Evaluation of a SOE Stack for Hydrogen and Syngas Production: a Performance and Durability Analysis

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Abstract

Solid oxide electrolyzer (SOE) are gaining growing interest in research because they can convert electricity into a chemical fuel with high efficiency. The present work investigates the performance of a 6-cell SOE stack (80 cm² active area) in electrolysis and co-electrolysis modes for producing hydrogen and synthetic fuel. Initially, the stack was operated and characterized in fuel cell mode at 750°C. Operation was then changed to electrolysis mode. The stack performance was characterized with four different inlet gas compositions of various ratios of inlet steam and carbon dioxide at temperatures of 700, 750 and 800°C. It was found that the stack performance depends primarily on the operation temperature and only to a small extent on the inlet gas composition. Finally, a steam electrolysis durability test of 1,500 hours was performed at a current density of –0.775 A cm⁻² (50% of reactant utilization) and at a temperature of 750°C. The voltage trend showed that no degradation could be observed, which is a very promising result. In conclusion, the investigated stack appears suitable for syngas production. In the future, co-electrolysis durability tests will be conducted to evaluate the effect of addition of carbon dioxide on the stack durability.

Keywords: Co-electrolysis, Durability Test, Fuel Cell, Hydrogens, Solid Oxide Electrolyzer (SOE), Solid Oxide Fuel Cell (SOFC), Stack Characterization

1 Introduction

The growing global need for electricity and the climate change mitigation call for efficient and clean means for power production and electricity storage. Solid oxide fuel cells (SOFC) and solid oxide electrolyzer (SOE) are efficient technologies for converting chemical energy to electrical energy and vice versa. They operate at temperatures ranging from 600 to 800°C. Co-electrolysis of steam and CO₂ is gaining attention because when powered by zero-carbon energy sources, it could be used to recycle captured CO₂ into carbon-neutral hydrocarbon fuels [1]. There are SOFC products already on the market, but SOE is still in the phase of research and development. Information of performance and durability at different experimental conditions is required for the progress of this technology both in terms of material development and the system level durability.

Steam electrolysis as well as co-electrolysis of steam and CO₂ by a SOE stack has been investigated by several research groups. Cinti et al. reported the performance of a 4-cell stack at 750°C with three different co-electrolysis compositions [2]. Diethelm et al. reported the performance of two 6-cell stacks in steam electrolysis at 600–700°C and in co-electrolysis at 750–850°C [3]. Alenazey et al. also reported the performance of a 6-cell stack at 750°C with two steam electrolysis compositions and four different co-electrolysis compositions [4]. Mouglin et al. reported the performance and the thermal cyclability of a 3-cell stack at 800°C [5]. Reytier et al. reported the area specific resistance of 10-cell and 25-cell stacks in steam electrolysis at 800°C [6].

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Several research groups also investigated the durability of SOE at stack level in steam electrolysis condition. Fu et al. reported 2% \( kh^{-1} \) degradation for a stack operated at 700°C at ~0.6 A cm\(^{-2} \) [7]. Brisse et al. reported several stack tests with degradation rates between 3 and 5% \( kh^{-1} \) [8]. Zhang et al. also reported durability test at stack level with four stacks degrading between 3 and 9% \( kh^{-1} \) and a fifth one showing no increase of voltage after 1,900 h. The reasons behind the good performance of that stack were not presented [9]. Diethelm et al. reported degradation rate for a stack operated with a current density of about ~0.3 A cm\(^{-2} \). The degradation rates were 3.6, 3.1 and 0.7% \( kh^{-1} \) for operation at 650, 750 and 800°C, respectively [3]. Fang et al. reported a durability test at 800 and 700°C with a current density of ~0.5 A cm\(^{-2} \). The degradation rates were 0.7 and 1.9% \( kh^{-1} \), respectively [10]. The general opinion is that the reported degradation rates are mostly too high for commercial applications.

