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Abstract
Premixed safety gas is conventionally used to keep the anode of a solid oxide fuel cell (SOFC) under reducing conditions during heat-up. This article presents the results of an experimental study to heat up a SOFC system and stack without the said premixed safety gases, i.e. by utilizing a natural gas pre-reformer and anode off-gas recycling (AOGR). Firstly, ex-situ experiments were conducted to investigate the operability of a pre-reformer during system heat-up. It was found that any oxygen fed to the reformer hinders the reforming reactions at low temperatures. Secondly, based on the ex-situ findings, series of heat-up cycles were conducted with a complete 10 kW system using AOGR and a planar SOFC stack. In these experiments it was found that the system heat-up is possible with fuel gas and steam only, without the need for premixed reducing safety gases. Use of the fuel gas instead of a premixed safety gas did not result in a significant performance loss in the SOFC stack. Therefore, such a heat-up strategy was developed for SOFC systems that reduces the need of premixed safety gas storage space and thus decreases the system cost.

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1. Introduction

Solid oxide fuel cells (SOFCs) enable energy production from different hydrocarbon fuels with high efficiency. SOFCs require high operating temperatures, e.g. 700–800 °C for anode supported cell types. Thus the fuel cell stack and other system components have to be heated up to operating temperature before the electricity production can begin. Lengthy heat-up times of several hours may be required to maintain the temperature gradient and the thermal stresses in the stack at acceptable level [1].

The nickel in the SOFC anode substrate has to remain at reduced state at elevated temperatures. This is accomplished by supplying sufficient amount of fuel or other reducing gas to the stack. If the reducing gas supply is discontinued, then the nickel in the anode substrate will start to re-oxidize, which will first deteriorate the cell performance and eventually destroy the SOFC by cracking the cell [2]. First signs of the oxidation of the nickel cermet anode have been measured as low as 290 °C [3], and it has been shown that the oxidation of the anode substrate proceeds more rapidly as the temperature increases [4]. Permanent damage to the cell may occur in a matter of minutes if there is forced oxygen supply to the anode [5]. Indeed, without the forced oxygen supply and by minimizing the time under oxidizing conditions at elevated temperatures, the redox tolerance of the stack can increase significantly [6]. Ideally, the re-oxidation could be avoided, if no oxygen is transported to anode. However, the anode supported SOFC stack is not a hermetically sealed device, and some air will eventually leak from the cathode side of the stack via the electrolyte or stack seals [7]. Additionally, ambient air can leak to the anode through other fuel system

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components (e.g. reformer or heat exchanger) or through connecting piping from the air system. Therefore, it is necessary to feed reducing gas to the stack during the heat-up cycle to displace the oxygen in the fuel system and to protect the stack from re-oxidation. Furthermore, it may be necessary to sustain the flow of reducing gas for several hours during the system heat-up and cool-down, while the stack temperature is still high enough for significant re-oxidation and cell damage. SOFC system concepts based on the anode off-gas recirculation (AOGR) achieve higher efficiencies and potentially simpler design when compared to systems without AOGR [8]. Therefore, they are considered technically advantageous, and there are studies where the AOGR has been successfully used in SOFC systems [9–11]. However, for a planar stack with cross-over leakage (air is leaking to fuel side and vice versa), utilization of AOGR complicates the heat-up procedure since there is a forced supply of oxygen to the fuel system due to the leakages. Furthermore, prior to starting the SOFC system electricity production, all fuel system components have to be heated up above the dew point before the recirculation of the anode off-gas with high steam content can be initiated. Otherwise, water could condensate to the system components (e.g. reformer catalysts and recirculation blowers), which would have detrimental effects on their operation.

The most straightforward way to provide a reducing gas supply is to utilize gas containers of premixed safety gas e.g. hydrogen–nitrogen mixtures. Indeed, due to its simplicity, this approach has been adopted by the majority of research laboratories that conduct research on solid oxide fuel cells or stacks. For example, the 10 kW demo unit at VTT [9] would consume ca. 5 bottles (50 L, 200 bars) of premixed safety gas with 4 vol.-% of hydrogen during a heat-up cycle. In commercial products however, this approach is not desirable, due to large amount of gases needed for heat-up cycles spanning several hours. The gas containers require additional space, and increase the cost of both installation and servicing of the system. Thus it would be beneficial if the reducing gas could be generated with the existing Balance-of-Plant equipment which is fundamental for system operation. The most obvious solution would be to utilize the fuel supply (e.g. natural gas), the pre-reformer and the start-up steam generator to produce hydrogen-containing natural gas reformate.

