



# **ELECTRODE ACTIVATION AND PASSIVATION OF SOLID OXIDE FUEL CELL ELECTRODES**

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# Electrode activation and passivation of solid oxide fuel cell electrodes.

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## Abstract

The performance of anode-supported cells with a composite LSM-YSZ cathode and an LSM current collector was investigated. Over the first 48 hours after application of a constant current the cell voltage was observed to increase up to 20%. When the current was switched off, the cell resistance increased significantly during the next four days at open circuit conditions. Apparently, at OCV conditions passivation of the cell occurs. Once the current is switched on again, the cell gradually activates again. Part of this activation / passivation process is fast enough to influence the resistance of a cell during *i*-V measurements (over less than 1 hour) and a considerable hysteresis in the cell voltage during *i*-V measurements can be observed.

Impedance spectroscopy was used to investigate the activation / passivation process and it was found that the series resistance and the part of the polarisation impedance above approximately 100 Hz was not influenced by the activation / passivation process. The part of the polarisation impedance between 1 and 100 Hz was highly influenced by the activation / passivation process and during cell polarisation this part of the polarisation impedance was up to 40 % lower than at open circuit conditions. This frequency range of the spectrum was also sensitive to the oxygen partial pressure at the cathode side indicating that it is the cathode that activates and passivates.

## Introduction

Testing of solid oxide fuel cells with respect to durability and performance is not trivial and several phenomena influence the performance of a fuel cell. Ultimately durability tests of fuel cells must take place for very long periods (years) in order to determine the lifetime. However, as a development tool, cell tests under severe operating conditions in order to increase the degradation rates is a possibility [1]. During accelerated testing of a cell at constant current for several hundred hours, the cell degradation may be hidden by an increase in the cell voltage during the first 50 to 100 hours after the current is switched on [2,3]. Single electrode investigations have shown that electrodes may activate [4] which may be responsible for increased performance at constant current. This initial increase in cell voltage was investigated for a number of cells within the framework of the CORE-SOFC project [5]. The cells were tested at constant current at either 850°C or 750°C. This paper reports results of cells tested at 750°C where significant activation was observed.

## Experimental

The cells tested in this study were nominally identical cells manufactured in a small series by ECN, The Netherlands, in the framework of the EU funded project CORE-SOFC. 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 on the cell). The cells were tested in an alumina test housing at Risø. The principle of the Risø cell test set-up is described elsewhere [6].

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 humidified 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. (For two of the tests, Kz020830-10 and -29, a small flow of moist 9% H<sub>2</sub>/N<sub>2</sub> was fed to the anode chamber already during the heating up). After the reduction the cells were cooled to 850°C and the cells were ready for test.

The cells were tested in moist hydrogen with approximately 5% water and wet hydrogen with 50% water (In the following referred to just as "moist" or "wet" hydrogen). Air was fed to the cathode side. The initial testing was by i-V curves at different fuel and airflows. The fuel flows ranged from 18 to 30 L/hour hydrogen and the airflows ranged between 5 and 170 L/hour.

For some of the cells the investigations also included impedance spectroscopy using a Solartron 1260 frequency response analyser. The frequency range for these measurements was 0.1 Hz to 100 kHz.

After the initial characterisation the cells were tested at constant conditions for more than 300 hours (except for cell Kz020830-24, which was only tested for 70 hours at constant conditions). Cells were 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 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 changes in the cell resistance. For the cells, where impedance spectroscopy was performed during the initial characterisation, further impedance spectroscopy was usually performed after the durability test.

Table 1: Operating conditions during the tests. The internally reformed methane had a steam to carbon ratio of approximately 2:1.

Cell	Temperature (°C)	Fuel gas composition	Current density	Fuel utilisation
Kz010614-4	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.25	14%
Kz010614-23	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.5	28%
Kz010614-6	750	50% H <sub>2</sub> , 50% H <sub>2</sub> O	0.75	42%
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%
Kz010614-42	750	95% H <sub>2</sub> , 5% H <sub>2</sub> O	1	28%
Kz010614-8	750	Internally reformed CH <sub>4</sub>	0.25	7%
Kz020830-10	750	Internally reformed CH <sub>4</sub>	0.5	14%
Kz020830-29	750	Internally reformed CH <sub>4</sub>	1	28%
Kz020830-24	850	Change in feed gasses		

## Results

For the cells tested at 750°C a pronounced activation / passivation was observed as shown in Figure 1, where a part of the test history of cell Kz010614-6 is shown. For this cell impedance spectroscopy was performed at various times and the results are shown in Table 2 and Figure 2.

