LONG-TERM MEASUREMENTS OF ANODE-SUPPORTED SOLID OXIDE FUEL CELLS WITH LSCF CATHODES UNDER VARIOUS OPERATING CONDITIONS

Michael Becker*, Andreas Mai**, Ellen Ivers-Tiffée*, Frank Tietz**
*Institut für Werkstoffe der Elektrotechnik (IWE)
Universität Karlsruhe, 76131 Karlsruhe, Germany
**Institute for Materials and Processes in Energy Systems (IWV)
Forschungszentrum Jülich, 52425 Jülich, Germany

ABSTRACT

Anode-supported SOFCs with La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (LSCF) cathodes, Ce_{0.8}Gd_{0.2}O_{2-δ} interlayers and yttria-stabilised zirconia electrolytes show a significantly higher power output than cells with (La,Sr)MnO_{3-δ}-based cathodes in single cell tests. However, these cells show a rather high degradation rate of 1.0 - 1.5 % per 1000 h. Therefore, the long-term stability of seven LSCF-based cells was evaluated over 1000 hours of operation under varied constant operating conditions to evaluate the parameters forcing the cell degradation. The tests were carried out at temperatures of 800°C and 700°C as well as at current densities of 0.3 and 0.6 A/cm². Furthermore, the influence of a higher reduction temperature of the anode was evaluated. The results show that it is vitally important to compare the degradation rates at identical operating points for evaluation of the parameters influencing the degradation. While a lower temperature resulted in a significantly reduced degradation, the current density and reduction temperature did not have a clear impact on the degradation.

INTRODUCTION

One aim of latest development activities in the field of solid oxide fuel cells (SOFC) is the reduction of the operating temperature to 600-800°C. This results in smaller mismatches in thermal expansion coefficient and interdiffusion of the materials used. Lower temperatures decrease the requirements on interconnector materials and therefore material costs. In addition, prolonged SOFC stack life time can be achieved. It was shown previously that using La_{0.58}Sr_{0.4}Co_{0.2}Fe_{0.8}O_{3-δ} (L58SCF) as the cathode material in anode-supported SOFCs leads to significantly higher power densities compared to SOFCs with (La,Sr)MnO_{3-δ}-based cathodes in the temperature range mentioned above (1, 2). That has also been shown by other authors (3-5). The higher performance of LSCF-based cathodes has also been demonstrated in SOFC stacks (6).

However, former endurance tests of single cells with 40 x 40 mm² LSCF cathodes under a constant load of 0.5 A/cm² showed a rather high loss in performance of 0.9 to 1.5% per 1000 h (see Figure 1), which is tolerable for mobile applications of SOFC systems, but not for stationary applications. In the past, degradation rates of complete SOFC stacks
were significantly higher than the rates measured for single cells, but nowadays the degradation rates of stacks have been reduced to values of 0.5 (cells with LSM-cathodes) to 3% (cells with LSCF-cathodes) (6). That makes it necessary to investigate the degradation mechanisms of single cells in more detail.

Since the degradation of cells with LSM cathodes in former measurements (7) was smaller than the degradation rates measured with LSCF cathodes on similar anode-supported thin film electrolyte SOFCs, it becomes necessary to take a closer look on the long-term behaviour of LSCF cathodes to achieve a more profound knowledge on the degradation behaviour.

**Figure 1. Long-term behaviour of SOFCs with 16 cm² L58SCF cathodes under constant load of 0.5 A/cm², at 750°C with 1 slm H₂+3% H₂O and air as gases (1).**

In order to investigate the reasons of the performance degradation and resulting determination of operating conditions with minimized degradation, seven single cells with L58SCF cathodes were tested in different operating conditions for at least 1000 h under constant operating conditions.

**EXPERIMENTAL**

**Cell Production and Cell Geometry**

The SOFCs used in this study are based on 50 x 50 mm² anode substrates (Ni/8YSZ) with an average thickness of about 1.5 mm. On these substrates, an anode functional layer (Ni/8YSZ, approx. 10 μm) and an electrolyte (8YSZ, approx. 10 μm) are deposited and co-fired at 1400°C. More details on the manufacturing procedures can be found elsewhere (8).

As described in an earlier paper (1), a Ce₀.₈Gd₀.₂O₂₋₅ (CGO, from Treibacher Auermet, Austria) interlayer was screen-printed on the electrolyte and sintered at 1300°C for 3 h,
resulting in a thickness of approx. 7 μm. This interlayer is used to prevent a chemical reaction between LSCF and 8YSZ, which otherwise forms an insulating layer of SrZrO₃. On top of this interlayer a La₀.₅₈Sr₀.₄Co₀.₂Fe₀.₈O₃₅ cathode (synthesised by spray drying, as described by Kontouros et al. (9), calcination temperature 900°C) was applied by screen-printing and sintered at 1080°C for 3 h, resulting in a thickness of approx. 45 μm.

