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Study of solid oxide electrolysis cells operated in potentiostatic mode: Effect of operating temperature on durability

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Abstract

Potentiostatic operation of solid oxide electrolysis cells (SOECs) at the thermoneutral voltage enables operation of the SOECs close to 100% electrical efficiency and simplifies the heat management at the stack and system level. In this work, we investigate the long-term durability of Ni/yttria-stabilized zirconia (YSZ) fuel electrode supported SOECs operated for electrolysis of steam at the thermoneutral voltage of 1290 mV, by testing cells at 800, 750, and 700 °C for periods exceeding 1000 h each. The cells show different initial performance due to different operating temperatures, but all experience a significant degree of initial degradation within the first 300 h, with a degradation rate of 2.80, 1.93, and 1.77 A cm$^{-2}$ kh$^{-1}$ (~1.80, 1.51 and 1.90 % kh$^{-1}$) for the cells tested at 800, 750, and 700 °C, respectively. Hereafter the cells show stable performance or even slight activation. After 300 h of operation, the cell tested at 750 °C exhibits performance comparable to the cell tested at 800 °C and more than 74% higher than the cell tested at 700 °C, and this is maintained until the end of the test, suggesting that among three operating temperatures 750 °C is the optimum one. The different degradation behavior of the cells is further investigated by electrochemical impedance spectroscopy (EIS) analysis and post-test microstructural characterization. The cause of degradation is discussed in terms of electrode overpotential. Our findings highlight the significance of operating temperature optimization on the long-term durability of SOECs when operated in potentiostatic mode.

Keywords: Solid oxide electrolysis cells; Operating temperature; Thermoneutral voltage; Potentiostatic; Durability
1. Introduction

Solid oxide electrolysis cell (SOEC) is a promising energy conversion technology for the future energy system based on increasing supply from renewable energy \(^{[1-2]}\). The SOECs can convert surplus electricity from renewable energy to hydrogen via electrolysis of H\(_2\)O or to syn-gas (a mixture of CO and H\(_2\)) via co-electrolysis of H\(_2\)O and CO\(_2\). The syn-gas can be used as feedstock to produce synthetic fuels such as gasoline, diesel, and methanol \(^{[3-7]}\). Compared to conventional low-temperature electrolysis cells, SOECs are generally operated at high temperatures of 650-850 °C, resulting in high energy efficiency because of fast reaction kinetics and favorable thermodynamics \(^{[8]}\). It is worth mentioning that the efficiency of SOEC is significantly impacted by the operating voltage, and a close to 100% power-to-gas efficiency can be reached if the SOEC is operated at the so-called thermoneutral voltage \(^{[9]}\). The thermoneutral voltage is defined as the operating voltage at which the Joule heat generated from the internal resistance of the cell compensates the heat demand required for the endothermic electrolysis process, and it corresponds to 100% electrolysis efficiency. For the cells operated above or below the thermoneutral voltage, heat would be either released to or absorbed from the surrounding environment to compensate for the change of enthalpy and free energy. The corresponding electrolysis efficiency will be higher or less than 100%. From the electrolysis system point of view, the net heat flux reaches zero at the constant thermoneutral voltage, which not only contributes to high system efficiency but also eases the heat management of SOEC stacks and systems during the stage of continuous hydrogen production, as in principle no extra heat needs to be provided to or be released from the stack in a perfect insulation case. In reality, the stack can be operated slightly above thermoneutral voltage to produce some extra heat, to compensate potential heat loss to the surroundings. In addition potentiostatic operation at thermoneutral voltage will ensure homogeneous temperature distribution inside the stack, thus avoiding or at least minimizing the degradation due to thermal fatigue caused by uneven temperature distribution \(^{[10-12]}\).

The long-term durability of SOECs and stacks has been extensively investigated in the past couple of decades. Most of the previously conducted long-term tests were carried out in galvanostatic mode \(^{[13-18]}\), i.e. current is kept constant while voltage is changing due to degradation or activation. A number of other studies investigated the stack and system characteristics upon varying current density, steam utilization or operating temperature etc. \(^{[11,19]}\). Only very few studies looked into the current degradation behavior of the cells operated
in potentiostatic mode \cite{20,21}. To the authors’ knowledge, no research has been reported on how the operating temperature influences both the initial performance and the lifetime degradation of SOEC operated in potentiostatic mode. Chen et al. investigated the degradation behavior of two cells with different oxygen electrodes operated potentiostatically at 1290 mV and 750 °C \cite{20}. Both cells are Ni/yttria-stabilized zirconia (YSZ) fuel electrode supported type, one with La$_{0.6}$Sr$_{0.4}$Co$_{0.2}$Fe$_{0.8}$O$_{3-\delta}$ (LSCF)/Ce$_{0.9}$Gd$_{0.1}$O$_{1.95}$ (CGO) and the other with (La$_{0.6}$Sr$_{0.4}$)$_{0.99}$CoO$_{3-\delta}$ (LSC)/CGO oxygen electrode. The two cells exhibited different initial performance and different long-term degradation behavior. Degradation happened mainly at the Ni/YSZ electrode for both cells. Large overpotential on the Ni/YSZ electrode was identified as the main cause of the degradation. Later Rao et al. made a comparative study of the durability of Ni/YSZ fuel electrode supported SOEC cells tested for co-electrolysis under galvanostatic and potentiostatic conditions \cite{21}. This study has shown that operating a SOEC in potentiostatic mode for co-electrolysis operation can prevent some causes for degradation. From a SOEC system point of view, the operating current density determines hydrogen production rate, while the time-dependent current density degradation behavior at e.g. thermoneutral voltage determines the economic payback period of the SOEC system investment \cite{22,23}. When operated potentiostatically, the current density is directly controlled by the cell operating temperature. The system operated at higher temperature can achieve higher initial current density (hence higher production rate), while the elevated operating temperature also increases the difficulty of selecting suitable stack component materials, and thus increases the system cost \cite{24,25}. The system operated at lower temperature allows for use of regular (and often cheaper) materials, like ferritic stainless steels for hot stack or BOP components. This will also reduce the risk of component failure due to high temperature corrosion or sealing leakage \cite{26,27}. However, lower operating temperature often results in lower production rate, thus reducing the economic benefits. Therefore, it is crucial to investigate the optimum working temperature when the SOEC is operated potentiostatically.