Table 2. Series ( $R_s$ ) and polarisation ( $R_p$ ) resistance for cell Kz010614-6 measured at the beginning, after a period at constant conditions (0.75A/cm<sup>2</sup>, 76 to 384 hours) and after further 100 hours at OCV (384 to 479 hours). Between 497 and 503 hours the cell was again at 0.75A/cm<sup>2</sup>. The values are for wet hydrogen (approximately 50% water). The ASR was determined at 750 mV from the *i*-V curves and was corrected for fuel utilisation using the method described in [7].

Time (h)	76	384	479	503	76h – 384h	384h – 479h	479h – 503h
$R_s$ ( $\Omega\text{cm}^2$ )	0.18	0.22	0.22	0.22	+22%	-2%	+2%
$R_p$ ( $\Omega\text{cm}^2$ )	0.78	0.73	1.13	0.78	-6%	+55%	-31%
$R_{\text{tot}}$ ( $\Omega\text{cm}^2$ )	0.96	0.95	1.35	1.00	-1%	+42%	-26%
ASR ( $\Omega\text{cm}^2$ )	0.86	0.77	1.16	0.88	-10%	+51%	-24%

The values of  $R_s$  quoted in Table 2 are the real parts of the impedance at 91 kHz, i.e. the spectra were not fitted to correct for the effect of inductances. The  $R_p$  values are the differences in the real part between 91 kHz and 91 mHz.

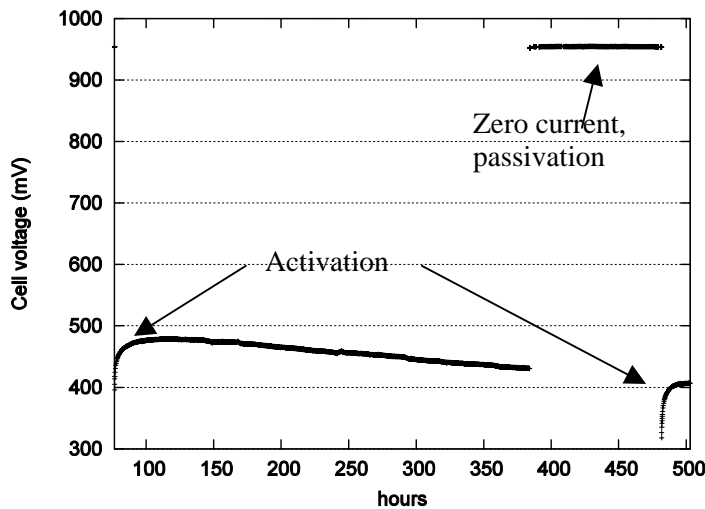


Figure 1. Cell voltage versus time for cell Kz010614-6. The cell was tested at 0.75 A/cm<sup>2</sup> at 750°C in wet hydrogen (50% H<sub>2</sub>O).

For all the cells tested at 750°C the activation / passivation phenomenon illustrated in Figure 1 was observed (Table 3). Generally, when the cells were subjected to high current densities, the activation was more pronounced than at low current densities as shown in Table 3.

