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Performance and Durability of Solid Oxide Electrolysis Cells

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Solid oxide fuel cells produced at Risø National Laboratory have been tested as electrolysis cells by applying an external voltage. Results on initial performance and durability of such reversible solid oxide cells at temperatures from 750 to 950°C and current densities from ~0.25 A/cm² to ~0.50 A/cm² are reported. The full cells have an initial area specific resistance as low as 0.27 Ωcm² for electrolysis operation at 850°C. During galvanostatic long-term electrolysis tests, the cells were observed to passivate mainly during the first ~100 h of electrolysis. Cells that have been passivated during electrolysis tests can be partly activated again by operation in fuel cell mode or even at constant electrolysis mode after several hundred hours of testing.

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In the perspective of the increasing interest in renewable energy, hydrogen economy, and CO₂ neutral energy production, reversible solid oxide cells (SOCs) are a potentially interesting technology. Using a solid oxide electrolysis cell can be a cost effective and efficient way to produce hydrogen by high-temperature electrolysis of steam (HTES). The cells can be operated as solid oxide fuel cells (SOFCs) for electricity production and as solid oxide electrolysis cells (SOECs) to produce hydrogen by high-temperature electrolysis of steam by applying an external voltage. Potentially, such reversible SOCss can be combined with already existing energy technologies. By converting surplus energy from nuclear power plants or renewable energy sources such as wind or solar, the SOCs can optimize the efficiency of such energy technologies and play an important role in the security of supply in future hydrogen-based energy systems. Some of the first results on hydrogen production by HTES using SOCs were reported more than two decades ago, where Dönitz presented results from the HOTELLY project for a single cell and stack including durability tests; however the project was stopped around 1990. Since then, intensive research and development in the field of SOFCs has taken place and the efforts have resulted in optimized materials giving high performing, long-term stable cells. The research within the field of HTES using SOC can easily benefit from the results obtained within the SOFC research.

For SOCs to become interesting from a commercial point of view, a low internal resistance of the cell is important, not only at start-up but also during thousands of hours of electrolysis operation as the hydrogen production price is proportional to the resistance of the cell. So far, only a few results on durability of high-performance SOECs have been reported in literature and even though the operation of the SOCs is reversible and can have comparable initial performance in electrolysis and fuel cell mode, the degree of passivation of the cells during long-term testing in fuel cell and electrolysis operation mode, respectively, can be dramatically different. Therefore, it is necessary not only to produce high-performance SOECs but also long-term stable electrolysis cells.

Results on performance and durability of SOECs are presented here. Polarization curves (IV-curves) at various test conditions have been recorded to monitor the initial performance for both fuel cell and electrolysis operation of the SOCs produced at Risø National Laboratory. Results from galvanostatic long-term electrolysis tests for four SOCs are given and the electrolysis testing is shown to lead to a significant passivation of the cells. A partial activation of an electrolysis tested cell by fuel cell operation is reported. Furthermore, an example is given of a 776 h electrolysis test, where the passivation of the electrolysis cell was followed by a partial activation at constant electrolysis conditions.