In this study, we report on the influence of operating temperature on the durability of state-of-the-art Ni/YSZ fuel electrode supported SOECs, when potentiostatically operated for electrolysis of steam at the thermoneutral voltage of 1290 mV. Different degradation behaviors are observed for the cells tested at different temperatures of 800, 750 and 700 °C. The degradation of cells is further investigated by electrochemical impedance spectroscopy (EIS) measurements and post-test microstructural characterization. Distributions of
relaxation times (DRT) and complex-non-linear-least-squares (CNLS) fitting applying equivalent circuit modeling are carried out to quantify the origin of the degradation. The cause of degradation is discussed in terms of electrode overpotential. The cell long-term durability and degradation behavior at different temperatures are evaluated in order to identify the optimum operating temperature of SOEC at thermoneutral voltage.

2. Experimental

The cells used for electrolysis testing in this work are fuel electrode supported SOEC cells from the same production batch. The cells consist of a NiO/3 mol.% Y₂O₃ doped ZrO₂ (3YSZ) mechanical support layer (~300 μm in thickness), a NiO/8 mol.% Y₂O₃ stabilized ZrO₂ (8YSZ) active fuel electrode layer (~10 μm), an 8YSZ electrolyte layer (~8 μm), a CGO inter-diffusion barrier layer (~6 μm) and a LSCF/CGO composite oxygen electrode (~30 μm). The cells were produced in two steps: In the first step the support layer, active fuel electrode, and electrolyte were produced via multilayer tape casting and co-sintering. In the second step, the CGO barrier layer and the oxygen electrode were applied on top of the YSZ layer by screen printing and sintering. The cells were produced in a footprint of 12 × 12 cm², and were further cut into a footprint of 5.3 × 5.3 cm² with an active oxygen electrode area of 4.0 × 4.0 cm². In this work, only the full cells with a configuration of Ni/YSZ/YSZ/CGO/LSCF/CGO are investigated.

The cell testing was carried out at DTU. Details on the test setup is described elsewhere [28-30]. The tests were started up by heating the cell (1 °C min⁻¹) up to 850 °C, with 20 l h⁻¹ air supplied to the oxygen electrode and 20 l h⁻¹ Ar to the fuel electrode. The NiO in the fuel electrode was reduced with 9% H₂ in N₂ for 2 hours before switched to pure H₂ with 4% steam for 1 hour. After reduction, the cell performance was characterized at various temperatures (850, 800, 750 °C) with 50 l h⁻¹ air or pure oxygen supplied to the LSCF/CGO composite oxygen electrode and 24 l h⁻¹ H₂O/H₂ (4, 20, and 50% H₂O in H₂) to the Ni/YSZ fuel electrode. The cell performance was characterized by measuring DC polarization curves (I-V curves) and AC electrochemical impedance spectra (EIS). For the durability testing, 50 l h⁻¹ pure oxygen was supplied to the LSCF/CGO composite oxygen electrode and 13.3 l h⁻¹ H₂O/H₂ (90/10) to the Ni/YSZ fuel electrode. The three cells were tested at different temperatures (800, 750, and 700 °C) at potentiostatic (1290 mV) electrolysis conditions. The
cells are denoted as Cell-800, Cell-750, and Cell-700 in this work. The gas flow rates were kept constant during the entire potentiostatic durability testing period. The cell performance was monitored by measuring current density and EIS throughout the testing periods. A Solartron 1255 frequency analyzer was used for measuring the EIS both at open-circuit voltages (OCV) and 1290 mV during the durability test. The EIS data were recorded in a frequency range from 96850 Hz to 0.08 Hz, 12 points per decade with a perturbation current of 3.75 mA cm$^{-2}$. In addition to the three long-term tested cells, a nominally identical cell (denoted as Cell-Ref) was selected as a reference to assess microstructural changes induced by the durability testing. Cell-Ref was exposed to reduction and initial performance characterization only.

A Zeiss Merlin scanning electron microscope (SEM) equipped with a field emission gun (FEG-SEM) for obtaining high resolution micrographs was employed for post-test microstructural characterization. Two SEM modes were used: backscattered electron (BSE) and low-voltage SEM. Polished cross-sections of Cell-800, Cell-750, Cell-700 as well as the Cell-Ref were selected for microstructural analysis. For each cell, a cross-section from the steam inlet area was vacuum embedded in Struers epoxy resin (Epofix), followed by grinding using SiC paper and polishing using 6, 3, 1, and 0.5 µm diamond paste. The polished cross-section samples were used firstly to examine the percolating network of Ni in the Ni/YSZ electrodes. For this purpose the samples without carbon coating were applied. An acceleration voltage of ~0.95 kV and an inlens detector were used. These low-voltage SEM micrographs provide information on the percolation characteristics of the electron conducting phase (Ni) in the Ni/YSZ electrode $^{[31]}$. The polished cross-sections were then carbon coated to eliminate surface charging when conducting the high-voltage SEM imaging. The samples were examined using the BSE detector and an accelerating voltage of 15 kV for microstructural characterization as well as Energy Dispersive X-ray Spectroscopy (EDS) elemental analysis.

