LONG-TERM TESTS OF DK-SOFC CELLS

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ABSTRACT

An important aspect of SOFC performance is long-term stability. Four "long-term" tests (1000-2000 hr) are presented and problems concerning the test set-up are discussed. The cells were tested at 850°C under four different sets of conditions with respect to current density and water vapor content. The performance was observed to decrease in all four cases. Depending on the conditions, the power density decreased between 0.3 and 4.6% over 1000 hrs of test. The area specific resistances of the cells were between 0.27 and 0.39 $\Omega \text{cm}^2$.

INTRODUCTION

Besides the development of cells with lower area specific resistances, the long-term stability of solid oxide fuel cells (SOFCs) is a key technological aim. The specific maximum tolerable degradation rate eventually depends on stack price. However, with expected lifetime requirements on the order of ~40,000 hr, the tolerable degradation on practical time scales in cell development programs will be very small, say 0.25 – 1%. This sets strong demands to the test methodology and instrumentation and makes long-term testing challenging since even small changes in auxiliary components of the test facility affects the apparent performance of the cell.

It has been reported (1) that Ni/YSZ cermets may lose up to 33% of the initial electrical conductivity due to aging of the cermet in an Ar/H$_2$/H$_2$O mixture at 1000°C for 4000 hr. The change in conductivity was ascribed to coarsening of Ni particles (1). Long-term degradation of complete cells has been reported to be due to loss of Ni from the cermet structure via volatile Ni(OH)$_2$ species (2). Microscopy has revealed that Ni can accumulate in cracks of the cermet or on the surface of the surroundings (2). Some studies have been performed on degradation mechanisms of SOFC, but the full understanding of the dependency on current load, fuel utilization, fuel gas composition and temperature has yet to come.

In this paper, the change in performance of four DK-SOFC cells (C0477, C0475, PC0030 and PSC0252, see Table I), tested for 1000-2000 hr is reported and discussed. Both the stability of the cells and the stability of auxiliary components like gas-distributor plates and glass seals are addressed. A problem with the interface between current collection foil and gas-distributor plate on the anode side was identified and is discussed at some length.
EXPERIMENTAL

The test set-up and test strategies in the Danish SOFC program were previously described (3) and are here only briefly summarized. The cell is held between two alumina blocks where the gas supply channels are fabricated. Air and fuel-gas are distributed to the cathode/anode through gas distributor plates (CCC and ACC respectively, see figure 1) placed on each side of the cell. These plates are made of the same materials as the electrodes and are thus good conductors. The gas distributor plates are in contact with a current collector foil placed on the current and voltage probes. The current collector foil is made of Au at the cathode side and Pt at the anode side. Two voltage probes are connected to each foil. Apart from monitoring the potential difference over the cell, in-plane potential differences in the current collector foils on both sides of the cell can be followed.

![Cell test set-up](image)

Figure 1. Cell test set-up. Only the anode part of the alumina house is shown. CCC and ACC are cathode coupling component and anode coupling component respectively.

In-house developed glass-ceramic seals are used at both sides of the cell (5). Monitoring the O₂ partial pressure at both the fuel inlet and outlet sides makes it possible to quantify the amount of fuel lost to the surroundings. This is done by comparing the difference between inlet and outlet H₂O:H₂ ratio with the current and OCV using Faraday’s law.

The tested cells are anode supported planar cells representing various steps in the cell development. The cells C0477 and C0475 are similar and different from PC0030 and PSC0252 (see Table I). The gas flow over the cell is plug-flow like, and area specific resistances (ASR) are calculated after correcting the data for fuel utilization (4). The active area is 4 x 4 cm² and all tests are performed in H₂ with different water partial pressures at the anode and air as the cathode gas.

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The first phase of the test period serves to establish a fingerprint of the cell. IV-curves are obtained under various gas-flows at 850°C and the cells are characterized by impedance spectroscopy. The cell is thereafter operated under a constant atmosphere and current load at 850°C for at least 1000 hr. Hereafter, further experiments to characterize details of the performance characteristics are carried out. In one case (C0477), the cell was tested for prolonged time at 950°C after the 1000 hr at 850°C.

RESULTS AND DISCUSSION

Stability of Tested Cells

The test conditions and the degradation in terms of power loss for the four cells are shown in Table I. All cells showed some degradation over the test period. The cell that experienced the strongest degradation after 1000 hr at constant conditions was C0477, which was tested with a constant current of 0.5 A cm⁻² and an inlet fuel gas composition of 50% H₂ and 52% H₂O. This is the condition where the high current density is combined with the high water concentration (Table I).

| Cell   | Inlet Conditions | P [W/cm²] 0 hr | P [W/cm²] 1000 hr| ΔP [%] | ASR [Ω cm⁻²] 0 hr | ASR [Ω cm⁻²] 1000 hr |
|--------|-----------------|---------------|-----------------|--------|-------------------|-------------------|
| C0477  | 52% H₂O         | 0.3870        | 0.3694          | -4.6   | 0.266             | 0.340             |
| PSC0252| 5% H₂O          | 0.4133        | 0.4095          | -0.9   | 0.361             | 0.363             |
| C0475  | 5% H₂O          | 0.2736        | 0.2705          | -1.1   | 0.315             | 0.366             |
| PC0030*| 5% H₂O OCV      | 0.3939        | 0.3875          | -1.6   | 0.393             | 0.418             |

Performance was calculated from IV-curves at I = 0.47A/cm²
ASR is corrected for fuel utilization
After 1000 hr at constant conditions
The columns labeled "0" hr shows the cell performance at the onset of the period with constant conditions.