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Figure 1. Schematic drawing of the SOCs for the electrolysis tests (top) and photo of the one half of the test setup in an alumina cell house (bottom): A: H₂O/H₂ tube inlet, B: Gas inlet holes for H₂O/H₂, C: Glass sealing, D: Current collector (Ni foil), E: Gas distributor, F: The cell and G: Gas outlet tube. Schematic drawing of the test setup is given in Ref. 11.
The polarization curves were measured using controlled current for each of the cells before and after the long-term electrolysis tests. The gas composition to the Ni/YSZ electrode is divided by the total number of \( \text{H}_2\text{O} \) molecules led to the cell. For all four tests, the test conditions and duration for the four electrolysis tests reported in this work. This gas composition to the Ni/YSZ electrode is kept constant at 1 atm when switching from open-circuit voltage (OCV) to electrolysis operation of the cell. This is advantageous for subsequent analysis of the possible changes in the oxygen electrode response observed in the electrochemical impedance spectra recorded during testing. The inlet gas composition to the hydrogen electrode was \( p(\text{H}_2\text{O}) = 0.7 \text{ atm} \) and \( p(\text{H}_2) = 0.3 \text{ atm} \) during electrolysis testing for all electrolysis tests reported in this work. This gas composition to the Ni/YSZ electrode is obtained by mixing 6 L/h \( \text{O}_2 \) and 17 L/h \( \text{H}_2 \) in a gas mixer and leading the mixture to the cell through the inlet tube (Fig. 1). All the gas compositions reported in this work are given as initial fuel compositions at the gas inlet of the cell. The results presented are four SOC electrolysis tests. The tests were performed at various temperatures and current densities. An overview of the electrochemical durability test conditions is given in Table I. The degree of steam conversion given in Table I is calculated as the number of converted water molecules using Faraday’s law, divided by the total number of \( \text{H}_2\text{O} \) molecules led to the cell. For all four tests, the test conditions were kept constant during electrolysis test and the tests were run galvanostatic.

A dc characterization has been performed by recording IV curves for each of the cells before and after the long-term electrolysis tests. The polarization curves were measured using controlled current method stepping 62.5 mA/s (cm²). The IV curves presented in this work are almost linear and the area specific resistances \( \text{ASR} \) and the gas composition to the negative electrode was \( p(\text{H}_2\text{O})/p(\text{H}_2) = 0.7 \text{ atm} \) and \( p(\text{H}_2\text{O})/p(\text{H}_2) = 0.5 \text{ atm} \).

Table I. Test conditions and duration for the four electrolysis tests. For all tests, oxygen was passed over the positive electrode, and the inlet gas composition to the negative electrode was \( p(\text{H}_2\text{O}) = 0.7 \text{ atm} \) and \( p(\text{H}_2) = 0.3 \text{ atm} \). The steam conversion is the number of converted water molecules (Faraday’s law) divided by the total number of \( \text{H}_2\text{O} \) molecules led to the cell.

<table>
<thead>
<tr>
<th>Test</th>
<th>Current density</th>
<th>Steam conversion</th>
<th>Temperature</th>
<th>Electrolysis test time</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>−0.25 A/cm²</td>
<td>14%</td>
<td>750°C</td>
<td>82 h</td>
</tr>
<tr>
<td>B</td>
<td>−0.50 A/cm²</td>
<td>28%</td>
<td>950°C</td>
<td>140 h</td>
</tr>
<tr>
<td>C</td>
<td>−0.50 A/cm²</td>
<td>28%</td>
<td>850°C</td>
<td>135 h</td>
</tr>
<tr>
<td>D</td>
<td>−0.25 A/cm²</td>
<td>14%</td>
<td>850°C</td>
<td>766 h</td>
</tr>
</tbody>
</table>

The initial performance of all cells was measured by recording IV curves at various temperatures and partial pressure of steam to the Ni/YSZ electrode. Figure 2 shows a comparison of such initial IV curves for the two cells with the highest and the lowest performance, namely, the cells used for tests B and C. The IV curves shown were recorded at 850°C and \( p(\text{H}_2\text{O})/p(\text{H}_2) = 1 \) atm to the oxygen electrode.

From the IV characteristic shown in Fig. 2, it is observed that no discontinuity occurs in the shift from fuel cell to electrolysis operation. The area specific resistances (ASR) at varying \( p(\text{H}_2\text{O})/p(\text{H}_2) \) ratios at 850°C for the cells used for tests B and C is given in Table II. It is seen from the numbers in Table II that, even though the slopes of the IV curves in Fig. 2 look identical for positive and negative current densities for each of the two cells, the ASR is larger when running the cells in electrolysis mode than in fuel cell mode. Voltages at distinct current densities were also compared. Both cells had an open-circuit voltage of 928 mV at 850°C and \( p(\text{H}_2\text{O})/p(\text{H}_2) = 1 \). Voltages of 821 and 1061 mV were measured at 0.50 A/cm² and −0.50 A/cm², respectively, for the cell with the highest performance (test B). The corresponding values for the cell having the lowest initial performance (test C) were 775 mV and 1091 mV at 0.50 A/cm² and −0.50 A/cm².