3. Results and discussion

3.1 Initial electrochemical performance

Figure 1a compares the initial $I$-$V$ curves of the three cells (Cell-800, Cell-750, and Cell-700) measured at 750 °C with 50% H$_2$O+50% H$_2$ supplied to the fuel electrode and pure O$_2$ to the oxygen electrode. The measured
OCVs are 983, 986, and 986 mV, for Cell-800, Cell-750, and Cell-700, respectively (Figure 1a), and are within 8 mV off the calculated Nernst potentials (991 mV), confirming proper sealing and gas-tightness of the electrolyte. Furthermore, the I-V results verify that the cells coming from the same production batch are alike, showing comparable performance, but differ slightly at current densities above 0.5 A cm². Figure 1b and 1c plots the Nyquist and Bode plots of the EIS data recorded at OCV. The three cells show almost identical ohmic resistance ($R_s$), but differ slightly in the polarization resistance ($R_p$). The main difference lies in the frequency range of ~1–10 kHz, where Cell-750 shows a bit higher resistance than Cell-800 and Cell-700. The impedance observed in this frequency range can be attributed to resistance contributions from the Ni/YSZ fuel electrode [30,32]. This indicates that Cell-750 initially had slightly fewer active sites in the Ni/YSZ fuel electrode, which may originate from the less well dispersed/phase distributed microstructure within the 16 cm² fuel electrode area. This could be caused by imperfect slurry preparation for the fuel electrode, such as agglomeration etc.

Figure 1. (a) Initial I-V curves, (b) Nyquist plots and (c) Bode plots of EIS data of Cell-800, Cell-750, and Cell-700 measured at 750 °C at OCV, with 50% H₂O+50% H₂ supplied to the fuel electrode and pure O₂ to the oxygen electrode.

To separate the different resistance contributions to the overall polarization resistance, $R_p$, the EIS data were further analyzed using the distribution of relaxation times (DRT) method [32-33]. Figure 2 gives a representative illustration of the EIS data recorded on Cell-800 at 750 °C under OCV with varying gas feeds to the electrodes, and the corresponding DRT plot. By applying the DRT method, the frequency ranges for the
different loss mechanisms occurring to the total impedance response of the cell can be determined. As shown in Figure 2c, five peaks can be identified from the DRT plot, corresponding to five different electrochemical processes (P1-P5). The integral area enclosed by a specific peak represents the resistance for that electrochemical processes [34-35]. The process P1 is almost independent of any gas change [32-33]. With increasing the ratio of H2O to H2 at the fuel electrode, the peaks for P2, P4, and P5 shift towards higher frequency, also with a significant decrease in the peak area. The processes P3, P4, and P5 exhibit a visible dependency on the gas to the oxygen electrode compartment, i.e. a change is detected when switching the gas supply to the oxygen electrode from O2 to air, while P2 exhibits only very limited sensitivity towards the changes in p(O2) on the oxygen electrode side. Based on the above and the previous studies on the same type of cells [28], the five peaks are allocated to the following electrochemical processes: The high-frequency process P1 is ascribed to the oxygen ion conduction in the composite electrode. Due to the high ionic conductivity of CGO as compared to that of YSZ, the main contribution of P1 is then expected to derive from the Ni/YSZ fuel electrode [32]; P2 is associated with the resistance originating from the charge transfer reaction at the triple-phase boundaries (TPB) of the Ni/YSZ fuel electrode; P3 is likely due to the oxygen evolution reaction at the active sites of the oxygen electrode [36-37]; The low-frequency processes P4 and P5 are usually related to the mass transport process by gas diffusion and the gas conversion polarization, respectively [38-42].
Figure 2. Inductance corrected EIS spectra recorded on Cell-800 at 750 °C under OCV with varying gas feed to the electrodes: (a) Nyquist, (b) Bode and (c) DRT plots.

3.2 Long-term durability

Durability tests were performed potentiostatically at 1290 mV with 90% H₂O+10% H₂ fed to the fuel electrode and pure O₂ to the oxygen electrode. Figure 3 shows the evolution of current density with time for the three cells tested at 800 °C (Cell-800), 750 °C (Cell-750), and 700 °C (Cell-700). Looking more closely at the test results, there was a similar degradation profile on all the cell group during the initial 300 h testing with a fast initial degradation, which started to level off after ~ 300 h of testing. Table 1 summarizes the measured current densities and the calculated degradation rates. The current was measured continuously throughout the durability test period. At 1290 mV, Cell-800, Cell-750, and Cell-700 reached an initial current density of 1.55, 1.28, and 0.93 A cm⁻², respectively, corresponding to a hydrogen production rate of 649, 536, and 390 mL cm⁻² h⁻¹ (Figure S1, “Supporting information”). However, rapid degradation (in terms of decreasing current density) occurred within the first 300 h for all the three cells. The current densities dropped to 0.71, 0.70, and 0.40 A cm⁻² at 300 h, with average degradation rates of 2.80, 1.93, and 1.77 A cm⁻² kh⁻¹ (~1.80, 1.51 and 1.90 % kh⁻¹). The maximum
degradation rates within 0-300 h reached 6.16, 3.09 and 3.30 A cm\(^{-2}\) kh\(^{-1}\) for Cell-800, Cell-750, and Cell-700, respectively. The current densities were then gradually stabilized at 0.69, 0.68, and 0.39 A cm\(^{-2}\), corresponding to hydrogen production rates of 289, 283, and 162 mL cm\(^{-2}\) h\(^{-1}\) (Figure S1, “Supporting information”). Even though the cell tested at 800 °C (Cell-800) initially was able to operate at 20% higher current density at 1290 mV than the cell tested at 750 °C (Cell-750), both cells reached similar long-term performance after 300 h. The cell tested at 700 °C had initially 27% lower current density as compared to Cell-750, and ended up having a 40% lower current density at 1050 h. In brief, after 300 h of operation, the cell tested at 750 °C exhibited performance comparable to the cell tested at 800 °C and more than 74% higher than the cell tested at 700 °C. The test at 800 °C was interrupted a few times. Cell-800 was hence exposed to four load cycles (SOEC-OCV-SOEC), but without notable changes in the cell performance. Cell-800 actually exhibited a bit better performance (slightly higher current density) after each unintended load cycle.

