EFFECT OF OPERATIONAL CONDITIONS ON LONG-TERM STABILITY OF SOFCs

Anke Hagen, Rasmus Barfod, Peter Vang Hendriksen, Yi-Lin Liu and Severine Ramousse
Risø National Laboratory
Frederiksborgvej 399, DK-4000 Roskilde, Denmark

ABSTRACT

The long-term stability of anode supported solid oxide fuel cells (SOFCs) was investigated as a function of operating temperature and current density. The largest degradation rate was observed at the lower operating temperature and higher current density of 750°C and 0.75 A/cm², respectively. Detailed characterization by impedance spectroscopy and post-test microscopy revealed that cathode degradation is the dominant contribution to the degradation under these conditions. A slight delamination at the cathode/electrolyte interface was observed. At higher operating temperatures, the degradation is generally less severe, even under higher current densities. Degradation rates as low as 2%/1000 h were observed at 850 and 950°C and 1.6 and 1.9 A/cm², respectively, over operating periods of 1500 hours.

INTRODUCTION

Long-term stability is an important requirement for the application of fuel cell technology. The total degradation of the cell performance while operated under constant conditions is the sum of contributions from all constituents of the test assembly (anode, cathode, electrolyte of the cell, their interfaces, and perhaps also auxiliary components (1)). For the cell constituents, degradation mechanisms like for example coarsening of nickel particles in the anode (2, 3), enrichment of impurities at the three-phase boundary (4), and changes of the microstructure in the cathode (5) have been discussed in the literature. The operating conditions affect these mechanisms differently. Besides degradation, activation processes, where cell performance increases over time, can occur under polarization. This effect could overlap with degradation, making evaluation more difficult. In order to assign the degradation behaviour of a given cell to a specific part of it, or even a specific process and further to predict its total lifetime in a justified manner, extensive testing and characterization is necessary.

In the present contribution, long-term tests running over 1500 h under constant operating conditions are reported. This test time was considered sufficient to evaluate the degradation for most of the applied conditions. However, in selected cases, the tests were extended in order to verify the found degradation courses.
EXPERIMENTAL

Anode supported SOFCs consisting of a Ni-YSZ anode, YSZ electrolyte, and LSM-YSZ cathode with an active area of 4 x 4 cm² were subjected to long term testing over periods of 1500 hours. The tests were performed in alumina test-houses using gold and nickel foil current collectors at the cathode and anode side, respectively. LSM and NiO/YSZ gas distribution components were used on the cathode and anode side, respectively. Standard glass ceramic composite seals (stoichiometric albite glass, 12.5 Na2O-12.5 Al2O3-75 SiO2 plus YSZ (6)) were used to seal the cell. Prior to testing, contact layers were applied on the cathode and anode of the cell. The test set-up and method is described in detail in (7). The tests were started by heating the cell in air to 1000°C with a heating rate of 1°C/min and reducing the anode at this temperature in humidified diluted hydrogen (9% in nitrogen, 4% water vapor) followed by pure humidified hydrogen.

After reduction, DC and AC characteristics were obtained at 850 and 750°C in air and humidified hydrogen as cathode and anode gas, respectively. Subsequently, the temperature was adjusted to operating temperature for the long-term tests. Air was used as cathode gas and a synthesis gas mixture on the anode side. The fuel gas was applied by mixing CO2 and hydrogen with a ratio of 1 to 4 or methane and water with a ratio of 1 to 2. At the conditions in the fuel gas inlet of the cell, an equilibrium mixture of CO:H2:H2O = 1:1:4 is obtained, corresponding to a steam to carbon ratio of two. The fuel utilization was adjusted to lie between 75 and 85% and controlled by measuring the oxygen partial pressures at the fuel outlet. The test matrix comprised the temperatures 950, 850, and 750°C and current densities in the range between 0.2 and 1.9 A/cm². Selected tested cells were subjected to post-test analysis (scanning electron microscopy).

RESULTS AND DISCUSSION

DC Characterization

When evaluating performance and stability of SOFCs, the efficiency \( \eta \) [1] and power density \( P \) [2] are key parameters:

\[
\eta = \frac{\Delta G}{\Delta H_{298}^0} \cdot \frac{U}{Emf} \cdot \alpha \tag{1}
\]

\[
P = U \cdot i \tag{2}
\]

where \( \Delta G \) is the change of the Gibbs energy, \( \Delta H \) the change of enthalpy, \( U \) the cell voltage, \( Emf \) the electromotive force, \( \alpha \) the fuel utilization, and \( i \) the current density.