The effect of temperature on the initial performance of the SOCs has also been investigated. Figure 3 shows an example of the effect of lowering the temperature from 850 to 750°C for the good performing cell used for test B. Both curves were recorded at \( p(\text{H}_2\text{O})/p(\text{H}_2) = 1 \). There is still continuity across OCV for the IV curve at 750°C but the ASR has more than doubled compared with the ASR values at 850°C (Table II). For the IV curve at 750°C in fuel cell mode the ASR is 0.44 Ω cm². For the IV curve at 750°C in electrolysis mode the ASR is 0.65 Ω cm² if the data to −0.75 A/cm² is included and the chord is used for the calculation of the ASR but

Table II. ASR for the cell with the highest (test B) and lowest (test C) performance at 850°C at varying steam content to the hydrogen electrode. ASR values calculated as the chord from OCV to the voltages measured at current densities of ±0.75 A/cm². For test C, \( p(\text{H}_2\text{O}) = 0.5 \text{ atm} \), fuel cell mode, only data to 0.67 A/cm² was available.

<table>
<thead>
<tr>
<th>( p(\text{H}_2\text{O}) )</th>
<th>0.05 atm</th>
<th>0.20 atm</th>
<th>0.50 atm (fuel cell)</th>
<th>0.50 atm (electrolysis)</th>
</tr>
</thead>
<tbody>
<tr>
<td>ASR _test B</td>
<td>0.28 Ω cm²</td>
<td>0.22 Ω cm²</td>
<td>0.21 Ω cm²</td>
<td>0.27 Ω cm²</td>
</tr>
<tr>
<td>ASR _test C</td>
<td>0.40 Ω cm²</td>
<td>0.35 Ω cm²</td>
<td>0.32 Ω cm²</td>
<td>0.34 Ω cm²</td>
</tr>
</tbody>
</table>
this number hides the observed hysteresis effect. Calculating the ASR value as the chord from OCV to the voltage measured at a current density of \(-0.50 \text{ A/cm}^2\) for the start and end part of the IV curve leads to ASR values of 0.70 \(\Omega\) cm\(^2\) and 0.60 \(\Omega\) cm\(^2\), respectively. The last part of this IV curve represents the more stable system. The hysteresis effects for this IV curve in electrolysis mode at 750°C is of course also clear from the measured voltages at \(-0.50 \text{ A/cm}^2\). An open-circuit voltage of 957 mV was measured at 750°C. Voltages of 1261 and 1309 mV were measured at \(-0.50 \text{ A/cm}^2\) for the first and last part of the electrolysis IV curve in Fig. 3. The same four trends have been observed for all cells tested in this work, namely, IV curves at 850°C have only minor differences in ASR for fuel cell and electrolysis operation of the cell; no passivation of the cell is observed to take place during electrolysis at 850°C, for electrolysis IV curves recorded at 750°C a passivation of the cell is observed and the initial performance of the cells is improved at increasing temperatures. IV curves were recorded at 750, 850, and 950°C.

