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The Identification of Degradation Parameters in SOC Using In-Situ and Ex-Situ Approaches

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Recent SOC activities focus on upscaling the applications to MW scales with target operation of several 10,000 hours. These long lifetimes require new approaches for durability testing. In the present study, the influence of different operating parameters on degradation was studied by long-term cell testing (in-situ treatment). Based on the results, accelerating parameters for ex-situ treatment were identified, which is a cheaper and time saving approach as compared to conventional cell/stack long-term testing. Two commercial SOC cell designs were studied: Anode supported cells (ASC) and Electrolyte supported cells (ESC).

Introduction

Solid oxide cells (SOC) have shown immense potential as efficient energy conversion technologies. Meanwhile, cost and durability continue to challenge the commercialization of these systems today (1,2). Different cell configurations have been developed since the past decades, Anode supported cells (ASC) and Electrolyte supported cells (ESC) being the most common with different cell compositions. Nickel (Ni) based cermets with Yttria Stabilized Zirconia (YSZ) or Gadolinium Doped Ceria/Cerium Gadolinium Oxide (CGO) fuel electrodes are the most common in both cell configurations.

One of the common degradation processes that have been reported for the fuel electrodes is with respect to microstructural changes in the Ni cermets. Ni-YSZ has been widely studied in the past preferentially in anode-supported configurations under different operating conditions and gas compositions (1–6). These electrodes have shown excellent performance and durability under long-term operation. In particular, at high current densities and in presence of high steam, there are still challenges related to loss of triple phase boundary (TPB) sites due to Ni migration and agglomeration under long-term operation (7–10). The Ni migration has been reported to be severe in case of electrolysis operation with high steam as compared to fuel cell operation (9,13). The presence of high steam may also result in Ni re-oxidation, which could result in mechanical fatigue of the cells, which can have a detrimental impact especially on ASC configurations (13). It was proposed by Mogensen et al. (14) that an applied current on the cells acts as a driving force for Ni migration. In comparison, the ESC configuration results in a more mechanically robust structure due to the thick, dense electrolyte support, however at the expense of a higher ohmic cell resistance, which typically requires higher operating temperatures. Ni-CGO fuel electrodes have been commonly used in the recent years in case of ESCs. These electrodes show a high impurity tolerance and good cell performance also at lower temperatures (15). Ni-CGO electrodes combat the challenges in loss of TPB with the
introduction of double phase boundary reaction sites, in which CGO, being a mixed ionic and electronic conductor (MIEC), aids the transport of both O$_2^-$ ions as well as electrons ensuring a longer cell operation (16). The challenges continue to exist with the Ni migration as well as Ni oxidation in oxidizing environments. Studies have reported that steam has an accelerating effect on the Ni migration and coarsening similar to Ni-YSZ based electrodes (17). Microstructural changes in Ni and CGO in the initial hours of operation under wet fuel conditions followed by an apparent plateau have been reported (17, 18). Furthermore, in Ni-CGO electrodes, Ni growth and migration is additionally also governed by CGO film formation on the Ni (17, 19) as well as the dissolution-precipitation process of CGO on the Ni particles (20). Rapid degradation was observed during operation under high current densities at high pH$_2$O/pH$_2$O ratios due to the formation of H$_2$O or hydroxyl layers on the NiO (21). As highlighted in the previous works, there is a strong interplay of the different operating parameters (steam, temperature, current density, operation mode) on the degradation processes. Thus, the identification of the impact of isolated parameters on cell performance remains a challenge.

This work aims to identify potential accelerating parameters towards cell degradation in both cell configurations while isolating their individual influence on the cell performance. Degradation studies were carried out on cells with ASC and ESC configurations under different fuel compositions and operating conditions. Cells were operated according to two approaches: (i) Cells operated with high steam compositions under load (in situ aging) in fuel cell or electrolysis mode and (ii) Cells exposed to similar gas compositions without any load (ex situ treatment). The cells aged using these two approaches are compared with each other with the aim to establish cheaper (preferentially accelerated) aging approaches.