The tests were carried out under constant current density and fuel utilization. Both, efficiency and power density, are proportional to the cell voltage under these conditions and changes of \( U \) with time translate thus directly to changes of efficiency and power density. The cell voltage decreased with increasing operating time, as shown in Fig. 1. The shape of the curves depended on the current density. At lower current densities, the decrease was more linear, whereas it was more exponential-like at higher current density (Fig. 1).
A simple way to calculate the degradation rate is to subtract the cell voltage at a given time from the initial cell voltage and to relate this value to 1000 hours operating time. This approach leads to different degradation rates depending on the test time used for calculation (see Fig. 1 and Fig. 2). Further, the cell voltage increased within the first 24 h in some tests. This result was already observed previously and could be due to cathode activation processes in the initial period under current load (8). This makes use of the initial cell voltage as basis for the degradation rate questionable. In this work, the degradation rate was therefore calculated as the difference between the initial ‘steady state’ cell voltage, i.e. the maximum cell voltage, and the cell voltage 300 or 1500 hours operating time thereafter, respectively. Both values were normalized to 1000 hours. The degradation rate after the shorter operating period yields important information about the initial degradation processes, whereas the latter one makes a prediction of lifetime more reliable. Two tests were extended beyond 1500 h operating time and showed a linearly decreasing cell voltage with a degradation rate like the one observed from 1200 to 1500 hours (9).

In Fig. 2, the degradation rates are shown as a function of current density and temperature:

**Figure 1.** Cell voltage as function of operating time and current density: 0.25 A/cm², 0.41 A/cm², and 0.75 A/cm² at 750°C.

**Figure 2.** Degradation rates after 300 (a) and 1500 (b) hours under current load as function of current density and temperature: 750°C (triangles), 850°C (circles), and 950°C (rhomb).
temperature. The degradation rates increased drastically with increasing current density, in particular when observing the first 300 hours (Fig. 2a). The sharp increase occurred at a lower current density at the lower temperature of 750°C.

After the whole period of 1500 hours (Fig 2b), the degradation rates were generally much smaller than after the first 300 h. But the effects of temperature and current density were qualitatively the same. The degradation rates at 850 (and 950) °C were again significantly smaller than at 750°C. At this lower temperature, the degradation rate still increased strongly with current density and was about ½ of the value observed after 300 h. At the higher temperatures, the degradation rate was only about 1/5 of the value after 300 h. This was due to the fact that the cell voltage decreased linearly and at a slow rate beyond 300 h operating time, i.e. the cell degradation reached almost a constant value at 850 and 950°C. Values as low as 2%/1000 h were obtained at 850 and 950°C at 1.6 and 1.9 A/cm² current density, which corresponds to very significant power densities.

The electrodes operate under much higher polarization at the lower temperature and it is relevant to evaluate degradation rate as a function of cell polarization \((Emf-U_{steady\,state})\). In Fig. 3, the degradation rates are re-plotted vs. the total cell polarization. The degradation rate increased nearly exponentially with increasing cell polarization. Interestingly, the trend was independent on the temperature when evaluated after 300 hours test (Fig. 3a). It thus seems that the underlying degradation mechanisms are similar in this period and that the initial degradation is more dependent on polarization than on temperature and current density. However, after 1500 hours test, the degradation rates increased more steeply at 750 compared to 850 (and 950) °C (Fig. 3b). Obviously, the degradation processes are more severe at lower temperatures. Looking at possible degradation mechanisms, nickel coarsening in the anode should be more pronounced at higher temperatures because of the higher mobility of species. The same should apply for the enrichment of impurities at the three-phase boundary, although also the thermodynamics of the formation of the specific phases is important. More information about the single contributions to the degradation can be expected from the electrochemical characterization prior to and after the test under constant operating conditions.
Impedance Analysis

In order to evaluate the degradation as a function of temperature and current density, in particular the high degradation rate at high current densities and 750°C (large polarization), impedance spectra obtained initially and after 1500 h test at constant conditions were compared. Two examples for each temperature are discussed here: one test at high and one at low polarization. In order to be able to compare characteristics directly before and after test, the impedance data were obtained at the same temperatures as the aging tests, i.e. for the tests performed at 750°C, also impedance spectra were recorded at 750°C (accordingly for the tests at 850°C).

