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# Solid oxide fuel cell performance under severe operating conditions

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## Abstract

The performance and degradation of Solid Oxide Fuel Cells (SOFC) have been studied at severe operating conditions. The nominally identical cells were manufactured in a small series by ECN in the framework of the EU funded project CORE-SOFC. The cells were of the anode-supported type of cell with a double layer LSM cathode. The Ni/8YSZ anode-substrate was manufactured by tape casting, while all the other cell layers were deposited by screen-printing. Cells were operated at 750°C and 850°C in hydrogen with 5% and 50% water at current densities ranging from 0.25 A/cm<sup>2</sup> to 1 A/cm<sup>2</sup> for periods of 300 hours or more. The area specific cell resistance, corrected for fuel utilisation, ranged between 0.20 Ωcm<sup>2</sup> and 0.32 Ωcm<sup>2</sup> at 850°C, and between 0.51 Ωcm<sup>2</sup> and 0.70 Ωcm<sup>2</sup> at 750°C.

The degradation of cell performance was found to be low (ranging from 0% to 8 %/1000 hours) at regular operating conditions. At severe operating conditions, voltage degradation rates of 20 to 40 %/1000 hours were observed depending on the test conditions.

Analysis of all the experimental data revealed an apparently critical cell voltage in the range of 700 to 750 mV. Above the critical cell voltage the degradation rates were low to insignificant, even at high current densities. If the cell voltage was decreased significantly below the critical value, either by increasing the current density, lowering the cell temperature or by changing the fuel composition, fast voltage degradation occurred.

Some cells were also tested using a different test procedure than the usual Risø procedure. The results obtained from these tests were not identical to the results obtained using the usual Risø test procedure indicating that the detailed test circumstances may be very decisive for the outcome.

## Introduction

Within the EU-funded CORE-SOFC project a number of nominal identical cells were tested at normal and severe operating conditions in order to determine the limits of safe operating conditions.

The severe conditions (accelerated test) also served another purpose. The determination of the durability and performance of solid oxide fuel cells is complicated by the long time necessary to test a cell under normal operating conditions if relevant figures for the degradation rates are to be achieved and typically several thousands of hours of test is necessary [1,2]. It is possible to gain information of the cell degradation by testing the fuel cells under severe operating conditions, thereby increasing the degradation rates and bringing the time of the individual cell test down to several hundreds of hours. Earlier investigations have indicated that high current densities and high water contents of the inlet fuel gas to the cell results in higher degradation rates than at low current and water pressure [2].

## Experimental

The cells tested in this study were nominally identical cells manufactured in a small series by ECN, The Netherlands. The cells were of the anode-supported type with a double layer LSM cathode. The Ni/8YSZ anode-substrate was manufactured by tape casting, while all the other cell layers were deposited by screen-printing. The overall cell dimensions were 5x5 cm with an active cell area of 4x4 cm (determined by the cathode area). In the work reported here all cells but one were tested in the usual alumina test housing at Risø which supplies the fuel gas and air as described in ref [3]. One cell was tested at Forschungszentrum Jülich (FZ-J).

After mounting in the furnace, the cells were heated to 1000°C at 60°C/hour. At 1000°C the mechanical load on the cell assembly was increased to ensure gas tight seals. Two hours after increasing the load the reduction of the anode and anode support was started. The reduction was in two steps where the first step was in 9% H<sub>2</sub> / N<sub>2</sub> for two to four hours and the second step was in hydrogen with approximately 5% water vapour for one hour. After the reduction the cells were cooled to 850°C and the cells were ready for test.

In most cases the cells were sprayed with a NiO contact layer on the anode side to ensure good contact to the anode current collector component (the NiO is reduced to Ni during anode reduction). This contact layer is not applied at FZ-J or ECN and therefore a few cells were also tested at Risø without this layer. At FZJ the cell are also mounted without the ceramic gas distribution components which is used in the Risø setup [3]. Furthermore the cells at FZ-J are heated with argon on the anode side until reduction in H<sub>2</sub>/Ar at 850°C whereas at Risø the cells are headed without anode gas until reduction in H<sub>2</sub>/N<sub>2</sub> at 1000°C. These slight differences in the test procedures may influence the observed cell degradation.