**Experimental setup**

Commercial, planar solid oxide cells provided by Sunfire (ESC) and Solid Power (ASC) were tested at Technical University of Denmark (DTU). The cells were laser cut to 5.3 cm x 5.3 cm with an active area of 16 cm$^2$. ASCs consist of a Ni-YSZ anode composed of a support and a functional layer (~250 µm in total), a dense YSZ electrolyte layer (8-10 µm), a CGO barrier layer (~5 µm) and a LSCF-CGO air electrode (~50 µm). ESCs have a thin Ni-CGO fuel electrode (~25 µm), a CGO layer close to the electrolyte (~2 µm), a Ni-CGO functional layer (15-20 µm) and a Ni contact layer (~5 µm), which aids contact with the Ni meshes for better current collection on the fuel electrode side. The electrolyte in the ESC is a dense YSZ electrolyte (80-85 µm), a CGO barrier layer and a LSCF-CGO air electrode (30-35 µm) and a LSMC contact layer (~5 µm). The cells were mounted on alumina test houses described in detail elsewhere (22). Gold seal was used for the anode side. As current collector, Nickel meshes (fine and coarse) and Gold mesh were used on the fuel electrode side and on the air electrode side respectively.

The cells were heated to 750 ºC for ASCs and 850 ºC for ESCs using Argon on the fuel electrode and air on the air electrode as per manufacturer’s protocols. The cells were then reduced firstly in diluted hydrogen on the fuel electrode (5% H$_2$ in N$_2$) for two hours followed by one hour under pure hydrogen. Thermocouples were located at the inlet and outlet of the cell. Cells were characterized using I-V curves and electrochemical spectroscopy impedance (EIS) measurements recorded at H$_2$:H$_2$O ratios of 96:4, 80:20 and
50:50 with an oxygen content of 0.21 (air) and 1 on the air electrode. These measurements were recorded at temperatures of 750 °C (ASC only), 800 °C, and 850 °C. The same characterization curves were recorded both prior to and post durability testing. Cells were operated under current (in situ aging). During this operation, EIS spectra were recorded at intervals of 8 h for in-situ tests. The aging under ex situ conditions was carried out in the same test setup, only without applying a load (current). During ex situ treatment, no I-V curves were recorded in order to avoid polarization of the cells. EIS were only recorded at 0 h, 500 h and 1000 h, to minimize impact of current. The long-term conditions under which the cells were tested are summarized in Table I.

**TABLE I.** Summary of different conditions of long-term (1000 h) in-situ operation and ex-situ treatments of the two cell configurations.

<table>
<thead>
<tr>
<th>Parameters</th>
<th>In-situ operation</th>
<th></th>
<th>Ex-situ treatment</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>ASC</td>
<td>ESC</td>
<td>ASC</td>
<td>ESC</td>
</tr>
<tr>
<td></td>
<td>96:4</td>
<td>60:40</td>
<td>10:90</td>
<td>60:40</td>
</tr>
<tr>
<td>H2 flow [l/h]</td>
<td>20</td>
<td>20</td>
<td>13</td>
<td>10</td>
</tr>
<tr>
<td>H2O flow [l/h]</td>
<td>0.8</td>
<td>8</td>
<td>6</td>
<td>0.4</td>
</tr>
<tr>
<td>N2 flow [l/h]</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>4.6</td>
</tr>
<tr>
<td>Total flow rate [l/h]</td>
<td>20</td>
<td>20</td>
<td>13</td>
<td>14.6</td>
</tr>
<tr>
<td>pH2O</td>
<td>4</td>
<td>40</td>
<td>90</td>
<td>2.7</td>
</tr>
<tr>
<td>Current density [A/cm²]</td>
<td>0.4</td>
<td>0.4</td>
<td>-0.4</td>
<td>0.2</td>
</tr>
<tr>
<td>Temperature [°C]</td>
<td>750</td>
<td>750</td>
<td>750</td>
<td>850</td>
</tr>
</tbody>
</table>

**Results and Discussions**

To understand the effect of the different parameters on the cell behavior, a detailed study of the different loss contributions to the total area specific resistance was carried out. This was performed based on results of I-V curves/ EIS during the initial performance characterization, carried out at a set of different temperatures and gas compositions. Furthermore, EIS spectra under different current loads were also recorded at chosen fuel compositions. The peak identification aids to further point out the differences between the two cell configurations (ASC, ESC) as well as the evolution of the different losses over time during aging under in-situ operation and ex-situ treatment.

