channels in the interconnect plate. Here, the fabrication and initial testing of porosity graded anode substrates is described. They are fabricated by dry pressing, a fabrication technique that can be scaled up. The technique was developed at EMPA for the fabrication of Ni-YSZ cermet anode supports [7, 8].

2 Experimental

Ceramic masses of NiO-YSZ were prepared by mixing slurries of premilled NiO (Aur-Remy, Cerac) and 8-YSZ (Tosoh, GTV) with water, dispersant, and binder (PEG). Various pore forming agents (carbon (Timrex), polypropylene fibres (KRENIT), and polyacrylate spheres (Porlat)) were added to the NiO-YSZ slurries, which were subsequently granulated by spray drying. The NiO (Cerac) particle size was modified by milling the powder down to the desired particle size distribution, expressed by the d$_{50}$-value.

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The composite granules were uni-axially pressed (50-100-150 MPa) into circular disks of 39 mm diameter. Single layer as well as multilayer pellets with a total thickness of 1–2 mm were pressed and further characterized with respect to their sintering behaviour. The samples were sintered in air at 1430 °C (nominal temperature) for 2 h. Subsequently, they were reduced at 800 °C for 1 h in 91% N_2/9% H_2 gas.

The linear shrinkage of the NiO-YSZ masses during sintering was determined by dilatometry. The geometrical density of the sintered porous bodies was determined by the Archimedes method or calculated from the dimensions of the sample and compared to the skeleton density measured with a helium pycnometer. The total porosity of the samples was calculated from the ratio of the geometric to the skeleton density. Additionally, mercury porosimetry was used to determine the open porosity of the sample, which is important with respect to the gas transport properties.

Suitable green / unfired multilayer anode substrates were coated with an 8-YSZ electrolyte layer by aerosol spraying with an isopropanol based low viscosity TZ8Y-S suspension, and were subsequently co-fired in air at 1430 °C for 2 h. The co-fired half cells were characterized in terms of their isopropanol permeability (as an indication of the electrolyte's gas tightness) and warping (measured as the maximum deviation from linearity by using a micrometer screw).

For electrochemical characterization, the co-fired half cells were completed with an LSCF-cathode, painted onto the electrolyte layer prior to electrochemical testing. Full-cell tests were conducted in dry and dilute hydrogen in a non-sealed set-up using Pt meshes for current collection.

3 Results and Discussion

As a first step, suitable pore formers for the aqueous NiO-YSZ slurries needed to be identified. Graphite, in the form of plates and spheres, with particle sizes (d_{50}) ranging from 5–50 microns could be dispersed into the slurries and processed further. In addition, trials with polymer fibres and polyacrylate spheres were unsuccessful due to problems with their dispersion and unsuccessful spray drying, respectively. Therefore, only graphite was investigated further.

In the next step, the influence of the individual NiO, YSZ, and carbon particle sizes on the resulting porosity and the microstructure were investigated for a carbon content of 10 vol.-%. The results for the total porosity are given in Figure 1. Apparently, the particle size of the pore former has no influence on the porosity, determined by helium pycnometry. The porosity can be slightly increased by using coarser ceramic powders of YSZ and NiO. This trend is expected since compared to finer fractions for larger particle sizes the sintering activity is reduced, which reduces the densification of the ceramic body. The slight reduction of the porosity when using coarser fractions of YSZ is attributed to a higher pack-
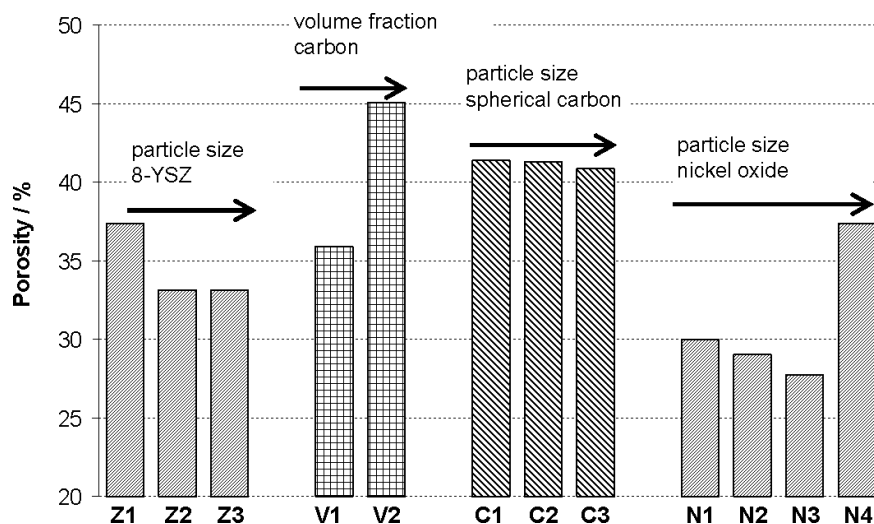