This work contributes to the progress of SOE research with a combination of an extensive test matrix and a durability run with a state-of-the-art 6-cell stack. The test matrix included three relevant operation temperatures (700, 750 and 800°C) and four gas compositions (0, 10, 25 and 45 vol.% \( \text{CO}_2 \) at inlet) selected to be representative of the cases in which the electrolyzer would be combined with a fuel synthesis process and produce hydrocarbons with different hydrogen-to-carbon ratios. The test was concluded with a 1,500 h steam electrolysis durability test that shows no sign of voltage degradation. This is an encouraging result, compared to the rather high degradation rates previously published in the field of SOE.

Section 2 below presents the theory of steam electrolysis and co-electrolysis. In Section 3 the test object, test equipment and methodology are described. Section 4 presents the results and discussion. Finally, Section 5 concludes the work.

2 Theory

Steam electrolysis is defined as splitting gaseous water to hydrogen and oxygen; Eq. (1):
\[
\text{H}_2\text{O} \rightarrow \text{H}_2 + 1/2 \text{O}_2.
\] (1)

Steam electrolysis consists of two half reactions. The first takes place at the cathode, the hydrogen electrode; Eq. (2):
\[
\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + \text{O}_2^-.
\] (2)

The second takes place at the anode, the oxygen electrode; Eq. (3):
\[
\text{O}_2^- \rightarrow 1/2 \text{O}_2 + 2e^-.
\] (3)

CO\(_2\) can be electrolyzed to its components as well; Eq. (4):
\[
\text{CO}_2 \rightarrow \text{CO} + 1/2 \text{O}_2.
\] (4)

In \( \text{CO}_2 \) electrolysis the anodic reaction stays the same as in steam electrolysis, but the cathodic reaction changes; Eq. (5):
\[
\text{CO}_2 + 2e^- \rightarrow \text{CO} + \text{O}_2^-.
\] (5)

Co-electrolysis is defined as electrolysis of both steam and \( \text{CO}_2 \) to syngas (\( \text{H}_2 + \text{CO} \)); Eq. (6):
\[
\text{H}_2\text{O} + \text{CO}_2 \rightarrow \text{H}_2 + \text{CO} + \text{O}_2.
\] (6)

Thermoneutral voltage is defined in Eq. (7):
\[
U_{\text{TN}} = -\Delta H/(nF)
\] (7)

where \( \Delta H \) is the change in enthalpy, \( n \) is the amount of electrons involved in the electrochemical reaction and \( F \) is the Faraday constant.

3 Experimental

The test object was a stack prototype manufactured by SOLIDpower. The stack had six planar hydrogen electrode supported cells and ferritic stainless steel interconnects coated with a MnCo\(_2\)O\(_4\) protective layer. The structure of the cells was based on a thin (ca. 10 μm) 8 mol.% Y\(_2\)O\(_3\) stabilized zirconia (YSZ) electrolyte supported by a porous Ni/YSZ hydrogen electrode (ca. 250 μm). The oxygen electrode was based on (La,Sr)(Co,Fe)O\(_3\)–\( d \) (LSCF) perovskite and the diffusion barrier layer applied on the electrolyte was a Gd\(_2\)O\(_3\)-doped CeO\(_2\). The active area of the cell was 80 cm\(^2\).

The highly instrumented, fully automated and UPS secured test station was designed and built in-house particularly for investigation of reversible operation of solid oxide cell stacks. Figure 1 presents schematically the test station. Inlet gas flows of chosen composition for operation in fuel cell, steam electrolysis or co-electrolysis mode were controlled by Bronkhorst mass flow controllers (F\(_{\text{in}}\)). The liquid water flow was controlled by a Bronkhorst CORI-TECH controller and the steam was generated by an EBZ electrical evaporator. Both in the hydrogen side and air side outlets there were online measurements of steam partial pressure with VAISALA HMT330 sensors (Hum\(_{\text{in}}\) and Hum\(_{\text{out}}\)). The proportion of oxygen in the hydrogen side outlet was measured with ABB AO2020 in order to measure potential leaks from the air side. The proportion of oxygen in the air side outlet was measured by SICK TRANSIC100LP (\( \text{O}_2 \)) in order to indirectly measure potential leaks and directly measure the produced oxygen in the electrolysis. Hydrogen side dried outlet gas mass flow rate was measured with a Bronkhorst mass flow meter (F\(_{\text{out}}\)). In co-electrolysis experiments the dried outlet gas was also sampled to gas bags and analyzed with Agilent Technologies 490 Micro Gas Chromatograph with Molecular Sieve 5 Å and PoraPLOT U columns, coupled with a thermal conductivity detector (TCD). Thermodynamic equilibrium calculations were performed with the Cantera toolbox [11] using GRI-Mech 3.0 reactions developed for natural gas combustion [12]. The gas inlet and
outlet temperatures (T) and pressures (p), as well as the individual cell voltages (U), were measured. The power supply was Delta Elektronika SM66-AR-110 and the electronic load Elektro-Automatik EA-EL 9160-200.