**Electrochemical Characterization**

The cells were characterized prior to durability tests under similar conditions for both cell configurations. The EIS spectra recorded at OCV using different gas compositions to the fuel and air electrodes were used to identify the different contributions of both the electrodes to the cell impedance for the two cell configurations. The gas shift was also performed at different temperatures to study further the temperature dependencies for the different processes. Using the Analysis of difference in impedance spectra (ADIS) and the
distribution of relaxation times (DRT) deconvolutions, the different loss contributions were identified. These are listed in Table II.

In case of ASC, three distinct peaks were observed for the fuel electrode contributions. The low frequency peak at ~1 Hz was identified to be gas transport process namely gas conversion and a middle frequency peak ~30-50 Hz as gas diffusion. Further, a high frequency peak >1 kHz was assigned to the charge transfer process. These are in accordance with previous studies on similar cells (23). For the ESC, the fuel electrode contributions were shifted to low frequencies owing to the high chemical capacitance of oxygen non-stoichiometry of CGO (24, 25). The low frequency peak between 0.1-1 Hz is assigned to the gas transport losses (in case of ESCs, which have thin electrodes, the gas diffusion losses also arise as a result of the Ni contact meshes). The charge transfer peak in the CGO based fuel electrode is observed at very low frequencies <0.1 Hz. This was observed also using symmetric cells reported by Riegraf et al (26).

The air electrodes of the two cell configurations were composed of similar materials, although with possible different microstructural properties. This would thus result in contributions at similar frequencies. Two distinct peaks were observed for the air electrode, where the low frequency ~0.1-10 Hz was attributed to the gas diffusion in the bulk. The middle frequency 5-30 Hz in case of ESC and >100 Hz for ASCs was attributed to the oxygen ion transfer kinetics and diffusivity in the bulk (27).

**TABLE II.** Summary of the different loss contributions in the different cell configurations (ASC and ESC) identified using gas shift EIS measurements.

<table>
<thead>
<tr>
<th>Loss contributions</th>
<th>ASC</th>
<th>ESC</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Fuel electrode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas conversion</td>
<td>1 Hz</td>
<td></td>
</tr>
<tr>
<td>Gas diffusion</td>
<td>30-50 Hz</td>
<td></td>
</tr>
<tr>
<td>Charge transfer</td>
<td>2-6 kHz</td>
<td>0.1-1 Hz</td>
</tr>
<tr>
<td><strong>Air electrode</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Gas bulk diffusion</td>
<td>0.3-10 Hz</td>
<td>0.1-0.5 Hz</td>
</tr>
<tr>
<td>O² diffusion and O₂ surface kinetics</td>
<td>0.1-1 kHz</td>
<td>5-30 Hz</td>
</tr>
</tbody>
</table>

**Durability studies- Anode supported cells**

The area specific resistances (ASR) was used as measure to study the development of cell performance over time. They were calculated using equation [1] where OCV is the measured OCV at the durability gas compositions before the durability operation (assuming no change of OCV during the operation), U is the measured cell voltage and j is the current density at which the cell is operated.