As mentioned above, when tested potentiostatically at 1290 mV, all the three cells suffer serious deterioration, especially within the first 300 h. Over the entire testing periods, the current density of Cell-800, Cell-750, and Cell-700 dropped by 0.86, 0.60, and 0.54 A cm\(^{-2}\), respectively. Note that Cell-800 was tested for 2290 h, while Cell-750 and Cell-700 were tested for 1300 and 1050 h, respectively. Most of the degradation happened within the first 300 h: the current density dropped about 0.84, 0.58, and 0.53 A cm\(^{-2}\), accounting for 98%, 96%, and 98% of the degradation over the entire testing period, for Cell-800, Cell-750, and Cell-700, respectively. From 300 h onwards, the cells are stabilized with negligible degradation.
Figure 3. Evolution of current density and its time derivative for the three cells during the long-term stability test at the thermoneutral voltage of 1290 mV. Feeding $13.3 \text{ l h}^{-1}$ H\textsubscript{2}O+H\textsubscript{2} mixture (H\textsubscript{2}O/H\textsubscript{2} = 90/10) to the Ni/YSZ electrode and $50 \text{ l h}^{-1}$ O\textsubscript{2} to the oxygen electrode.
Table 1. Summary of cell degradation in terms of changes in current density. The unit of current density is A cm$^{-2}$.

<table>
<thead>
<tr>
<th>Cell ID</th>
<th>Testing period, h</th>
<th>$i_{in}$</th>
<th>$i_{300h}$</th>
<th>$i_{final}$</th>
<th>$\Delta i_{final}$</th>
<th>$\Delta i_{300h}$</th>
<th>$\Delta i_{300h}/(i_{in}-\Delta i)$, % kh$^{-1}$</th>
<th>$\Delta i_{final}/\Delta i$, %</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-800</td>
<td>2290</td>
<td>1.55</td>
<td>0.71</td>
<td>0.69</td>
<td>0.86</td>
<td>0.84</td>
<td>1.80</td>
<td>97.8</td>
</tr>
<tr>
<td>Cell-750</td>
<td>1300</td>
<td>1.28</td>
<td>0.70</td>
<td>0.68</td>
<td>0.60</td>
<td>0.58</td>
<td>1.51</td>
<td>96.3</td>
</tr>
<tr>
<td>Cell-700</td>
<td>1050</td>
<td>0.93</td>
<td>0.40</td>
<td>0.39</td>
<td>0.54</td>
<td>0.53</td>
<td>1.90</td>
<td>98.3</td>
</tr>
</tbody>
</table>

To assign the degradation behavior to a specific part of the cells, or even a specific process, Figure 4 illustrates the development of the resistances during the measurement at 1290 mV for the three cells plus the corresponding DRT analysis. An enlarged view of the DRT plots is further provided in Figure S2 (“Supporting information”), where the 10 – 10,000 Hz frequency range covering the P2 and P3 peaks are enlarged. Regardless of the working temperature, the resistances of the three cells increased sharply during the first 300 h of the durability tests, especially for the polarization resistances. The peaks in the DRT plot enables a frequency split-up of the different polarization resistance contributions. The characteristic frequency of P2 decreased significantly for Cell-800, meanwhile, the area enclosed by P2 increased markedly, although it has been offset by the negative contribution resulting from the decrease of current density.$^{[38]}$ This implies that at the higher temperature of 800 °C the major degradation originated from the Ni/YSZ fuel electrode (charge transfer reaction). For Cell-700, the integral area of the P2 and P3 peak increased sharply and their characteristic frequency decreased. As for the increase of P3, it may be ascribed to the degradation from the LSCF/CGO electrode or it may be simply a matter of the P2 peak increasing and shifting downwards in frequency to cover P3 region. The detailed breakdown analysis will be shown later.
Figure 4. Nyquist and DRT plots of the impedance spectra recorded during the potentiostatic testing period at 1290 mV with 13.3 l h\(^{-1}\) 90% H\(_2\)O–10% H\(_2\) fed to the fuel electrode and 50 l h\(^{-1}\) pure O\(_2\) to the oxygen electrode.

