Short communication

Influence of anode thickness on the power output of solid oxide fuel cells with (La,Sr)(Co,Fe)-type cathode

Norbert H. Menzler [a],[*], Vincent A.C. Haanappel [b]

[a] Forschungszentrum Jülich, Institute of Energy Research, IEF-1: Materials Synthesis and Processing, 52425 Jülich, Germany
[b] Forschungszentrum Jülich, Institute of Energy Research, IEF-3: Fuel Cells, 52425 Jülich, Germany

ARTICLE INFO

ABSTRACT

The influence of the thickness of the anode (functional layer) on the power output of anode-supported solid oxide fuel cells with a lanthanum–strontium–cobalt–ferrite cathode was investigated. The anode was applied by vacuum slip casting and the thickness varied between 1 and 22 μm. All other material and microstructural parameters were kept constant. Single cells with dimensions of 50 mm × 50 mm and with an active cathode area of 40 mm × 40 mm were manufactured and tested in an alumina housing with air as oxidant and hydrogen with 3% water vapour as the fuel gas.

Results have shown that SOFCs with anodes between 1 and 13 μm have slightly better performance than those with thicker anodes (~1.7 A cm^{-2} versus 1.5 A cm^{-2} at 800 °C and 0.7 V). The current densities were discussed with respect to cell area specific resistance, helium leak rate of the half-cell, and microstructure.

1. Introduction

The performance of a solid oxide fuel cell (SOFC), as a multi-layered structure, is governed by two aspects: the materials (their chemical composition) and the microstructure. Based on anode-supported cells (ASCs) with lanthanum–strontium–manganite (LSM) cathodes the influences of many manufacturing and microstructural parameters were characterized [1–3].

The aim of achieving higher power densities for ASCs leads to the development of other perovskite-type cathode materials, e.g. lanthanum strontium cobalt ferrites (LSCF).

After developing LSCF as a cathode material, the cells were assembled in a first approach as for the LSM-cathode cells, which means equivalent materials and layers for the anode substrate, the anode and the electrolyte. To question is whether these layers are also optimal for the LSCF cathode cells. The support itself does not influence the basic electrochemical reaction at the electrodes, thus it can be kept unchanged. The electrolyte must also be dense and thin to reduce ohmic losses in both cases, thus it can be left unchanged. Since the oxygen reduction reaction on the cathode is the power-limiting factor of the overall SOFC reactions, the electrochemical performance of this type of cell is not affected by the thickness of the anode. However, it can be suggested that if the anode thickness is chosen too thin, the limiting factor changes from the cathode to the anode side reactions. This paper deals with the adaptation of the anode layer thickness to cells with LSCF cathode aiming for a sensitivity analysis regarding the dependence between electrochemical performance and anode thickness.

2. Experimental

Standard half-cells (substrate–anode–electrolyte) according to the quality protocols of Forschungszentrum Jülich were used as the basis for the investigations. The substrate was prepared by warm pressing of Coat-Mix® powder, pre-sintering and subsequently coating by vacuum slip casting (VSC) with an anode of varying thickness between 1 and 22 μm. The thickness was adapted by changing the solid fraction within the VSC suspension. After electrolyte coating by VSC, the three-layer laminate was sintered at 1400 °C to electrolyte gas-tightness. The gas-tightness of all the samples was characterized by He leak testing as described in Ref. [4]. After leak rate characterization, a CGO layer was applied by screen printing and sintered at 1250 °C. Subsequently, the LSCF cathode was also deposited by screen printing and sintered at 1080 °C. The LSCF stoichiometry is La$_{0.58}$Sr$_{0.40}$Co$_{0.20}$Fe$_{0.80}$O$_{3-\delta}$ [5,6] and the stoichiometry of the CGO is Ce$_{0.90}$Gd$_{0.10}$O$_2$. The NiO powder was supplied by Baker (NiO green, Mallinkrodt Baker, Griesheim, Germany), the 8YSZ for the substrate by Unitec Ceramics (FYT13-005H, Stafford, United Kingdom), that for the anode and the electrolyte by Tosoh (TZ8Y, Tokyo, Japan), the CGO was from Treibacher (Althofen, Austria) and the LSCF was made in-house via a spray drying process (on a nitrate basis) and calcination [7]. After

