Poisoning of Solid Oxide Electrolysis Cells by Impurities

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The production of synthetic hydrocarbon fuels from renewable energy is a solution to reduce oil consumption and carbon dioxide emissions without the need for modifications of existing infrastructure, e.g., in the production of methane (also called synthetic natural gas) or petrol/diesel, the infrastructure already exists in many countries. The raw material for synthetic hydrocarbon fuels is synthesis gas (H$_2$ + CO), which traditionally is produced via coal gasification or steam reforming of natural gas. Both processes consume fossil fuels and emit greenhouse gases. Co-electrolysis of H$_2$O and CO$_2$ (H$_2$O + CO$_2$ + electricity → H$_2$ + CO + O$_2$) using renewable energy sources may be an alternative route for producing synthesis gas without consumption of fossil fuels and without emitting greenhouse gases. CO$_2$ capture from air and/or recycling or reuse of CO$_2$ from energy systems in combination with co-electrolysis of H$_2$O and CO$_2$ seems to be an attractive method to provide CO$_2$ neutral synthetic hydrocarbon fuels.9-11 Solid oxide electrolysis cell (SOECs) have the potential for cost competitive production of hydrogen,14 carbon monoxide,11 and synthesis gas,1,15 providing lifetimes exceeding 5–10 years.11,14

Steam electrolysis (H$_2$O + electricity → H$_2$ + $\frac{1}{2}$O$_2$) in solid oxide cells (SOCs) for hydrogen production was under development during the early 1980s,16-18 and has again become increasingly investigated during recent years as a green energy technology.19,20 Only limited studies have reported electrolysis of CO$_2$ (CO$_2$ + electricity → CO + $\frac{1}{2}$O$_2$) in SOCs.11,17,21-27 Most of this work was performed in platinum and nickel-based SOCs at NASA as a means of producing oxygen.17,21,22 Co-electrolysis of H$_2$O and CO$_2$ is more complicated than the two separate electrolysis reactions because the equilibrium for the water gas shift (WGS)/reverse water gas shift (RWGS) reaction (CO + H$_2$O ↔ CO$_2$ + H$_2$) is easily reached over nickel catalysts at the operating temperatures of the SOECs and occurs in parallel with the electrochemical reactions.13 So far, the co-electrolysis of H$_2$O and CO$_2$ has only been presented in a few studies.15,29-32 Relatively little information on the long-term stability of Ni/ytria-stabilized zirconia (YSZ)-based SOECs is available. A few studies have reported short-term (shorter than 500 h)12,35 and long-term (longer than 500 h)13,15,24,36-44 durability. Even though the initial performance may be quite similar in the electrolysis and fuel cell mode, the cells degrade much faster in the electrolysis mode than in the fuel cell mode.39,45,46 When operating Ni/YSZ–YSZ–lanthanum strontium manganite (LSM)/YSZ SOECs at mild conditions, the cells have a limited degradation on the LSM/YSZ electrode, whereas the main degradation occurs on the Ni/YSZ cathode.39,42 One of the most discussed phenomena for Ni/YSZ electrode degradation in general [both solid oxide fuel cell (SOFC) and SOEC] is the influence of impurities.9,15,24,37,39,47-59 For SOFCs the poisoning effect of sulfur is the most discussed, whereas for SOECs the impurities are rarely identified. The impurities tend to migrate to the grain boundaries, blocking the active triple phase boundary (TPB), which leads to an increase mainly in the polarization resistance. Also for SOECs, the segregation of impurities to the TPB in the Ni/YSZ electrode was speculated to cause the observed degradation when operated at mild conditions (H$_2$O, CO$_2$, or H$_2$O–CO$_2$ mixtures),15,19,24,37,39,40 although no firm evidence for this degradation mechanism for SOECs has been presented. We have recently shown that removing these impurities may result in electrolysis durability with only limited degradation when operated at low current densities.3,37

The aim of the present study is to examine the degradation of Ni/YSZ-supported SOECs when applied for the electrolysis of H$_2$O, CO$_2$, and co-electrolysis of H$_2$O and CO$_2$ in detail by electrochemical impedance spectroscopy (EIS) and to investigate the influence of impurities on the performance and durability of the SOECs.

**Experimental**

Planar Ni/YSZ-supported SOCs of 5 × 5 cm with an active electrode area of 4 × 4 cm were used for all experiments. The cells were produced at Risø DTU.45,60 and had a 10–15 μm thick Ni/YSZ cermet electrode; a 10–15 μm thick YSZ electrolyte and a 15–20 μm thick strontium-doped lanthanum manganate composite LSM/YSZ electrode. The cells were supported by an ~300 μm thick porous Ni/YSZ layer.60-61 At startup, the nickel oxide in the Ni/YSZ electrode was reduced to nickel in hydrogen at 1000°C.60-61 It was previously published that test components, such as the application of glass sealings,39 may have a significant negative effect on the long-term stability of these cells. To eliminate the glass sealings, three different cell assemblies were used for characterization of the cells (see Fig. 1). The cell assemblies used for each specific experiment are described in Table I. For all the cell assemblies, the cell was sandwiched between the gas distributor/contact components at each electrode. A gold or platinum foil at the side of the LSM/YSZ electrode and a nickel foil at the side of the Ni/YSZ electrode were used to pick up the electrode current. For cell assembly 1, the test house was assembled using albit glass seals and gas distributor/contact components, which were made of the same material as the respective electrodes.62 For cell assembly 2 (Fig. 1), the

