ABSTRACT

The properties of solid oxide fuel cell (SOFC) cathodes consisting of (La,Sr)(Fe,Co)O$_3$-type (LSFC) perovskites were examined. For this purpose, anode-supported single cells with yttria-stabilised zirconia (8YSZ) electrolytes were used. On the electrolyte, a Ce$_{0.8}$Gd$_{0.2}$O$_2$-$_8$ (CGO) interlayer and the LSFC cathode were screen-printed. Emphasis was placed on the effect of changing material properties and processing parameters; i.e. the influence of sintering temperature of the CGO interlayer and composition of the LSFC cathode. It was found that the performance was best for sintering temperatures of the CGO interlayer of at least 1300°C. A La$_{0.58}$Sr$_{0.4}$Fe$_{0.8}$Co$_{0.2}$O$_3$-$_8$ cathode, together with a CGO interlayer, considerably improved the overall power densities (0.77 W/cm$^2$ at 750°C) compared to SOFC with a La$_{0.65}$Sr$_{0.3}$Mn$_{0.3}$O$_2$/8YSZ composite cathode (0.39 W/cm$^2$). This was particularly the case for operating temperatures between 650 and 750°C. Regarding a La$_{0.8}$Sr$_{0.2}$Fe$_{0.8}$Co$_{0.2}$O$_3$-$_6$ cathode, the higher lanthanum content resulted in lower electrochemical performance.

INTRODUCTION

One of the main goals of solid oxide fuel cell (SOFC) development nowadays is to reduce the operating temperature from 800-1000°C to 750°C or below. Higher temperatures result in corrosion of steel stack components and, as a consequence, in intolerable stack degradation. Reducing the operation temperature is, however, associated with a decrease in power density of the SOFC, mainly due to higher overpotentials at the cathode (see 1, 2). From this point of view, new cathode materials with an increased electrocatalytic activity compared to state-of-the-art La$_{1-x}$Sr$_x$MnO$_3$-$_8$ (LSM)-based perovskites need to be developed. In addition to a high electronic conductivity, these materials should provide a high ionic conductivity leading to a wider three-phase-boundary at the cathode/electrolyte interface and faster surface exchange kinetics, which both lead to an increased overall power density of the fuel cell.

In the last few years, much attention has been attracted by cobalt- and iron-containing perovskites with the general formula La$_{1-x}$Sr$_x$Fe$_{1-z}$Co$_z$O$_3$-$_8$ (LSFC) (see 3, 4) as these have both a higher oxygen ion conductivity and faster surface exchange kinetics.
compared to LSM. However, these materials pose disadvantages such as incompatibilities with the 8YSZ (8 mol% yttria-stabilised zirconia) electrolyte; i.e., a high thermal expansion coefficient (5) compared to YSZ and undesired chemical reactions (6). Therefore, a Ce₀.₈Gd₀.₂O₂₋₄ (CGO) interlayer is needed to overcome these disadvantages (7). The objective of this contribution is to investigate the electrochemical performance of LSFC-based SOFC in comparison with single cells containing a LSM/YSZ-composite cathode. In particular, attention is paid to different sintering temperatures of the CGO interlayer and different compositions of the LSFC cathode.

EXPERIMENTAL

SOFC Preparation and Characterization

Anode-supported single cells used in this study, are based on an anode substrate (Ni/8YSZ) with an average thickness of about 1.5 mm. The anode substrate (dimensions: 50 x 50 mm²) is produced by warm pressing using a so-called Coat-Mix® material and presintering at 1230°C. An anode functional layer (Ni/8YSZ, thickness: approx. 10 µm) and the electrolyte (8YSZ, thickness: approx. 10 µm), both deposited by vacuum slip casting, were co-fired at 1400°C. More details about the manufacturing procedures can be found elsewhere (8).

