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An operation strategy for mitigating the degradation of solid oxide electrolysis cells for syngas production

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HIGHLIGHTS

• Durability of three cells under different operation conditions was investigated.
• Ni-YSZ fuel electrode degradation mechanisms are discussed.
• Lowering the conversion and \( \text{H}_2\text{O} + \text{CO}_2 \) concentration in two steps reduces degradation.
• An operations strategy that mitigates degradation is proposed.

ABSTRACT

Three cells were tested under different conditions to mimic the situation with stacks arranged in gas flow series or parallel. The effects of reactant conversion ratio and inlet gas composition on the cell performance and durability were studied. The cells were operated under \(-1\, \text{A/cm}^2\) at 800 °C for \( \text{H}_2\text{O} + \text{CO}_2 \) co-electrolysis. Flows were adjusted to realize the same overall production of syngas. Detailed electrochemical characterization was performed before, during and after the aging test and microstructural changes after aging were investigated. The results show that a gas-flow series arrangement is advantageous as it leads to reduced cell degradation: Reducing the \( \text{H}_2\text{O} + \text{CO}_2 \) conversion from 56% of a gas flow “parallel” case (Cell P) to 28% in the upstream of the series connected cells (Cell SU) and 39% in the downstream one (Cell SD) reduces the overall cell voltage degradation rate from 372 mV/kh for Cell P to 140 mV/kh and 69 mV/kh for Cells SU and SD, respectively. This is tentatively ascribed to the “milder” overall conditions realized in the gas flow series case, where the average as well as maximum polarization (and local current density) is reduced relative to the parallel flow case.

1. Introduction

The transition from a fossil fuel energy system to one based on renewable energy sources is widely accepted as a need for reducing the global anthropogenic \( \text{CO}_2 \) emission. However, the widespread implementation of renewable energy sources such as wind and solar energy requires efficient and large capacity energy storage due to the intermittent nature of these sources. Also pathways for producing synthetic green fuels for hard-to-be-electrified sectors of society such as aviation and shipping is needed. Solid oxide cells (SOCs) technology has drawn great interest for such applications in recent years, due to their high power to fuel efficiency and excellent reversibility between solid oxide fuel cell (SOFC) operation mode for power generation and solid oxide electrolysis cell (SOEC) mode for fuel production. The capability of co-electrolysis of \( \text{H}_2\text{O} \) and \( \text{CO}_2 \) further makes SOEC attractive for bio-gas upgrading and syngas production [1–3], the latter being an intermediate in the synthesis of higher value chemicals like methanol or dimethyl ether (DME). High performance and durable operation are the keys to bring down the cost of fuel production from SOECs. Better understanding of the degradation mechanism and further optimizing the operation conditions to reduce degradation will help to advance the SOEC technology to the market.

In recent years, significant efforts have been devoted to the study of the SOEC degradation [4–13], and countering strategies have been

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proposed to mitigate the degradation [14–16]. Recent development and degradation mechanisms have been reviewed [17–19]. Severe degradation phenomena have been reported especially when operating the SOEC under high current densities or high over-potentials [5,8]. For example, for cells using a lanthanum strontium manganite - yttria stabilized zirconia (LSM-YSZ) oxygen electrode, formation of small cavities inside YSZ grains and cracks along the grain boundary close to electrolyte - oxygen electrode interface have been reported [7,20–22].

The reason for this has been attributed to the high oxygen partial pressure established inside the electrolyte close to the electrolyte-oxygen electrode interface under strong polarization [13,23–25]. The application of better performing oxygen electrodes such as lanthanum strontium cobaltalite (LSC)- or lanthanum strontium cobalt ferrite (LSCF)-based electrode which in general has a lower polarization resistance than the LSM based electrodes, has effectively mitigated such problems [26].

At the Ni-YSZ electrode, besides loss of percolation between Ni and Ni grains [12,37,38], and loss of contact between zirconia and Ni [7,29], nano ZrOx extrusion from the Ni bulk has been observed [30]. Changes in Ni-YSZ electrode microstructure caused by Ni migration from the most active part of the electrode to the support layer has also been reported on long term SOEC durability tests and the underlying mechanisms discussed in Refs. [12,29,31]. Studies on the Ni-YSZ electrode supported cells have also showed that impurities play major role in the Ni-YSZ electrode degradation. The presence and distribution of impurities such as Si, Ca and Na has been mapped on SOECs applied for H2O, CO2 and H2O + CO2 co-electrolysis using time-of-flight secondary ion mass spectrometry (TOF-SIMS) [32]. It has been found out that the impurities enrichment (and distribution) varied with feedstock compositions and was most significant for the case of high steam. Impurities in the inlet gas even below ppm of sulfur concentration has been reported to have detrimental effect on the SOEC performance [33,34]. Cleaning the inlet gas before feeding it to the cell has been demonstrated to improve the durability of the cells [35]. However, impurities like Si, Ca may also come from the raw materials of the cell or the glass sealant applied at the cell periphery and hence cleaning the gas is not enough to avoid impurity related cell degradation at high steam partial pressure.