The impedance spectra were recorded in hydrogen and with high degree of humidification (25%), in order to diminish the resistances arising from diffusion and gas conversion (10). The impedance spectra were fitted to an equivalent circuit consisting of an inductance, a serial resistance, and five resistance/constant phase element units. The two arcs at the lowest frequencies were assigned to diffusion and gas conversion and the three arcs at higher frequencies to cathode and anode processes (11, 12). The electrode resistance, $R_p$, was calculated as the sum of these three high frequency resistances ($R_p=R_1+R_2+R_3$). This measure thus comprises all anode and cathode losses (chemical and electrochemical of nature) other than diffusion and conversion losses. The shown spectra are representative for the tests performed at high and low current densities and at 750 and 850°C. The obtained resistance values are summarized in Table 1.

| $T$ (°C) | $i$ (A/cm²) | $Rs$ (Ω*cm²) | $Rp$ (Ω*cm²) |
|----------|--------------|---------------|---------------|
|          |              | Before test   | After test    | Before test | After test |
| 750      | 0.25         | 0.18          | 0.21          | 0.37        | 0.55       |
| 750      | 0.75         | 0.10          | 0.19          | 0.41        | 0.65       |
| 850      | 0.25         | 0.06          | 0.06          | 0.12        | 0.19       |
| 850      | 1.76         | 0.07          | 0.08          | 0.14        | 0.16       |

Figure 4. Impedance spectra prior to (rhombs) and after (triangles) testing at 750°C for 1500 h at 0.25 A/cm² (a) and 0.75 A/cm² (b), spectra were recorded at 750°C at 25% humidity, characteristic frequencies in Hz are indicated.
After the test at 750°C and lower current density, showing the smaller degradation rate, only a slight increase of the serial resistance was observed, whereas the polarization resistance had increased by ∼50% (Table 1, Fig. 4a). After the test at high current density having the higher degradation rate, the whole impedance spectrum shifted significantly to higher resistance values after test (Fig. 4b), reflecting an increase of the serial resistance. In addition, the polarization resistance had increased significantly (by ∼60%, see Table 1).

Also for the tests at 850°C, impedance spectra were recorded prior to and after the test under constant current load. The results for the test under low (0.25 A/cm², Fig. 5a) and high (1.75 A/cm², Fig. 5b) current density are compared in Fig. 5 (for resistance values see Table 1). In both tests, the voltage degradation rates were rather low (see also Fig. 3b). Both impedance spectra pairs show the same characteristics as already observed for the cell tested at 750°C and low current density (see Fig. 4 and Table 1): The serial resistances hardly increased, whereas the polarization resistances increased significantly (Table 1).

It thus seems, that the dominating degradation mechanism at 750°C and high current density is different from the dominating degradation mechanism for the three other examples (low polarization at 750°C and both polarizations at 850°C).

Note, that the values in Table 1 (increase of polarization resistances, in particular) indicate significant degradation of the cells tested at lower current densities at 750 and 850°C. This finding seems to be in contrast to the observation of the low degradation rate while following the cell voltage (see black triangle and circle in Fig. 3b). A part of this apparent discrepancy can be ascribed activation processes that superimpose the degradation under current load.

After the test at higher polarization and 750°C, a significant increase of both, serial as well as polarization resistance was observed. Such a result could be explained by a small delamination between one electrode and electrolyte. The separation between the layers causes an increase of the serial resistance, but also of the polarization resistance as the active area decreases. If flaws (delamination zones) have a lateral extension larger than the electrolyte thickness, the active area will effectively decrease on both electrodes even
though delamination only occurs on one electrode, due to the low capacity of the thin, relatively poorly conducting zirconia for sustaining in plane currents (see e.g. (12)).

An exclusive increase of the polarization resistance as observed for the lower current densities at 750 and 850°C, on the other hand, could be due to changes in the microstructure of the electrode, which might hinder effective gas adsorption, dissociation, and reaction at the three-phase boundary. From the results discussed so far, electrode processes, as characterized by the polarization resistance, play an important role in the degradation, although a distinction between mechanisms at the different current densities and temperatures cannot be made yet.

It is known from previous detailed characterization how anode and cathode processes are reflected in the different frequency regions of the cell impedance spectrum (11). Accordingly, two of the three high frequency electrode arcs are supposed to be dominated by cathode processes (they depend on the oxygen partial pressure). It was suggested that the process with the highest summit frequency (~60000 Hz) is due to the transport of oxygen species at the LSM-YSZ interface and that the arc with a summit frequency around 1000 Hz is due to the dissociative adsorption of oxygen and transport to the three-phase-boundary (13). The arc with a summit frequency < 10000 Hz includes charge transfer between Ni and YSZ at the anode. These frequency values are valid at 850 °C for cells described in (14) with no degradation. At 750°C the frequencies are shifted to 12000 and 150 Hz for the cathode dominated processes, and to 1500-3000 Hz for the anode dominated process. Using this model, the contributions of these processes to the total resistance of a cell at 850 and 750°C were determined. The three high frequency resistances $R_1$, $R_2$, and $R_3$ are listed in Tab. 2.