Fig. 1 Influence of the particle sizes and the amount of pore formers on the porosity of NiO-YSZ anode supports. D_{50} 8-YSZ: Z1, 12.9 μm; Z2, 16.7 μm; Z3, 35.6 μm; vol.-% C: V1, 10%; V2, 30%; D_{50} carbon: C1, 5.6 μm; C2, 23.2 μm; C3, 51.9 μm; D_{50} NiO: N1, 0.5 μm; N2, 1.0 μm; N3, 2.4 μm; N4, 6.2 μm.
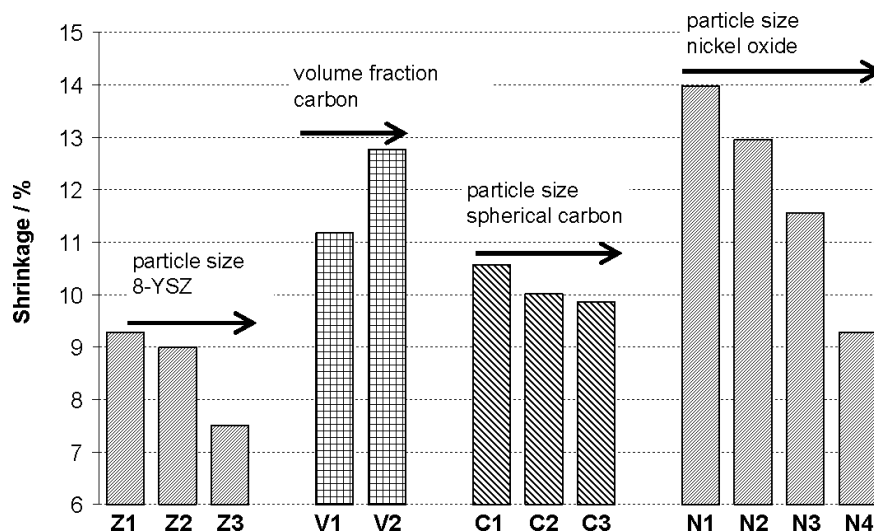

Fig. 2 Influence of the particle sizes and the amount of pore formers on the shrinkage of NiO-YSZ anode supports. D_{50} 8-YSZ: Z1, 12.9 μm; Z2, 16.7 μm; Z3, 35.6 μm; vol.-% C: V1, 10%; V2, 30%; D_{50} carbon: C1, 5.6 μm; C2, 23.2 μm; C3, 51.9 μm; D_{50} NiO: N1, 0.5 μm; N2, 1.0 μm; N3, 2.4 μm; N4, 6.2 μm.

ing density arising from the multi modal particle size distribution.

Microstructural investigations clearly showed that the particle size of the pore former corresponds to the size and shape of the pores remaining after sintering. The porosity increased by almost 10% by increasing the carbon content from 10 vol.-% to 30 vol.-%.

Shrinkage during sintering is considered to be an important parameter for the co-sintering of the various NiO-YSZ layers in a graded anode support. The variation of the coarse and fine powder fractions in the NiO-YSZ masses, as well as the influence of the pore former on the shrinkage during sintering, have been investigated on single layer pellets (see Figure 2).