From an economic point of view, operation of SOECs at high current density and high reactant conversion benefits the fuel production cost (as the CAPEX of the plant is reduced). However, in general the degradation rate of the SOEC increases with increasing current density and reactant conversion [8,22,36,37]. For the case of co-electrolysis care also has to be taken when choosing the operation conditions to avoid carbon deposition; this has been reported to occur at 60% conversion of H2O + CO2 [38].

In large electrolysis systems of several MW due to the finite number of cells currently stacked in state of the art stacks (~100 to few 100’s) and the modest cell size typically applied (~100–500 cm2), many SOEC stack modules will have to be operated together. The individual stack modules will be connected electrically in series and/or parallel considering operation strategy, risk mitigation and voltage requirements of the surrounding grid and power electronics. Also with respect to gas flow, one may envisage both series and parallel connection. In a series connection, a certain amount of gas is fed first to an upstream unit, the gas-output of which is the input for a similar down-stream unit. Alternatively, the same amount of gas can be split in two and fed to the two stacks in parallel. The overall reactant flow per stack area is the same in the two cases described, and if the stacks are operated to provide the same overall fuel production, the reactant conversion per cell length is much higher for the case of the parallel flow than for the series connection. The pressure drop associated with the gas passage on the other hand will be higher for the series connected case. Since, for the series connection the targeted conversion per length is smaller, so will be the average polarization as well as the maximum current density experienced on the cells. Hence, this type of operation can be considered milder for the cells. For arriving at the stack module connection that maximizes performance and durability, it is important to understand the effect of the connections on the cell performance, since it will influence the reactant conversion rate as well as the inlet gas composition in the down stream part. In this work we present a detailed comparison of the cell durability tracked over 1000 h under different reactant utilization and inlet gas composition chosen to mimic “gas-flow series” and gas-flow parallel. The cells were operated in co-electrolysis mode at 800 °C and were operated to provide the same amount of syngas for the two cases. From detailed post-aging-test structural characterization the implication of the operation conditions on the mechanisms of degradation is discussed.

2. Experimental

Planar hydrogen electrode supported solid oxide cells were used in this study. The cells consist of a porous Ni - 3% Y2O3 doped ZrO2 support electrode (~300 μm in thickness) and a Ni - 8% Y2O3 doped ZrO2 (Ni-YSZ) active electrode (10 μm in thickness), a ~8 μm thick 8 mol% Y2O3 stabilized ZrO2 (YSZ) electrolyte, a Ce0.8Gd0.2O1.95 (CGO) inter-diffusion barrier layer (~5 μm in thickness) made by screen printing and a L0.5Sr0.5Co0.8Fe0.2O3 (LSCF)-CGO composite oxygen electrode (~25 μm in thickness). Detailed description of the cell production can be found in Ref. [39]. The total cell area is 5.3 cm2 with an active electrode area of 4 cm × 4 cm (16 cm2). For testing, an alumina cell test house was used, with further details described elsewhere [40]. The cell is “sandwiched” between gas distribution layers (corrugated Au and Ni meshes on the oxygen electrode and fuel electrode side, respectively), current collector layers (Au and Ni foils on the oxygen and the fuel electrode side, respectively), and the alumina cell test house. The cell was sealed at its edges with glass. The gases supplied to the Ni-YSZ electrode were cleaned by passing through 8 g of a “gas cleaning bed” before entering the cell test house, following the procedure described by Ebbesen and Mogensen [41]. At start up, the cell was heated up to 850 °C with 20 L/h Ar supplied to the Ni(O)-YSZ electrode compartment and 20 L/h Air supplied to the oxygen electrode compartment. The fuel electrode was reduced in H2 + 4% H2O at 850 °C for 2 h before electrochemical characterizations were performed.

In this work, four nominally identical cells prepared in the same production batch were used. These shall in the following be labelled with reference to the flow conditions during the aging tests conducted; Cell “P” (parallel flow), Cell “SU” (series flow, upstream), Cell “SD” (Series flow, downstream) and Cell reference. Cell reference is used as a “reference cell” which only experienced the initial performance characterization and cooling down and no prolonged (1000 h) aging. Cells P, SU and SD experienced an initial performance characterization, a durability test of more than 1000 h at constant conditions and a final performance characterization. The initial performance characterization on all cells was carried out by measuring DC polarization (I-V) curves and AC electrochemical impedance spectra (EIS) at 850, 800 and 750 °C.