All subsequent layers (40 x 40 mm²) are applied by screen printing using pastes based on ceramic powder, an ethyl cellulose binder (Sigma) and a terpineol-based solvent (Dupont 8250). The La₀.₆₅Sr₀.₃MnO₃₋₄ powder was synthesised by spray drying, as described by Kontouros et al. (9). La₀.₆₅Sr₀.₃Fe₀.₈Co₀.₂O₃₋₄ was prepared by a citrate complexation (Pechini) route (10), while the La₀.₅₈Sr₀.₄Fe₀.₈Co₀.₂O₃₋₄ powder was provided by ECN (Energy Research Centre of the Netherlands, Petten). Ce₀.₈Gd₀.₂O₂₋₄ powder was purchased from Treibacher Auermet (Austria). All cathode powders underwent a calcination step between 700 to 900°C until crystallographic single-phase purity was achieved. This purity was proven by X-ray diffraction using a Siemens D500 equipped with a mono-chromated Cu Kα radiation source.

Regarding the LSFC-based single cells, the CGO interlayer (thickness: 7 µm) applied between the electrolyte and cathode was sintered between 1200 and 1350°C. Afterwards, the LSFC cathode (thickness: 45 µm) was deposited and sintered at 1080°C. The LSM-based composite cathode consisted of a pure La₀.₆₅Sr₀.₃MnO₃₋₄ layer (thickness: approx. 45 µm) and a cathode functional layer (thickness: approx. 15 µm) of 60 wt. % La₀.₆₅Sr₀.₃MnO₃₋₄ and 40 wt.% 8YSZ, the latter layer acting as the electro-catalytically active layer.

Characterization of the microstructure of the anode-supported single cells was performed using scanning electron microscopy (LEO 1530 (Gemini)) equipped with an energy dispersive X-ray (EDX) analysis system.

Electrochemical Measurements

Electrochemical measurements of the single cells were performed in an alumina test housing. In order to obtain sufficient electronic contacts, on the anode side a Ni mesh, and on the cathode side a Pt mesh were used. Sealing of the gas compartment was
obtained by a gold seal. After closing the furnace, a gas flow of argon was introduced at the anode side, and an air flow at the cathode side. The temperature was slowly increased to the reduction temperature. After reaching this temperature, the anode of the single cells was reduced by replacing stepwise the argon with hydrogen. Water vapour (3 vol%) was added by saturating the hydrogen gas through a water bubbler (super saturation and condensation) to the desired dew point. The total gas flow of hydrogen and air were both set at 1000 ml/min (STP) using mass flow controllers. The electrochemical performance was measured between 650 and 800°C.

RESULTS AND DISCUSSION

Microstructure and Element Composition

Effect of the presence of a CGO interlayer. Figures 1 and 2 show backscattered SEM micrographs including element mappings of polished cross sections of the cathode/electrolyte interface without and with the presence of a CGO interlayer.

![Backscattered SEM micrograph and element distribution of the cathode/electrolyte interface of La0.58Sr0.4Fe0.8Co0.2O3-δ cell without CGO interlayer.](image)

Without this CGO interlayer (Figure 1) where La0.58Sr0.4Fe0.8Co0.2O3-δ was deposited directly on the electrolyte and sintered at 1080°C, a strontium and zirconium-rich phase, probably SrZrO3, is formed near the interface. The formation of this Sr-rich phase results in a higher A-site deficiency in the perovskite LSFC. This probably caused the formation of a Co-rich phase distributed inhomogeneously in the cathode layer. The formation of a continuous SrZrO3 layer between the 8YSZ electrolyte and the LSFC cathode will finally increase the ohmic resistance, resulting in failure of the SOFC. In Figure 2, the influence of the CGO interlayer is shown. This interlayer successfully prevents the formation of SrZrO3 and, consequently, the Co-rich phase in the cathode. Cracks visible in the lower part of the CGO interlayer were formed during preparation of the cross sections.

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Microstructure of the LFSC vs LSM/YSZ cathode. The microstructure of the cathode plays a vital role in the performance of the cathode and, thus, in the performance of the whole SOFC. Figures 3 and 4 show SEM micrographs of the microstructure of a LSM/YSZ cathode functional layer deposited on a 8YSZ electrolyte, and a LSFC cathode together with a CGO interlayer and a 8YSZ electrolyte, respectively.

The microstructure of the LSFC cathode is slightly coarser than that of the LSM/YSZ cathode functional layer. For the mixed-conducting LSFC cathode, the active area is not limited to the cathode/electrolyte interface, which is normally the case for LSM-based cathodes. Therefore, a coarser structure was chosen to provide sufficient gas supply and sufficient contact with the CGO interlayer.