The gas tightness of the stack was evaluated at room temperature by a pressurizing method instructed by the manufacturer. The stack was judged adequately leak tight. The stack was first tested in fuel cell mode to compare the performance to the quality assurance data from the manufacturer and then tested in the electrolysis mode, both steam electrolysis and co-electrolysis of steam and CO₂.

In electrolysis mode, steam electrolysis condition and three different co-electrolysis conditions (Table 1) were tested at furnace temperatures of 700, 750 and 800°C. In each gas composition, a 10% hydrogen volume fraction was added in order to maintain at all times a reducing atmosphere for the nickel catalyst, and only the ratio of steam and CO₂ was varied. The different inlet gas compositions were selected to be representative of the cases in which the electrolyser would be combined with a fuel synthesis process and produce hydrocarbons with different hydrogen-to-carbon ratio. The flow rate to the hydrogen electrode was 12 NmL min⁻¹ cm⁻². All the furnace temperature ramps were 1°C min⁻¹.

The steam electrolysis composition is referred to as SE and the co-electrolysis compositions are referred to as C₁, C₂ and C₃. The volumetric flow rate figures are given in normal temperature and pressure conditions (T = 0°C, p = 1 atm): normal liters per minute (NL min⁻¹). The air flow was set to 24.69 NL min⁻¹ (51 NL min⁻¹ cm⁻²) in all conditions in order to have constant, abundant amount of air flow over the oxygen electrodes to decrease oxygen concentration and temperature gradients over the cells. Finally, a durability test was run in steam electrolysis mode with a current density of -0.775 A cm⁻² corresponding to reactant utilization ratio (RU) 0.50, a temperature of 750°C and an air flow of 5.76 NL min⁻¹. The current density was chosen to be such that the average voltage over all the six cells was close to the thermoneutral voltage 1.285 V. The air flow was lowered for the durability test in order to increase the oxygen concentration on the air side to expose the stack to a more challenging condition.

The characterization methods of the stack were polarization curves with constant gas flows, calculation of the area specific resistance (ASR) and finally the durability run to examine the long term durability in constant conditions. The ramp rate of the polarization curves was 1 A min⁻¹. ASR was calculated from the slope in the linear part of the polarization curve.

| Table 1 | The fuel inlet gas flow fractions for each composition. |
|---------|--------------------------------------------------------|
|         | H₂ / – | H₂O / – | CO₂ / – |
| Steam electrolysis (SE) | 0.10 | 0.90 | 0.00 |
| Co-electrolysis 1 (C₁) | 0.10 | 0.80 | 0.10 |
| Co-electrolysis 2 (C₂) | 0.10 | 0.65 | 0.25 |
| Co-electrolysis 3 (C₃) | 0.10 | 0.45 | 0.45 |

Fig. 1 Test station diagram.
4 Results and Discussion

4.1 Performance in Fuel Cell Mode

The performance of the stack was initially tested in fuel cell mode and compared to the quality assurance data provided by the manufacturer. The measured polarization curve is presented in Figure 2. The operation conditions were similar to the manufacturer’s reference: furnace temperature was 750°C, the hydrogen side inlet gas flows were 1.73 NL min⁻¹ of dry H₂ and 1.15 NL min⁻¹ of dry N₂ and the air side inlet flow was 16.5 NL min⁻¹ of dry air. The purpose of hydrogen dilution with nitrogen was to simulate typical hydrogen-rich SOFC fuels like natural gas reformate. The open circuit voltage (OCV) was measured 1.16 V corresponding to the value measured by the manufacturer. This indicates that the stack sealing was not affected by the thermal cycles and transport between the manufacturer’s and VTT’s premises. The current density of the cells at an average voltage of 0.8 V was 0.28 A cm⁻² which again corresponded to the manufacturer measurement. The fuel utilization ratio (FU) was 0.54 at 0.28 A cm⁻². The average ASR was 0.8 Ω cm². Similarly, as in the quality assurance document, the cell 6 voltage was noted to be lower than the voltages of the other five cells which were very well in line with each other. This difference in performance was because of design issues that have been fixed in the subsequent stack prototypes.