In this article, the heat-up of a SOFC system and stack without using the premixed safety gases is investigated experimentally. Firstly, ex-situ experiments are conducted in a stand-alone reformer test bench. The experiments were done to realize the restrictions of reforming at low temperature in a system with AOGR and air leakage (i.e. forced oxygen supply to the fuel system). Secondly, series of heat-up cycles were done with a complete 10 kW SOFC system using AOGR and a planar SOFC stack. The results of the ex-situ experiments were applied to devise a safe heat-up procedure that would not damage the stack and removes the need for premixed safety gas. The performance of the stack was investigated after each heat-up to evaluate possible damage to the stack due to these heat-up procedures. There are several studies where the heat-up of a SOFC has been investigated by modelling [1,12–18], but to the authors’ knowledge, no experimental work with a complete planar SOFC system utilizing AOGR has been published previously.

2. Experimental

2.1. Ex-situ reformer experiments

The ex-situ experiments were conducted in a separate reformer test bench described in detail in Ref. [19]. The aim of the experiment was to assess the activity of the catalyst at low temperature in steam reforming (Eq. (1)) using different inlet gas mixtures. This information is highly relevant to conduct the heat-up experiment on the SOFC system. The light-off temperature was determined by the reformer inlet gas temperature at which the reformer starts to convert methane to hydrogen according to Eq. (1).

\[ \text{CH}_4 + \text{H}_2\text{O} \rightarrow \text{CO} + 3\text{H}_2 \]  

(1)

The reformer included a commercial precious metal monolithic catalyst (Süd-Chemie). The gas composition at the reformer outlet was monitored continuously with an online gas analysis equipment (IR-based for CH\textsubscript{4}, thermal conductivity for H\textsubscript{2} and paramagnetic for O\textsubscript{2}, Sick Maihak S700 series). Due to different channels cross-sensitivity, the analyser results should be used to evaluate trends and not as quantitative measurements. The temperature of the inlet gas was ramped up from 200…250–550 °C with a rate of ca. 2 °C min\textsuperscript{-1}. The gas hourly space velocity (GHSV i.e. gas volume flow at NTP divided by catalyst volume) used was ca. 32,000 h\textsuperscript{-1}. The different inlet gas mixtures investigated (Table 1) are relevant to SOFC system operated on natural gas including an anode-off gas recycling (AOGR) loop during first stages of the heat-up, where the fuel and steam supply have just been initiated. At that time, the temperature of both the pre-reformer and the stack are low and little or no reforming activity is expected to occur. Without reforming reactions, the gas

<table>
<thead>
<tr>
<th>Run Gas flow/NLPM</th>
<th>Natural gas</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
<th>0.5</th>
</tr>
</thead>
<tbody>
<tr>
<td>H\textsubscript{2}O</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>N\textsubscript{2}</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
<td>10</td>
</tr>
<tr>
<td>H\textsubscript{2}</td>
<td>–</td>
<td>–</td>
<td>0.2</td>
<td>0.05</td>
<td>0.1</td>
<td>0.15</td>
<td>0.4</td>
</tr>
<tr>
<td>Air</td>
<td>–</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
<td>0.5</td>
</tr>
<tr>
<td>H\textsubscript{2}/O\textsubscript{2}</td>
<td>0</td>
<td>2</td>
<td>0.5</td>
<td>1</td>
<td>1.5</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>
recirculating in the fuel system consists of the inlet flows i.e. fuel gas and steam as well as air originating from stack leakages. The test gas in run 1 consisted of natural gas (ca. 98% methane [19]), steam and nitrogen. A small fraction of air was introduced in the run 2–7 to simulate the effect of the presence of oxygen originating from air leakage to the fuel system and into the recycled gas. In the other test gases (run 3–7), hydrogen was added with varying H₂/O₂ ratio from 0 to 4 according to the Eq. (2).

\[
\text{O}_2 + 2\text{H}_2 \leftrightarrow 2\text{H}_2\text{O} 
\]

(2)

2.2. System heat-up experiments

The heat-up experiments were conducted on VTT’s 10 kW SOFC demo unit [9]. The VTT demo unit consists of two interconnected modules, the balance of plant (BoP) module and the stack module, containing a planar SOFC stack (Fig. 1). The fuel system utilizes an AOGG loop, which enables operation without external steam supply when the stack current and single-pass fuel utilization are high enough. Ambient air is fed to the air system with a blower and filtered with a particle filter. Other system components include e.g. heat exchangers, catalytic burner and reformer which are necessary to maintain the thermal balance of the system and stack during operation. The SOFC stack was designed, manufactured and installed into the demo unit by Versa Power Systems (VPS), and it consisted of 64 planar anode supported cells with 550 cm² of active area [20]. The SOFC stack is located inside a thermally insulated and gas-tight module designed by VPS. Internal temperature of the stack is measured with thermocouples inserted at various locations inside the stack. Voltage is measured from each cell.