The cells were tested in moist hydrogen with approximately 5% water and wet hydrogen with approximately 50% water (In the following termed moist and wet hydrogen). Air was fed to the cathode side. The initial testing was by i-V curves at different fuel and air flows. The fuel flows ranged from 18 to 30 L/hour moist hydrogen and the air flows ranged between 50 and 170 L/hour. i-V curves was also obtained in moderately wet hydrogen with approximately 20% water vapour. For some of the cells the initial investigations also included impedance spectroscopy using a Solartron 1260 frequency response analyser. The frequency range for these measurements was 100 kHz to 0.1 Hz.

A few cells were tested with internally reformed methane with a steam to carbon ratio of approximately 2:1. In these cases methane was fed to a mixture of approximately 5% hydrogen in water vapour prior to the cell. The small amount of hydrogen in the feed water vapour was in order to ensure reducing conditions at the anode at all times. Prior to the test in internally reformed methane these cells were characterised in hydrogen in the same way as the other cells.

The 18 cell tests that are reported in this paper are listed in table 1 along with the test conditions.

After the initial testing the cells were tested at constant conditions for more than 300 hours. Each cell was tested at 0.25, 0.5, 0.75 or 1 A/cm<sup>2</sup> as shown in table 1. Before the cells were tested at constant conditions, i-V curves were obtained at the same fuel flow, air flow and temperature as the conditions during the test at constant conditions.

After the test at constant conditions, i-V curves were obtained in order to determine the magnitude of any change in the cell resistance. For the cells, where impedance spectroscopy was performed during the initial testing, further impedance spectroscopy was usually performed after the test at constant conditions.

Cell	Temperature (°C)	Fuel gas composition	Current density (A/cm <sup>2</sup> )	Fuel utilisation (%)
Kz010614-4	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.25	14
Kz010614-6	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.75	42
Kz010614-8	750	Internally reformed CH <sub>4</sub>	0.25	7
Kz010614-10	850	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.5	28
Kz010614-23	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.5	28
Kz010614-25	750	95% H <sub>2</sub> , 5% H <sub>2</sub> O	0.25	7
Kz010614-28	750	95% H <sub>2</sub> , 5% H <sub>2</sub> O	0.5	14
Kz010614-30	850	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.5	28
Kz010614-32	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.5	28
Kz010614-34	850	95% H <sub>2</sub> , 5% H <sub>2</sub> O	1	28
Kz010614-42	750	95% H <sub>2</sub> , 5% H <sub>2</sub> O	1	28
Kz010614-46	850	95% H <sub>2</sub> , 5% H <sub>2</sub> O	0.5	14
Kz020830-7	850	50% H <sub>2</sub> , 50% H <sub>2</sub> O	1	56
Kz020830-8	850	50% H <sub>2</sub> , 50% H <sub>2</sub> O	1	56
Kz020830-10	750	Internally reformed CH <sub>4</sub>	0.5	14
Kz020830-17	750	95% H <sub>2</sub> , 5% H <sub>2</sub> O	0.43	12
Kz020830-29	750	Internally reformed CH <sub>4</sub>	1	28
Kz010614-3	750	97% H <sub>2</sub> , 3% H <sub>2</sub> O	0.5	14

Table 1: Operating conditions during the test at constant conditions. The cells tested in internally reformed methane used a steam to carbon ratio of approximately 2:1. The air utilisation was in all cases less than 20%. The cell Kz010614-3 was tested at FZ-J.