4.2 Steam Electrolysis

Steam electrolysis polarization curve recorded at 750°C is presented below in Figure 3. As above in the fuel cell mode, the cell six performance differs from the rest of the cells also in the electrolysis mode. The polarization was recorded up to the current density of –0.75 A cm⁻² corresponding to RU 0.49. The average voltage at that point was 1.29 V, which corresponds closely to the thermoneutral voltage 1.285 V. Comparatively, Alenazey et al. [4] recorded a steam electrolysis polarization curve with a stack with similar design and materials at the same temperature. The fuel side gas flows were identical but the air flow was 77% smaller: 5.76 NL min⁻¹. At the same current density of –0.75 A cm⁻² the Alenazey group reported an average voltage of about 1.18 V meaning a very good performance.

Figure 4 below presents the substantial effect of the temperature to the stack performance. At a temperature of 700°C and a current density of –0.40 A cm⁻² the average cell voltage was 1.25 V. Diethelm et al. did experiments with a 6-cell LSCF stack with 50 cm² active area [3]. At the same temperature, gas flows and current density the group reported similar performance to this work, an average cell voltage of about 1.27 V. The benefits of lowering the temperature are that most of the thermally activated degradation phenomena such as the interconnect oxidation can be decreased. On the other hand, the higher the temperature the higher the performance because of the higher electrode kinetics and cell ionic conductivity. By increasing the temperature from 700 to 800°C the current density required to reach the thermoneutral voltage (1.284-1.287 V) could be doubled from –0.45 to –0.90 A cm⁻².

There are reports in the literature of steam electrolysis experiments at 800°C with the same 90% H₂O/10% H₂ hydrogen electrode inlet gas composition ratio but with different type of stacks and with different absolute gas flow rates. Mougín et al. [5] reported an average voltage of about 1.16 V for a 3-cell stack at –0.80 A cm⁻². Reytier et al. [6] reported cell voltages of as low as 1.0–1.1 V for 10-cell and 25-cell stacks at –0.80 A cm⁻², however the reactant utilization was much lower since the absolute gas flows in the hydrogen side were double to this work: 24 NmL min⁻¹. Direct comparison of the stack performances to this work is difficult because of different experi-
mental conditions, but with the information available the tested short stack is in line with steam electrolysis references from the literature.

### 4.3 Effect of Inlet Gas Composition

Figure 5 below shows that the volumetric fraction of CO₂ in the inlet gas mixture has an increasing effect to the voltage, albeit relatively small. At a current density of –0.65 A cm⁻² the stack mean voltages in steam electrolysis and co-electrolysis conditions C1, C2 and C3 were 1.25, 1.27, 1.30 and 1.34 V, respectively. It can be seen that the effect of increasing CO₂ inlet fraction increases slightly the area specific resistance, however to a smaller extent than the effect of increasing the temperature.