\[
\frac{ASR}{m\Omega cm^2} = \frac{OCV - U}{j} \quad [1]
\]
The change in resistances during long-term in-situ operation of the ASCs in fuel cell (FC) and electrolysis (EC) mode with different hydrogen: steam compositions are shown in Figure 1. The open circuit voltages (OCV) are different for the three tests at the beginning of the durability testing due to the different fuel compositions. This leads to different initial ASR values (see Figure 1). Furthermore, steam has a positive impact on the cell ASR as observed during the initial cell characterization studies. This has been previously shown both in Ni-YSZ as well as Ni-CGO based fuel electrodes (28, 29). The different initial ASR values make a fair comparison of degradation rates expressed in %/kh difficult. Therefore, also the absolute values of degradation are given. In case of the cells operated in fuel cell mode with 4% steam in hydrogen, the ASR change during the initial ca. 500 h of operation is found to be negligible and then gradually increases to ca. 10 mΩcm²/kh (~3 %/kh) towards 1000 h. During operation in fuel cell mode with the higher steam content of 40% in hydrogen, a larger degradation rate of the ASR of ca. 100 mΩcm²/kh (~35 %/kh) within the initial few 100 hours was observed. The cell degradation rate reduced thereafter and becomes more stable with a rate of ca. 35 mΩcm²/kh (~12 %/kh) by the end of 1000 h. The degradation of the ASR shows a distinctly different trend for the cell operated in electrolysis mode (EC, in Figure 1). There is a steep increase of the ASR for the first 100 h. Afterwards, the ASR increase becomes slower and reaches a more constant increase after ca. 600 h of ca. 50%/kh. It is noteworthy that the degradation rates over the last ca. 500 h of operation under all three test approaches reach similar values of ca. 35-42 mΩcm²/kh.

A closer look at the different resistance contributions was done to understand the degradation mechanisms based on the selected operation parameters in more detail. The ohmic and polarization resistances obtained from EIS during operation are shown in Figure 2. For the in-situ operated cell with 4% steam, there was a slight increase of the ohmic resistance (Rs) within the first 50 h, and then a stabilization. At ca. 900 h, the Rs dropped due to fluctuations in the temperature for unknown reasons. In case of the fuel cell operation with 40% steam in hydrogen, (see curve in Figure 2a) the Rs increased from ~0.145 Ωcm² to ~0.165 Ωcm² corresponding to an increase of ca. 20 mΩcm²/kh (~12 %/kh), which was significantly larger than under less humid fuel conditions. Close to 850 hours, there was an abrupt decrease of Rs, the reason for which is not known at present. For the electrolysis mode operated cell (Figure 2a), the cell experiences an average Rs increase rate of ca. 7 mΩcm²/kh (~2.8 %/kh). The results indicate that the rate of increase of Rs is highest for the cell operated with 40% steam under FC mode with close to 20 mΩcm²/kh, followed by the cells operated with 90% steam under EC mode with ca. 6 mΩcm²/kh and the cell operated in fuel cell under more dry conditions with ca. 4.5 mΩcm²/kh, i.e. with rather similar Rs degradation rates. The ex-situ aging for the ASC configuration with 90:10 H₂O:H₂ (indicated by the black dot in Figure 2) is ongoing.
Figure 1. Evolution of ASR over time for ASCs operated at 750 °C using air on the air electrode and 60:40 H₂:H₂O at 0.4 A/cm², fuel cell mode, 96:4 H₂:H₂O at 0.4 A/cm² fuel cell mode, and 10:90 H₂:H₂O at -0.4 A/cm², electrolysis mode.

Figure 2. Evolution of a) ohmic resistance and b) polarization resistance over time for ASC at 750 °C using air on the air electrode and 60:40 H₂:H₂O at 0.4 A/cm², FC, 96:4/H₂:H₂O at 0.4 A/cm², FC and 10:90/H₂:H₂O at -0.4 A/cm², EC; Ex situ treatment in 10:90/H₂:H₂O at 750 °C. Values obtained from EIS during aging.

The polarization resistance changes during operation of the two ASCs in fuel cell mode were identical in both steam contents in hydrogen. Both Rp increase with a rate of 20-25 mΩcm²/kh (~10-15 %/kh) over the 1000 h of operation. During operation of the ASC in electrolysis mode, Rp increased with a higher rate although with a decreasing trend over time. In the initial 500 h the rate of degradation fell from ~80 %/kh to 30 %/kh. After ca. 700 h, the Rp increased with a smaller rate of ca. 23 mΩcm²/kh (~20 %/kh) and thus a similar rate as the ASCs operated in fuel cell mode. Thus, the changes of Rp were rather similar upon operation in either electrolysis or fuel cell mode after the initial few 100 hours regarding the Rp.