The active area of the applied cathode was 10 x 10 mm². Additionally, two reference electrodes in gas flow direction in front of and behind the cathode were applied (see cathode layout in (10)). These three electrodes were separated from the electrolyte by a single CGO interlayer with lateral dimensions of 12 x 30 mm².

**Set-up for Electrochemical Measurements**

For electrochemical characterisation of the cells the IWE has constructed two identical software-controlled test benches that can operate up to 1200 °C with an accuracy of 0.25% of the temperature set point, given by thermocouple type S. A gas supply unit is installed to feed the cells with 6 selectable gases on both sides, cathode and anode. The mass flow controllers (MFC) used have a metering precision of 0.5% of the measured value and 0.1% of the measurement range's terminal value at a flow rate of 300 sccm and 150 sccm (for oxygen on anode side) respectively. The current is set by a power supply unit from Agilent (model 6012C) with a range from 0-2 A and an accuracy of 0.2%. All cell voltages are recorded by the data acquisition unit “Agilent 34970A” with 6 ½ digits (22 bits) of resolution, which means less than 0.1 V total accuracy for typical measurement values of SOFC single cells. Additionally an error of not more than 0.004% dc V per 1-year at 25°C is guaranteed.

The SOFC single cell electrodes were contacted on the anode side with nickel meshes and with gold meshes on the cathode side. The meshes were mounted in an Al₂O₃ contact block including gas channels of 1 mm² in cross section and 10 mm length to guide the supplied gases along the electrodes (10).

During the total measurement period, the steam amount in the anode gas was set to 5.5% corresponding to an open circuit voltage (OCV) of 1.072 mV at 800°C and 1.092 mV at 700°C, respectively. This was measured at the reference electrode located in front of the working electrode in the gas flow direction. Assuming that the electrolytes do not become leaky during the measurement period, this gives reliable information on the stability of operating conditions (e.g. drift of MFCs). It was therefore recorded for each cell during the total measurement period of at least 1000 hours.

In order to investigate the influence of temperature and current density on the single cells’ degradation, the measurements were carried out at 700°C and 800°C and at current densities of 0.3 and 0.6 A/cm². All cells were fed with air as oxidant. Additionally, the reduction temperature of the anode substrate was set to 900°C instead of 800°C for cell 7 (see Table 1). This was done to establish a coarser anode microstructure which might be more resistant to sintering effects during operation of the cell. Further measurements with the same current densities and temperatures, but with only 5% instead of 21% oxygen in the cathode gas are currently underway and will be the subject of a future publication.
Table 1. Long-term operating conditions of tested cells. All cells were operated with 250 sccm air on the cathode side and 250 sccm H2 including 5% H2O on the anode side.

| Cell   | j/A/cm² | T / °C | T_{reduction NiO—>Ni} |
|--------|---------|--------|------------------------|
| Cell 1 | 0.6     | 800    | 800                    |
| Cell 2*| 0.6     | 700    | 800                    |
| Cell 3 | 0.6     | 700    | 800                    |
| Cell 4*| 0.3     | 800    | 800                    |
| Cell 5 | 0.3     | 800    | 800                    |
| Cell 6 | 0.3     | 700    | 800                    |
| Cell 7 | 0.6     | 800    | 900                    |

* Reproducibility test of the long-term measurements of cells 3 and 4

Since the total time for the measurements was about one year, there were no statistics planned for every single parameter set. For this reason every single cell was treated by the identical test procedure before and after the long-term measurement. The procedure of operation is shown in principle in Figure 2. During the initial and finishing procedure the cells have been characterised at temperatures of 600°C – 800°C in steps of 50 K. At each temperature, the gas composition (N2/O2 and Ar/O2) and partial oxygen pressure were varied. For all these parameter settings the cells were characterised by I-V-curves and electrical impedance measurements. This was done to obtain information on degradation behaviour of the cells under various comparable operating conditions (set points).

Figure 2. Principal operation of cell test procedure.

RESULTS

Reproducibility of the Measurements

The open circuit voltage at 800°C with 250 sccm air and 250 sccm dry H2 was always higher than 1.18 V which means a very gas tight sealing (≤ 0.5% H2O resulting from reaction with O2 from surrounding air) and therefore a very good separation of reducing
anode gas from cathode material. That means in general a negligible influence of steam on degradation of the cathode material.