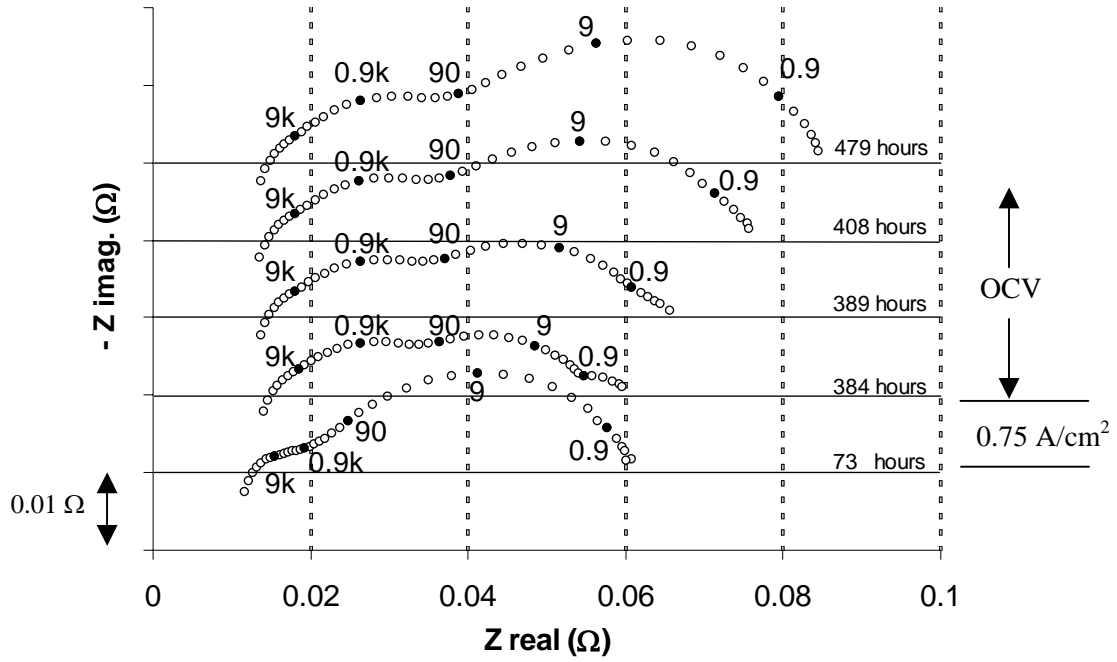


Figure 2. Impedance spectra for cell Kz010614-6 at 750°C. The current density between 73 and 384 hours was 0.75 A/cm<sup>2</sup> whereas the cell was at OCV between 384 and 479 hours. The numbers at the curves give the frequencies (solid symbols).

Table 3: Cell resistance and cell voltage right after the current was switched on and after 48 hours at constant current. The cells where  $x\text{H}_2\text{O}$  is marked with an asterisk were tested in internally reformed methane with a steam to carbon ratio of 2 to 1. The area specific resistances are corrected for fuel utilisation at the indicated current density according to [7].

Cell	$x\text{H}_2\text{O}$	$i$ A/cm <sup>2</sup>	$U_{\text{start}}$ mV	$U_{48\text{h}}$ mV	$\Delta U$ mV	$\text{ASR}_{\text{start}}$ $\Omega\text{cm}^2$	$\text{ASR}_{48\text{h}}$ $\Omega\text{cm}^2$	$\Delta\text{ASR}$ $\Omega\text{cm}^2$
Kz010614-4	0.5	0.25	785	784	-1	0.63	0.63	0
Kz010614-23	0.5	0.5	548	633	85	0.77	0.6	-0.17
Kz010614-6	0.5	0.75	396	478	82	0.72	0.61	-0.11
Kz010614-25	0.05	0.25	851	870	19	0.82	0.75	-0.07
Kz010614-28	0.05	0.5	670	711	41	0.75	0.67	-0.08
Kz010614-42	0.05	1	376	488	112	0.65	0.54	-0.11
Kz010614-8	*	0.25	795	812	17	0.85	0.79	-0.06
Kz020830-10	*	0.5	563	636	73	0.87	0.72	-0.15
Kz020830-29	*	1	287	431	114	0.70	0.56	-0.14

Initially the area specific cell resistances (ASR) corrected for fuel utilisation [7] were in the range of 0.63 to 0.87  $\Omega\text{cm}^2$ , but during the first 48 hours the cells were subjected to constant current, the cell resistances decreased (up to 0.17  $\Omega\text{cm}^2$ , Table 3).