**ECS**

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Electrolysis of H$_2$O, CO$_2$, and co-electrolysis of H$_2$O and CO$_2$ was studied in Ni/ytria-stabilized zirconia (YSZ) electrode supported solid oxide electrolysis cells (SOECs) consisting of a Ni/YSZ support, a YSZ electrolyte, and an lanthanum strontium manganite (LSM)/YSZ oxygen electrode When applying the gases as received, the cells degraded significantly at the Ni/YSZ electrode, whereas only minor (and initial) degradation was observed for either the Ni/YSZ or LSM/YSZ electrode. Application of clean gases to the Ni/YSZ electrode resulted in operation without any long-term degradation, in fact some cells activated slightly. This shows that the durability of these SOECs is heavily influenced by impurities in the inlet gases. Cleaning the inlet gases to the Ni/YSZ electrode may be a solution for operating these Ni/YSZ-based SOECs without long-term degradation.

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glass seal and gas distributor/contact component on the side of the Ni/YSZ electrode were replaced with a nickel seal and a nickel mesh.\textsuperscript{13} External gas leaks were minimized by applying Ni/YSZ paste (to fill any irregularities) at the side of the Ni/YSZ electrode. For cell assembly 3, the gas distributors at both electrodes were replaced with a metal mesh as gas distributor/contact component (nickel mesh on the side of the Ni/YSZ electrode and platinum mesh on the side of the LSM/YSZ electrode).\textsuperscript{15} The use of platinum mesh on the side of the LSM/YSZ electrode avoided stresses induced by uneven weight on the two sides of the cell. Further, the use of a sealing material was avoided by lowering the gas distribution/contact component and current collector into a wide channel made in the alumina cell housing. In this case, the cell rests directly on the alumina housing. Gas leaks were minimized by applying Ni/YSZ paste at the side of the Ni/YSZ electrode and platinum paste at the side of the LSM/YSZ electrode. For all assemblies, the metal seals and meshes are assumed to contribute negligible to the electrochemical/catalytic activity because their surface area is low compared to the surface area of the electrodes.

Several voltage probes were drawn through the alumina block to measure the cell voltage and the in-plane voltage. The in-plane voltage is measured across each electrode by probes contacting the electrode near the gas inlet and outlet. The in-plane voltage, which reflects an uneven current distribution, is usually below 1 mV due to the high conductivity of the metal foils applied for current collection. Thus, an in-plane voltage of, say 1 mV, reflects that a significant current flows in-plane through the metal foil due to the uneven current distribution across the cell. The cells were placed in a furnace to operate the SOCs at the desired temperature. Steam was produced by reacting oxygen with hydrogen at the inlet to the alumina cell housing.

To investigate the effect of the impurities in the applied gases, the initial performance and durability of the SOCs were examined by producing steam and supplied to the Ni/YSZ electrode (4% H2O–96% H2, 20% H2O–80% H2, and 50% H2O–50% H2) and pure oxygen or air supplied to the LSM/YSZ electrode. For the investigation of CO2 electrolysis and co-electrolysis of H2O and CO\textsubscript{2}, additional ac and dc characterization was performed with H2O–CO\textsubscript{2}–H2–CO mixtures supplied to the Ni/YSZ electrode.

The dc characterization of the cell was performed by recording polarization curves [current density–voltage (i-V) curves] in both electrolysate and fuel cell mode by varying the current. AC characterization was performed by EIS using an external shunt and a Solartron 1255B or 1260 frequency analyzer at frequencies from 82 kHz to 0.08 Hz. The impedance data were corrected using the short-circuit impedance response of the test setup. From the impedance spectra, the ohmic (serial) resistance (R\textsubscript{o}) was taken as the value of the real part of the impedance measured at 82 kHz. The polarization resistance (R\textsubscript{p}) was taken as the difference in the real part of the impedance at 82 kHz and 0.08 Hz. The total area specific resistance of a cell was calculated as the total ac resistance of the real part (R\textsubscript{p} + R\textsubscript{o}) to 0.08 Hz) of the impedance measured at open-circuit voltage (OCV).

**Durability of the SOECs.**—The durability of the SOCs during H2O and CO\textsubscript{2} electrolysis and co-electrolysis of H2O and CO\textsubscript{2} was examined for nine identical cells, all operated at 850°C (see Table I). Three experiments were performed with the gases applied as received. The cell voltage histories when applying the gases as received for H2O electrolysis (50% H2O–50% H2, 850°C, −0.50 A/cm\textsuperscript{2}),\textsuperscript{13,24} CO\textsubscript{2} electrolysis (70% CO2–30% CO, 850°C, −0.25 A/cm\textsuperscript{2}),\textsuperscript{13,24} and co-electrolysis (45% CO2–45% H2O–10% H2, 850°C, −0.25 A/cm\textsuperscript{2})\textsuperscript{15} were previously reported. For all tests applying the gases as received, oxygen was supplied to the LSM/YSZ electrode to avoid any transients in the polarization resistance. The specific degradation rates when applying the gases as received were impossible to reproduce, see for example Refs. 15, 24, 39, and 42.