Table 2 gives the mean values and standard deviations of the power densities of all tested cells. The power densities at 0.7 V and at temperatures from 600 to 750°C are taken from the I-V-curves measured during initial test procedure. Over this temperature range, the standard deviation is 0.012 W/cm² to 0.05 W/cm². This demonstrates the high reproducibility of the cell production and the test bench set-up including the contact between cell electrodes and metal meshes. The measured power densities are approximately the same than for similar cells with 40 x 40 mm² cathodes (1).

Table 2. Mean value and standard deviation of the power densities at 0.7 V of measured cells.

| Temperature (°C) | 750       | 700       | 650       | 600       |
|-----------------|-----------|-----------|-----------|-----------|
| Power density (W/cm²) | 1.09 ± 0.05 | 0.67 ± 0.03 | 0.37 ± 0.018 | 0.18 ± 0.012 |

To obtain an impression on the reliability of the measurements, two tests with two different parameter sets were run under equal conditions for approx. 550 hours (see Figure 3). That does not of course produce highly reliable statistics, but gives more confidence in interpretation of the measured data. The difference in cell voltage of cells 2 and 3 is less than 1% and constant over the total measurement period of 550 h. This also indicates the accuracy of the measurements. Even more important is the nearly identical behaviour of the voltage over time for those cells. This shows that the observed degradation processes can be clearly distinguished from measurement inaccuracies.

Figure 3. Comparison of cell voltage behaviour of two times two cells in identical operating conditions. The difference of cell voltage of cells 2 and 3 is only 7 mV at 0 h (<1%) and 6.5 mV at 550 h of long-term test duration.

**Degradation During the Long-term Tests**

Figure 4 and Figure 5 show the time relationship of the cell voltages during the long-term measurements. All cells show a decrease of the cell voltage over time. Interpreting the
results of these curves, it seems that the degradation in performance is higher at an operating temperature of 700°C compared to 800°C and higher for 0.6 A/cm² compared to 0.3 A/cm² (see relative voltage drops per 1000 h given in the first row of Table 3). For example, cell 2 (T = 700°C; j = 0.6 A/cm²) shows a decrease of the voltage of 3.6% per 1000 h, while the voltage of cell 4 (T = 800°C; j = 0.3 A/cm²) decreases by only 2.3% per 1000 h. However, it has to be considered that these voltages were measured at different incomparable operating points of the SOFC, which falsifies the conclusions to some extent (see next section).

The time relationship of the cell voltages demonstrates a significant difference between the cells operated at 700°C and 800°C. While the voltage drop at 700°C is approximately linear, the voltage drop at 800°C has a slope that decreases over time, which points to a degradation effect that saturates over time (e.g. sintering or diffusion processes). This trend can be fitted very well with an exponential function and an additional linear term.

The reasons for the different degradation behaviour for cells operated at 700°C and 800°C are not clear yet, but changes in cathode stoichiometry, including diffusion processes, are assumed to be one of the reasons. The degradation of the electrolyte’s conductivity appears to be a negligible effect, when looking at resistances that were initially calculated from impedance measurements. This is in agreement with the degradation of the conductivity of 8YSZ published by Norby et al. (11). They measured a decrease of approx. 0.01 S/cm per 1000 h in air or hydrogen at 800°C.

**Comparison of Measurements Before and After the Long Term Tests**

As stated above, the comparison of the degradation rates of the different cells exclusively by means of the cell voltage drop is difficult and leads to no clear conclusion, because different operating points are compared. To circumvent this problem, I-V-curves were measured before and after the long-term measurements. Figure 6 shows two I-V-curves measured at 700°C for cell 6 before and after the long-term test. While the open cell voltage has not changed at all and while the cell voltage is lower after long-term
measurement at any current density, the cell resistance must have increased during the 1050 hours of operation. Therefore, the calculated degradation rates of cell voltage are different at different operating points, namely increasing with higher current densities and lower operating temperature. A comparison of the current densities at a fixed voltage (e.g. 0.7 V) leads to even higher degradation rates. Therefore, the degradation rate of this cell can be determined as 2.5% per 1000 h (at 0.3 A/cm²) or 16.6% per 1000 h (at 0.7 V) for the same cell, depending on the viewpoint and operating point respectively.

Figure 6. Two degradation values at two operation points: at 0.3 A/cm² a voltage drop of 2.5% (1) and at 0.7 V (2) a current density loss of 16.6 %. (I-V-curves measured on cell 6 at 700°C).