* Corresponding author. Tel.: +49 2461 613059; fax: +49 2461 612455.
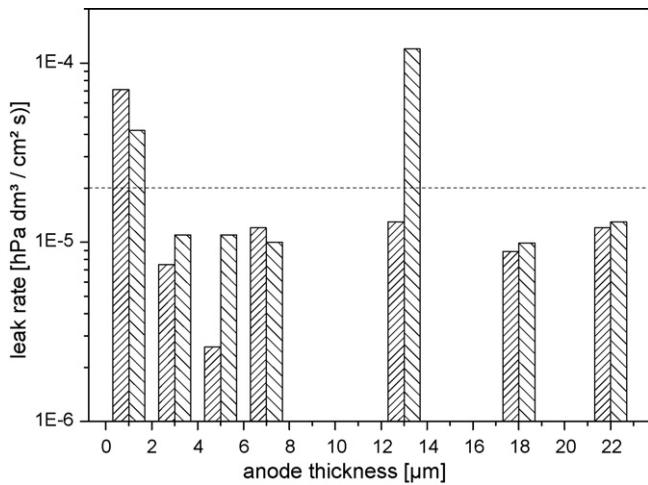E-mail address: n.h.menzler@fz-juelich.de (N.H. Menzler).

Fig. 1. He leak rates of the half-cells as a function of the anode thickness (two samples were measured of each anode thickness); the dotted line marks the internal threshold value.

preparing the single cells, they were characterized electrochemically in an alumina single cell housing as described in Ref. [8]. Post-test examination was done by scanning electron microscopy (SEM) of polished cross-sections using a Zeiss SEM microscope (Ultra 55).

3. Results and discussion

First the gas-tightness of the half-cells (electrolyte + anode + substrate) was characterized by He leak testing. Fig. 1 shows the results. The values are given in $hPa\,dm^3\,(cm^2\,s)^{-1}$ and calculated to a pressure difference of 100 hPa (measurement at a difference of 1000 hPa). The internal threshold for electrolyte gas-tightness is $2 \times 10^{-5}\,hPa\,dm^3\,(cm^2\,s)^{-1}$. This value is typically obtained with the standard anode thickness of 7 μm and an electrolyte thickness of 10 μm. The measured leak rates fit this value very well with one exception. Both cells with the thinnest anode (1 μm) exhibit leak rate values of 4 to $7 \times 10^{-5}\,hPa\,dm^3\,(cm^2\,s)^{-1}$, which are one to two times that of the threshold. Additionally, one cell prepared with a 13-μm-thick anode layer is also above the threshold. All others show lower values. Although these three cells exceed the threshold they were tested in the single cell unit. The reason for their exceeding the threshold will be discussed in the SEM characterization section. It should be noted here that all half-cells were tested in the oxidized state of the anode and the substrate. It is known that the value in the reduced state, as for operation, is higher – typically by one order of magnitude. Table 1 lists the open cell voltages (OCV) of all samples at 800 °C. The OCV values ranging from 1080 to 1085 mV correspond well with the theoretical Nernst voltage (at the given parameters, the theoretical value is 1100 mV). The slightly lower OCV values are probably due to a slightly higher water vapour concentration. No tendency for significant differences in the OCV values for thinner or thicker

anodes was measurable. The reason for this may be that the rise in the leak rate due to anode reduction varies, which ultimately leads to leak rate values higher by approx. a factor of 10–50 than in the oxidized state, and, moreover, it is not measurable whether a half-cell with a lower leak rate in the oxidized state also has the lowest leak rate in the reduced state.