## Results

During the initial testing at 850°C the area specific cell resistance at 500 mV corrected for fuel utilisation (calculated by the method described in [4]) ranged between 0.2 and 0.34  $\Omega\text{cm}^2$  as shown in figure 1

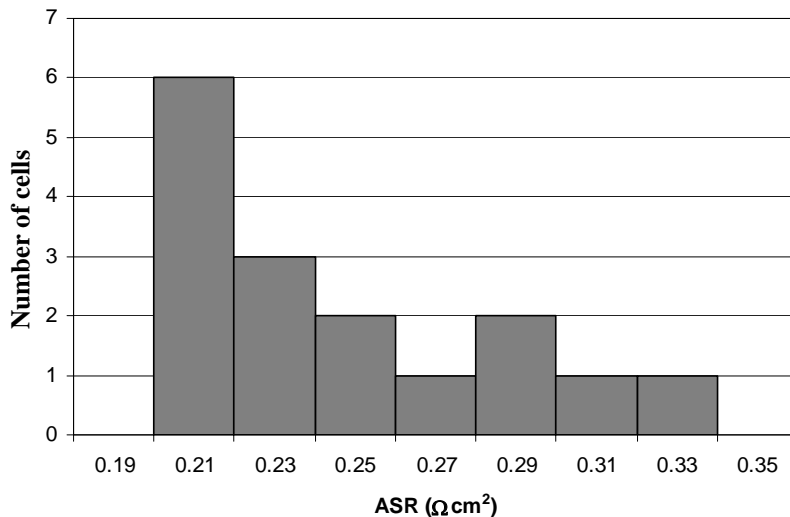


Figure 1: Reproducibility of cell performance in terms of the (fuel utilisation corrected) area specific cell resistance (ASR) at 850°C and 500 mV in moist hydrogen (5% H<sub>2</sub>O) as measured during the initial characterisation.

The degradation rates observed at various operating conditions with hydrogen as fuel gas are presented in table 2 and the degradation rates observed for the cells tested in internally reformed methane is reported in table 3. For the cells tested at 750°C a pronounced activation of the cell occurred during the first 50 hours the cell was at a constant current density. For the cells where this activation was observed, the reported degradation rates was determined during the later part of these tests where it is assumed that the activation process has completed. The activation / passivation of the cells are reported in [5]. As an example of a cell that did not degrade under moderately harsh conditions the test

history of cell Kz010614-34 is shown in figure 2. This cell was tested in moist hydrogen with approximately 5% water vapour at 855°C for approximately 350 hours at a current load of 1 A/cm<sup>2</sup>. During this time, almost no degradation in cell performance was observed (Figure 3). The cell voltage was 770 mV after 75 hours at constant current and 250 hours later the cell voltage was 766 mV. Figure 2 further shows three tests performed at 750°C at very similar conditions. The one tested using the usual Risø procedure degraded rapidly.

Current density (A/cm <sup>2</sup> )	T (°C)	95%H <sub>2</sub> – 5%H <sub>2</sub> O		50%H <sub>2</sub> – 50%H <sub>2</sub> O	
		Degradation	Cell voltage	Degradation	Cell voltage
0.25	850				
0.25	750	10	870mV	6	790mV
0.5	850	0	770mV	0	725mV
0.5	750	265	710mV	100 – 180	600mV
1	850	9	770mV	98	600mV
1	750	176	480mV		
0.75	750			180	475mV

Table 2: Degradation rates (μV/hour) and cell voltage after 50 hours at constant current at different operating conditions.

For the cells where low degradation rates were observed, minor changes in the impedance spectra was observed. An example of this is shown in figure 3 where impedance spectra for cell Kz010614-34 are shown. For the cells where large degradation rates were observed large changes in the individual arcs in the impedance spectra was observed as shown for cell Kz010614-28 in figure 4. In some cases the medium frequency part (between 1 and 200 Hz) of the polarisation resistance decreased significantly during the time the cell was at constant current. In the case of cell Kz010614-6 the polarisation resistance between 1 and 200 Hz decreased 50% and at the same time the high frequency part (above 200 Hz) increased 48%.