Figure 7 shows the relative power drops $\Delta p$ at different temperatures for all cells. This confirms the relationships mentioned above: at operating points that are more "demanding" for the SOFC (low temperatures, high current densities) the calculated degradation is higher than for less "demanding" operating points.

In addition to the voltage drops measured during the long-term tests, Table 3 shows the relative power drops $\Delta p$ per 1000 h for the five cells that were operated for at least 1000 h. The values have been calculated from the ratio of the power densities measured at a certain operating point ($j = 0.3$ and 0.6 A/cm² or $V = 0.7$ V; $T = 750°C$) before and after the long-term test:

$$\Delta p = \left(1 - \frac{p_{after}(j, V)}{p_{before}(j, V)} \right) \times \frac{1000}{t_{total}}$$  \hspace{1cm} [1]$$

While the voltage drops during operation were higher for lower temperatures and higher currents (first row in the table), this impression is somewhat changed when looking at the relative power drops from the I-V-curves (other rows). The cells that were operated at 700°C (No. 3, 6) show significantly smaller degradation rates under all conditions than the cells operated at 800°C (No. 1, 5 and 7). This indicates a thermally activated degradation process (e.g. sintering or diffusion process). From these values it can also be seen that the current density seems to have little influence on the degradation processes.
At 700°C the degradation rates are nearly the same after operation at 0.3 and 0.6 A/cm², while at 800°C a clear correlation is at least not visible. A significant influence of the reduction temperature, which was set to 900°C instead of 800°C for cell 7, is also not visible.

Figure 7. Relative difference in the power densities measured at 0.3 A/cm² before and after the long-term cell tests at different temperatures. Values in grey circle correspond to line 3 in Table 3.

Table 3. Decrease in cell performances at various operating points (in % per 1000 h).

| Cell | 800°C 0.6 A/cm² | 700°C 0.6 A/cm² | 800°C 0.3 A/cm² | 700°C 0.3 A/cm² | 800°C 0.6 A/cm² |
|------|-----------------|-----------------|-----------------|-----------------|-----------------|
| 1    | 2.3%            | 3.6%            | 2.3%            | 2.1%            | 3.3%            |
| 3    | 2.0%            | 1.2%            | 3.2%            | 1.0%            | 3.3%            |
| 5    | 4.1%            | 2.4%            | 5.6%            | 2.0%            | 5.9%            |
| 6    | 22%             | 13%             | 26%             | 12%             | 24%             |

Relative voltage drop during long-term test

Relative power drop $\Delta p^2$
- at $j = 0.3$ A/cm²
- at $j = 0.6$ A/cm²
- at $V = 0.7$ V

Total operating time 1130 h 1048 h 1051 h 1056 h 1056 h

*anode reduction temperature of cell 7: 900°C; all other cells: 800°C
\(^1\)calculation: $1 - (\text{cell voltage}_{(1000\text{h})}/\text{cell voltage}_{(after \text{ initial test})})$
\(^2\)decrease of the power density at 750°C taken from I-V-measurements after and before the long term tests

The measured degradation rates are in the same range as the degradation rates measured by Barfod et al. (12) for anode supported SOFCs with LSM-based cathodes at 850°C and 0.47 A/cm². Müller et al. (13) observed degradation rates of 0.3% per 1000 h for electrolyte-supported SOFC with LSM-based cathodes at 950°C, which were strongly dependent on the fuel utilisation. In both publications, coarsening of nickel in the anode
at these elevated temperatures is regarded as one of the reasons for the degradation. Coarsening of the nickel particles in the fine structured anode functional layer was also seen by Simwonis (14) after 2100 h of exposure at 800°C and 0.1 A/cm². In contrast to the findings of these authors and the results in this paper, Rietveld et. al. (4) observed no degradation of the cell voltage for anode-supported SOFCs with LSCF-based cathodes at 700°C for 1000 h at a current density of 0.4 A/cm².

For a verification of the findings in this article, further investigations are planned with a lower oxygen partial pressure (5% O₂ on the cathode side). Additionally, a detailed interpretation of the impedance measurements will follow, allowing determination of the contribution of polarisation and ohmic resistances to the change in total resistance. To find the reasons for the performance degradation, examinations of some of the samples by means of transmission and scanning electron microscopy (TEM/SEM) and secondary ion mass spectroscopy (SIMS) are currently underway.