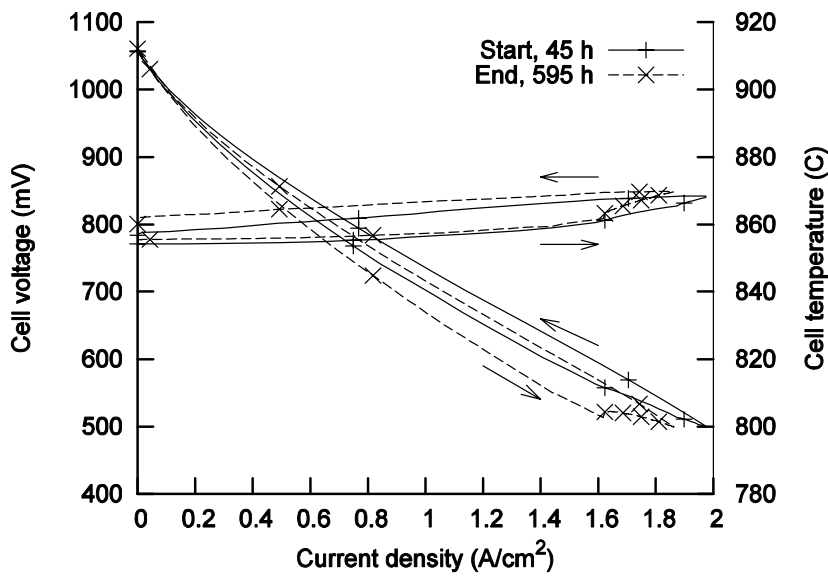


Figure 3.  
*i*-V curves and cell temperature obtained initially and at the end of the test of cell Kz020830-24 at 850°C. The airflow was 140 L/hour and the fuel flow was 24 L/hour H<sub>2</sub> with approximately 5% H<sub>2</sub>O

The activation / passivation was also observed during *i*-V curves as shown in Figure 3 in the form of the hysteresis loop for the individual *i*-V curves. All the tested cells showed such hysteresis loops under electrical loading. Also it was in many cases observed that the current densities obtained right after a period at constant current were larger than the initial ones, as illustrated in Figure 4.

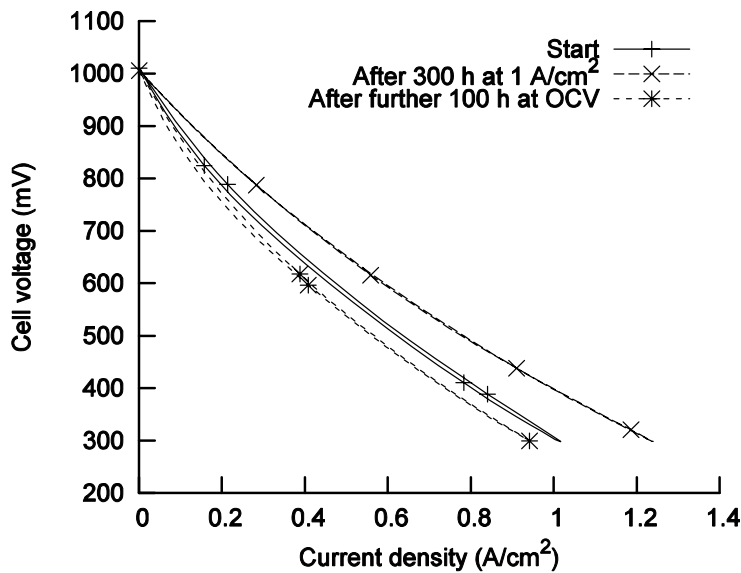


Figure 4:  
*i*-V curves for cell Kz020830-29 obtained before and after 300 hours at 1 A/cm<sup>2</sup> at 750°C in internally reformed methane (S:C ~ 2:1).

Cell Kz020830-24 was tested at different temperatures and at different anode and cathode gas compositions. Figure 5 shows impedance spectra obtained at 853°C and with different gasses fed to the cathode of the cell.