Furthermore, to quantitatively split up the total area specific resistance (ASR) into contributions from the different electrode processes, the CNLS method using the Ravdav software was used to fit the equivalent circuit model depicted in Figure 5(a) to the experimental impedance data. The model was built on DRT results and previously reported research \(^{29,33,43-45}\). Figure 5(b-d) gives a representative illustration of Nyquist plots in comparison with simulated EIS for Cell-800, Cell-750, and Cell-700 at 10 h and 300 h of the long-term stability test. The impedance spectra of Cell-800 was fitted with the circuit B, while the impedance spectra of Cell-750 and Cell-700 were fitted with the circuit A. Note that in circuit B, the R6 additional resistance in series with the L6 inductance as part of the P5 process describes the low frequency loop appearing at the frequencies below 0.5 Hz, which has been shown to derive from the reduction of Zr\(^{4+}\) in Ni/YSZ fuel electrode \(^{29,46-47}\). An illustrative example of Cell-800 showing experimentally measured and simulated impedance spectra and the relative differences between them for \(Z_{\text{real}}\) and \(Z_{\text{imag}}\) over the entire frequency range can be found in Figure S3 (“Supporting information”). As shown in Figure S3(c), the residuals (relative errors) are distributed uniformly along the frequency axis, showing no systematic deviation. For most of the spectra obtained in this work, the relative error lies below 2%, thus demonstrating the validity of the model. Above 10,000 Hz, inductive contributions caused by the electrical wiring become noticeable \(^{45}\), but the deviation is still below 4%. The above shows the validity of our models and the fitting. The quantitative results from EIS analysis are further
listed in Table S1 (“Supporting information”). Figure 5(e-g) summarizes the values of \( R_s \) and resistances associated with various electrode processes from the EIS analysis for the three tested cells. \( R_{\text{ion}} \) related to the transmission of oxygen anions (corresponding to P1), while \( R_{\text{Ni/YSZ,TPB}} \) represents the charge transfer reaction in the Ni/YSZ electrode (corresponding to P2). \( R_{\text{ion}} \) and \( R_{\text{Ni/YSZ,TPB}} \) commonly constitute the Ni/YSZ electrode polarization resistance \( R_{\text{Ni/YSZ}} \). From Figure 5(b-d), we observe that the initial high-frequency \( R_p \) contribution of Cell-800 is higher than that of Cell-750 and Cell-700. It is expected that the high-frequency \( R_p \) contribution could be ascribed to the Ni/YSZ-TPB resistance (\( R_{\text{Ni/YSZ,TPB}} \)) which increases with current density [38]. As shown in Figure 5(b,e), for Cell-800, the ohmic resistance was observed to increase considerably from 0.094 to 0.166 \( \Omega \) cm\(^2\), increased by 77\%, meanwhile, the \( R_{\text{Ni/YSZ}} (R_{\text{ion}}+R_{\text{Ni/YSZ,TPB}}) \) was increased by 0.284 \( \Omega \) cm\(^2\), contributing more than 84\% of the total increase of the \( R_p \). It was found that both \( R_s \) and \( R_p \) suffer serious deterioration, and particularly the fuel electrode (\( R_{\text{Ni/YSZ}} \)) exhibited the most severe degradation. This effect could be ascribed to the processes where the Ni grains are detached from each other and/or from the YSZ scaffold and redistributed/agglomerated in the Ni/YSZ active layer [33,48-50], and this was supported by SEM images as shown later in Figure 8. While in the case of Cell-700, the cell itself has higher initial ohmic resistance and polarization resistance, mainly ascribed to the lower operating temperature, thus the lower ionic conductivity in the electrolyte and the ionic conducting phase in the Ni/YSZ three-phase boundaries [51]. The polarization resistance of Cell-700 increased more during the first 300 h as shown in Figure 5(d,g), \( R_{\text{Ni/YSZ}} \) increased considerably from 0.200 to 0.688 \( \Omega \) cm\(^2\) (increased by 244\%). Besides, \( R_{\text{LSCF/CGO}} \) of Cell-700, representing reaction at the oxygen electrode (corresponding to P3), was increased by 0.152 \( \Omega \) cm\(^2\), which was more severe than that of the Cell-800 (0.029 \( \Omega \) cm\(^2\)) and Cell-750 (0.048 \( \Omega \) cm\(^2\)). The polarization resistance of both fuel electrode and oxygen electrode of Cell-700 increased significantly compared with the case of Cell-800 and Cell-750. This effect may be ascribed to the fact that the oxygen electrode suffers degradation when operated under 1 A cm\(^2\) at the lower operating temperature which was observed in our previous study [52]. These could include effects such as the breakup of LSCF grains and the formation of nanoparticles (e.g. lanthanum zirconate) at the electrode/electrolyte [52-55]. The combination of \( R_{\text{diff}} \) (corresponding to P4) and \( R_{\text{conv}} \) (corresponding to P5) accounts for the total gas concentration polarization resistance \( R_{\text{conc}} \). The \( R_{\text{conc}} \) has little change in the condition of long-term stability
testing since gas concentration polarization is only mildly temperature-dependent\textsuperscript{[56]}. Overall, Cell-750 exhibited the lowest degradation in resistance as compared to Cell-800 and Cell-700.

Figure 5. (a) Equivalent circuit models used in fitting the impedance spectra obtained in this work. Model B was used to fit the spectra with a low-frequency inductance loop, whereas Model A was used for the rest, (b-d) Nyquist plots in comparison with simulated EIS and (e-g) Summary of simulated values of $R_s$ and resistances associated with each of the electrode processes for Cell-800, Cell-750, and Cell-700 at 10 h and 300 h of the long-term durability test at the thermoneutral voltage of 1290 mV.