CONCLUSIONS

To investigate the long-term behaviour of LSCF cathodes on anode-supported SOFC single cells with 8YSZ electrolytes and CGO interlayers, seven cells were electrochemically characterized at temperatures of 800°C and 700°C as well as at current densities of 0.3 and 0.6 A/cm². Furthermore, the influence of a higher reduction temperature was evaluated. All cells showed a very high reproducibility in cell performance during the initial test. Cells running under identical conditions over several hundred hours also showed equal degradation behaviour. Both these findings lead to a high confidence of measurement data even with a small database. The degradation rates were higher than in earlier experiments (shown in Figure 1) at similar conditions. This might be caused by the larger edge to surface area ratio, which is 4 for 1 cm² compared to 1 for 16 cm² cathodes, which enhances the influence of degradation effects at the edges of the cathode.

When using the cell voltage for evaluation of degradation behaviour of SOFC single cells, the comparison must be done at identical operating points. Comparing the cell performances before and after the long-term tests, a significant influence of the operating temperature on the degradation was obvious, whereas there was no clear influence caused by different current densities or a higher nickel oxide reduction temperature. All cells operated at 800°C showed very similar degradation behaviour. The degradation process slowed down after several hundred hours of operation. In contrast, the slope of the cell voltage of the cells operated at 700°C was nearly identical during the total time of characterization. The most likely reasons for the observed degradations include changes of the cathode stoichiometry due to diffusion processes, a further formation of SrZrO₃ at the CGO-YSZ interface and coarsening of the anode or the cathode microstructure.

ACKNOWLEDGMENTS

The authors thank the staff of the FZJ-IWV-department, Jülich, for processing the anode substrates and electrolyte layers. The financial support from the Bundesministerium für...
REFERENCES

1. A. Mai, V.A.C. Haanappel, S. Uhlenbruck, F. Tietz, D. Stöver, *Solid State Ionics*, submitted, (2004).
2. A. Mai, Ph.D. thesis, Ruhr-Universität Bochum, Germany, (2004).
3. N. Dekker, B. Rietveld, J. Laatsch, F. Tietz, in *6th European Solid Oxide Fuel Cell Forum*, M. Mogensen, Editor, pp. 319-328, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
4. B. Rietveld, P. Nammensma, J.P. Ouweltjes, N. Dekker, in *5th European Solid Oxide Fuel Cell Forum*, J. Huijsmans, Editor, 2, pp. 716 - 720, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2002).
5. E. P. Murray and S. A. Barnett, in *SOFC-VI*, S. C. Singhal and M. Dokiya, Editors, *PV 99-19*, p. 369, The Electrochemical Society Proceedings Series, Pennington, NJ, (1999).
6. R. Steinberger-Wilckens, I. C. Vinke, L. Blum, L. G. J. de Haart, J. Remmel, F. Tietz, W. J. Quadakkers, in *6th European Solid Oxide Fuel Cell Forum*, M. Mogensen, Editor, 1, pp. 11-19, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
7. L.G.J. de Haart, I. C. Vinke, A. Janke, H. Ringel, F. Tietz, in *SOFC-VII*, H. Yokokawa and S. C. Singhal, Editors, *PV 2001-16*, pp. 111-119, The Electrochemical Society Proceedings Series, Pennington, NJ, (2001).
8. H. P. Buchkremer, U. Diekmann, D. Stöver, in *2nd European Solid Oxide Fuel Cell Forum*, B. Thorstensen, Editor, p. 221, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (1996).
9. P. Kontouros, R. Förthmann, A. Naoumidis, G. Stochiniol, E. Syskakis, *Ionics*, 1, 40 (1995).
10. A. Weber, A. Müller, D. Herbstritt, E. Ivers-Tiffee, in *SOFC-VII*, H. Yokokawa and S. C. Singhal, Editors, *PV2001-16*, pp. 952-962, The Electrochemical Society Proceedings Series, Pennington, NJ (2001).
11. T. Norby, P. A. Osborg, H. Raeder, in *2nd European Solid Oxide Fuel Cell Forum*, B. Thorstensen, Editor, p. 315, European SOFC Forum, Oberrohrdorf, Switzerland, (1996).
12. R. Barfod, S. Koch, Y. L. Liu, P. H. Larsen, P. V. Hendriksen, in *SOFC- VIII*, S. C. Singhal and M. Dokiya, Editors, *PV 2003-07*, pp. 1158-1166, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
13. A. C. Müller, A. Weber, D. Herbstritt, E. Ivers-Tiffee, in *SOFC-VIII*, S. C. Singhal and M. Dokiya, Editors, *PV2003-07*, pp. 196-199, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
14. D. Simwonis, Ph.D. thesis, Ruhr-Universität Bochum, Germany, (1999).