The durability tests were performed under galvanostatic co-electrolysis conditions at 800 °C under a co-electrolysis current density of 1 A/cm2 with pure oxygen supplied to the LSCF-CGO electrode. The latter was chosen for facilitating comparison with previous tests and to ensure a well defined and invariant conditions on the oxygen electrode. The fuel flow and loading of the cells were selected to reflect two different operation strategies as illustrated in Fig. 1. The test Cell P was used to simulate the operation scenario 1, where two stacks are operated at the same current density and same reactant conversion and fed with gas in “parallel”. On the tests of Cell SU and Cell SD, the conditions were chosen to simulate operation scenario 2, where the two stacks operate in gas flow series. Thus the gas flow to cell SU is twice that fed to Cell P and the conversion over the cell is only half of that experienced on Cell P. The operation voltage is chosen to give the same current density as in the two other tests (~1
A/cm³), whereby the overall conversion on SU and SD is equal to the conversion on Cell P (50%). The total amount of syngas produced running cells SU and SD equals the amount produced by two cells operated like test Cell P. It has been reported that at such operation temperature, water gas shift (WGS) reaction is fast enough to reach chemical equilibrium [42]. The theoretical equilibrium outlet gas compositions therefore can be calculated based on the inlet gas composition and applied current. The detailed test conditions of the three tested cells and outlet gas composition are summarized in Table 1. Cell P was tested with 45% CO₂ + 45% H₂O + 5% H₂ + 5% CO supplied to the Ni-YSZ electrode, with a H₂O + CO₂ conversion of 56%. The gas supplied to the Ni-YSZ electrode for Cell SU was the same gas composition as to Cell P but with doubled flow rate, thus the H₂O + CO₂ conversion for Cell SD is 39%. The aging test was terminated after 1000 h at constant current and inlet gas composition conditions.

The impedances spectra were measured under zero DC current (during fingerprint) or under current (during durability test) with a Solartron 1255B frequency analyzer using an external shunt in series with the cell. The spectra were recorded from 96850 to 0.08 Hz with 12 points per decade and were corrected using the short circuit impedance response of the real part (fingerprint) or under current (during durability test) with a Solartron 1255B frequency analyzer using an external shunt in series with the cell. From the impedance spectra, the ohmic (serial) resistance (Rₛ) was taken as the value of the real part of the impedance measured at 96850 Hz and the polarization resistance (Rₚ) was taken as the difference in the real part of the impedance at 96850 Hz and 0.08 Hz. The total area specific resistance of a cell was calculated as the total resistance of the real part (Rₛ + Rₚ) of the impedance. For current-voltage (iV) characterization in SOFC mode, a current scanning step of 0.002 A/cm² was applied at constant density below 0.05 A/cm² and cell voltage between 600 mV and 700 mV. At current density above 0.05 A/cm² and cell voltage above 700 mV, a 0.05 A/cm² current scanning step was used. In SOEC mode, the current scanning step was 0.002 A/cm² at electrolysis current density below 0.05 A/cm² and cell voltage between 1150 mV and 1250 mV, and 0.05 A/cm² at electrolysis current density above 0.05 A/cm² and cell voltage below 1150 mV. Each scanning step takes 5 s.

The microstructure of all four cells was analyzed using a Supra 35 scanning electron microscope (SEM) equipped with a field emission gun (FE-SEM, Carl Zeiss) and for chemical analysis the Supra 35 equipped with an energy-dispersive X-ray spectrometer (EDXS) and a microanalysis software NSS from Thermo Electron Corporation. Polished cross-sections along the flow path from inlet to outlet were prepared for four cells. For the back-scattered electron (BSE) mode, an accelerating voltage of 15 kV was used. The samples were coated with carbon to eliminate surface charging.

3. Results

3.1. Initial performance characterization

Fig. 2 shows the iV initial characterization of the three tested cells with 24 L/h 50% H₂ + 50% H₂O supplied to the Ni-YSZ fuel electrode compartment and 50 L/h pure oxygen applied to the LSCF-CGO oxygen electrode compartment. The open circuit voltage of the three tested cells are 972, 974 and 975 mV for Cell P, Cell SU and Cell SD respectively, which are very close to the theoretical Nernst potential of 977 mV calculated at the test condition. The tested cells show very similar performance as can be seen from the iV curves. Minor difference can be observed, which might be due to the furnace temperature difference or slight unintended variations between the cells (e.g. average electrolyte thickness, slightly different firing temperatures, etc.). The good reproducibility of the cell’s initial performance enables comparison of the different degradation behavior of the cells when operated at different conditions/scenarios.