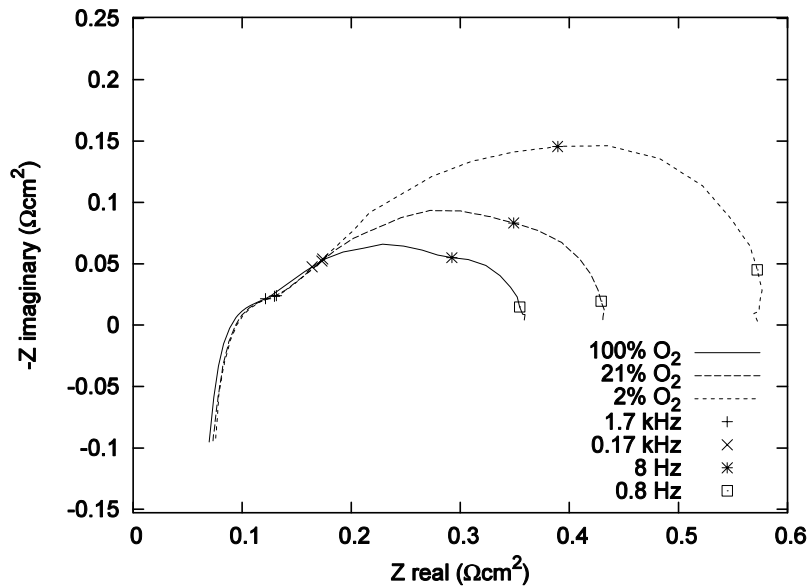


Figure 5. Impedance spectra obtained at 853°C for cell Kz020830-24 with different amounts of oxygen in the cathode gas. The anode gas was wet hydrogen (~20% H<sub>2</sub>O).

The polarisation resistance at frequencies below 200 Hz was strongly affected by the change in the cathode gas, whereas the polarisation resistance above this frequency was almost unaffected. The influence of different anode gas compositions was also investigated, and Figure 6 shows the impedance spectra for cell Kz020830-24 at 853°C with different gasses fed to the anode.

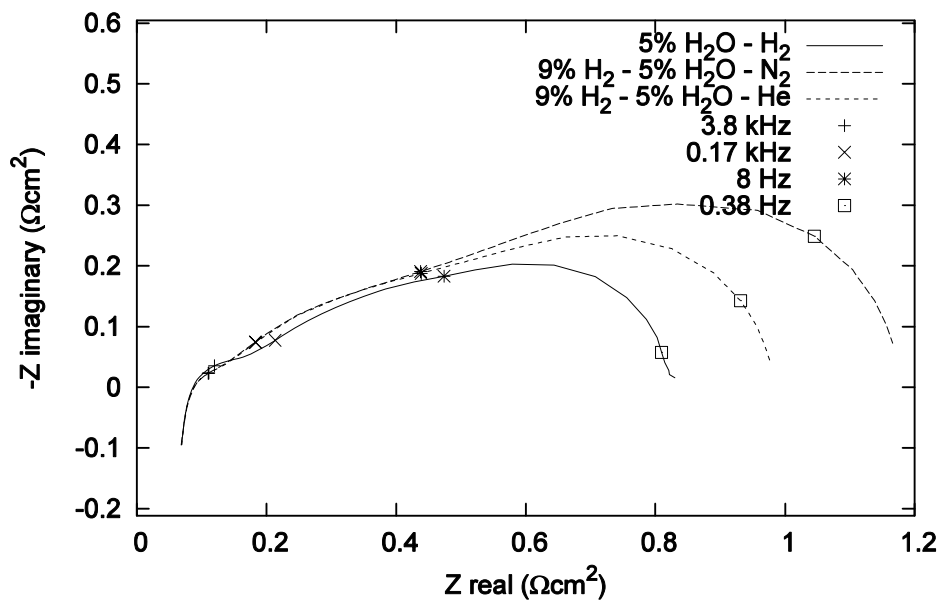


Figure 6. Impedance spectra for cell Kz020830-24 obtained at 853°C with different fuel gas compositions: H<sub>2</sub>(5% H<sub>2</sub>O), 9% H<sub>2</sub>-5% H<sub>2</sub>O-N<sub>2</sub> and 9% H<sub>2</sub>-5% H<sub>2</sub>O-He. Air was fed to the cathode side of the cell.

The low frequency part of the polarisation resistance (below 10 Hz) was strongly influenced by changes in the anode gas composition, whereas the medium frequency part of the polarisation resistance (in the range 10 to 200 Hz) was almost unaffected by changes in the anode gas.

All the cells tested at 750°C were also initially tested at 850°C. The activation energy for the cell resistance was found to be between 1 and 1.2 eV between 750°C and 850°C.