3.3 Performance comparison before and after the durability test

Additionally, $I$-$V$ curves of the three tested cells in respective temperatures before and after the long-term degradation tests were measured and plotted in Figure 6. Due to a smaller increase in ASR, the change in the slope of $I$-$V$ curves for Cell-750 is smaller than in the case of Cell-800 and Cell-700. With regard to the current densities measured at 1250 mV, the current densities of the three cells (Cell-800, Cell-750, and Cell-700)
dropped from 1.52, 1.18, 0.830 A cm\(^{-2}\) before durability testing to 0.859, 0.813, and 0.390 A cm\(^{-2}\), respectively, corresponding to degradation of 43, 31, and 53%, respectively. Cell-750 has the smallest change in electrolysis current density. It should be noted that the OCVs of Cell-800, Cell-750, and Cell-700 are 850, 885, and 892 mV (theoretical Nerst potentials are 874, 893, 913 mV) before durability testing and dropped to 837, 883, and 890 mV afterwards, respectively.

Figure 6. I-V curves measured before and after the durability test at 800, 750, and 700 °C with 13.3 l h\(^{-1}\) 90% H\(_2\)O–10% H\(_2\) fed to the Ni/YSZ electrode and 50 l h\(^{-1}\) pure O\(_2\) fed to the LSCF/CGO oxygen electrode.

Impedance spectra recorded before and after the durability test at OCV illustrate the deterioration from individual processes. Nyquist plots in comparison with simulated EIS for Cell-800, Cell-750, and Cell-700 measured at 750 °C and OCV are shown in Figure 7(a,b,c), and the summary of results from equivalent circuit modeling of EIS are presented in Figure 7(d,e,f) and Table S2 (“Supporting information”). The impedance spectra were fitted with the CNLS model of circuit A described in Figure 5(a). With regard to the results from equivalent circuit modeling, initially, the three tested cells have similar resistance contributions from the individual processes as expected, as the three tested cells are from the same production batch. After the durability test, Cell-750 shows the least degradation. Only a slight increase of the ohmic resistance was observed, whereas the polarization resistance had increased by 53% as shown in Figure 7(b,e). The entire impedance spectrum of Cell-800 shifted evidently towards higher resistance values as shown in Figure 7(a), reflecting an increase of the
ohmic resistance. In addition, the polarization resistance had increased significantly (up to 170%). It should be noted that $R_{\text{Ni/YSZ}}$ was observed to increase roughly by a factor of 4 after the durability test of Cell-800. For Cell-700, the $R_{\text{LSCF/CGO}}$ increased from 0.016 to 0.026 $\Omega \text{ cm}^2$, or a relative increase of 63%, which can be seen in Figure 7(c,f) and Table S2.

Figure 7. Measured and simulated impedance spectra (a,b,c) and summary of results (d,e,f) from equivalent circuit modeling of EIS recorded for the three cells before and after the durability test. Impedance spectra were recorded at 750 °C and OCV, with 24 l h$^{-1}$ 50%$\text{H}_2\text{O}+50\%\ \text{H}_2$ supplied to the fuel electrode and 50 l h$^{-1}$ $\text{O}_2$ to the oxygen electrode.

3.4 Microstructure analysis

In the present work, Figure 8 and Figure S4 (“Supporting information”) presents the BSE and low-voltage images of the polished cross-sections of the inlet part of the three tested cells Cell-800, Cell-750, Cell-700, as well as a reference cell (Cell-Ref). This work focused on the Ni/YSZ electrode to assess the microstructure changes that occurred at the Ni/Ni and Ni/YSZ interfaces and Ni grains. Figure 8 shows the low-voltage (right) images of the Ni/YSZ hydrogen electrode to visualize the Ni agglomeration and loss of percolating network. These results clearly showed increase of the Ni particle size after long-term testing in the three cells Cell-800, Cell-750, Cell-700. Furthermore, the loss of Ni/Ni electrical conducting path (a significant lack of percolating
Ni) in the active Ni/YSZ electrode was detected in all the three cells. The degree of the percolation loss is the most pronounced for Cell-800. Figure 8(a) and Figure S4(a) further reveal an increasing number of large pores (more than 1 μm in diameter) in the electrochemically active fuel electrode layer and a decrease of porosity in the neighboring support layer in Cell-800. The porosity change indicates the redistribution/agglomeration of Ni grain particles [48] (Figure 8a). Furthermore, some dark rims (continuous or discontinuous) around the Ni grains (indicated by the blue circles in Figure 8a (left)) were detected in the active fuel electrode of Cell-800, indicating that the Ni grains are detached from the YSZ scaffold [33]. As previously reported, the dark rims are associated with the presence of Zr-oxide nano-particles on the surface of Ni grains, causing the detachment. This has previously been identified as one of the major degradation mechanisms for Ni/YSZ electrodes under SOEC operation [49]. In addition to changes at the interface, black dots (indicated by the red circles in Figure 8a), which are inclusions inside Ni grains, are also found in the fuel electrode. Corresponding EDS point analyses provide the information that the black dot (Point 1 in Figure S5, “Supporting information”) contains a significant amount of Si and this is not detected in Point 2, indicating that these black dots are silicon oxide [49-50]. However, in the cases of active fuel electrode of Cell-750 and Cell-700, as shown in Figure 8(b,c), neither Ni grains detach from the YSZ nor black dots (silica) are detected. The microstructure is rather similar to that of Cell-Ref (Figure 8d). This is in good agreement with the results obtained from electrochemical characterizations, where Cell-750 and Cell-700 show relatively mild degradation when comparing with the electrochemical performance of Cell-800.