3.2. Voltage and resistance evolution during durability testing

The cell voltages and the cell voltage degradation rates recorded during the aging tests are reproduced in Fig. 3a. The degradation rate at any time during the test is calculated using the equation \( \frac{\Delta V}{\Delta t} = \frac{V(t)}{t} \), where \( \Delta t \) is the time interval between two voltage readings. Cell P, Cell SU and Cell SD were operated at constant current for a little longer than 1000 h (1030, 1190 h and 1063 h respectively). An overview of the cell

<table>
<thead>
<tr>
<th>Test</th>
<th>Inlet equilibrium gas composition</th>
<th>Current density</th>
<th>Conversion</th>
<th>Theoretical outlet equilibrium gas composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cell P</td>
<td>13.4 L/h 45% CO₂ + 45% H₂O + 5% H₂ + 5% CO</td>
<td>-1 A/cm²</td>
<td>56%</td>
<td>20% CO₂ + 19% H₂O + 31% H₂ + 30% CO</td>
</tr>
<tr>
<td>Cell SU</td>
<td>26.8 L/h 45% CO₂ + 45% H₂O + 5% H₂ + 5% CO</td>
<td>-1 A/cm²</td>
<td>28%</td>
<td>33% CO₂ + 32% H₂O + 18% H₂ + 17% CO</td>
</tr>
<tr>
<td>Cell SD</td>
<td>26.8 L/h 33% CO₂ + 32% H₂O + 18% H₂ + 17% CO</td>
<td>-1 A/cm²</td>
<td>39%</td>
<td>20% CO₂ + 19% H₂O + 31% H₂ + 30% CO</td>
</tr>
</tbody>
</table>

Fig. 2. Initial iV characterizations of Cell P, Cell SU and Cell SD at 800 °C with 50% H₂ + 50% H₂O and O₂ supplied to the fuel electrode and oxygen electrode compartment, respectively.
voltages and average degradation rates measured for the three durability tested cells is given in Table 2. Strong degradation was observed on Cell P, which operated at same current density and with the same inlet gas composition as Cell SU, but with twice the reactant conversion.

Fig. 3 presents the serial resistance $R_s$, polarization resistance $R_p$, and area specific resistance, $\text{ASR} = (R_s + R_p)$ that were extracted from the EIS data measured during the durability test. Different degradation behaviors were observed for the three tested cells. For $R_s$, the initial values for the three cells were very close. Cell SU and Cell SD exhibited very low and similar overall degradation rates of 24 and 20 m$\Omega$ cm$^2$/1000 h, respectively. Cell P in contrast exhibited a degradation rate of nine times higher (185 m$\Omega$ cm$^2$/1000 h). The $R_p$ of Cell SU and Cell SD increased at a more or less constant rate, whereas Cell P showed accelerated degradation rate after the initial 200 h operation. For $R_p$, Cell P and Cell SU show very similar degradation trends, with an initial fast degradation that subsequently slows down, whereas Cell SD showed a constant and overall smaller degradation rate during the entire operation period. The initial $R_p$ difference between Cells P and SU is mainly due to the different reactant conversion rates, i.e. 56% for Cell P and 28% for Cell SU, which results in different average gas-compositions over the cells. Table 3 presents an overview of the initial and final values as well as the degradation rates of $R_s$, $R_p$ and ASR.

### 3.3. EIS and DRT analysis during durability test

Fig. 4 presents the EIS Nyquist plots (left) and their corresponding distribution of relaxation times (DRT) plots (right) of the EIS measured during the co-electrolysis operation. The EIS plots in Fig. 4 show a large impedance increase on Cell P, especially on the $R_s$ values, while Cell SU and Cell SD show much smaller changes in impedance. The DRT method which allows distinguishing the different characteristic time constants physio-chemical processes that give rise to the impedance of a cell provided that the processes have different characteristic time constants [43] was applied to further elucidate the cells’ degradation behavior. Five distinguishable peaks can be identified and are presented in Fig. 4 (right). The corresponding electrochemical/chemical processes have been reported previously in Refs. [44,45]. All the processes show increasing resistance during the durability testing. For the first high frequency peak (~30 kHz) which is mainly originated from the oxygen ion transport processes in the Ni-YSZ composite electrode, Cell P shows a noticeable DRT peak area increase whereas relatively small change can be observed on Cell SU and Cell SD. For the second high frequency peak (7–10 kHz) which can be attributed to the Ni-YSZ charger transfer process, both Cell P and Cell SU show a remarkable increase in the DRT peak area together with a shift of the summit frequency from around 10 KHz to a few hundred Hz. The change on the middle frequency process (~100 Hz) which is mainly associated with the LSCF-CGO oxygen electrode, shows a similar trend as the first high frequency process, where Cell P shows a stronger degradation, but Cells SU and Cell SD show only small changes. For Cell SD only minor changes on the DRT peaks are observed.