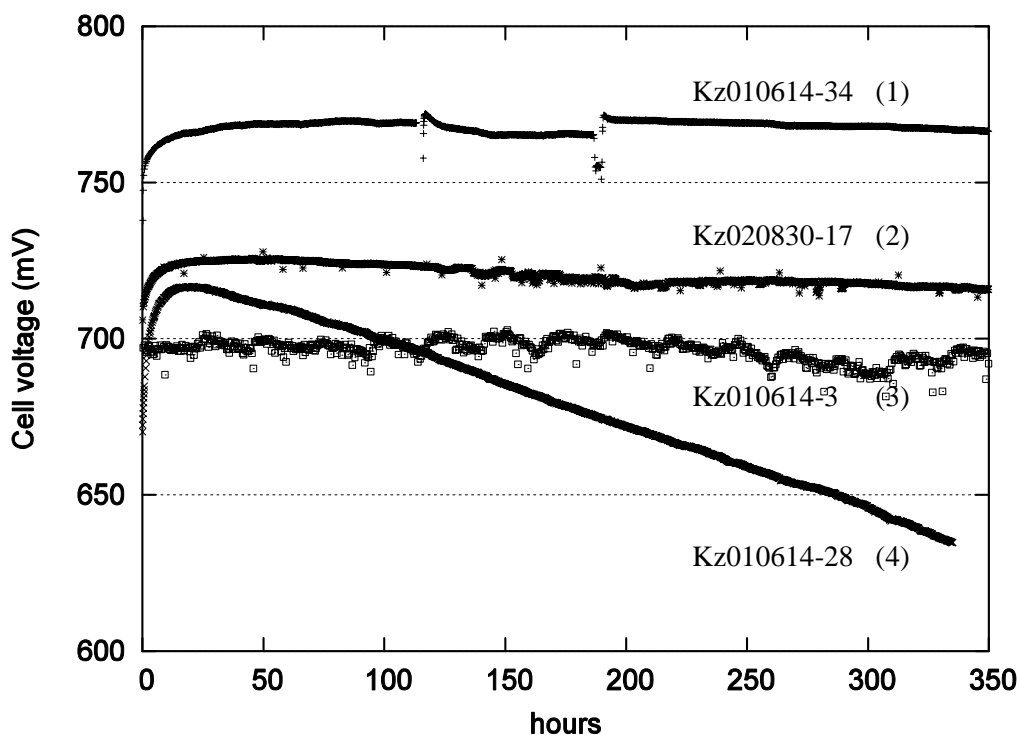


Figure 2. Cell voltage versus time for cell Kz010614-34 (1), Kz020830-17 (2), Kz010614-3 (3) and Kz010614-28 (4). All cells were tested in moist hydrogen (between 3 and 5% water) and the time where the current was set to the constant conditions is set to 0. Cell (1) was tested at 850°C at 1 A/cm<sup>2</sup>. The cells labelled (2), (3) and (4) were tested at 750°C. Cell (2) was tested at 0.43 A/cm<sup>2</sup>

whereas (3) and (4) was tested at  $0.5 \text{ A/cm}^2$ . In the case of cell (3), the cell was tested for approximately 700 hours at  $0.5 \text{ A/cm}^2$  at a lower fuel utilisation before the 350 hours shown in the figure. Cells (1) and (4) were assembled according to the usual Risø procedure, cell (2) was tested at Risø using a similar procedure as at FZ-J and cell (3) was tested at FZ-J.

Current density ( $\text{A/cm}^2$ )	Temperature (C)	Degradation rate ( $\mu\text{V}/\text{hour}$ )	Cell voltage (mV)
0.25	750	12	813
0.5	750	71	637
1	750	173	432

Table 3. Degradation rates for the cells tested in internally reformed methane. The cells were tested with a steam to carbon ratio of approximately 2:1.

### Discussion

The observed degradation rates ranged between 0 and  $300 \mu\text{V}/\text{hour}$  depending on the operating conditions. At high water content and high current density the degradation rates were generally higher than at low current densities and water concentrations. This is consistent with earlier findings [2]. At  $850^\circ\text{C}$  low to insignificant degradation was observed at  $0.5 \text{ A/cm}^2$  irrespective of the water partial pressure (within the investigated range:  $x\text{H}_2\text{O} = 0.05 - 0.5$ ) at  $750^\circ\text{C}$  low degradation was only observed at  $0.25 \text{ A/cm}^2$  as shown in table 2.

Impedance spectroscopy was used to investigate which part of the fuel cell was responsible for the observed degradation as both the anode and / or cathode may degrade over time [6,7]. Figure 3 shows the impedance spectra for cell Kz010614-34 obtained before and after 350 hours at  $850^\circ\text{C}$  and  $1 \text{ A/cm}^2$ . Although the total resistance is almost unchanged, the medium frequency part of the polarisation resistance (between 1 and 200 Hz) decreased somewhat during the experiment.