The electrolysis durability was examined with cleaned inlet gases for six identical SOCs at the same conditions as when applying the gases as received. Two cells were tested for CO\textsubscript{2} electrolysis at 850°C and a current density of −0.25 A/cm\textsuperscript{2} (70% CO2–30% CO); these cells are denoted as A\textsubscript{CO2} and B\textsubscript{CO2}. Two cells were tested for H2O electrolysis durability at 850°C and a current density of either −0.25 A/cm\textsuperscript{2} or −0.50 A/cm\textsuperscript{2} (50% H2O–50% H2); these cells are denoted as A\textsubscript{H2O} and B\textsubscript{H2O}.
respectively. Also, two cells were tested for co-electrolysis durability at 850°C and a current density of ~0.25 A/cm² (45% H₂O–45% CO₂–10% H₂); these cells are denoted as A₉Ο₂–CΟ₂ and B₉Ο₂–CΟ₂. For these six SOCs except A₉Ο₂-CΟ₂, oxygen was supplied to the LSM/YSZ electrode. For A₉Ο₂–CΟ₂, air was supplied to the LSM/YSZ electrode. For AH₂O–CΟ₂, air was 50% CO₂–50% CO, whereas for H₂O electrolysis the shift was performed by subtraction of two spectra where a gas shift was made for one electrode only. The change in impedance is calculated according to Eq. 2-4, where \(\frac{\partial Z'(f_{\text{Ni/YSZ}})}{\partial \ln(f)}\) for the gas shift in CO₂–CO₂ (II) or in H₂O–CO₂ (III) at the Ni/YSZ electrode or the shift in O₂–H₂ (IV) at the LSM/YSZ electrode is shown

\[
\frac{\partial Z'(f_{\text{Ni/YSZ}})}{\partial \ln(f)} = Z'(f)_{\text{Ni/YSZ}} - Z'(f)_{\text{Ni/YSZ}, \text{before electrolysis}}
\]

\[
\frac{\partial Z'(f_{\text{LSM/YSZ}})}{\partial \ln(f)} = Z'(f)_{\text{LSM/YSZ}} - Z'(f)_{\text{LSM/YSZ}, \text{before electrolysis}}
\]

The difference in the gas shift before and after durability tests for the Ni/YSZ or the LSM/YSZ electrode is calculated, as shown below, where \(\Delta Z\) for the gas shift at the Ni/YSZ electrode and \(\Delta Z\) for the gas shift at the LSM/YSZ electrode is shown in Eq. 5 and 6, respectively.

\[
\frac{\Delta Z'(f_{\text{Ni/YSZ}})}{\partial \ln(f)} = \frac{\Delta Z'(f_{\text{Ni/YSZ}})}{\partial \ln(f)} - \frac{\Delta Z'(f_{\text{LSM/YSZ}})}{\partial \ln(f)}
\]

**Results**

**Initial electrochemical characterization of the SOCs.**—The results of this initial ac characterization for the nine cells are summarized in Table I. Some variation in the ohmic resistances is observed, whereas the polarization resistances for the nine cells were reproducible in the different gas mixtures. The variation in the ohmic resistance was mainly a consequence of variations in the contact between the current collector, gas distribution component, and the cell. In general, for the cells using assemblies 2 and 3, good contact was ensured, which clearly improved the reproducibility.

**Durability of the SOECs when applying gases as received.**—Cell voltage and in-plane voltage during CO₂ electrolysis.—After testing the initial performance of the cell, durability in electrolysis mode was examined at 850°C with 70% CO₂–30% CO supplied to the Ni/YSZ electrode and a current density of ~0.25 A/cm². The evolution of the cell voltage and in-plane voltage with time for the test is shown in Fig. 2A.

During the initial electrolysis period (50 h), the cell voltage increased slightly, corresponding to a passivation rate of 0.217 mV/h. The loss in cell performance during CO₂ electrolysis was at least partly reversible when introducing hydrogen; the term passivation is therefore used to describe the loss in performance. Hereafter, the passivation rate increased to 0.454 mV/h (passivation rate from 300 to 400 h). After operation for ~500 h the cell voltage leveled off, and the cell voltage reached a plateau with a limited passivation rate of only 0.032 mV/h.

The in-plane voltage for the Ni/YSZ electrode (Fig. 2A) increased corresponding to the increase in cell voltage. After operation for ~100 h, the in-plane voltage leveled off. Subsequently, the in-plane voltage decreased to the same value as when the electrolysis period was started. During the long-term passivation where the cell voltage increased only slightly, the in-plane voltage remained close to stable.

**Cell voltage and in-plane voltage during H₂O electrolysis.**—Electrolysis durability was tested at 850°C with 50% H₂O–50% H₂
Table I. Cell assembly and initial characterization of the nine SOCs. Area-specific polarization resistances calculated from EIS for the cells when characterized in 20% H₂O–80% H₂, 50% H₂O–50% H₂, 50% CO₂–50% CO, 70% CO₂–30% CO, and 45% CO₂–45% H₂O–10% H₂ at OCV and 850°C.