### Table 2
Overview of the initial and final values as well as the degradation rates of $R_s$, $R_p$ and ASR during the durability test.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Initial $R_s$</th>
<th>Final $R_s$</th>
<th>$R_s$ degradation m$\Omega$ cm$^2$/1000 h</th>
<th>Initial $R_p$</th>
<th>Final $R_p$</th>
<th>$R_p$ degradation m$\Omega$ cm$^2$/1000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>0.074</td>
<td>0.265</td>
<td>185</td>
<td>0.253</td>
<td>0.528</td>
<td>296</td>
</tr>
<tr>
<td>SU</td>
<td>0.085</td>
<td>0.11</td>
<td>24</td>
<td>0.13</td>
<td>0.31</td>
<td>149</td>
</tr>
<tr>
<td>SD</td>
<td>0.078</td>
<td>0.10</td>
<td>20</td>
<td>0.16</td>
<td>0.25</td>
<td>83</td>
</tr>
</tbody>
</table>

### Table 3
Overview of the initial and final values as well as the degradation rates of the three durability tested cells.

<table>
<thead>
<tr>
<th>Cell</th>
<th>Initial OCV, mV</th>
<th>Initial voltage at $-1$ A/cm$^2$, mV</th>
<th>Final voltage at $-1$ A/cm$^2$, mV</th>
<th>Test duration at $-1$ A/cm$^2$, h</th>
<th>Overall degradation, mV/1000 h</th>
<th>Last 200 h degradation, mV/1000 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>881</td>
<td>1150</td>
<td>1533</td>
<td>1030</td>
<td>372</td>
<td>430</td>
</tr>
<tr>
<td>SU</td>
<td>884</td>
<td>1093</td>
<td>1257</td>
<td>1190</td>
<td>140</td>
<td>20</td>
</tr>
<tr>
<td>SD</td>
<td>953</td>
<td>1149</td>
<td>1223</td>
<td>1063</td>
<td>69</td>
<td>64</td>
</tr>
</tbody>
</table>
3.4. Post-mortem analysis

For all the long-term tested cells, the observed microstructural changes are more pronounced at the gas inlet and middle of the cell than at the outlet. Due to the length limitation, only results from the inlet of the cells are presented in this work. The selected fuel gas outlet microstructure images can be found in the supplementary materials (Fig. S1 and Fig. S2). Fig. 5 shows the BSE images of the Ni-YSZ electrode at the steam inlet of four cells. It is found that the porosity of the active fuel electrode layer (within ca. 5 μm from the electrolyte-electrode interface) was increased, while the porosity in the outer active electrode layer and neighboring support layer (within 5–20 μm from the electrolyte-electrode interface) is decreased. The porosity change in Cell P is the most significant among the three tested cells and becomes less along the gas flow path.

Porosity change in the active electrode of Cell SU happens mostly within ca. 5 μm from the electrode-electrolyte interface. To quantify the porosity change, images were taken at the location close to the steam inlet of each cell. The area in each SEM image was divided into four sub-areas as indicated in Fig. 6d: inner active electrode (5 × 82 μm), outer active electrode (5 × 82 μm), neighboring support electrode (support electrode next to the active electrode, 10 × 82 μm) and the support electrode (25 × 82 μm). The porosity in each sub-area was analyzed using the software ImageJ [46] and results are plotted in Fig. 5e. Even with the cell to cell variations (area to area variations) clear differences are observed between the cells: 1) The porosity variation from the electrode/electrolyte interface towards the support becomes more significant on aging in co-electrolysis, and 2) a significant porosity increase is observed in the inner electrode layer. The porosity change is caused by Ni redistribution; the Ni moves from the inner initially most active part of the electrode layer to the outer part of this and to the neighboring support layer. This is further evidenced by the EDS line scan results reproduced in Fig. 5f. An area covering both the active electrode and the neighboring support (similar to the ones shown in Fig. 5d and as marked in red square in Fig. 6d) was selected for EDS spectral imaging. Based on the collected EDS spectra, an integrated EDS line scan was made as illustrated in Fig. 6d and the Ni/(Y + Zr) ratio was derived. This analysis was carried out at both gas inlet and outlet of the four cells. A distinct depletion in Ni close to the electrode-electrolyte interface (marked with gray in Fig. 5f) is observed in all the tested cells compared to the reference (black curve lies highest in the inner 6–10 μm).