The shrinkage could be tailored between 7.5% and 14%, depending on the grain size distribution, and is mainly influenced by the NiO-powder morphology in the chosen masses. While the shrinkage decreased by only half a percent when the carbon size increased from 5 to 52 microns, a change in the carbon content from 10 to 30 vol.-% slightly increased the shrinkage, by about 2%.

From the analysis of the porosity, microstructure, and shrinkage, layers with different porosities were identified and fabricated as 2-layer pellets to be characterised regarding their sintering behaviour. The thicknesses of the individual layers were 0.5–0.7 mm leading to a total thickness of slightly more then 1 mm. The pellets were inspected after sintering in air to check how much they had warped, due to differing shrinkages. For the masses investigated, a difference in shrinkage of 0.5% could be tolerated without causing warping during sintering. A combination of layers with higher shrinkage showed bending towards the layer with the higher shrinkage rate during sintering.

From these results, suitable combinations of layers (masses), in order to build up a porosity graded anode support, were identified. The masses were based on NiO with a d_{50}-value of 6.23 microns and a ratio of fine to coarse 8-YSZ of 1:2. The pore former content was 10 vol.-%, starting with carbon plates and followed by layers of spherical carbon particles of average size 5.6, 23, and 52 microns. The microstructure of a 4-layer anode support is shown in Figure 3. The total thickness of the anode support is 2 mm, consisting of 0.5 mm thick layers (after sintering). The two right hand layers show a clear increase in the pore size compared to the left half of the porous layer in which the pore size is clearly lower. Although these results show the feasibility of the concept and of the fabrication process, the microstructure in Figure 3 suggests rather large pores with tight access necks, which are not considered advantageous for gas transport through the porous anode support. Indeed, mercury porosimetry did not indicate the formation of large pores, as observed in the SEM, confirming the conclusion that they are rather isolated.
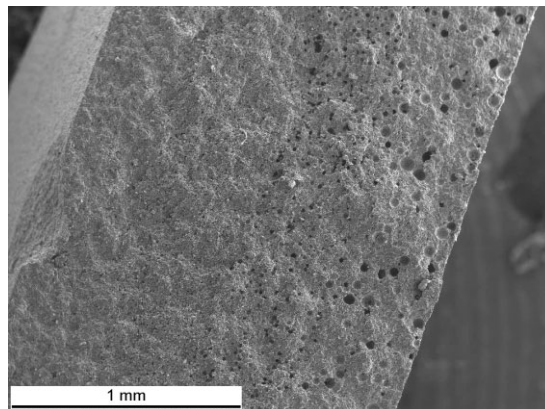

Fig. 3 Four layer anode support with graded porosity.

In order to increase the number of larger pores, the carbon content was increased to 20 and 30 vol.-% leading to an increase in the porosity, to 34 and 40%, respectively. Microstructural analysis confirmed that the amount of closed and isolated large pores also decreased. The average pore sizes were determined to be 1.4 (20 vol.-% C) and 3.5 (30 vol.-% C) microns, after sintering.

YSZ coated half cells were characterised with respect to their co-sintering behaviour before reduction. The electrolyte thickness was between 5 and 10 microns after sintering, which corresponded well to the thickness estimated from the spraying process and time. Table 1 gives an overview of the co-firing behaviour of different multi-layer anode supports with the YSZ electrolyte. It should be noted, that the shrinkage of the free electrolyte is around 19% and thus significantly higher than the free shrinkage of the substrates.

A sample with a matched shrinkage of the anode substrate layers to around 10.4% showed a bending towards the electrolyte layer (denoted (+) in Table 1). A special case occurred in the bending of a half cell consisting of an anode substrate with two layers of un-matched shrinkage (e.g., no. 95 and no. 101). These samples were bent slightly in the opposite direction, namely towards the anode substrate (denoted (-)). Since each individual layers thickness was around 0.5 mm and was kept almost constant for the different layers, the observed bending is attributed to the differences in shrinkage rather then the thickness of the layers involved.