<table>
<thead>
<tr>
<th>Gas composition to the Ni/YSZ electrode</th>
<th>Gas composition to the LSM/YSZ electrode</th>
<th>Cell assembly 1</th>
<th>Cell assembly 2</th>
<th>Cell assembly 1</th>
<th>Cell assembly 2</th>
<th>Cell assembly 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20% H₂O–80% H₂</td>
<td>Air</td>
<td>0.21</td>
<td>0.19</td>
<td>0.19</td>
<td>0.18</td>
<td>0.19</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>0.18</td>
<td>0.15</td>
<td>0.15</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td>50% H₂O–50% H₂</td>
<td>Air</td>
<td>0.14</td>
<td>0.13</td>
<td>0.15</td>
<td>0.14</td>
<td>0.15</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>0.11</td>
<td>0.10</td>
<td>0.12</td>
<td>0.10</td>
<td>0.12</td>
</tr>
<tr>
<td>50% CO₂–50% CO</td>
<td>Air</td>
<td>0.21</td>
<td>0.18</td>
<td>0.20</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>0.17</td>
<td>0.15</td>
<td>0.17</td>
<td>0.15</td>
<td>0.17</td>
</tr>
<tr>
<td>70% CO₂–30% CO</td>
<td>Air</td>
<td>0.24</td>
<td>0.20</td>
<td>0.23</td>
<td>0.22</td>
<td>0.23</td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td>0.19</td>
<td>0.17</td>
<td>0.19</td>
<td>0.17</td>
<td>0.20</td>
</tr>
<tr>
<td>45% CO₂–45% H₂–10% H₂</td>
<td>Air</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td></td>
<td>Oxygen</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

a The increased ohmic resistance for these experiments is most likely caused by nonoptimal contact between the current collector, contact components, and the cell (as have been the experience with cell assembly 1, Fig. 1).
b The increased resistance for cell A_H₂O–CO₂ compared to the remaining experiment was mainly observed in R_s. This increase in resistance is most likely due to the small amount of contact points between the contact component (mesh) and the LSM/YSZ electrode for this experiment. When increasing the amount of contact points at the LSM/YSZ electrode (B_H₂O–CO₂) more predictable ohmic resistance was obtained.
c We have previously shown that the gas composition to the Ni/YSZ electrode is in WGS–RWGS equilibrium. The thermodynamic equilibrium composition for the co-electrolysis mixture is 40% CO₂, 50% H₂O, 5% CO, 5% H₂ at 850°C.
Electrolysis of CO₂

Time −40% CO₂−5% CO−5% H₂ at 850°C. The evolution of the cell CO₂−10% H₂ supplied to the Ni/YSZ electrode and a current density of 70% CO₂−30% CO, 50% H₂O−50% H₂, and C co-electrolysis (850°C, −0.25 A/cm², 45% H₂O−45% CO₂−10% H₂).

supplied to the Ni/YSZ electrode and a current density of −0.50 A/cm². The evolution of cell voltage and in-plane voltage with time for the test is shown in Fig. 2B.

During the initial electrolysis period, the cell voltage increased slightly, corresponding to a passivation rate of 0.080 mV/h during the first 50 h of operation. Hereafter, the passivation rate increased to 0.683 mV/h (passivation rate from 100 to 200 h). After operation for −250 h the cell voltage started to level off, where after it decreased again (activation). The activation rate measured from 400 to 500 h of operation was 0.497 mV/h. After activation of the cell, a long-term degradation rate of 0.015 mV/h was observed (700–1100 h).

The in-plane voltage for the Ni/YSZ electrode (Fig. 2B) follows the first derivative of cell voltage with time. After operation for −125 h the in-plane voltage levels off. Subsequently, the in-plane voltage decrease to the same value as when the electrolysis period was started. During activation a decrease to a negative in-plane voltage occurs. During the long-term degradation where the cell voltage increased only slightly, the in-plane voltage remained close to stable.

Cell voltage and in-plane voltage during co-electrolysis of H₂O and CO₂ — After testing the initial performance of the cell, durability in electrolysis mode was tested at 850°C with 45% H₂O−45% CO₂−10% H₂ supplied to the Ni/YSZ electrode and a current density of −0.25 A/cm². The thermodynamic equilibrium composition for the co-electrolysis mixture is 50% H₂O−40% CO₂−5% CO−5% H₂ at 850°C. The evolution of the cell voltage and in-plane voltage with time for the entire test is shown in Fig. 2C.

The cell voltage during co-electrolysis shows the same trend (passivation/activation) as during H₂O electrolysis (Fig. 2B), although the initial period with low passivation is not as pronounced. The initial (50 h) passivation rate during co-electrolysis was 0.377 mV/h. Hereafter, the passivation rate increased to 0.594 mV/h (passivation rate from 100 to 150 h). After operation for −200 h, the cell voltage started to level off, whereafter it decreased again. The activation may be separated into two periods: first a period with a low activation rate of 0.067 mV/h (activation rate from 400 to 600 h) followed by a period with an increased activation of 0.138 mV/h (activation rate from 700 to 900 h). After the activation of the cell, a long-term degradation of 0.003 mV/h was observed during the last 50 h of operation. Also the in-plane voltage for the Ni/YSZ electrode shows the same trend as during H₂O electrolysis (Fig. 2B). The in-plane voltage increases initially. After operation for −75 h the in-plane voltage levels off. Subsequently, the in-plane voltage decreases to the same value as when the electrolysis period was started. During the initial activation, the in-plane voltage remained close to stable, whereas during the fast activation, a decrease to a negative in-plane voltage occurs. During the long-term degradation where the cell voltage increased only slightly, the in-plane voltage remained close to stable.