Fig. 6 shows high magnification images of the four cells at the gas inlet. In Cell P, many gaps (~hundred nm or less) are formed between the Ni and zirconia especially close to the electrolyte layer. These gaps appear as dark rings (continuous or discontinuous) around the Ni grains. Such gaps are not observed in the reference nor in the two cells aged under milder conditions (Cell SU, SD). In a few places in Cell P inclusions inside the Ni grains were found (small black dots). Such inclusions are not seen in the reference nor in Cells SU and SD. The formation of gaps around Ni reflects a detachment of Ni-Ni and Ni-YSZ at the interfaces, which will weaken or block the conduction path of electron or oxygen ion, causing loss of active TPBs. This is likely the microstructural origin of the increased ASR. It will increase Rp due to the reduced TPB area and will also result in a decrease in the total cross sectional area available for ionic transport through the zirconia phase and as Ni moves away from the electrolyte the “effective electrolyte thickness” (the total distance

Fig. 4. EIS (Left) and DRT (Right) of the three durability tested cells during co-electrolysis operation under -1A/cm².
Fig. 5. BSE images analysis of Ni-YSZ electrode. a), b), c) and d): Images at the inlet of cell P, Cell SU, Cell SD and Cell Reference e): Porosity at the inlet of the Ni-YSZ active electrode and support electrode and f): Atomic ratio of Ni/(Y + Zr) at the inlet and outlet of the active Ni-YSZ electrode and the support derived from integrated EDS line scans.
the charge has to transport in form of ions) will also increase - both these
effects lead to an increase of Rs.
EDS point analysis were performed to identify the element compositions of the inclusions inside of Ni grains at the fuel gas inlet of Cell P. 6 points were selected as marked in Fig. 6 e and the results are presented in Table 4. It is identified that the inclusions contain significant amounts of Si. This has been found in previous studies [12, 30]. Si can be evaporated from a glass sealant or may originate from the raw materials (impurities). During the operation process it can be transported by the fuel gas flow, then deposit at active TPBs in the fuel electrode. Under high polarization, SiO$_2$ can be subsequently reduced to Si and dissolved into the Ni grains. Once the polarization stops, the Si reacts with oxygen that is dissolved in Ni and forms SiO$_2$ inside the Ni grain.

4. Discussion

The three tested cells initially showed the same electrical/electrochemical performance as documented in Fig. 2. However, the cells show different degradation behavior during operation under different gas compositions and reactant conversions. Operation temperature and current density was the same for all three cell tests.

4.1. Effect of reactant conversion rate

Cell P and Cell SU experiences the same inlet gas composition and consequently show very similar OCV values (881 mV for Cell P and 884 mV for Cell SU) before starting the durability test. Even though the two cells operated at the same temperature and current density, Cell P show much higher degradation than Cell SU. This is ascribed to the different flows and thus different reactant conversion realized over the cells i.e. 56% and 28% for Cell P and Cell SU, respectively. Decreasing the reactant conversion by a factor of two the overall degradation decreased from 337 mV/1000 h to 140 mV/1000 h and when considering the last 200 h of test decreased from 430 mV/1000 h to 20 mV/1000 h. From the impedance, it is clear that the initial degradation of both Cell P and Cell

![Fig. 6. High magnification BSE images of the Ni-YSZ electrode at the inlet of four cells: a) Cell P, b) Cell SU, c) Cell SD, d) Cell reference and e) Selected points marked as red circles for EDS analysis of Cell P. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)](image-url)

<table>
<thead>
<tr>
<th>Table 4</th>
</tr>
</thead>
<tbody>
<tr>
<td>EDS point analysis on the active Ni/YSZ electrode layer at the inlet of Cell P. The locations selected for analysis are shown in Fig. 6e.</td>
</tr>
<tr>
<td>Element (at.%)</td>
</tr>
<tr>
<td>---</td>
</tr>
<tr>
<td>point 1</td>
</tr>
<tr>
<td>point 2</td>
</tr>
<tr>
<td>Point 3</td>
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<td>Point 4</td>
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<td>Point 5</td>
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<td>Point 6</td>
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</table>
SU are dominated by the increase of $R_p$, after the initial degradation period, the two cells show similar $R_p$ degradation behavior. The long-term degradation for Cell P is dominated by an increasing $R_p$, whereas this is not the case for Cell SU that shows a stable $R_p$ during the entire operation period. The rapid increase of $R_p$ could in principle be caused by several different types of microstructural degradation phenomena: i) loss of electronic connection path, ii) formation of resistive reaction products, iii) partial delamination for example between electrode and electrolyte or iv) a consequence of the Ni redistribution and loss of Ni-Ni contact and Ni/YSZ contact, which will lead to decreased cross-sectional area for ionic transport in the porous zirconia phase and increased effective electrolyte thickness as contact to the innermost Ni particles is lost. It is clear that the rapid increase of $R_p$ is not caused by a delamination as in this case a simultaneously rapid increase of $R_p$ should be expected. Hence, we conclude that the increased $R_p$ and the steadily increasing $R_p$ observed in Cell P are consequences of the observed damages to the Ni-network, with local loss of contact and overall loss of Ni from the inner electrode zone.