After the test of the initial performance of each of the SOCs, durability tests at constant galvanostatic electrolysis conditions were conducted. The resulting development of the cell voltages is shown in Fig. 4. For all tests, the cell voltage increased due to an increase in the internal resistance of the cells. The increase in cell voltage had a tendency to take the form of an “S”-curve and level off after \(\sim 100\) h of electrolysis or less. The least pronounced passivation over 135 h of electrolysis was observed for the high-temperature test B, which actually started out with a minor activation of the cell. The most significant passivation occurred for test A where the cell voltage increased from 1055 to 1275 mV within only 82 h of electrolysis. As the cell voltage seems to have stabilized at 1275 mV, electrolysis test A was stopped. The development of the polarization resistance monitored by EIS recorded during the pronounced passivation observed for test A is described and analyzed elsewhere. Another and a very simple way to monitor the passivation of the cell used for test A is by comparison of IV curves recorded before and immediately after the electrolysis test and these two IV curves are shown in Fig. 5. The passivation of the cell has led to an increased slope of the IV curve. Data from the IV curve were applied to calculate the conversion corrected ASRs as the internal resistance of the cell depends on test conditions such as the reactant utilization. The over voltage will not be equal at the gas-inlet and gas-outlet and therefore a conversion correction has been made for the ASR using an iterative calculation method as discussed elsewhere. The conversion corrected ASRs are included in Fig. 5. A significant hysteresis effect is observed for the IV curve recorded immediately after the electrolysis test A. This hysteresis effect corresponds to a partial activation of the cell obtained during the recording of the IV curve in fuel cell mode after electrolysis test A. In Fig. 5, the direction of time is indicated by arrows. Qualitatively, the course of the cell voltage for test C seems to be similar to that of test A (Fig. 4) but test C was run for a longer time than test A. Figure 6 shows a
“zoom-in” on the development of the cell voltage for test C from 55 to 135 h of electrolysis test time. This reveals that a decrease in the cell voltage corresponding to a decrease in the internal resistance of the cell took place at the end of the test. Electrolysis test C was stopped unintentionally due to a failure in steam supply causing steam starvation for the electrolysis process. After ending test C, the cell was run at constant fuel cell condition at 850°C, a current density of 0.5 A/cm² and \( p(\text{H}_2) = 0.95 \text{ atm} \) to the hydrogen electrode and \( p(\text{H}_2\text{O}) = 0.05 \text{ atm} \). Figure 7 shows that the cell voltage increased by 49 mV during the 97 h of constant fuel cell operation of the cell and this correspond to a partial activation of cell C. Test D was run at even milder conditions than test C, in the sense that the current density was lowered to −0.25 A/cm².

Figure 7. Cell voltage (black line) measured during constant fuel cell operation after electrolysis test C. Conditions during fuel cell operation was: 850°C, 0.5 A/cm². \( \text{O}_2 \) was passed over the oxygen electrode and the gas composition to the hydrogen electrode was \( p(\text{H}_2) = 0.95 \text{ atm} \) and \( p(\text{H}_2\text{O}) = 0.05 \text{ atm} \).

The difference in the slope of the IV curves is slightly larger for electrolysis mode than for fuel cell mode. Figure 9, it is observed that numeric maximum for \( Z_{\text{imag}} \) decreases from a frequency of ca. 7 kHz after 1 h of electrolysis to a frequency of −2 kHz after 45 h of electrolysis and down to −400 Hz at the most passivated state after 116 h of electrolysis testing. Furthermore, the imaginary part of the Bode plot shows minor increase/decrease in \( Z_{\text{imag}} \) for the impedance at a frequency of 1–5 Hz, which is ascribed to gas conversion impedance.

Nyquist and the Bode plots show that \( R_s \) stays constant during the whole electrolysis test D. From the imaginary part of the Bode plot in Fig. 9, it is observed that numeric maximum for \( Z_{\text{imag}} \) decreases from a frequency of ca. 7 kHz after 1 h of electrolysis to a frequency of −2 kHz after 45 h of electrolysis and down to −400 Hz at the most passivated state after 116 h of electrolysis testing. Furthermore, the imaginary part of the Bode plot shows minor increase/decrease in \( Z_{\text{imag}} \) for the impedance at a frequency of 1–5 Hz, which is ascribed to gas conversion impedance.