The dried fuel outlet gas was sampled into gas bags to be analyzed with the GC in all co-electrolysis (C1, C2, C3) compositions at 700, 750 and 800°C. Gas was sampled after stabilization of the stack at thermoneutral voltage. The thermoneutral voltages and corresponding current densities in the different conditions can be found in Table 2. Table 2 presents also the results of gas analysis of the dried outlet gas from the hydrogen side. These results can be compared with the expected compositions at thermodynamic equilibrium, in order to verify if equilibrium is reached at the stack fuel outlet in the tested conditions. The thermodynamic equilibrium was calculated taking into account the inlet gas flows to the hydrogen side, the amount of oxygen migrating to the oxygen electrode calculated from the current, assuming a faraday efficiency of 100% and the stack outlet temperature. The measured values are compared with the calculated equilibrium values in Figure 6 for a measurement taken at 750°C with the C1 composition. Firstly, no methanation seems to take place in the stack, which is in accordance with thermodynamics. This holds true for all the conditions tested. Secondly, some oxygen is present (around 2%), which comes certainly from the sampling process to the gas bag. The oxygen present is unlikely to come from an internal leak in the stack because at this temperature, oxygen would have reacted rapidly with hydrogen and moreover, the online oxygen measurement of the outlet gas did not detect any oxygen in any co-electrolysis condition. The presence of nitrogen (about 6%) is also very likely related to the sampling process, given the O₂/N₂ ratio of 1/4 in ambient air and 1/3 in this measurement, yet it is not possible to know if part of the nitrogen originates from an internal leak in the stack. The gas sample illustrated in Figure 6 exhibited the highest content of oxygen and nitrogen, therefore it was the most contaminated by leak, probably due to a gas bag of lower quality. The measured hydrogen fraction is found lower than the equilibrium value. This holds true for all samples. The reasons for this deviation are multiple: (i) outward leak from the gas bag since the small hydrogen molecule leaks faster than the other molecules, (ii) consumption of hydrogen in the stack fuel side by oxygen leak from the oxygen side or from ambient, (iii) hydrogen leaking from the fuel side to ambient or air side of the stack, (iv) there might be faradic losses due to electronic conductivity of the electrolyte or (v) error from the GC (about 3% of the measured value).

For a more systematic view of the deviation between equilibrium and measured values, Figure 7 illustrates the deviation between measured and equilibrium values for hydrogen, carbon monoxide and carbon dioxide. The deviation is calculated by subtracting equilibrium value from the measured value. As one can see, the largest deviations are found for the hydrogen channel, with an average deviation of 3%-unit. The average deviation for carbon monoxide and dioxide channel is 1%-unit and 1.5%-unit. Altogether, the deviation is relatively small and part of it can be explained by leaks inside the stack and leaks.
during the sampling process. This indicates that we can expect the outlet composition to have a good match with equilibrium. This is a useful information for system modeling of combined co-electrolyzer and fuel synthesis plant. For future stack tests, the sampling procedure will be changed and the gas sampling will be made by a sampling line rather than gas bag. This should significantly decrease leak from and to the gas bags and thus yield more accurate results.

### 4.4 Area Specific Resistance Mapping

In Figure 8 below the average ASR is plotted. The ASR is measured in the linear part of the polarization curve at three different temperatures as a function of CO$_2$ fraction in the hydrogen electrode inlet gas. It can be seen that the ASR is affected substantially by the operating temperature. The lowest ASR value of 0.51 $\Omega$ cm$^2$ was recorded in steam electrolysis at 800°C. Reytier et al. [6] reported significantly lower ASR values in steam electrolysis at 800°C: for a 10-cell stack the

#### Table 2  Co-electrolysis parameters and dried fuel outlet gas analysis data. See Table 1 for the inlet gas compositions. Air inlet: air 24.69 NL min$^{-1}$ of dry air. Percentages in round numbers for better readability. Error $\pm$ 3%.

| Sample / °C | 700 | 750 | 800 |
|------------|-----|-----|-----|
| Fuel inlet / – | C1  | C2  | C3  |
| $U_{\text{thermoneutral}} /$ V | 1.299 | 1.323 | 1.359 |
| $i /$ A cm$^{-2}$ | 0.49 | 0.49 | 0.48 |
| CH$_4$ / % | 0 | 0 | 0 |
| CO / % | 6 | 12 | 19 |
| CO$_2$ / % | 18 | 33 | 46 |
| H$_2$ / % | 74 | 53 | 33 |
| O$_2$/Ar / % | 1 | 1 | 0 |
| N$_2$ / % | 3 | 2 | 1 |
| SUM / % | 103 | 101 | 100 |

Fig. 6  Gas analysis of dried hydrogen side outlet gas in co-electrolysis experiment with C1 composition at 750°C. Fuel inlet: 0.58 NL min$^{-1}$ of dry H$_2$, 0.58 NL min$^{-1}$ of dry CO$_2$ and 4.61 NL min$^{-1}$ of steam. Air inlet: 24.69 NL min$^{-1}$ of dry air. The values measured by gas chromatography are compared to the calculated thermodynamic equilibrium values.