Effect of different sintering temperatures of the CGO interlayer. Figures 5 and 6 show SEM micrographs of cross-sections of two different CGO interlayers; i.e., one
sintered at 1200°C (Figure 5) and the other at 1300°C (Figure 6). Cross sections of a CGO interlayer sintered at 1100°C (not depicted here) provided insufficient adhesion with the 8YSZ electrolyte. A sintering temperature of 1200°C led to a porous layer with sintering bridges between the CGO interlayer and the electrolyte. Higher sintering temperatures; i.e., 1300°C and 1350°C, resulted in a coarser structure of the CGO interlayer together with a good contact with the underlying electrolyte. However, at these high sintering temperatures, an interdiffusion zone at the interface of the two layers is formed (cf. the different fracture morphology in the YSZ layer in Figures 4 and 6), which probably may influence the electrochemical performance (7). Nevertheless, for a good ionic conductivity of the CGO layer, sintering at temperatures ≥ 1200°C seemed desirable.

Therefore, electrochemical tests were performed on LSFC-based single cells as a function of these sintering temperatures, i.e. 1200, 1300, and 1350°C.

Electrochemical Characterization

The electrochemical performance; i.e., current density (A/cm²) at 700 mV, area specific resistance (mΩ cm²), and activation energy (kJ/mol), of a reference (LSM/YSZ-based single cells) and single cells with an LSFC (La₀.₅Sr₀.₄Fe₀.₆Co₀.₄O₃-δ) cathode as a function of the sintering temperature of the CGO interlayer are given in Table 1. The fuel gas used here consists of H₂ with 3% H₂O (gas flow: 1000 ml/min), the oxidant was air (1000 ml/min).

From this table, it can be concluded that replacing the LSM-based cathode by a LSFC-cathode including a CGO interlayer results in a significant improvement of the electrochemical performance. In particular, for the temperature region 650 to 750°C and in the case of the presence of a CGO interlayer sintered at 1300 or 1350°C, the current density at 700 mV was about twice the averaged value of the reference LSM single cells. In addition, an obvious decrease of the area specific resistance and a slightly lower activation energy were obtained.

Figure 5. CGO layer sintered at 1200°C. Figure 6. CGO layer sintered at 1300°C.
The electrochemical performance increased with increasing sintering temperature of the CGO interlayer, while the activation energy is hardly influenced. For a good electrochemical performance of these types of single cells, a sintering temperature of at least 1300°C is needed. Figure 7 shows a set of current-voltage curves of La0.58Sr0.4Fe0.8Co0.2O3-δ-based single cells as a function of the sintering temperature of the CGO interlayer.

In addition to the above described experiments, measurements were performed with an LSFC cathode of the composition La0.8Sr0.2Fe0.8Co0.2O3-s. The higher La content and, consequently, a lower Sr content reduces the thermal mismatch between the LSFC cathode and the underlying CGO interlayer (5). In this case, the sintering temperature of the CGO interlayer was 1200°C. The electrochemical data of this series of cell tests are also given in Table 1.

Table 1. Electrochemical data from anode-supported single cell tests.

| Temperature (°C) | Current density at 700 mV (A/cm²) | Lao.58Sr0.4Fe0.8Co0.2O3-δ | Lao.8Sr0.2Fe0.8Co0.2O3-s |
|-----------------|-------------------------------------|---------------------------|-------------------------|
|                 |                                     | CGO (1200°C)      | CGO (1300°C)      | CGO (1350°C)      | CGO (1200°C)      |
| 650             | 0.22 ± 0.03                         | 0.32 ± 0.05         | 0.49 ± 0.01         | 0.45 ± 0.01         | 0.28 ± 0.03         |
| 700             | 0.36 ± 0.08                         | 0.56 ± 0.09         | 0.75 ± 0.01         | 0.78 ± 0.01         | 0.46 ± 0.04         |
| 750             | 0.55 ± 0.11                         | 0.83 ± 0.10         | 1.10 ± 0.03         | 1.14 ± 0.01         | 0.69 ± 0.04         |
| 800             | 0.92 ± 0.05                         | 0.99 ± 0.12         | 1.28 ± 0.07         | 1.32 ± 0.03         | 0.87 ± 0.04         |