C0477 was tested with an inlet H₂ flow of 12 l/hr and a H₂O inlet flow of 13 l/hr. The constant current load of 0.5 A cm⁻² corresponds to a fuel utilization of approximately 30% corresponding to a water concentration of 66% at the outlet. The performance of C0477 decreased by 4% (= 30 mV) during the first 100 hr at constant conditions. The rate of degradation then leveled off as seen in figure 2. The total performance loss after 1000 hr on constant conditions was 4.6% (= 37mV). The ASR increased from 0.266 to 0.340 Ω cm⁻² over the entire test period. The cell voltage varies a little over the test period, which is seen in all tests. This is ascribed to variations in fuel gas composition or the cell temperature. However, the 4% performance loss observed initially for C0477 cannot be explained by these variations.

PSC0252 was tested with same current load but at a lower water concentration compared to C0477. The inlet H₂-flow was 15 l/h, and the fuel utilization in the period with constant conditions was 24% corresponding to a water concentration of 28% at the outlet. The performance of PSC0252 only decreased by 0.9 % (= 4mV) after 1000 hr of test. The
Fast initial degradation observed for C0477 was not observed for PSC0252 as seen in figure 3. The ASR increased from 0.361 to 0.363 Ωcm² over 1000 hr.

Figure 2. Test history of C0477. Tested at 0.5 A/cm² with 52% water in the fuel. Between 225 - 275 hr, the inlet fuel gas contained only 5% H₂O. Vertical lines are due to IV-curves (downwards) or periods at OCV (upwards).

C0475 was tested at a constant current of 0.25 A/cm² and with 5% H₂O in the fuel gas. The inlet H₂-flow was 9 l/hr, and the resulting fuel utilization was approximately 20% which corresponds to an outlet concentration of 24% water. The cell voltage slowly decreased during the test, corresponding to a performance loss of 1.1% over 1000 hr (= 11 mV) as seen in figure 4. The ASR increased from 0.32 to 0.37 Ωcm².

Figure 3. Test history of PSC0252 tested at 0.5 A/cm² with ~5% H₂O in fuel. Between 350 and 380 hr, there was no current load and an inlet fuelgas composition of 8.6% H₂, 86.6% N₂ and 4.8% H₂O. Vertical lines are due to IV-curves (downwards) or periods at OCV (upwards).

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The performance of PC0030 that was kept at OCV was calculated from occasional IV-curves at I = 0.47 A cm\(^{-2}\). In spite of the mild conditions, a degradation of the performance of 1.5\% over 1000 hrs was observed.

Figure 4. Test history of C0475 tested at 0.25 A cm\(^{-2}\) and with 5\% H\(_2\)O in fuel. Between 275 – 375 hr, the inlet fuel composition and the current load is changed. Vertical lines are due to IV-curves (downwards) or periods at OCV (upwards)

**Stability of Auxiliary Components**

As discussed under experimental, with the two voltage probes it is possible to measure the in-plane potential difference in the Pt-foil and to follow this with time. The changes in the in-plane potential differences in the Pt foil over the first 1200 hrs of test of PSC0252 are shown in figure 5. The in-plane voltage difference increases during the first approximately 1000 hr test from initially 10\(^{-3}\) mV to about 0.8 mV. A similar trend is observed for C0475 where the in-plane potential difference increases from 0 mV to 1.5 mV as shown in figure 5.

Figure 5. In-plane voltage at the Pt foil for cells number C0475 and PSC0252.
All tested cells display significant changes in the in-plane potential difference in the Pt foil. The potential difference increases steadily from an initial value of $10^{-6}$ V to the mV range. The in-plane potential difference of the Au foil at the cathode side does not show similar changes. The voltage range for the in-plane Au voltage is $10^{-6}$ V during the whole test period.

The in-plane potential difference in the Pt-foil is an in-direct measure of the ACC-Pt interface resistance. Due to the high conductivity of the current collector the in-plane potential difference is expected to be very small ($10^{-6}$ V). However, large changes in the in-plane potential difference can be a sign of a redistribution of the current density from the ACC to the Pt-foil and thereby an indication of a contact problem at the ACC-Pt interface. Therefore the potential difference over the ACC-Pt interface is now being measured directly by use of an extra voltage probe. Results of a recent test are shown in figure 6. It is seen that the cell voltage and the potential difference over the ACC-Pt interface decreases simultaneously. Initially the contribution to the ASR of this interface resistance was only 0.5 m$\Omega$cm$^2$ corresponding to 0.2% of the measured resistance. However, after 750 hr the resistance at this interface contributes to the total resistance by 34 m$\Omega$cm$^2$ which is approximately 12% of the total resistance.