The current–voltage characteristics were measured with increasing current load by a sequential step change of $0.0625\,A\,cm^{-2}$ starting from zero until the voltage dropped below 0.7 V or until the maximum current load of $1.25\,A\,cm^{-2}$ was reached. Calculations of the area specific resistance (ASR) at 0.7 V are based on linear regression or linear extrapolation. The ASR, defined as dV/di, is determined from the slope of the best fitting line over the measurement data within the interval 0.65–0.75 V. If the cell output does not drop below 0.7 V, the ASR is determined on the basis of the five final measurement data. The ASR values are listed in Table 1. The ASR varies between 170 and $210\,m\Omega\,cm^2$, which are typical values for these types of cells. There is no distinct dependence of the ASR on the anode thickness. The reason for this may be that the anode contributes less to the overall ASR value. Thus a slight difference in the anodic ASR is superimposed by the other cell components (ohmic losses of electrolyte and overpotentials of the cathode side). The current densities measured at 0.7 V between 650 and 900 °C are summarized in Fig. 2a. For better comparison, the current densities at a fixed temperature (800 °C) are extracted from Fig. 2a and shown in Fig. 2b. From both figures it is obvious that the current densities measured can be divided into two groups: one group from a thickness of 1–13 μm and the other from 18 to 22 μm. Results from the first group scatter around $1.7\,A\,cm^{-2}$ and from the second one around $1.5\,A\,cm^{-2}$. Since the calculated ASR is fairly constant but some slight tendency to rise occurred between the current densities (at 0.7 V and 800 °C), it is suggested that the activation polarization differs with changing anode thickness. Indeed, a former study with impedance spectroscopy by Mai et al. [4] revealed differences in the anodic reactions (anode diffusion and/or charge transfer).

A comparison of the anode microstructures is shown in Fig. 3. The following conclusions can be drawn from Fig. 3:

- for the thinnest anodes (1 and 3 μm) no clear anode layer exists; in most cases the anode material only smoothes the roughness of the underlying substrate, only forming a partly layered structure
- an anode layer is formed beginning at a thickness of 5 μm; but the nominal layer thickness and the measured layer thickness are only equal at 7 μm
- for the thicker anodes (>7 μm) the nominal and the real thickness are in very good agreement
- in all cases the anode shows a fine, homogeneous microstructure which is typical of layers deposited by VSC
- the electrolyte is dense with some remaining closed porosity and its thickness is ~10 μm (as desired)
- the barrier layer thickness is around 5 μm and porous; this is also typical of a relatively low sintering temperature of 1250 °C and is not ideal, but up to now no better microstructure has been obtained by ceramic processing of CGO layers; if there is a

Table 1
OCV and ASR of the cells at 800 °C; fuel gas: hydrogen with 3% water vapour, oxidant: air.