In order to get more knowledge about the degradation in different modes under different degrees of steam in hydrogen, EIS spectra recorded prior and post durability were analyzed. With this approach, the end state of the cell as compared to the fresh state is characterized, disregarding changes during aging. The EIS of the cell operated in 40 % steam in hydrogen as fuel cell are shown in Figure 3a. This was the cell with the largest degradation of the ohmic resistance during aging. In addition to these changes of ohmic resistances that were discussed earlier and observed during the FC operation (see Figure 3a), it is possible to assign a specific frequency region for the changes of the polarization resistance. It is in the
high frequency region, attributed to the charge transfer in the fuel electrode of the ASC. A minor change was observed also at the low frequency region below 1 Hz which could indicate an increase in the gas conversion loss contribution. This increase might be attributed to changes in the Ni particles due to migration and needs to be analyzed further by looking at the cell microstructures. In the middle frequencies, close to 1000 Hz, there is a change observed as well, which can be attributed to the oxygen electrode resistances, i.e. the fuel cell operation over 1000 h leads to degradation of both electrodes of the ASC.

EIS spectra recorded prior to and post cell operation as electrolysis cell at 10:90 H2:H2O inlet fuel composition for 1000 h at -0.4 A/cm² are shown in Figure 3b. In terms of the ohmic resistances, there was no significant changes observed as a consequence of the durability operation, i.e. the Rs degradation observed during the test did not lead to a permanent change after the durability test. Looking at the polarization resistances, the contributions at the low frequencies are fairly unchanged before and after durability operation. The most significant changes are observed at the high frequency (> 500 Hz) region which corresponds to the charge transfer losses of the fuel electrode. It can be concluded that the change in this region is accelerated in the EC operation in comparison to the FC operation. This can be attributed to both a higher overpotential experienced by the EC operation as well as the higher steam content in the fuel feed leading to changes of the TPB sites. In addition, the peaks at middle frequency ca. 30-50 Hz, are seen to shift to a higher frequency after EC operation, and to increase slightly in the peak height at ca. 100 Hz, both indicating an increase of resistances owing to the TPB degradation at the oxygen electrode as well as gas diffusion.

Figure 3. Nyquist, Bode and DRT plots (top, middle, bottom) for EIS recorded before and after durability testing at 750 °C with 80:20 H2:H2O at OCV for cell operated at a) 60:40 H2:H2O composition with 0.4 A/cm², FC for 1000 h b) 10:90 H2:H2O composition with -0.4 A/cm², EC for 1000 h
Durability studies- Electrolyte supported cells

Two cells were operated in fuel cell mode using 96:4 and 60:40 H₂: H₂O ratios as fuel and with air to the air electrode at 850°C under current density of 0.2 A/cm². Figure 4 shows the ASR vs. operating time under current. The ASR degradation rate of the cell with 4% steam in hydrogen in FC mode is larger in the initial ca. 150 h and is more stable afterwards with a degradation rate of ca. 16 mΩcm²/kh (~2.6%/kh). The ASR of the cell in FC mode with the higher steam content of 40% stays rather constant in the first ca. 200 h and increases afterwards to ca. 60 mΩcm²/kh (~11%/kh).

![ASR vs. operating time plot](image)

**Figure 4.** ASR evolution of cells during in-situ operation for 1000 hours at 850 °C using air on the air electrode and 60:40 H₂:H₂O at 0.2 A/cm², fuel cell mode, 96:4 H₂:H₂O under 0.4 A/cm² fuel cell mode.