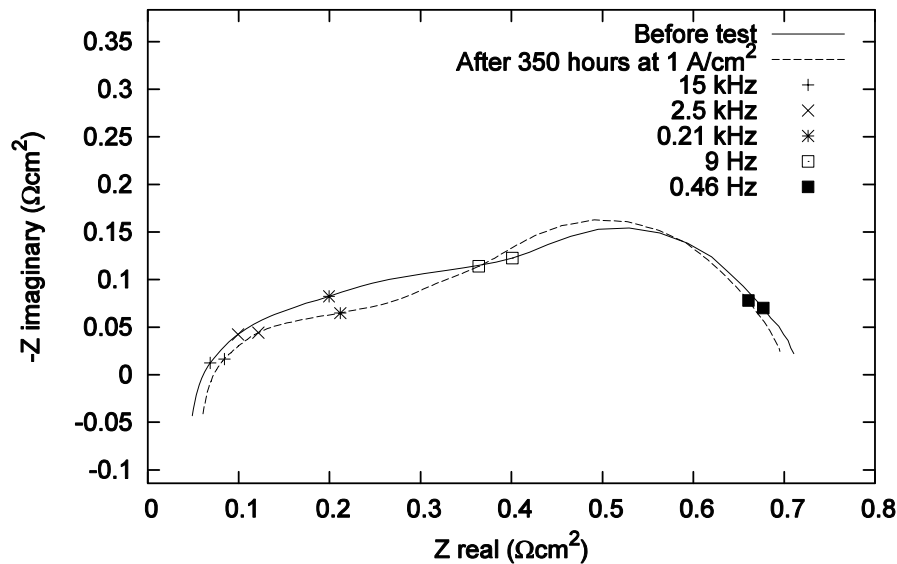


Figure 3. Impedance spectre for cell Kz010614-34 obtained before and after 350 hours at  $1 \text{ A/cm}^2$  in hydrogen (5%  $\text{H}_2\text{O}$ ) at  $855^\circ\text{C}$ .

Below 10 Hz the impedance spectra was influenced by diffusion and fuel conversion [8,9,10] whereas the cathode influences the medium frequency part (1 to 200 Hz) and the anode mainly influences the high frequency part (above 200 Hz) for these types of cells [5].

For the cells where high degradation rates were observed, the largest effect was observed in the high frequency part of the polarisation resistance (above 200 Hz) as shown in figure 4. The high frequency part of the polarisation resistance (above 200 Hz) increased almost 100% whereas the low frequency part only increased 60%. The increase in the low frequency part (below 200 Hz), however, is partly due to cathode passivation [5] as the spectra shown in Figure 4 (after 320 hours at  $0.5 \text{ A/cm}^2$ ), was obtained 60 hours after the current was switched off.

The degradation rates reported in table 2 indicate that a voltage limit exists above which low to insignificant cell degradation is observed. In the case of a cell temperature of 850°C this limit appears to be approximately 700 mV whereas at 750°C it is approximately 750 mV. The reason for this apparent voltage limit is not well understood, but perhaps the polarisation of the anode is responsible as the impedance investigations indicate that it is the anode that is responsible for the observed voltage degradation. Apparently, the fuel gas composition is not critical for the degradation except that the fuel gas composition influences the cell voltage and thereby indirectly the maximum current density if the cell voltage must stay above the limit. This is shown by comparing cell Kz010614-8 and Kz020830-10, These cells were run for 300 hours in internally reformed methane and at 0.25 or 0.5 A/cm<sup>2</sup> respectively (table 1). In the case of the cell that was run at 0.25 A/cm<sup>2</sup> the cell voltage was above 800 mV and the degradation was low (12 μV/hour) whereas the other cell, which was run at higher current and thus lower cell voltage degraded faster (table 3).