In Fig. 10, the IV curves (850°C, \( p(\text{H}_2\text{O}) = 0.46 \text{ atm} \) and \( p(\text{H}_2) = 0.53 \text{ atm} \), air to the oxygen electrode) in fuel cell and electrolysis operation before and after electrolysis test D is shown. Only a limited increase in the ASR is observed for the IV curve after electrolysis test D. The difference in the slope of the IV curves is slightly larger for electrolysis mode than for fuel cell mode. Figure 11 shows two fuel cell mode IV curves recorded just before electrolysis test D and immediately after finishing the electrolysis operation of the cell. These IV curves are almost identical. The partial activation of the cell that was caused by recording a fuel cell IV curve immediately after test A (Fig. 5), was not observed for this test D. IV curves for test D were also recorded at the same conditions as those for test A in Fig. 5 (fuel cell operation, 750°C, \( p(\text{H}_2\text{O}) = 0.05 \text{ atm} \) and \( p(\text{H}_2) = 0.95 \text{ atm} \)). For those IV curves, the ASR increased from 0.54 Ω cm² before test to 0.61 Ω cm² after the electrolysis test but no noticeable activation effect was observed for the fuel cell mode IV curve recorded after electrolysis test D.

**Discussion**

**Initial performance of the SOECs.**—The continuity of the IV curves (Figs. 2 and 3) close to OCV verifies that even though these cells were produced and optimized for fuel cell use, they can work as reversible SOCs. In general the initial ASR obtained from IV curves was lower in fuel cell mode than in electrolysis mode (Table II). Table IV lists some initial performances obtained from IV curves in electrolysis mode for SOECs reported in literature. As discussed by Mogensen et al. the concept of area specific resistance for

<table>
<thead>
<tr>
<th>Time</th>
<th>1 h</th>
<th>45 h</th>
<th>116 h</th>
<th>317 h</th>
<th>767 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>( R_s )</td>
<td>0.131 Ω cm²</td>
<td>0.135 Ω cm²</td>
<td>0.133 Ω cm²</td>
<td>0.132 Ω cm²</td>
<td>0.126 Ω cm²</td>
</tr>
<tr>
<td>( R_p )</td>
<td>0.163 Ω cm²</td>
<td>0.321 Ω cm²</td>
<td>0.455 Ω cm²</td>
<td>0.322 Ω cm²</td>
<td>0.224 Ω cm²</td>
</tr>
<tr>
<td>( R_p/R_s(1 \text{ h}) )</td>
<td>1</td>
<td>2.0</td>
<td>2.7</td>
<td>2.0</td>
<td>1.4</td>
</tr>
</tbody>
</table>
SOFCs is often used, though no generally accepted definition seems to exist. Because the ASR depends on fuel utilization, a more direct description of the cell performance is given by the conversion corrected ASRs (Fig. 5 and 11). Unfortunately, conversion corrected ASRs or information enabling the calculation of it, is not always reported in literature. Therefore, the listing of ASRs given in Table IV is simply obtained by taking the slopes of the reported IV curves in the linear regions. The references in Table IV have been selected as they represent results for cells and test conditions close to those applied for the IV curves for the cells tested in this work. Table IV shows that the reversible SOCs produced at Risø National Laboratory have the best initial performance.

Only a few of the results on full electrolysis cells reported in literature include long-term testing and, therefore, a comparison of the long-term electrolysis testing results presented here with results for similar electrolysis cells is difficult. One of the few successful long-term electrolysis tests was reported by Dönitz et al.17 They ran a 1000 h single cell test at 1000°C and no notable passivation was observed. But it should be pointed out that the microstructure of their electrodes was more coarse than for the SOECs tested in this work, and the starting point for their testing, that is the initial ASRs for their cells at 1000°C, was even larger than the ASR that was measured for Risø cells at 850°C (test D) after the partly passivation during the 766 h of electrolysis test.