4.2. Effect of inlet gas composition

Cell SU and Cell SD have the same volumetric inlet gas flow and were operated at the same current density, but with different inlet gas compositions. The $\text{H}_2\text{O} + \text{CO}_2$ concentration for Cell SU was around 1.4 times higher than for Cell SD. The difference in the $\text{CO}_2$ concentration in the fuel gas inlet has been reported to have minor influence on the cell performance since only a small fraction of $\text{CO}_2$ is converted by the electrochemical process [42,47]. Nevertheless, the OCV as indicated from Table 2 for Cell SD was 953 mV, significantly higher than those for Cells P (881 mV) and SU (884 mV). Cell SU exhibits a high initial degradation rate of 140 mV/1000 h in the first 400 h, afterwards, the degradation rate decreases to around 20 mV/1000 h in the last 200 h. On the contrary, Cell SD exhibits almost constant degradation rates and in the last 200 h the degradation rate is around 64 mV/1000 h.

4.3. Effect of operation strategies

The specific power consumption of the syngas production can be calculated using equation $E = n/P$, where $E$ is the power consumption per m$^3$ of syngas produced and $n$ is the syngas volume production rate calculated by Faradays equation, and $P$ is the consumed power which is a product of current and cell voltage. The $E$ for parallel connection operation was calculated based on Cell P, and for serial connection operation was calculated based on the average of Cell SU and SD and the results are presented in Fig. 7. Initially the parallel connection is less efficient than the serial connection and the deviation becomes larger and larger with time due to the stronger degradation observed for Cell P. Thus from an economy point of view, it is clearly advantageous to operate the stacks in gas flow series.

To further identify the cause of the degradation and the reasons for the difference in behavior of the cells tested under different operation conditions, the polarizations of the individual electrodes has been estimated. This is done from the EIS measurements carried out at the start of the durability test right after the cell was exposed to a co-electrolysis current density of $-1 \text{ A/cm}^2$. From the DRT and the fitting of the impedance spectra, the overall cell loss could be broken down into four major terms associated with purely ohmic losses, fuel electrode losses, oxygen electrode losses and losses due to reactant conversion. From the estimated resistance the polarization realized at $-1 \text{ A/cm}^2$ as applied at the beginning of the aging test has been calculated as the integration of resistances over the measured current densities. The results are listed in Table 5. It can be seen that the three tested cells have very similar electrolyte and electrode over-potential. Cell SU and Cell SD show slightly lower over-potential on the Ni-YSZ electrode than Cell P. Since the reactant conversion over Cell P is equal to the sum of the conversions over SU and SD, the EMF gain experienced from inlet to outlet of Cell P is close to the sum of the values of Cells SU and SD as reported in Table 5. Small differences are observed reflecting either small unintended differences in cell characteristics or more likely some of the mentioned non-linearities (the fuel electrode polarization resistance is smaller in the gas-compositional range characteristic of Cell SD than for Cell P conditions. In any case the difference between the over-potentials are less than 15 mV.

Furthermore, it is worth to note that the over-potentials listed in Table 5 are averaged over the whole cell area, i.e. the average over-potential characteristic of the average $\text{H}_2\text{O} + \text{CO}_2$ concentration from gas inlet to gas outlet. Due to the applied current and associated gas conversion, the local EMF (Nernst voltage characteristic of the local composition) increases from inlet to outlet which results in an uneven distribution of current/over-potential along the flow direction. The influence of inlet gas composition and reactant gas conversion on the current distribution can be estimated by following the method described in Refs. [48,49]. Fig. 8 illustrates the simulated current distribution as a function of the cell length in the $\text{H}_2\text{O} + \text{CO}_2$ flow direction. It is worth to note that the estimation only considers the effect of the reactant gas conversion on the current distribution along the reactant flow direction. If the electrode polarization resistance is also gas composition (e.g $P_{\text{H}_2\text{O}}$) dependent, this will affect the current distribution and the local temperature as well. These contributions may result in an even larger current distribution due to the reduction of $P_{\text{H}_2\text{O}}$ thus increasing the Ni-YSZ TPB resistance along the gas flow direction [11]. However, these contributions are often smaller than the effect of the EMF-variations as also shown in Table 5. It is clear from Fig. 8 that the unevenness in the current density distribution decreases from Cell P > Cell SU > Cell SD, even though they were operated under the same nominal co-electrolysis current density of $-1 \text{ A/cm}^2$.