EIS during electrolysis applying gases as received.— Significant degradation of the SOECs was observed when applying the inlet gases as received. To investigate the origin for the degradation, impedance spectra were recorded during electrolysis, as shown below.

Electrolysis of CO₂. Nyquist plot of the measured impedance during CO₂ electrolysis as well as ADIS (Δ ΔZ′/Δ ln(f)) during electrolysis are shown in Fig. 3. Figure 3A shows that no change is observed in the ohmic resistance during electrolysis testing and that the observed cell degradation is caused solely by a change in the polarization resistance of the cell. The start of electrolysis is used as the reference time for the ADIS shown in Fig. 3. The differences in impedance spectra recorded during CO₂ electrolysis show initial increases at −200 to 300 Hz (initially close to 1000 Hz) and at −2000 Hz (Fig. 3B). After electrolysis for −100 h, the increase in
Figure 4. (A) Nyquist plot of impedance spectra recorded during \( 	ext{H}_2\text{O} \) electrolysis. ADIS (B) during the initial passivation of the cell (0–140 h), (C) during the entire passivation period (0–260 h), and (D) during activation and long-term degradation of the cell (260–1315 h).

Figure 5. (A) Nyquist plot of impedance spectra recorded during \( 	ext{H}_2\text{O} \) electrolysis. ADIS (B) during the initial passivation of the cell (0–80 h), (C) during the entire passivation period (0–200 h), and (D) during activation and long-term degradation of the cell (200–1340 h).

the peak at \( \sim 2000 \) Hz leveled off (Fig. 3B), whereas a continued increase in impedance was observed at \( \sim 300 \) Hz, which shifted to \( \sim 80 \) Hz with time (Fig. 3C).

Electrolysis of \( 	ext{H}_2\text{O} \). The Nyquist plot of the measured impedance during \( 	ext{H}_2\text{O} \) electrolysis as well as ADIS (\( \Delta \), \( \partial \, Z'(f)/\partial \ln(f) \)) during electrolysis is shown in Fig. 4. Figure 4A shows that no change is observed in the ohmic resistance during electrolysis testing, whereas the observed cell degradation is caused solely by a change in the polarization resistance of the cell. The start of electrolysis is used as the reference time for the ADIS shown in Fig. 4. During the initial passivation of the cell (0–0 h, Fig. 2), an increase in impedance is observed at around 300–400 (initially close to 1000 Hz) and \( \sim 2000 \) to 3000 Hz (Fig. 4B). After electrolysis for \( \sim 50 \) to 100 h, the increase at \( \sim 2000 \) to 3000 Hz leveled off, whereas a continued increase in impedance was observed at \( \sim 600 \) to 700 Hz (Fig. 4B), which shifted to \( \sim 150 \) to 200 Hz with time (Fig. 4C).

During activation of the cell (250–600 h, Fig. 2), the impedance peak observed at \( \sim 150 \) to 200 Hz decreased, whereas the peak at \( \sim 2000 \) to 3000 Hz remained stable or increased only slightly (Fig. 4D). After activation, an increase in impedance (compared to the start of electrolysis) was observed at \( \sim 2000 \) to 3000 Hz similar to the initial loss in performance. After 600 h of operation (long-term degradation, 600–1315 h, Fig. 2), an increase in impedance is only observed between \( \sim 4000 \) and 5000 Hz (Fig. 4D).

Co-electrolysis of \( 	ext{H}_2\text{O} \) and \( 	ext{CO}_2 \). The Nyquist plot of the measured impedance during co-electrolysis of \( 	ext{H}_2\text{O} \) and \( 	ext{CO}_2 \) as well as ADIS (\( \Delta \), \( \partial \, Z'(f)/\partial \ln(f) \)) during electrolysis is shown in Fig. 5. Figure 5A shows again that no change is observed in the ohmic resistance during electrolysis testing, whereas the observed cell degradation is caused solely by a change in the polarization resistance of the cell. The start of electrolysis is used as the reference time for the ADIS shown in Fig. 5. During the initial passivation of the cell (0–50 h, Fig. 2), an increased impedance is observed at around 300–400 (initially close to 1000 Hz) and \( \sim 2000 \) to 3000 Hz (Fig. 5B). After electrolysis for \( \sim 50 \) to 100 h, the increase at \( \sim 2000 \) to 3000 Hz leveled off (Fig. 5B), whereas a continued increase in impedance was observed at \( \sim 600 \) to 700 Hz (Fig. 5B), which shifted to \( \sim 100 \) Hz with time (Fig. 5C).

During activation of the cell (200–1200 h, Fig. 2), the impedance observed at \( \sim 100 \) Hz decreased, whereas the peak at \( \sim 2000 \) to 3000 Hz remained stable (Fig. 5D). After activation, an increase in impedance (compared to the start of electrolysis) was observed at \( \sim 2000 \) to 4000 Hz similar to the initial loss of performance.

Gas shift analysis by EIS. — Gas shifts on both the Ni/YSZ and LSM/YSZ electrodes were performed before and after electrolysis testing for all tests. The gas shifts enable breakdown of the imped-
The main passivation occurs at the Ni/YSZ electrode. The main difference as the tests shown above in the inlet gases was examined for six cells at identical electrolysis conditions as the tests shown above (Fig. 2). The evolution of cell voltage and in-plane voltage for the remaining cells. The total degradation of the cell was only 6 mV during the 1350 h.