For the oxygen side, as shown in Figure S6 (“Supporting information”), SEM analysis did not show any noticeable microstructural change in either the CGO barrier layer or the LSCF/CGO oxygen electrode, and the adhesion between the different layers (electrolyte, barrier layer, and oxygen electrode) of the tested cells seems to remain intact after the long-term stability test at thermoneutral voltage of 1290 mV.
Figure 8. BSE (left) and low-voltage (right) images of the Ni/YSZ hydrogen electrode. (a) Cell-800, (b) Cell-750, (c) Cell-700 and (d) Cell-Ref. The blue and red circles in (a) highlight dark rims around Ni grains and inclusions inside Ni grains. For low-voltage (right) images, White: percolating Ni; light gray: non-percolating Ni; black: porosity; and dark gray: YSZ.

3.5 Electrode overpotential

Based on the aforementioned results on the three durability tests performed at 800, 750, and 700 °C, there seems to be no linear relation between the degradation rate and the operating temperature. Recent work has shown that SOECs suffer roughly linear and irreversible degradation at high electrode overpotentials [33,49,57].
SOECs operated at thermoneutral potential but at different temperatures are expected to reach different initial current densities, which will affect the distribution of the overpotential across the cell. To further clarify this, with the results from equivalent circuit modeling of EIS recorded during potentiostatic testing (Table S1, “Supporting information”), the overpotential distribution on the different components of the three tested cells at 10 h and 300 h of the long-term stability test at the thermoneutral voltage of 1290 mV was estimated [58] and is presented in Table 2. The overall cell overpotential was calculated as the difference between cell voltage (1290 mV) and the Nernst potential. The ohmic part of the overpotential was calculated as the product of $R_s$ and current density. The remaining part was deemed as the electrode overpotential and was distributed proportionally according to the corresponding resistance values. For Cell-800, $\eta_{Ni/YSZ}$ was about 169 mV at 10 h of the durability testing period, higher than that of Cell-750 ($\eta_{Ni/YSZ} \approx 124$ mV) and Cell-700 ($\eta_{Ni/YSZ} \approx 140$ mV). In our prior work, we found that for fuel electrode overpotential below 160 mV, Ni migration was not significant but Ni migration occurred to a significant degree at fuel electrode overpotential between 160 mV and 300 mV [33]. The Ni/YSZ microstructure undergoes irreversible changes, including Ni particle morphology changes, coarsening and even the reduction of Zr$^{4+}$ and the formation of ZrO$_2$ nanoparticles on the Ni surface when operated at high overpotentials [33,49,57]. The ohmic resistance, therefore, increased due to the loss of electrical conducting path [33,49,57]. The Cell-700 operated at a lower temperature exhibit a lower current density, however, its overpotential of the oxygen electrode ($\eta_{LSCF/CGO} \approx 59$ mV) was higher than that of Cell-800 ($\eta_{LSCF/CGO} \approx 33$ mV) and Cell-750 ($\eta_{LSCF/CGO} \approx 44$ mV). These findings suggested that testing at a lower temperature may result in higher $\eta_{LSCF/CGO}$, which cannot be neglected as a contribution of the degradation processes. According to the long-term electrolysis test results presented here, it is clear that the local overpotential plays an essential role in the irreversible degradation. When the cell is operated potentiostatically at 1290 mV, the operating temperature has only a minor influence on the overall cell overpotential, due to the fact that the cell OCV varies very little with temperature. However, varying temperature does change how the overall cell overpotential is distributed onto different parts of the cell, due to difference in the activation energy of various electrochemical processes. This can be controlled by temperature adjustments during operation of the SOECs, to ensure stable operating conditions for both the fuel electrode and the oxygen electrode. From a commercial system point of view, electrolysis testing at 750 °C at 1290 mV with the lowest initial fuel electrode overpotential seems to be the optimum operating temperature.
for the planar Ni/YSZ fuel electrode supported SOECs studied in this work.

Table 2. Estimated overpotential contributions for the three cells at 10 h and 300 h of the durability testing period (potentiostatically at 1290 mV, 90% H₂O–10% H₂ fed to the fuel electrode and 50 l h⁻¹ pure O₂ to the oxygen electrode).

<table>
<thead>
<tr>
<th>Simulated overpotential (mV)</th>
<th>ηᵣ</th>
<th>ηᵣNi/YSZ</th>
<th>ηᵣLSCF–CGO</th>
<th>ηᵣDIFFconc</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell-800-10h</td>
<td>105</td>
<td>169</td>
<td>31</td>
<td>134</td>
</tr>
<tr>
<td>Cell-800-300h</td>
<td>108</td>
<td>236</td>
<td>33</td>
<td>62</td>
</tr>
<tr>
<td>Cell-750-10h</td>
<td>124</td>
<td>124</td>
<td>25</td>
<td>127</td>
</tr>
<tr>
<td>Cell-750-300h</td>
<td>77</td>
<td>203</td>
<td>44</td>
<td>78</td>
</tr>
<tr>
<td>Cell-700-10h</td>
<td>143</td>
<td>140</td>
<td>28</td>
<td>87</td>
</tr>
<tr>
<td>Cell-700-300h</td>
<td>66</td>
<td>210</td>
<td>59</td>
<td>64</td>
</tr>
</tbody>
</table>