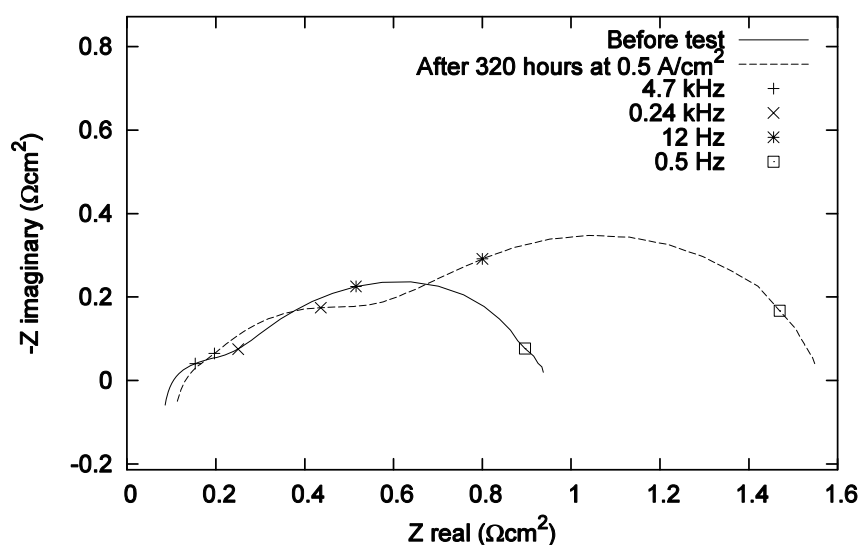


Figure 4. Impedance spectra for cell Kz010614-28 obtained before and after 320 hours at 0.5 A/cm<sup>2</sup> in hydrogen (20% H<sub>2</sub>O) at 750°C.

Different test procedures (e.g. reduction profile, sealing materials etc.) may result in large differences in the observed degradation rates under otherwise equal conditions. This is illustrated by comparing the results obtained for cells Kz010614-3, Kz010614-28 and Kz020830-17 (Figure 2). These cells were tested under almost identical conditions. Whereas the results for Kz020830-17 and Kz010614-3 are comparable, the degradation found for Kz010614-28 was much higher. The first two cells were reduced at 850°C and were mounted without the Ni contact layer whereas Kz010614-28 was reduced at 1000°C with the Ni contact layer.

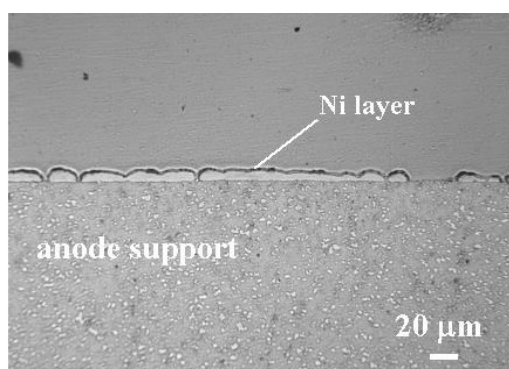


Figure 5: Light micrograph showing a cross section of the anode support and the Ni-contact layer applied to establish contact to the gas-distributor plate in the test-house.

The observed differences in the degradation rates indicate that the exact test procedure may be critical for the observed degradation rate of the individual fuel cell. Figure 5 shows a micrograph of the Ni contact layer after reduction and the layer is rather dense in some areas. This may result in higher water partial pressures at the anode due to the limited diffusion cross section. It is therefore possible that the presence of the Ni contact layer is at least partially responsible for the differences in degradation observed between the usual Risø test procedure and the FZ-J procedure, which does not include the Ni contact layer on the anode support.

### Conclusion

The degradation rate for a Ni-YSZ anode supported type of solid oxide fuel cells was found to be dependent on the test procedure as well as on the fuel gas composition and current density.

Apparently, a critical cell voltage exists below which fast cell degradation is observed. This limit appears to be in the vicinity of 700 mV at 850°C and 750 mV at 750°C.

If fuel gas composition and current density is adjusted so that the cell voltage is above this limiting voltage low degradation rates in the order of 0 to 20  $\mu\text{V}/\text{hour}$  is observed.

If the fuel gas composition and cell temperature can be adjusted accordingly, cells can be tested at current densities up to 1  $\text{A}/\text{cm}^2$  for more than 300 hours without significant degradation.

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