Durability of the SOECs when cleaning the inlet gases.—Cell voltage and in-plane voltage.—To test the effect of impurities in the inlet gases, experiments with cleaned inlet gases were performed. The durability during electrolysis when applying cleaned inlet gases was examined for six cells at identical electrolysis conditions as the tests shown above (Fig. 2). The evolution of cell voltage and the corresponding in-plane voltage for the remaining cells. From the cell voltage measured during H2O electrolysis, CO2 electrolysis, and co-electrolysis of CO2 and H2O (Fig. 7), the degradation was close to zero for A\textsubscript{H2O-CO2} and A\textsubscript{H2O-CO2}. Whereas surprisingly, a minor activation occurred during electrolysis of H2O (A\textsubscript{H2O} and B\textsubscript{H2O}) and co-electrolysis of H2O and CO2 when supplying oxygen to the LSM/YSZ electrode (B\textsubscript{H2O-CO2}).

The cell voltage during CO2 electrolysis increased slightly during the initial 20 h of operation (cell A\textsubscript{CO2}: from 973 to 975 mV and cell B\textsubscript{CO2}: from 977 to 980 mV). Thereafter no degradation was observed during the remaining electrolysis period. The cell voltage after 70 h of operation was 974 mV for cell A\textsubscript{CO2}, and the cell voltage after 600 h of operation was 980 mV for cell B\textsubscript{CO2}. The spikes in cell voltage for cell B\textsubscript{CO2} at 295 and 363 h of electrolysis operation were caused by a sensor break in the oven temperature control, causing a lowering of the cell temperature to 795 and 835°C, respectively. Also the corresponding in-plane voltage for cell B\textsubscript{CO2} shows no change during the electrolysis operation.

Also the cell voltage during H2O electrolysis increased during the initial electrolysis period. For cell A\textsubscript{H2O} (operated at −0.25 A/cm²), the cell voltage increased slowly from 1014 to 1018 mV (during the first 250 h of electrolysis operation). Hereafter, the
The cell voltage decreased to the initial value of 1014 mV after 600 h of operation. During the initial 50 h of electrolysis operation, the cell voltage increased from 1089 to 1100 mV for cell B_{H2O} (operated at −0.50 A/cm²). Hereafter, the cell voltage decreased to 1080 mV after 375 h of operation. No activation/degradation was observed during the last 55 h of electrolysis operation. The in-plane voltage for cell B_{H2O} increases initially; after operation for ~100 h the in-plane voltage levels off and subsequently decreases.

The cell voltage during co-electrolysis of CO₂ and H₂O also increased during the initial electrolysis operation. During the initial 50 h of electrolysis operation, the cell voltage increased from 1089 to 1100 mV for cell B_{H2O} (operated at −0.50 A/cm²). Hereafter, the cell voltage decreased to 1080 mV after 375 h of operation. No activation/degradation was observed during the last 55 h of electrolysis operation. The in-plane voltage for cell B_{H2O} increases initially; after operation for ~100 h the in-plane voltage levels off and subsequently decreases.

The cell voltage during co-electrolysis of CO₂ and H₂O also increased during the initial electrolysis operation. During the first 150 h of electrolysis operation, the cell voltage increased from 912 to 917 mV for cell A_{H2O,CO2} (operated with air to the LSM/YSZ electrode). After the first 150 h of operation, no degradation was observed; the cell voltage after 600 h of operation was 917 mV. The initial increase in cell voltage for cell B_{H2O,CO2} (operated with oxygen to the LSM/YSZ electrode) occurred during the first 25 h only (the cell voltage increased from 909 to 914 mV). Similar to the cells operated in 50% H₂O–50% H₂, the cell voltage decreased after this initial period. After the first 25 h of operation, the cell voltage decreased to 906 mV after 350 h of operation. During the remaining test period, no change in cell voltage was observed; the cell voltage after the 520 h of operation was 906 mV.

**EIS during electrolysis when cleaning the inlet gases.**—When cleaning the inlet gases, notable passivation/activation was only observed for cell B_{H2O}. The cell voltage increased from 1099 to 1100 mV for cell B_{H2O} after 350 h of operation. The Nyquist plot of the measured impedance as well as ADIS (ΔZ’/f)/ln(f) during electrolysis of H₂O is shown in Fig. 8.

**Discussion**

**Initial performance.**—Some variation in the ohmic resistances is observed, whereas the polarization resistances for the nine cells were reproducible in the different gas mixtures. The variation in the ohmic resistance was mainly a consequence of variations in the contact between the current collector, gas distribution component, and the cell. In general, for the cells using assemblies 2 and 3, good contact was ensured, which clearly improved the reproducibility. The varying ohmic resistances may induce increased local current densities (because of uneven contact), which if large enough may induce ohmic degradation (as the local current density is increased to a level where ohmic degradation may occur³⁸). No ohmic degradation was observed for any of the current test, showing that the variation in the ohmic resistances did not lead to any degradation.