### Table 2. Electrode resistances determined from impedance data by using the model presented in (11) and (12).

| $T$ (°C) | $i$ (A/cm²) | $R_1$ (Ω*cm²) | $R_2$ (Ω*cm²) | $R_3$ (Ω*cm²) |
|---------|-------------|---------------|---------------|---------------|
|         | Before test | After test     | Before test   | After test    | Before test   | After test   |
| 750     | 0.25        | 0.13          | 0.19          | 0.11          | 0.18          | 0.13         | 0.18         |
| 750     | 0.75        | 0.14          | 0.13          | 0.11          | 0.10          | 0.16         | 0.43         |
| 850     | 0.25        | 0.06          | 0.06          | 0.02          | 0.08          | 0.03         | 0.05         |
| 850     | 1.76        | 0.08          | 0.11          | 0.02          | 0.02          | 0.05         | 0.03         |

The results at 750°C and low current density show a slight increase of all three resistance contributions (Table 2). In contrast, after test at high current density, the resistance $R_3$ increased much more than $R_1$ and $R_2$. This resistance is assigned to a cathode process (11). Hence it is the cathode that degraded most at 750°C and high current density. After the tests at 850°C, all resistances remained the same before and after test or increased only slightly, which makes conclusions difficult (Table 2).

A better assignment of the cell constituents, which were mostly affected by degradation, is obtained by plotting the imaginary part of the impedance data vs. frequency before and after test (Fig. 6 and 7). The frequencies ascribed to the cathode and anode processes discussed above are marked in the two figures. The test at 750°C and low current density, in which the voltage degradation rate was rather low, showed small changes over the
whole frequency range from 80 to 26000 Hz (Fig. 6a) and confirms the evaluation based on the data in Tab. 2. For the test with the high degradation rate at 750°C (Fig. 6b), the most marked increase appeared at a frequency of 260 Hz, which is in the low frequency region of cathode processes. In addition, also anode processes, reflected around a frequency of 1300 Hz, are affected, however to a smaller extent.

For the cell tested at 850°C and lower current densities, the change in the imaginary part spans over a large frequency region from 180 to 12000 Hz (Fig. 7a). These findings are thus similar for both temperatures, 850 and 750°C, at the same current densities. The cell tested at 850°C and high current density showed the largest increase in the imaginary part of the impedance spectrum around a frequency of 2600 Hz, i.e. a region, where cathode processes dominate (Fig. 7b), like the cell tested at 750°C under high current density, although the increase was much smaller. In addition, the region assigned to anode processes changed slightly.

Figure 6. Imaginary part of impedance vs. frequency prior to (rhombus) and after (triangles) testing at 750 °C for 1500 h at 0.25 A/cm² (a) and 0.75 A/cm² (b), spectra recorded at 750°C at 25% humidity.

To summarize these observations one can state that degradation at the cathode is most prominent at high current densities and 750°C. It seems also, that cathode degradation occurs at high polarization at 850°C operating temperature, though not to such an extent.

Figure 7. Imaginary part of impedance vs. frequency prior to (squares) and after (circles) testing at 850°C for 1500 h at 0.25 A/cm² (a) and 1.75 A/cm² (b), spectra were recorded at 850°C at 25% humidity.
as at 750°C. At low current densities, also anode processes are visibly involved in the degradation both at 750 as well as 850°C and it seems that all constituents contribute more evenly to the degradation.

**Post-test Analysis**

Post-test microscopic analysis was performed on the tested cells with the aim to identify degradation processes after 1500 h operating at constant current density. The most severe degradation was observed after test at high current density at 750°C. As conclusion from the previously discussed impedance results, the focus was on the cathode/electrolyte interface.

In Fig. 8, the SEM images of the cells tested at 750°C and discussed above are shown. At the cell tested at high current density, a small gap (< 500 nm) between cathode and electrolyte was observed over a part of the interface (Fig. 8b). A similar gap was also found in another sample tested at high current density and 750°C (not shown in this paper). In contrast, the cell tested at low current density at 750°C had an intact interface cathode/electrolyte (Fig. 8a). The same picture was also obtained on other cells tested under similar conditions (not shown in this paper). The delamination on the cell subjected to stronger polarization at 750°C could thus explain the increase of both, serial and parallel resistance (in the arc assigned cathode processes) as seen in the impedance spectra before and after the testing.