Long-term galvanostatic electrolysis tests at various temperatures and current densities.—In view of the fact that the cells are from the same production batch and have very similar initial performance (Fig. 2), the development of the cell voltages in Fig. 4 illustrates the effect of variation of the temperature and the current density for the electrolysis tests. Comparing test A and D, the only difference is the temperature of 750°C and 850°C, respectively. The difference in temperature for the two tests gives rise to a considerable difference in the increase of the cell voltage. While the cell voltage for test D only increased by 58 mV over 116 h, the increase was 220 mV over 82 h for the low-temperature test A. The same trend for the increase in cell voltages is seen when comparing test B (30 mV from t = 0 h to t = 135 h) and test C (135 mV over 92 h), where the only difference in operation conditions were the temperatures of 850 and 950°C, respectively. The effect of changing the current density is seen by comparing test A and D. The same inlet gas composition was applied but changing the current density from $-0.25 \text{ A/cm}^2$ to $-0.50 \text{ A/cm}^2$ also changed the steam utilization from 14% to 28%.

Previously, Jensen17 found evidence for a build-up of impurities containing silicon in the three-phase-boundary (TPB) for a Ni-YSZ model system and Liu18 found segregated silicon containing impurities in a tested half cell by scanning and transmission electron microscopy. Such a build-up of impurities could lead to an increase in cell voltage as observed in Fig. 4, where the cell voltage curve levels off when the impurity build-up at the Ni-YSZ TPB stops (all impurities collected). A subsequent decrease in the cell voltage could be due to a conversion of the impurity phase, e.g., crystallization of the glass, see below. The tendency for the course of the cell voltage for all four tests to take the form of “S-curves” supports the explanation for the passivation of the electrolysis cells given by Jensen et al.17 By deconvolution of the EIS recorded during electrolysis, it was shown that the rate limiting step for the steam electrolysis using SOCs was due to a process at the TPB in the Ni/YSZ electrode and it was argued that it is related to an increase in the diffusion path length during the passivation of the electrolysis cell. This phenomenon was explained as impurities building up at the TPB in the Ni/YSZ.

Activation of an electrolysis cell.—To the best of our knowledge, the passivation of an electrolysis cell followed by a partial
activation at constant electrolysis conditions, as obtained for electrolysis test D, has not been reported for solid oxide electrolysis cells previously. This phenomenon has been observed for several of the electrolysis tested cells. Furthermore, the EIS recorded during this long-term electrolysis test D did not only lead to polarization resistances being equal during passivation and the subsequent activation of the cell; the EIS with the same $R_p$ recorded during passivation and activation are identical at each measured frequency (Fig. 9). This strongly suggests that it is the same processes that are the rate limiting step both during the passivation and the following activation of the electrolysis cell. The analysis of the EIS during electrolysis for the first 116 h points towards that the rate limiting step responsible for the passivation of the cell can be diffusion at the TPB caused by an increased diffusion path length.\(^{25}\) If the passivation of the cell used for test D is due to a build-up of glassy phase impurities at the TPB of the hydrogen electrode, then a plausible, but not yet experimentally verified, explanation for the subsequent partial activation of the cell could be a break-up of the glass caused by crystallization of these glassy phases. Such break-up would lead to a decrease in the diffusion path length and enable the complete overlap of the EIS recorded during passivation and activation of the cell as observed in Fig. 9. Impurities containing silica have been observed by scanning electron microscopy and detected by energy dispersive spectroscopy in the hydrogen electrode of the electrolysis tested cells. Further microscopy work is in progress. The partial activation of the cell by running an IV curve in fuel cell mode after the electrolysis test has not only been observed for test D but also for other tests, where a fuel cell IV curve was recorded immediately after electrolysis testing an IV curve in fuel cell mode after electrolysis testing of steam it can be concluded that:

The IV curves show that the SOECs tested in this work performs very well compared with similar SOECs reported in literature. From the results presented here using DK-SOFCs for high temperature electrolysis of steam it can be concluded that:

The cells produced at Risø National Laboratory can be operated both as fuel cells and electrolysis cells.

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References