**Cell voltage degradation.**—A long-term degradation for the SOECs during electrolysis was observed by the course of the cell voltage (Fig. 2) and the increase in impedance (Fig. 3-5) for the three tests applying the gases as received. As described above, small variations in the initial ohmic resistances was observed, whereas the polarization resistances for the nine cells were reproducible. Consequently, the degradation of the cells, which shows as degradation in the polarization resistance only, is solely a consequence of the operating conditions and not caused by different initial performances.

From the cell voltage shown in Fig. 2, there is a long-term polarization rate between 0.454 and 0.683 mVh⁻¹ regardless of the electrolysis conditions. The specific degradation rates when applying the gases as received are difficult to reproduce.¹⁵,²⁴,³⁹,⁴² However, this study clearly shows that degradation rates can be reproduced and that no degradation occurs when applying cleaned inlet gases. In other words, the durability of these SOCs is heavily influenced by impurities in the inlet gases when operated in electrolysis mode.

**Evaluation of the degradation processes by gas shift analysis.**—When performing ADIS on the gas shift at OCV (Fig. 6), a significant change in ΔZ’/f was found for the Ni/YSZ electrode (ΔZ’/f)/ln(f) of the SOEC when applying the gases as received. As described above, small variations in the initial ohmic resistances was observed, whereas the polarization resistances for the nine cells were reproducible. Consequently, the degradation of the cells, which shows as degradation in the polarization resistance only, is solely a consequence of the operating conditions and not caused by different initial performances.

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initial in-plane voltage. During activation (by the removal or rearrangement of impurities), a similar in-plane voltage development, although with negative sign, would occur.

Degradation mechanism.— The evolution of cell voltage and in-plane voltage as well as the gas shift analysis when applying the inlet gases as received, indicates that the degradation/passivation is related to adsorption of impurities at active sites in the Ni/YSZ electrode as illustrated in Fig. 9. Because of the extreme low impurity concentration and the impurities adsorb in the anode support layer first, and thereafter in the active anode layer, initially a low passivation rate is observed followed by an increased passivation rate. This agrees with the hypothesis that the degradation is due to impurities, as previously proposed by our group.9,15,19,23,37,38,50,41,43,49 The impurities may originate from the inlet gases,15,24 or may originate from the test setup, e.g., Si species originating from the glass seal used in assembly 1. In our prior work, the Si-containing impurities were observed to accumulate at TPB boundaries in the Ni/YSZ electrode (determined postmortem by scanning electron microscopy).15,41,49 The passivation/activation phenomenon was a consequence of these silica impurities. A similar passivation/activation phenomenon was observed during co-electrolysis of H2O and CO2 (Fig. 2, 4, and 5), when operated without the use of a glass sealing, and no silica could be detected by postmortem of the cell in this study. Consequently, silica segregation from the glass seal can certainly not alone describe the observed passivation/activation phenomena during electrolysis. Cleaning the inlet gases (CO2, CO, and H2) completely eliminates the observed degradation and almost eliminates the passivation. Therefore, the observed passivation/activation phenomenon is caused by the adsorption of impurities from the inlet gases. As previously discussed, the presence of minute concentrations of sulfur in carbon dioxide, carbon monoxide, and hydrogen in the inlet gases may lead to the observed passivation.15,25 Traces of hydrogen sulfide (H2S) were detected by mass spectroscopy in all the gases as supplied in this study, whereas no sulfur could be detected in the cleaned gases. The amount of impurities is in the ppb level,24 which makes detection extremely difficult.

When applying clean gases, a long-term activation is observed only when water is present. This indicates that water influences the long-term activation. It may be speculated that impurities [e.g., Na (133 ppm), Si (33 ppm), or Al (26 ppm)] in the raw materials may be removed as hydroxides as previously suggested for silica species.40,41 thereby freeing active sites and improving the activity.

It may further be speculated that the presence of sodium or alumina migrating from the raw material to the surface, as determined for YSZ25 (and eventually to the gas phase), result in the activation when applying the gases as received (Fig. 2), as especially sodium may bind sulfur as NaHS or Na2S thereby capturing/removing sulfur from the active sites. Pretreatment of the cell (e.g., with steam) to force these “impurities” to the surface may be a possibility to decrease the degradation, although this probably only has a limited effect as the impurities are “saturated”/covered eventually. Another possibility for the activation is that the glassy phase that block the TPB may crystallize, which has a less blocking effect at the TPB. In this case, steam would decrease the viscosity of the glass, which increases the crystallization kinetics.

Even though the initial performance is similar in electrolysis and fuel cell mode, the cells degrade much faster in electrolysis mode compared to fuel cell mode, where no degradation was observed for identical SOFCs operated at a current density of 0.25 A/cm2,45 when applying gases of the same purity.21 For H2O electrolysis, CO2 electrolysis, and co-electrolysis, the volume flow toward the TPB is higher than the volume flow away from the TPB. Further, steam is a good solvent/“evaporator” that during H2O electrolysis and co-electrolysis gets reduced to H2 at the TPB creating a transport gradient toward the TPB. This indicates that the driving force of the impurities would be toward the TPB in electrolysis mode. Likewise, in fuel cell mode, the volume flow and water gradient, and thereby the driving force for the impurities would be away from the TPB. Consequently, when operating the SOCs as electrolysis cells, the effect of impurities may be more pronounced compared to operation in fuel cell mode.