**CONCLUSIONS**

A number of long-term tests of anode supported SOFCs were carried out at 750, 850, and 950°C at different current densities. The cell voltage decreased with the operating time, more exponential-like at high current densities and linearly at low current densities.

The degradation rate increased as a function of current density, in particular for the lower operating temperature of 750°C. Here, it increased at significantly lower current densities than during test at 850°C.
When evaluating the voltage degradation rate as a function of cell polarization, it increased at all three operating temperatures similarly during the first 300 h operating time. However, the degradation rate increased more steeply at 750°C than at 850 (and 950) °C when evaluated after 1500 h operating time.

Impedance analysis revealed, that the test at 750°C and high current density, led to a significant increase of serial as well as polarization resistance. Specifically, the polarization resistance in the cathode dominated part of the impedance spectrum increased. A high polarization of the cell at 750°C seems to affect the cathode more than the other constituents of the cell. Also at 850°C and high current density, the cathode is more affected by degradation processes, however, to a smaller extent than at the lower temperature. During operation at low current density the degradation seems to be more evenly distributed over the whole cell, at 750 as well as 850°C.

Microscopic post-test analysis, with focus on the cathode part, showed a delamination between cathode and electrolyte for the most degrading cell operated at 750°C, thereby confirming the conclusions drawn from impedance analysis.

ACKNOWLEDGEMENTS

The authors thank K. Hansen, O. Hansen, and S. Koch for technical assistance. The financial support by Danish Public Service Organization, project PSO-Eltra-5302 is gratefully acknowledged.

REFERENCES

1. R. Barfod, Y.-L. Liu, P. H. Larsen, P. V. Hendriksen, in SOFC VIII, S. C. Singhal and M. Dokiya, Editors, PV2003-07, p. 1158, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).
2. D. Skarmoutsos, F. Tietz, P. Nikolopoulos, Fuel Cells, 1, 243 (2001).
3. A. Ioselevich, A. A. Kornyshev, W. Lehnert, Solid State Ionics, 124, 221 (1999).
4. Y. L. Liu, S. Primidahl, M. Mogensen, Solid State Ionics, 161, 1 (2003).
5. F. Umemura, K. Amano, H. Michibata, A. Kimura, in SOFC-IV, M. Dokiya, O. Yamamoto, H. Tagawa, and S. C. Singhal, Editors, PV95-1, p. 649, The Electrochemical Society Proceedings Series, Pennington, NJ, (1995).
6. J. G. Larsen, P. H. Larsen, and C. Bagger, “High Temperature Sealing Materials,” US Patent Ser. no. 60/112039, pending.
7. M. Mogensen, Peter Vang Hendriksen in High Temperature Solid Oxide Fuel Cells, Fundamentals, Design, and Applications, S. C. Singhal, K. Kendall, Editors, Chapter 10, Elsevier, (2003).
8. S. Koch, M. Mogensen, P. V. Hendriksen, N. Dekker, B. Rietveld, in Sixth European Solid Oxide Fuel Cell Forum Proceedings, M. Mogensen, Editor, p. 1000, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).
9. N. Christiansen, S. Kristensen, H. Holm-Larsen, P. Halvor Larsen, M. Mogensen, P. V. Hendriksen, S. Linderoth, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p. 20, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

10. P. V. Hendriksen, S. Koch, M. Mogensen, Y. L. Liu, P. H. Larsen, in *SOFC VIII*, S. C. Singhal and M. Dokiya, Editors, PV2003-07, p. 1147, The Electrochemical Society Proceedings Series, Pennington, NJ, (2003).

11. R. Barfod, A. Hagen, S. Ramousse, P.V. Hendriksen, M. Mogensen, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p. 960, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).

12. R. Barfod, M. Mogensen, T. Klemensoe, A. Hagen, Y. L. Liu, P. V. Hendriksen, *these proceedings*.

13. M. J. Joergensen, PhD thesis, Keele University, UK, (2001).

14. A. Hagen, M. Menon, S. Ramousse, P. H. Larsen, R. Barfod, P. V. Hendriksen, in *Sixth European Solid Oxide Fuel Cell Forum Proceedings*, M. Mogensen, Editor, p. 960, European Fuel Cell Forum, Oberrohrdorf, Switzerland, (2004).