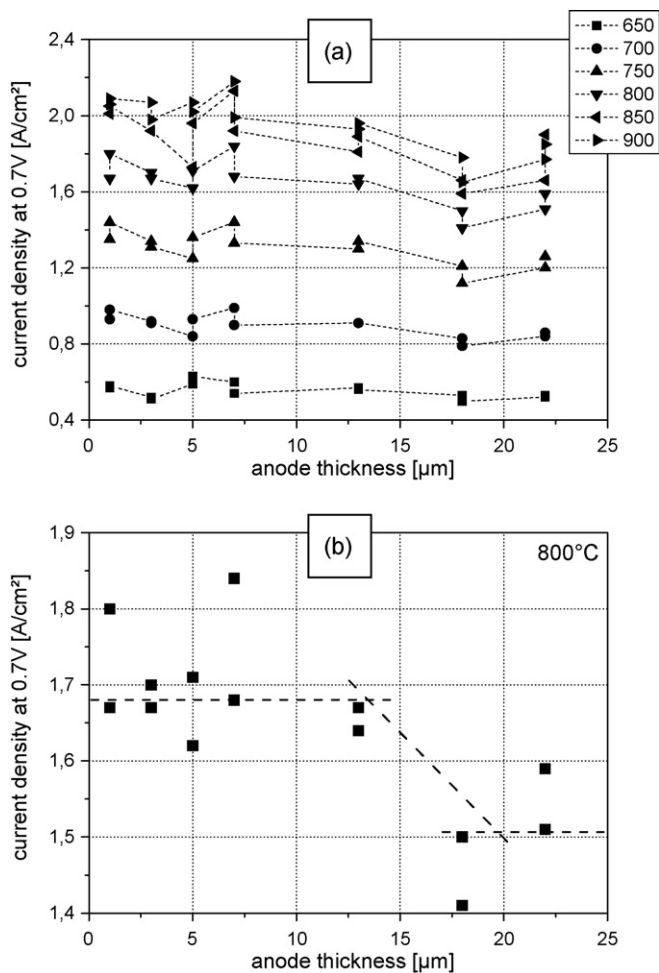| Anode thickness [μm]	OCV cell 1 [mV]	ASR cell 1 [mΩ cm²]	OCV cell 2 [mV]	ASR cell 2 [mΩ cm²]
1	1082	199 ± 7	1081	173 ± 2
3	1081	191 ± 2	1083	186 ± 1
5	1083	198 ± 2	1082	185 ± 2
7	1082	177 ± 2	1082	187 ± 2
13	1080	189 ± 4	1083	184 ± 1
18	1081	202 ± 3	1084	211 ± 2
22	1085	197 ± 1	1081	188 ± 2

Fig. 2. Measured current densities at 0.7 V; (a) as a function of anode thickness and operating temperature and (b) at 800 °C (the dashed lines are a guide for the eyes).

Fig. 3. SEM micrographs of cell cross-sections after cell testing (layers of each cell from bottom to top: substrate, anode, electrolyte, barrier, cathode; the horizontal cracks are due to sample preparation).

necessity for a dense barrier layer techniques like physical vapour deposition or sputtering need to be applied [9]

- the cathode thickness is ~40 μm, but the cathode and the barrier layer are of equivalent thickness for all cells
- since the substrate, the electrolyte, the barrier layer and the cathode are kept constant in microstructure and thickness, the slight measured differences in current density can only be attributed to the anode