| Temperature (°C) | Area Specific Resistance (mΩ cm²) | Lao.58Sr0.4Fe0.8Co0.2O3-δ | Lao.8Sr0.2Fe0.8Co0.2O3-s |
|-----------------|-----------------------------------|---------------------------|-------------------------|
|                 |                                   | CGO (1200°C)      | CGO (1300°C)      | CGO (1350°C)      | CGO (1200°C)      |
| 650             | 1327 ± 312                        | 1030 ± 144           | 644 ± 15            | 731 ± 8            | 1076 ± 15          |
| 700             | 767 ± 248                         | 556 ± 51             | 440 ± 20            | 404 ± 15           | 643 ± 9            |
| 750             | 517 ± 174                         | 390 ± 43             | 270 ± 16            | 251 ± 9            | 445 ± 16           |
| 800             | 343 ± 64                          | 314 ± 34             | 233 ± 16            | 221 ± 11           | 337 ± 4            |

Generally, the electrochemical performance of single cells with the cathode composition La0.8Sr0.2Fe0.8Co0.2O3-s was lower than that for cells with a La0.58Sr0.4Fe0.8Co0.2O3-δ cathode. However, comparing the data with the averaged values of the reference LSM/YSZ single cells, it can be concluded that, except for the test temperature of 800°C, the performance of La0.8Sr0.2Fe0.8Co0.2O3-s-based single cells was slightly improved; i.e., higher current densities and a lower area specific resistance were obtained.
CONCLUSIONS

Changing material properties and processing parameters can significantly affect the electrochemical performance of anode-supported single cells. In this paper, attention was paid to the influence of sintering temperature of the CGO interlayer on the microstructure and the electrochemical performance of the LSFC-based SOFC. In addition, some preliminary experiments were performed with a different LSFC cathode composition. Results have clearly shown that an LSFC cathode together with a CGO interlayer significantly improves the overall power densities compared to the LSM/YSZ reference cells. The presence of this CGO interlayer between cathode and electrolyte is needed to prevent the formation of SrZrO3 near the cathode/electrolyte interface. This oxide leads to failure of the SOFC.

The best performance was obtained with sintering temperatures of at least 1300°C for the CGO interlayer. Lower sintering temperatures resulted in lower performances, which can be ascribed to insufficient adhesion between the CGO interlayer and the 8YSZ electrolyte. Comparing results from two different LSFC cathodes; i.e., La0.58Sr0.4Fe0.8Co0.2O3-δ and La0.58Sr0.2Fe0.8Co0.2O3-δ, it was concluded that a higher La-content reduces the electrochemical performance. The power densities for the La0.58Sr0.4Fe0.8Co0.2O3-δ cells were also higher than the results published by Rietveld et al. (11) for cells with a La0.6Sr0.4Fe0.8Co0.2O3-δ cathode and a Ce0.9Y0.1O1.95 interlayer.

Further research is still needed to optimise the material properties and processing parameters in order to reach higher electrochemical performance. Furthermore, the long-term stability of the LSFC-based cathodes for anode-supported single cells has to be proven.

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Figure 7. Current-voltage curves at 700°C of La0.58Sr0.4Fe0.8Co0.2O3-δ-based single cells as a function of the sintering temperature of the CGO interlayer (fuel gas: H2 (3% H2O) = 1000 ml/min, oxidant: air = 1000 ml/min).
ACKNOWLEDGMENTS

The authors wish to thank the staff of the FZJ-IWV-department, Jülich, Germany, for processing the anode substrates and electrolyte layers; namely, Mr. F. J. Dias, Mrs. M.-T. Gerhards, Mr. M. Kampel and Mr. Blaß and for performing the electrochemical measurements; in particular, Mrs. C. Tropartz, Mrs. B. Röwekamp, and Mr. H. Wesemeyer. In addition, thanks go to Dr. Rietveld, ECN, Petten, The Netherlands, for providing the $\text{La}_{0.58}\text{Sr}_{0.4}\text{Fe}_{0.8}\text{Co}_{0.2}\text{O}_3$ powder. Financial support from the Bundesministerium für Bildung und Forschung (BMBF), Verbundprojekt Erneuerbare Energien under Contract No. 01SF0039 is gratefully acknowledged.

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