In all the cases, the highest current density is expected at the inlet of the cell where the difference between $U_{\text{cell}}$ and $\text{Emf}_{\text{gas}}$ is the largest. The uneven distribution of the current density corresponds to a similar distribution of the over-potential along the cell from the inlet to outlet. The local fuel electrode over-potential at the inlet part is thus much higher than those listed in Table 5 (20% higher for “P” and 10% higher for SU). The high local over-potential at the inlet can be concluded to accelerate the microstructural degradation - it is at the inlet where we observe the Si-inclusion, the strongest porosity increase and the most significant loss of Ni connection to neighboring phases. At the inlet the

![Fig. 7. Power consumption comparison for syngas production for parallel and series connection.](image-url)
fuel electrode polarization is estimated to be 85 mV. At the inlet of Cell SD where the polarization is estimated to be 59 mV no such inclusions were seen, no gaps were observed and the porosity increase (absolute number) is only 4–5% contrary to case P where it is 7–8%. There is a tendency that Ni de-wets zirconia under strong cathodic polarization and wets better under strong anodic polarization [31]. The observations here made are consistent with this finding; e.g. loss of contact close to the electrolyte (de-wetting), Ni transports to the outer less polarized areas, the effects seen more strongly the stronger the local polarization (comparing P and SD). Such trends have been observed in several studies of aging SOEC-cells [12,29,50,51]. Furthermore, it is unlikely for the case at hand that the local polarization has been strong enough to partially reduce YSZ, which has in some cases been suggested to case at hand that the local polarization has been strong enough to partially reduce YSZ, which has in some cases been suggested to lead to formation of YSZ crystallites on the Ni-surface (after larger total pressure drop over the stack. The total flow path length in terms of the stack life time.

partially reduce YSZ, which has in some cases been suggested to lead to formation of YSZ crystallites on the Ni-surface (after larger total pressure drop over the stack. The total flow path length in terms of the stack life time. 

In a practical application, series gas flow connection will entail a larger total pressure drop over the stack. The total flow path length doubles and the available cross sectional area for gas passage is reduced to half. Hence, the blower or compression work will increase which has to be taken into consideration when comparing economical merits at the system balance-of-plant (BOP) level. SOEC units must in future be operated close to the thermo-neutral point, as this has huge advantages both with respect to overall efficiency but also with respect to mitigating problems due to thermal gradients and induced stresses. Operation of the stack/modules under thermo-neutral conditions will be slightly more complicated in the gas flow serial connection case than in the parallel flow case. If the area of both sub-modules is identical, so will be the current density as the same total current runs through both sub-modules. Since the current density is thus the same and the average EMF is different, both modules will not be at the thermo-neutral potential simultaneously. To realize thermo-neutral operation for the gas flow series case one would have to vary the footprint between the two submodules or operate them in a manner where they are effectively operating at two slightly different temperatures.

5. Conclusion

In this work, the degradation of three SOE cells have been studied mimicking two different operation strategies; either with a gas-flow series arrangement or gas-flow in parallel arrangement. Even though the cells have been operated under the same current density and the same temperature, large differences in degradation rates were observed. With the same inlet gas composition, lowering the reactant utilization from 62% to 28% leads to a significant reduction of the serial resistance degradation rate. Degradation took place primarily on the fuel electrode, and the degradation becomes less severe from fuel gas inlet to outlet. The results show that a gas-flow series connection can be beneficial for the overall SOEC life time. In the gas-flow series-connection the variation in gas-composition over the cell is smaller than for the parallel case, thus less maximum polarization experienced by the fuel electrode (especially at the fuel electrode gas inlet). Since in general degradation rates of SOECs increases with increased electrode polarization, this increased local max polarization is considered the reason for the stronger degradation observed for the parallel connection case. Further techno-economic analysis must be carried out at module level to assess which of the gas-flow arrangements that eventually is the more beneficial – certainly, when operating at the high current densities applied here (−1 A/cm²) it is highly advantageous for a cell durability point of view to place cells in gas-flow series.

CRediT authorship contribution statement

Xiufu Sun: Conceptualization, Investigation, Writing – original draft. Yuliang Liu: Formal analysis, Writing – original draft. Peter Vang Hendriksen: Writing – review & editing, Discussions on data interpretations. Ming Chen: Conceptualization, Writing – review & editing, Funding acquisition, Project administration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jpowsour.2021.230136.

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