## Discussion

During the test of the cells, it was observed that the cell resistance in some cases was lower after several hundred hours under constant current than before. For all the cells tested at 750°C the cell voltage increased during the first 48 hours at constant current as exemplified in Figure 1. The reduction in cell resistance after a period at constant current is illustrated in Figure 4, where i-V curves obtained right before and right after 300 hours at 1 A/cm<sup>2</sup> are shown. The cell resistance (corrected for fuel utilisation) after 300 hours at 1 A/cm<sup>2</sup> was only 0.73 Ωcm<sup>2</sup> (at 750 mV) as opposed to 1.05 Ωcm<sup>2</sup> before the 300 hours at constant current.

The observed increase in the cell voltage after the current has been switched on, and the difference in cell voltage observed between increasing and decreasing current during i-V curves, can result from at least four factors. First of all, if ohmic heating of the cell increases the mean temperature of the cell, the conductivity of the electrolyte increases [8,9] and the polarisation resistance of the electrodes decreases as the electrochemical processes at the electrode – electrolyte interfaces are thermally activated [10,11]. Thus, an increase in the cell temperature decreases the cell resistance. Secondly, the anode may activate, and thirdly the cathode may activate. Indeed LSM based cathode materials have been shown to activate [4]. Fourthly, in principle, changes in the gas flow to the cell will also influence the cell voltage as the fuel or air utilisation changes [7].

Thermal effects can not be ruled out when addressing the difference in the cell voltage observed during i-V curves as the temperature during i-V curved was not constant due to a current induced heating of the cell (Figure 3).

However, the observed increase in the cell voltage during the first 2 days under constant current is not due to thermal effects. If the decrease in the cell resistance when a cell is at constant current is due to a thermal effect, then the cell temperature should have increased by more than 30°C. (Estimated for the case of cell Kz020830-29 using an activation energy of 1.2 eV). The cell temperature increased approximately 8°C within the first hour (5°C within 10 minutes) after the current was switched on and then remained constant. However, as the cell voltage continued to increase for almost 50 hours, another mechanism must account for the observed increase in cell voltage after the cell temperature has stabilised. As the gas flows were kept constant during the period at constant current, changes in the fuel and / or air utilisation cannot account for the increased cell voltage leaving electrode activation as the responsible mechanism.

When the cells had been operated at high current densities, the increase in cell voltage due to activation was generally higher than when the cells were operated at lower current density. However, there is no simple correlation between the decrease in cell resistance and the current density during the test as shown in Table 3.

Impedance spectroscopy was used to investigate if the anode or the cathode was the main contributor to the observed activation. At 850°C the polarisation resistance between 1 and 200 Hz was found to be influenced by changes in the cathode gas composition as shown in Figure 5.



The low frequency part (below 10 Hz) of the polarisation resistance was influenced by changes in the anode gas composition. This is to be expected as gas conversion and diffusion influences the cell impedance at frequencies below 10 Hz [12-14]. Impedance spectra obtained before and after the cell had been at constant current showed that only the part of the polarisation resistance between 1 and 200 Hz was influenced by the cell activation (Figure 2). This is the same frequency range which was influenced by changes in the cathode gas composition, showing that it is predominately the cathode that is responsible for the observed activation / passivation.

Based on the knowledge of LSM-YSZ single electrode behaviour and the frequency range influenced by the activation / passivation process, it is proposed that changes in the oxygen bond-breaking activity and / or oxygen surface diffusion on the cathode is likely responsible for the activation / passivation [15].

## Conclusions

Electrode activation was found to influence the cell voltage during galvanostatic tests of solid oxide fuel cells during the first 50 hours after the current is switched on.

When the cells were tested at high current densities, the increase in cell voltage was generally higher than at low current densities.

The decrease in cell resistance during activation was found to be up to  $0.17 \Omega\text{cm}^2$ , corresponding to more than 20% of the cell resistance.

It was found that the impedance in the frequency range from 1 to 200 Hz was strongly affected by the activation / passivation process which indicated that the cathode is responsible for the decrease in cell resistance during constant current.

When the current to the cell was switched off after several hundred hours at constant current, the impedance between 1 and 200 Hz increased to the original value during approximately 100 hours.

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