A comparison of the He leak rates, the OCV values and the SEM microstructures did not show any explanation for the higher leak rates for the cells with the thinnest anode. However, the measured OCV cannot completely explain the results either because the values for all cells were very good and comparable. However, from the manufacturing experience at our institute it is known that fine-structured layers on top of coarse-structured porous supports need to have a minimum thickness to cover all roughness and porosity forming a dense and gas-tight layer. If a layer, e.g. the electrolyte on the anode substrate, is too thin it cannot densify to gas-tightness anywhere. Single spot-like defects govern the measured leak rates. Thus it is possible that the thinnest anode cannot safely cover all the surface roughness and porosity of the substrate and thus the measured leak rates are higher than for cells with thicker anodes. This cannot easily be confirmed by SEM cross-sectional characterization because one of the spot defects needs to be prepared. However, if they cannot be localized by optical microscopy on the surface it
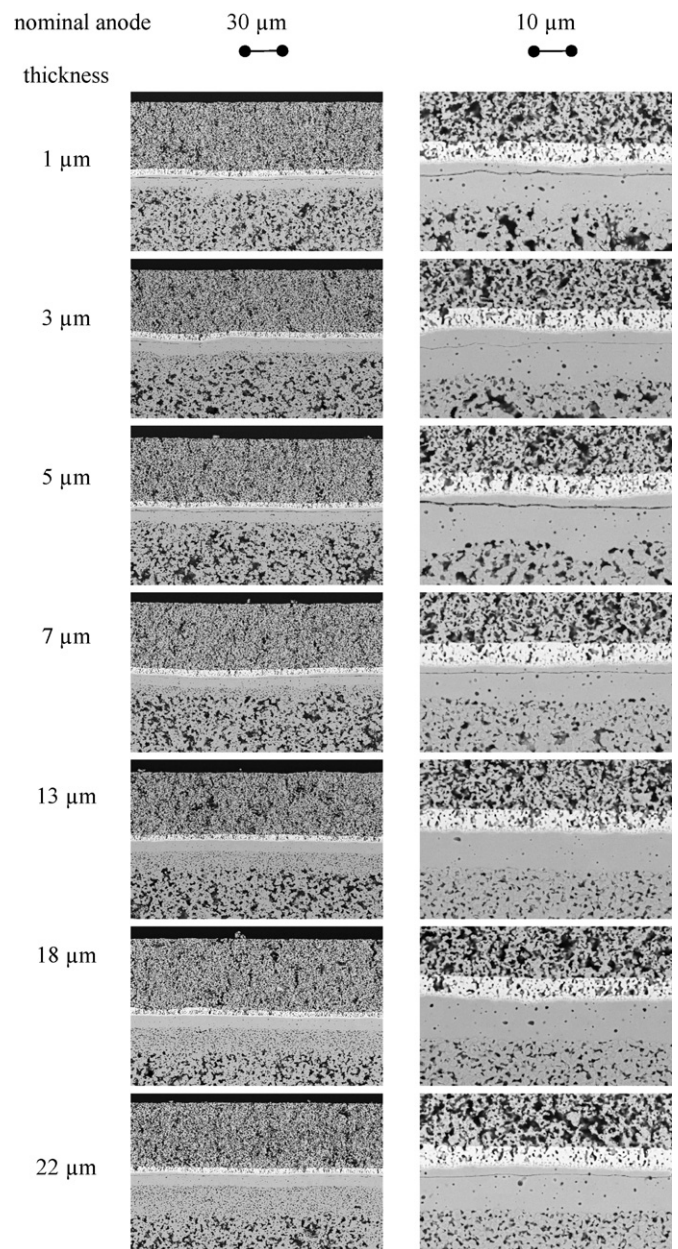
would be extremely unlikely that they would be prepared during sample grinding and polishing.

4. Conclusions

Summarizing the post-test SEM examinations with the measured current densities and the characterizations performed during cell manufacturing lead to the following conclusions:

- nearly all cells fulfil the He leak rate threshold irrespective of the anode thickness; only the samples with the thinnest anode have slightly higher leak rates; slightly higher leak rates in the oxidized state may not additionally cause higher leak rates for the electrolyte after anode reduction
- after anode reduction all samples show OCV values corresponding to the theoretical values, indicating a gas-tight electrolyte under the chosen conditions

- the current densities are split into two groups; the first one with an anode thickness of 1–13 μm with values of 1.7 A cm^{-2} and the second one with the thicker anodes having current densities of around 1.5 A cm^{-2}; earlier investigations on cells with LSM cathodes showed a more pronounced influence of the anode thickness on the power output of such cells [10]. No obvious differences occurred in the ASR as a function of the anode thickness of the LSCF cathode cells since the contribution of the anode resistance is negligible with respect to the overall ASR. The only difference in the current density can be explained by differences in the anode activation overpotential. However, based on these measurements, no in-depth explanation can yet be given. Additional measurements with half-cells focusing in more detail on the anode layer will be necessary to obtain greater insight into the influence of the anode thickness on electrochemical performance (e.g. impedance spectroscopy)
- SEM micrographs show less good layer formation for thin anodes, but good layers for thicknesses above 5 μm; all anodes are porous and homogeneous
- intensive impedance spectroscopy on comparable cells only reveals differences in the anodic reaction mechanism (anode diffusion and/or charge transfer); therefore the slight measured differences in current density can be attributed to the variations in anode thickness

Single cell testing at low fuel utilization shows that anode thicknesses between 1 and 13 μm have no influence on the current density of anode-supported SOFCs with CGO barrier layer and LSCF cathodes. Thicker anodes reduce the current density by approximately 10%. SEM characterization after single cell testing shows uniform anode microstructures for anode thicknesses above 5 μm and only partly layered structures below 7 μm.

Acknowledgements

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