A closer look at the overall cell performance was done by plotting the cell resistance changes with time in terms of both the ohmic and polarization contributions obtained from EIS during cell operation (see Figure 5). In addition to the EIS for the cells aged during FC operation, the results of EIS recorded on two ex-situ aged cells over time in 60/40 steam/hydrogen fuel and two temperatures are shown in the same Figure 5. It has to be noted that there was no current applied during the ex situ aging treatment for those two cells. The ohmic resistances of the two cells operated in-situ cells with polarization as fuel cells did not change significantly. In case of the high steam content in hydrogen, there was a slight increase after ca. 800 h, with a rate of ca. 12 mΩcm²/kh (~3.2%/kh). During the ex-situ treatment at two temperatures, only three EIS were recorded (at the start, 500 h and at the end of the durability testing over 1000h) in order to limit the influence of any current. The ohmic resistances change in significantly different trends as compared to the in-situ operated cells (see Figure 5a).

Ohmic contributions obtained from EIS of the cells during both the ex-situ treatments showed a significant increase at a rate of ca. 92 mΩcm²/kh for both treated cells (25%/kh and 45%/kh for 850 °C and 950 °C respectively). It seems that the degradation rate of the ohmic resistance during the treatment at 950 °C starts to decrease with time, to 72 mΩcm²/kh (35% /kh). It is difficult to explain the significantly larger degradation of the ohmic resistance of the ex-situ treated cells as compared to the operated cells under otherwise similar conditions (same steam/hydrogen and temperature, but without polarization, in Figure 5). One would suspect that polarization of cells would result in
additional degradation or at least the same, but not less. A potential cause could be that cells from different commercial batches were used in the in-situ operation cells and the ex-situ treatment. A repetition of the tests with cells from the same batch are currently running, together with a micro structural analysis.

Figure 5. Change of (a) ohmic and (b) polarization resistances over time during in-situ operation of cells in FC mode (60:40 and 96:4) and ex situ treatment (no current) at 850 °C, 60:40 hydrogen: steam and 850 °C, 60:40 hydrogen: steam

Comparing the polarization resistances, the cell with 96:4 H₂:H₂O fuel composition shows the highest initial polarization resistance due to the lower steam content and applied fuel cell current. A similar trend of ca.15 mΩcm²/kh (ca.10 %/kh) Rp degradation in the initial 400 hours was observed as for both the FC operated cells. However, for the fuel cell operation in higher steam content, an increase to ca. 36 mΩcm²/kh (~20 %/kh) followed ca. 400 h operation. For the case of both the ex-situ treated cells, a rate of ca. 35-37 mΩcm²/kh (~45 %/kh) was observed in the first 500 h. In the next 500 h, the slope of the ex-situ operated cells reduced slightly. The absolute change in the polarization contributions of both in-situ and ex-situ aged cells with 40 % steam is 0.036-0.038 Ωcm², which indicates, that similar Rp aging can be achieved by treating the cell in steam with and without FC polarization. This value is about 4 times higher than for the cell aged in FC mode with only 4% steam in hydrogen. This shows that high steam content has a significant effect on the degradation of the polarization resistance in case of ESCs.

To understand the changes of the different cell component contributions upon long-term aging, the EIS of the cells (both in situ operation and ex situ treatment) were recorded prior to and after the aging processes. They are shown in Figure 6. The EIS prior to the aging treatments should be the same, as they were recorded under the same EIS conditions at OCV (Figure 6a and Figure 6b). However, this is not the case; both the ohmic and the polarization resistances are different. These differences could be due to the use of different cell batches for the two aging processes as mentioned before. Further investigations are currently in progress.
Figure 6. Nyquist, Bode and DRT plots (top, middle, bottom) of EIS recorded prior to and after aging recorded at 850 °C with 80:20 H₂:H₂O fuel compositions with air to the air electrode at OCV for cell operated at a) 60:40 H₂:H₂O composition with 0.2 A/cm², FC for 1000h b) 60:40 H₂:H₂O composition at 850°C (ex-situ aging) for 1000 h