Fig. 7  Deviation between measured and calculated equilibrium values for hydrogen, carbon monoxide and carbon dioxide. Measurements taken from fuel outlet gas in the nine different co-electrolysis conditions. See Table 2 for details.

Fig. 8  Area Specific Resistance Mapping

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average ASR was 0.21 \( \Omega \) cm\(^2\) and for a 25-cell stack 0.24 \( \Omega \) cm\(^2\). However, the stacks were of different design and the gas feeds different, which makes the comparison difficult. Diethelm et al. [3] reported an average ASR of 0.92 \( \Omega \) cm\(^2\) in steam electrolysis at 750 °C, whereas the corresponding value recorded in this work is 0.58 \( \Omega \) cm\(^2\). Again, the direct comparison is difficult because of different experimental conditions. The increase of the ASR as a function of the CO\(_2\) fraction (0–0.45) is relatively linear and of the same magnitude (0.1–0.2 \( \Omega \) cm\(^2\)), independent of the temperature. The higher the temperature and the lower the CO\(_2\) fraction the lower the ASR.

### 4.5 Durability Test

The results of the durability test are illustrated in Figure 9. The stack was held in steam electrolysis conditions for 1,500 hours at 750 °C. Between 100 and 500 h the cell 5 voltage exhibited a sequence of about 20 mV lower performance compared to the voltage before and after, probably due to a change of mechanical contact between the cell and the interconnect plate. At 850 h all cell voltages momentarily dropped because the stack was accidentally pressurized due to a closed condensation water valve in the air outlet. The pressurization resulted in pushing air to the fuel side and causing combustion in the stack, also seen as a rise of the outlet temperatures in Figure 10. At 1,100 h there was an automatic shutdown triggered by pressure increase due to condensation in a pressure measurement pipe. The problem was immediately fixed and the experiment restarted to similar experimental conditions.

The average degradation rate was calculated to be negative, –9 mV kh\(^{-1}\) (–0.7% kh\(^{-1}\)), which means the performance improved in terms of voltage during this period. This result is in contrast with many degradation rates reported in the literature as detailed in the introduction. This result is indeed encouraging, however it would need to be confirmed by a similar durability test and complimentary experiments on this type of stack before concluding that this stack does not degrade over 1,500 hours.

In fuel cell mode, the voltage measurement is a very good measurement of the stack performance, because it is precise and easy to measure continuously and it indicates how much electrical power is produced in a stack. Conversely, in electrolysis mode, the voltage indicates how much electrical power is needed to produce hydrogen and does not indicate directly how much hydrogen is recovered from the stack. This is especially relevant considering that any air leakage to the hydrogen side in the stack would cause combustion of hydrogen and produce steam, which is the reactant of the cathode half-reaction. Therefore, leakage into the fuel side can possibly decrease the voltage (by reducing transport losses), while the actual efficiency of the stack is reduced by the loss of hydrogen, which was experimentally demonstrated by Morel et al. [13]. However, this effect would be expected only when the transport losses are significant, i.e., after the linear part of the polarization curve.

Figure 10 shows that the outlet temperatures did not increase, but decreased. This is in line with the voltage decrease: the stack operation shifted towards endothermic mode. The fuel outlet thermocouple behavior at 0–50 h is explained by a contact issue in the thermocouple.

The fuel outlet humidity and flow rate were measured as described in the experimental chapter (Figure 1). This data over the durability test is illustrated in Figure 11. Air outlet humidity and oxygen concentration data is unfortunately not
available for the durability test because of condensation problems in the sampling line. Figure 11 shows that the hydrogen outlet humidity did not rise during the durability test but stayed at about 470 hPa. The curve is wavy, indicating that the detector might not have been reliable in the prevailing temperature (100–150°C) and humidity. The detector became faulty at 1,000 h but was repaired and replaced at 1,450 h. Linear fit over the whole time range gives a humidity decrease rate of 3 hPa per 1,000 h. Given the long time period, this indicates that the humidity indeed stayed stable in the long term.