A possible explanation for this behaviour is illustrated in Figure 4. The first layer in the anode support with a reduced

Table 1 Summary of the co-firing results for various multi-layer anode supports with a 5–10 micrometer YSZ electrolyte. The individual layers in the anode support are called L1/L2/L3/L4 from the electrolyte side if needed. (+) and (–) indicate bending towards the electrolyte and the anode, respectively.

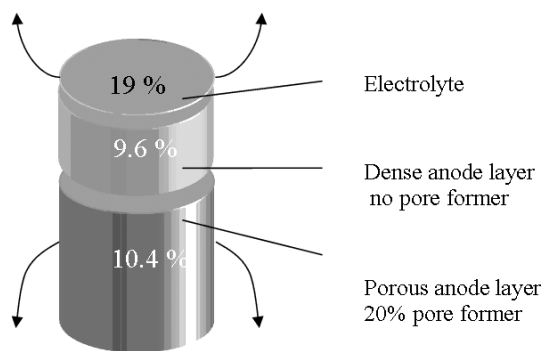| ID	Anode substrate				Half-cells
	No. layers	Carbon / vol.-%	Shrinkage /%	Thickness / mm	Warpage / mm
85	1	0	9.6	3	(+) 0.3 – 0.4
34	4	10/10/10/10	matched 10.4 – 10.9	3	(+) 0.7 – 1.1
40	4	10/10/10/10	matched 10.4 – 10.9	2.1	(+) 0.9 – 1.2
95	2	0/20	not matched 9.6/10.4	2.9	(–) 0.3 – 0.6
96/100	2	0/20	matched 10.4	2.9	(+) 2.0 – 2.5
101	2	0/30	not matched 9.6/10.4	2.9	(–) 0.9 – 1.0
98/102	2	0/30	matched 10.4	2.9	(+) 1.8 – 2.1

Fig. 4 Schematic representation of warpage in a coated two-layer graded anode. Numbers indicate the shrinkage of the respective layer.

shrinkage behaviour compared to both the electrolyte layer and the subsequent NiO-YSZ layer in the anode support seems to compensate for the opposing stresses. However, this could be expected to impose a huge mechanical stress on the electrolyte layer and crack formation is likely to occur. However, it was found that the electrolyte layer remained impermeable to isopropanol, an indication for effective densification. Apparently, the electrolyte layer is able to, at least partly, sustain the tensile stresses caused by the layered structure of the anode support. As discussed previously [9], a super plastic flow may occur in the TZ8Y-S powder used here, permitting an elongation under tensile stress [10].

The above results indicate dense electrolyte layers prior to the reduction of the anode support during SOFC start-up. The reduction of the anode and anode support can introduce further mechanical stresses, which may cause cracking of the electrolyte layer. Preliminary full cell tests [11] show reduced open circuit potentials and increased ohmic resistances. This is a first indication of microcracks, which lead to fuel loss and possible partial oxidation of the Ni-YSZ anode, thus reducing performance.

4 Conclusion

The fabrication of multilayer Ni-YSZ anode supports with different microstructures has been demonstrated by building up porosity graded anode supports with a thickness of 2–3 mm by dry pressing. Up to 30 vol.-% of spherical carbon, with diameters ranging from 5 to 50 microns, could be incorporated into the ceramic masses, which allowed tailoring of the microstructure in the anode support. The initial results on co-firing multilayer anodes and thin YSZ electrolytes indicate that further consideration of the mechanical properties of the laminated structures and superplasticity within the electrolyte layer are needed to further understand and optimize the electrolyte deposition and co-firing of graded multilayer structures. In addition, further electrochemical characterization and long-term testing are clearly needed in order to further validate the concept of porosity graded pressed anode supports for SOFCs. In particular, the reduction of the anode

can cause additional mechanical stresses on the electrolyte layer, which could lead to electrolyte cracking during the start up phase of the SOFC cell.

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