The results for the cell operated in FC mode at 0.2 A/cm² and 40% steam in hydrogen are shown in Figure 6a. The ohmic contribution is found to change by ~0.02 Ωcm², which is consistent with the observations of Rs during fuel cell operation (see Figure 5a). The cell experiences degradation in two different processes at low frequency polarization resistance assigned to the charge transfer resistances as well as diffusion term in the oxygen electrode (both <1 Hz). A slight increase was also observed at a frequency close to 20 Hz which indicates changes in the oxygen electrode but to a much lesser extent in comparison to the fuel electrode losses. In Figure 6b, the EIS spectra for the ex-situ aged cell in the same fuel composition of 60:40 H₂:H₂O and at the same temperature of 850 °C is shown. During the ex-situ aging, the cell experienced significant changes in the ohmic contributions. The magnitude of change was higher after ex-situ treatment compared to in-situ operation. The change was about 0.1 Ωcm². This is 5 times higher than for the fuel cell operated under similar conditions. In case of the ex-situ aged cells, the degradation of the electrodes was more prominent at the middle frequency region around 50 Hz owing to the oxygen kinetics. Only a slight increase was observed in the low frequency region. In case of both the in-situ operated cell and the ex-situ aged cell an increase of the resistances at low frequencies (at ~0.1 Hz) is observed to a similar extent.
Furthermore, the effect of higher temperature was studied using the ex-situ aging approach. EIS recorded prior to and after ex situ aging at 950 °C and 60:40 H₂:H₂O fuel composition is shown in Figure 7. The ohmic resistance in this case increases by 0.22 Ωcm². This is about ~5 times higher than the in-situ aged cell (which increases by 0.048 Ωcm² when comparing the EIS recorded at 800 °C under 80:20 H₂:H₂O fuel with air) with similar fuel composition as the cell operated at 850 °C in fuel cell mode and also slightly higher that the ex situ treated cell at 850 °C by 0.05 Ωcm². Higher aging temperature is seen to induce more changes in the diffusion and electrochemical contributions (~30Hz) of the oxygen electrode in comparison to the fuel cell operated cells as well as the ex-situ aged cells under similar fuel compositions. Furthermore, a peak appears at the low frequency region after 1000 h of aging at ca 0.1 Hz. This has been previously assigned to the charge transfer resistance due to the loss of reaction sites. This degradation effect was observed during ex situ aging at 850 °C and during operation in fuel cell mode at the same temperature to a much lower degree. Thus, loss of the reaction sites at the fuel electrode can be induced by high temperature and in combination with certain content of steam in the hydrogen fuel. For more detailed understanding of the changes, microstructural changes for the cells aged using the two approaches will be to be examined.
Conclusions

Two commercial cell configurations, ASC and ESC were aged under different conditions to understand the effect of isolated parameters on the cell durability. For this purpose, one set of cells was operated with different steam: hydrogen ratios in FC or EC mode (in situ operation). Another set of cells was treated at the same fuel gas composition and at different temperatures without applying a load (ex-situ treatment).

For the ASCs, the most significant changes were observed at the high frequency region assigned to the charge transfer contribution on the fuel electrode under long-term operation. A higher steam content under fuel cell operation leads to an increased degradation of the ohmic resistance at a rate of ca. 20 mΩcm²/kh. The polarization resistances remained fairly similar in 60:40 or 96:4 hydrogen: steam fuel, whereas the cell operated in electrolysis experienced a different trend with a degradation rate of the polarization resistance that decreases over time. Operating the cell in electrolysis mode increased the degradation of the processes observed at summit frequencies close to 1 kHz (charge transfer) and 100 Hz (Oxygen electrode kinetics), indicating that overpotential and high steam content accelerate the cell degradation.

For ESCs, the cells experienced degradation of the ohmic contributions, in particular during ex situ treatment, as well as processes at the low and middle frequency (ca. 0.1-0.5 Hz and ~50 Hz) assigned to the charge transfer and oxygen kinetics, respectively. Degradation of the charge transfer processes were observed to a significant extent on the ex-situ treated cell with 60:40 hydrogen: steam, at 950 °C. This indicates that high temperature and high steam content (likely induced further with overpotential at lower temperatures) causes this degradation phenomenon on ESCs.

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