4. Conclusion

In summary, we demonstrated that the operating temperature can have a large influence on the durability of SOECs when tested potentiostatically. Three durability tests on state-of-the-art Ni/YSZ fuel electrode supported SOECs were performed at 800, 750, and 700 °C for electrolysis of steam at thermoneutral voltage of 1290 mV. Rapid degradation occurred in the first 300 h in all three tests, where the current density of Cell-800, Cell-750, and Cell-700 dropped from 1.55, 1.28, and 0.93 A cm⁻² to 0.711, 0.700, and 0.398 A cm⁻², respectively, corresponding to degradation rates of 2.80, 1.93, and 1.77 A cm⁻² kh⁻¹. Accordingly, after 300 h of operation, the cell tested at 750 °C exhibited performance comparable to the cell tested at 800 °C and more than 74% higher than the cell tested at 700 °C. Hereafter all the cells showed stable performance or even slight activation. The EIS results indicate that the major degradation can be attributed to the Ni/YSZ electrode for all the three cells. The increase in the Rₘ and RₘNi/YSZ,TPB, which were determined from the EIS data recorded before and after the durability test, were 0.029 and 0.126 Ω cm⁻² kh⁻¹ for Cell-800, 0.013 and 0.035 Ω cm⁻² kh⁻¹ for Cell-750, 0.008 and 0.037 Ω cm⁻² kh⁻¹ for Cell-700, respectively. Severe microstructural deteriorations including Ni redistribution/agglomeration and the disconnection between Ni and YSZ were observed in the Ni/YSZ electrode for Cell-800. In contrast, no obvious microstructure damage was observed for Cell-750 and Cell-700. Such
different degradation behaviors of the cells were ascribed to the difference in electrode overpotential. Based on the results, it appears that the electrolysis testing at 750 °C at thermoneutral voltage results in the lowest initial fuel electrode overpotential and is the optimum operating temperature for the Ni/YSZ fuel electrode supported SOECs studied in this work. Prolonged durability testing is recommended to observe the truly long-term degradation and validate the above conclusion. The optimization of other operating parameters (operating voltage, gas flow rate, etc.) to avoid irreversible long-term degradation will be further systematically analyzed in our future study.

Acknowledgments
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Supporting information

Study of solid oxide electrolysis cells operated in potentiostatic mode: Effect of operating temperature on durability

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Table S1. Resistances obtained from equivalent circuit fitting of EIS recorded at 10 h and 300 h of the electrolysis durability testing at 1290 mV shown in Figure 5.

<table>
<thead>
<tr>
<th>Simulated resistance (Ω cm²)</th>
<th>Cell-800</th>
<th>Cell-750</th>
<th>Cell-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>0.094</td>
<td>0.166</td>
<td>0.072</td>
</tr>
<tr>
<td>Rion</td>
<td>0.100</td>
<td>0.128</td>
<td>0.028</td>
</tr>
<tr>
<td>RNi/YSZ,TPB</td>
<td>0.128</td>
<td>0.384</td>
<td>0.256</td>
</tr>
<tr>
<td>RLSCF/CGO</td>
<td>0.043</td>
<td>0.072</td>
<td>0.029</td>
</tr>
<tr>
<td>Rdiff+Rconv</td>
<td>0.181</td>
<td>0.134</td>
<td>-0.047</td>
</tr>
<tr>
<td>Rp,sum</td>
<td>0.546</td>
<td>0.884</td>
<td>0.338</td>
</tr>
</tbody>
</table>

Table S2. Results from equivalent circuit fitting of EIS (shown in Figure 7) recorded at OCV and 750 °C before and after the durability test.

<table>
<thead>
<tr>
<th>Simulated resistance (Ω cm²)</th>
<th>Cell-800</th>
<th>Cell-750</th>
<th>Cell-700</th>
</tr>
</thead>
<tbody>
<tr>
<td>Rs</td>
<td>0.102</td>
<td>0.131</td>
<td>0.029</td>
</tr>
<tr>
<td>Rion</td>
<td>0.020</td>
<td>0.040</td>
<td>0.020</td>
</tr>
<tr>
<td>RNi/YSZ,TPB</td>
<td>0.028</td>
<td>0.154</td>
<td>0.126</td>
</tr>
<tr>
<td>RLSCF/CGO</td>
<td>0.016</td>
<td>0.038</td>
<td>0.022</td>
</tr>
<tr>
<td>Rdiff+Rconv</td>
<td>0.039</td>
<td>0.045</td>
<td>0.006</td>
</tr>
<tr>
<td>Rp,sum</td>
<td>0.103</td>
<td>0.277</td>
<td>0.174</td>
</tr>
</tbody>
</table>
Figure S1. Evolution of current density and hydrogen production rate with time for the three cells tested at the thermoneutral voltage of 1290 mV. Feeding 13.3 l h\(^{-1}\) H\(_2\)O+H\(_2\) mixture (H\(_2\)O/H\(_2\) = 90/10) to the Ni/YSZ electrode and 50 l h\(^{-1}\) O\(_2\) to the oxygen electrode.

Figure S2. DRT plots of the impedance spectra recorded during the potentiostatic testing period at 1290 mV with 13.3 l h\(^{-1}\) of 90\% H\(_2\)O–10\% H\(_2\) fed to the fuel electrode and 50 l h\(^{-1}\) pure O\(_2\) to the oxygen electrode.
Figure S3. (a) CNLS fits of inductance corrected impedance spectra of Cell-800 at 10 h of durability test at the thermoneutral voltage of 1290 mV. The corresponding Bode plots (b) and relative residual plots (c).
Figure S4. BSE images of the Ni/YSZ hydrogen electrode. (a) Cell-800, (b) Cell-750, (c) Cell-700 and (d) Cell-Ref.

Figure S5. BSE images with EDS point analyses on Ni grains performed with an accelerating voltage of 15 kV, Point 1 (black dot – inclusion inside the Ni grain) and Point 2 (Ni grain without inclusion).
Figure S6. BSE images of the LSCF/CGO oxygen electrode. (a) Cell-800, (b) Cell-750, (c) Cell-700 and (d) Cell-Ref.