If there would have been an air leak from the oxygen electrode to the hydrogen electrode, there would have been steam production. Because the electric current and hence the steam consumption at the hydrogen electrode remained the same, the steam partial pressure would have grown in the outlet stream in case of a described leak. Figure 11 shows also the stable flow of about 2.7 NL min⁻¹ of dried hydrogen. In case of an air leak from the oxygen electrode to the hydrogen electrode, the flow rate of dried hydrogen in the outlet would have reduced because some hydrogen would have reacted with oxygen from the leaked air, generating steam. On the other hand, the flow rate would have increased because of nitrogen from the leaked air. However, small changes of the leak rate have a minimal impact on the dried outlet flow, therefore the flow rate measurement is not considered reliable to assess leak rate changes. Unfortunately, there is no gas analysis data available from the durability run, hence it is not possible to know the fraction of nitrogen in the hydrogen outlet flow. In order to better follow the leak progression in the stack, online gas chromatography will be performed for future stack durability tests.

Figure 12 presents polarization curves in electrolysis and fuel cell modes at three different times: before any characterization was performed, after co-electrolysis operation characterization (corresponding to before the durability test) and after the durability test. The polarization curves in fuel cell mode reveal that the open circuit voltage decreased over time, indicating that leakage increased during the test. The biggest open circuit voltage drop (86 mV) and hence leakage increase happened during the characterization in co-electrolysis. In comparison, the difference of open circuit voltage before and after the durability test is only 16 mV. This drop of open circuit voltage points at a moderate increase of the leakage also during the durability test, which is in contrast with the fact that humidity in the hydrogen outlet did not increase during the durability run (Figure 11). However, a change of 16 mV is still small. In contrast, the polarization curves in electrolysis mode reveal limited changes over time with an 8 mV drop in the
open circuit voltage both for the initial characterization and the durability test. This result is coherent because leaks in electrolysis mode have a much more limited effect on the OCV due to the high fraction of steam. The effect of leak might be seen in the transport limited region of the polarization curve (Figure 12), however, the polarization curves in electrolysis mode where only performed up to the thermoneutral voltage at which the transport limited region is not yet reached. For this reason, it would be expected that the increase in leakage would have only a limited effect during the durability test as the current corresponded to the linear section of the polarization curve.

In conclusion, no voltage degradation neither hydrogen outlet humidity increase was measured during 1,500 h in steam electrolysis mode, which is an encouraging result since numerous articles have reported voltage degradation in similar conditions. However, experiments in fuel cell mode revealed that leaks appear to have increased mainly during co-electrolysis characterization and to a minor extent during the durability test.

In electrolysis, there is already large partial pressure of steam on the hydrogen electrode side and steam formation caused by leakage is not seen in the voltage as clearly as in the operation in the fuel cell mode. Because of this, there is a limitation of using voltage measurement for performance measurement in electrolysis. In addition to the voltage measurement, it would be relevant to measure the humidity, flow rate and composition of the hydrogen side outlet gas over time, despite such measurement is more work intensive and relatively less accurate.

5 Conclusion

The present work investigated the performance of a 6-cell SOE stack in electrolysis and co-electrolysis modes. The initial stack characterization in fuel cell mode was done at 750 °C. The stack performance was then characterized in electrolysis mode with four different inlet gas compositions of various ratios of inlet steam and carbon dioxide at temperatures of 700, 750 and 800 °C. It was found that the stack performance depends primarily on the operation temperature and only to a small extent on the inlet gas composition. Experiments in fuel cell mode revealed that leaks appear to have increased during co-electrolysis. A steam electrolysis durability test of 1,500 hours was performed at a current density of –0.775 A cm⁻² at a temperature of 750 °C. The voltage trend showed that no degradation could be observed. In the future, durability tests in co-electrolysis operation will be conducted to evaluate the effect of addition of carbon dioxide on the stack durability.

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List of Symbols

| Symbol | Definition                  |
|--------|----------------------------|
| ASR    | area specific resistance   |
| FU     | fuel utilization ratio     |
| GC     | gas chromatograph          |
| OCV    | open circuit voltage       |
| RU     | reactant utilization ratio |
| SOE    | solid oxide electrolyser   |
| SOFC   | solid oxide fuel cell      |
| YSZ    | yttria stabilized zirconia |

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