Degradation mechanism monitored by EIS.— Careful examination of the evolution in impedance during the passivation/degradation of the SOECs, performed by ADIS (Fig. 4), shows that the same two passivation/degradation processes occur during electrolysis of CO2, H2O, and co-electrolysis of CO2 and H2O when applying the inlet gases as received. One degradation process is characterized by a characteristic frequency at ~1000 to 3000 Hz (initial degradation). A second passivation phenomenon occurs at a characteristic frequency at ~100 to 200 Hz.

Passivation characterized by a frequency of 100–200 Hz.— Based on the characteristic frequency and the gas shift analysis (Fig. 6), the passivation phenomena (100–200 Hz) may be assigned to a degradation of the Ni/YSZ electrode.

Figure 10 shows the ADIS (Δ, δ Z′(f)/δ ln(f)) during activation for H2O electrolysis and co-electrolysis of H2O and CO2. The activation of the cell is mainly influenced by the process characterized by the frequency at 100–200 Hz (Fig. 10). The start of the activation...
period (260 and 200 h for H2O and co-electrolysis, respectively) is used as the reference time for the ADIS shown in Fig. 10. That the activation is influenced by a process characterized by the frequency at 100–200 Hz strongly suggests that it is the same process that is affected both during the passivation and the following activation of the electrolysis cell.

It was previously discussed that a single process occurred during the degradation/passivation and activation of the cell and that this single process was characterized by a frequency shifting down from 2000 Hz to ~100 to 200 Hz during the passivation and shifting back to 2000 Hz during activation.39 Nevertheless, the carefully performed ADIS, as shown in this study, shows that two processes occur: one process that passivates and may activate again (100–200 Hz) and the other process which only shows degradation (1000–3000 Hz) (Fig. 4).

When a clean system is studied, e.g., by using cell assemblies 2 or 3 and clean inlet gases, the passivation/degradation of the Ni/YSZ electrode, with a characteristic frequency of 100–200 Hz can be fully eliminated, showing that this process is related to adsorption of impurities at the TPB. The characteristic frequency of 100–200 Hz may be assigned to a partial blockage of the TPB in the Ni/YSZ electrode caused by adsorption of impurities.

**Initial degradation characterized by a frequency of 1000–3000 Hz.**—It may be debated whether the initial degradation characterized by a frequency of 1000–3000 Hz is related to the Ni/YSZ or LSM/YSZ electrode. Based on the characteristic frequency, the minor initial degradation may be assigned to a degradation of the LSM/YSZ electrode.64 However, the contribution from the Ni/YSZ was observed as low as 2000 Hz.39 Further, the initial degradation of the Ni/YSZ electrode (mainly characterized 100–200 Hz) shifted down from just below 1000 Hz to the 100–200 Hz (see above and Fig. 4 and 5). This means that at low degradation, the degradation related to the Ni/YSZ electrode may be observed at ~1000 to 2000 Hz, and the minor initial degradation may therefore be assigned to a degradation of the Ni/YSZ electrode.

Regardless of the electrode assignment, it seems that the initial degradation may be affected by the current density (higher initial degradation when operating at ~0.50 A/cm² compared to when operating at ~0.25 A/cm², Fig. 2 and 7A).

Assuming that the degradation is related to the LSM/YSZ electrode, from Fig. 7A and 8, it seems like the minor initial degradation is reversible (passivation), similar to the kinetics observed during formation of volatile scales.72,73 Formation of such volatile impurity phases may originate from impurities in the raw materials such as silica and sodium. In this case, the degradation is caused by impurities in the raw materials and the TPB electrode, which is characterized by a frequency of ~100 to 200 Hz, can be eliminated by cleaning the inlet gases to the Ni/YSZ electrode. Cleaning the inlet gases resulted in cell operation without any long-term degradation.

**Conclusion**

Degradation of Ni/YSZ-based SOECs, when applied for H2O electrolysise, CO2 electrolysise, and co-electrolysis of H2O and CO2, was examined. Several long-term durability tests at 850°C and ~0.25 to ~0.5 A/cm² were performed. When applying the gases as received, the cells passivated/degraded with a rate between 0.45 and 0.70 mV/h over the first few hundred hours and a long-term degradation between 0.003 and 0.032 mV/h, regardless of the electrolysis conditions. However, when applying clean inlet gases, no degradation was observed; in fact some cells activate slightly. The durability of these SOECs is heavily influenced by impurities in the inlet gases.

When operating the cells at current densities up to at least ~0.5 A/cm², only polarization degradation is observed and no ohmic degradation. The polarization degradation can be divided into two degradation mechanisms, one at the Ni/YSZ electrode (with a characteristic frequency of 100–200 Hz in the impedance spectra), which is heavily influenced by impurities and one minor initial degradation occurring either at the Ni/YSZ or LSM/YSZ electrodes (with a characteristic frequency of ~1000 to 3000 Hz). The long-term activation of the cells when introducing steam may be caused by the removal of impurities from the cell (raw material).

The degradation occurring at the Ni/YSZ (with a characteristic frequency of 100–200 Hz) electrode can be completely eliminated by cleaning the inert gas to the electrode, whereas the degradation at the LSM/YSZ electrode is not affected by cleaning the inert gas. The degradation of these SOECs is thereby caused by the adsorption of impurities, and cleaning the inlet gases to the Ni/YSZ electrode may be a solution for operating these Ni/YSZ-based SOECs without any long-term degradation.

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