![Figure 6](image)

**Figure 6. Changes in the potential difference over the ACC-Pt interface and the simultaneous change of the cell voltage of an on-going test.**

**Impedance Analysis**

If the ACC-Pt interface gives rise to an increased resistance due to bad contact it should be observed by impedance spectroscopy as a contribution to the serial resistance $R_s$. It is seen from Table II that the serial contribution to the resistance has increased relative to the polarization resistance during the time of test.

It should be noted the numbers in Table II are not directly comparable to the data in Table I. The resistance measured in Table II reflects the cell characteristics just before termination of the test. In several cases harsh tests were performed after the 1000 hr test at constant conditions (Table I) and prior to the impedance experiments in Table II. For instance C0475 was operated galvanostatically with very high fuel utilization.
Table II. Impedance data of the four tested cells.

|        | Rs [mΩ]* | Rp [mΩ]* | Rs/Rp |
|--------|----------|----------|-------|
|        | Start    | End      |       |
| C0477  | 8        | 35       | 24.8  |
|        |          |          | 41    |
|        | 0.32     | 0.9      |       |
| PSC0252| 7.2      | 11.3     | 18.5  |
|        |          |          | 26.9  |
|        | 0.39     | 0.42     |       |
| C0475  | 7.3      | 239.5    | 15.7  |
|        |          |          | 40.9  |
|        | 0.46     | 5.8      |       |
| PC0030 | 9.6      | 33.8     | 18.5  |
|        |          |          | 33    |
|        | 0.52     | 1.0      |       |

* Active area is 16 cm²

Stability of the Glass-Seals and Gas-Leakage

To investigate the durability of the glass seals, the gas leakage was calculated initially and after 1000 hr of test. The results are presented in Table III. Three tests did not show any changes in gas leakage over the test period. Only C0477 displayed a change, but the gas leak cannot explain the changes in performance. A better initial performance of the seals is desirable but the seals show satisfactory performance over the time tested.

Table III. Gas leakage of four tests.

| Cell   | Gas leakage [%] |
|--------|-----------------|
|        | Start | 1000 hr |
| C0477  | 1     | 3       |
| PSC0252| 4     | 4       |
| C0475  | 1     | 1       |
| PC0030 | 2     | 2       |

Post-Test Analysis of Cells

Post-test analysis performed by light microscopy and SEM did not show any severe failures like delamination of electrodes and electrolyte or holes in the electrolyte. As shown in Figure 7, the Ni grains in the anode have coarsened after test for cell C0477.

Figure 7. Histogram of Ni grain size of (a) C0477 after test, and (b) a sister cell of C0477 before test.
The number of the small grains (0-0.5 μm) is considerably reduced. The size distribution shifts to the larger end but the size of the largest grains is only slightly increased. The measurements also show that the total area fraction of Ni in the anode is reduced from 26% before test to 19% after test. A similar effect was observed for C0475 but it was less pronounced. The stronger change of C0477 may be ascribed to increased Ni mobility in this case since the vapor pressure of volatile Ni species (such as Ni(OH)₂) increases with increasing water concentration in the gas mixture and temperature (2).

Post-Test Analysis of the ACC-Plate

Microscopy revealed that for all ACC-plates investigated, the Ni concentration at the ACC-Pt interface is reduced after test (figure 8). The effect is most pronounced for C0477 that was tested at the highest water pressure and also experienced prolonged testing at 950°C. As discussed above, this may be ascribed to increased Ni mobility. Ni depletion at the ACC-Pt interface will reduce the number of contact points, which can account for the observed increase in the in-plane voltage difference in the Pt foil.

Figure 8. Optical microscopy of ACC from the test of C0477. After test (top) and a not-tested, reduced ACC (bottom).
CONCLUSIONS

With the test set-ups used, it is possible to perform tests over thousands of hours. Glass seals do not show significant changes for >1000 hr of test. One problem of the test-houses has been clearly identified. The interface between the anode gas distributor (ACC) and the current collector (Pt-foil) is not sufficiently stable. During test, Ni seems to withdraw from the interface and thereby the contact between the two layers is partly lost resulting in an increased resistance.

The cells are stable for 1000 hr test, i.e. the electrolyte is dense and delamination at the electrode-electrolyte interfaces is not observed. However, the cells degrade between 0.9 – 4.6% in power density during test depending on the conditions. The degradation was highest for the cell tested at high water partial pressure and at high current load. Some part of the observed degradations was demonstrated to lie outside the cell in the interface between Pt and ACC.

Ni coarsening at the anode was seen by microscopy. The coarsening may also contribute to the observed cell degradation.

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