Fuel system gases were analysed at reformer inlet (Rin), anode inlet (Ain) and anode outlet (Aout) (Fig. 1). Anode outlet gas is recycled back to system inlet thus the recycling gas has

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Fig. 1 – VTT 10 kW demo unit layout with fuel system gas sampling locations. Reproduced and adapted from Ref. [9]. Copyright 2011, The Electrochemical Society.

![Fig. 1 – VTT 10 kW demo unit layout with fuel system gas sampling locations. Reproduced and adapted from Ref. [9].](image)

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Fig. 2 – Standard start-up (a) Stack temperature (solid line) and current (dashed line) (b) Flow rate of premixed safety gas (dashed line), fuel (dotted line) and steam (solid line).
the same composition. Continuous gas analysis for CH₄, CO, CO₂, H₂ and O₂ is done with online gas analysis equipment.

The heat-up of the stack and the system was accomplished primarily with the electric heater of the stack module, which heated up the inlet stack air as well as the stack and the surroundings close to the operating temperature (Fig. 1). Secondly, the heat-up was assisted by a smaller electric heater present in the AOG loop. The reformer did not have an electric heater thus necessitating the need of temporary hydrogen pulse to start the reforming reactions in the pre-reformer and the stack, which is described in more detail in the following chapters. The rate of temperature change of the stack was below 3 °C min⁻¹ during all heat-up cycles.

A standard laboratory style heat-up and start-up cycle has been previously established for this particular SOFC system (Fig. 2). The standard start-up consists of three different phases.

1. Heat-up phase. Premixed safety gas of 4 vol-% hydrogen and 96 vol-% of nitrogen (70 NLPM) is supplied to the fuel system, and air is supplied to air system with a blower (500 NLPM). AOG is used continuously with an AOG flow rate above 90 NLPM at all times.

2. Transition to fuel. After the heat-up phase, once the stack temperature is ca. 700 °C, a gradual transition from the premixed safety gas to fuel and steam supply is initiated. Once the transition is completed, premixed safety gas supply is stopped whereas 5 NLPM of natural gas and 20 NLPM of steam are supplied to fuel system.

3. Load-up phase. After transition to fuel gas, a load-up phase is commenced, where the stack current is first ramped up to 150 A, and later to 200 A which is the nominal operating current. During the load-up phase, the natural gas, steam and AOG flow rates are changed proportionally to the stack current. The external steam supply is stopped at 115 A, once sufficient stack fuel utilization and concurrent transport of oxygen via the cell electrolyte are established. At higher currents, the fuel flow rate is increased, and the fuel system and the stack are kept free of carbon formation by AOGR alone.

In the experimental heat-up cycles devised for this study, the standard heat-up procedure was altered by dividing the heat-up into two distinct phases (Fig. 3).

1. Heat-up phase 1. Firstly, the stack is heated above 200 °C and all other components in the fuel system, e.g. reformer, AOGR blower and heat exchangers, to at least 100 °C (Fig. 3(a)). Similarly to the standard heat-up, AOG is in operation and cathode air is fed with a blower.

2. Transition to fuel. Firstly, the steam supply is started once the minimum stack temperature is above 200 °C (Fig. 3). For safety reasons, the supply of hydrocarbon fuel was initiated only once the minimum measured in-stack temperature has reached 300 °C. This approach was chosen to eliminate the risk of accidental formation of toxic nickel carbonyl compounds in the SOFC stack. Reformer light-off was accomplished by a short-term hydrogen pulse.

<table>
<thead>
<tr>
<th>Table 2 – Summary of different system heat-up cycles (HUs).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Standard</td>
</tr>
<tr>
<td>HU phase 1 gas supply</td>
</tr>
<tr>
<td>Stack max. temperature at transition to fuel</td>
</tr>
<tr>
<td>HU phase 2 gas supply</td>
</tr>
</tbody>
</table>
3. Heat-up phase 2. The system is heated up close to stack operating temperature with fuel reformate used as reducing safety gas.

4. Load-up. The load-up procedure remains similar for both standard and experimental heat-up cycles.

In order to assess the feasibility to heat-up a system without premixed safety gases, the demo unit and the SOFC stack were subjected to three different experimental heat-up cycles (HUs). The operational conditions were changed successively to more severe with respect to the possibility of re-oxidizing the stack (Table 2) i.e. higher stack maximum temperature was allowed before the transition to reducing fuel gas was done. Another important distinction between different heat-up cycles should be emphasized. Premixed safety gas (70 NLPM) was supplied during phase 1 only in HU1 (see Table 2). For HU2-3 there was no premixed safety gas supplied at all (see Table 2 and Fig. 3(b)). Instead, the gas during phase 1, circulating in the fuel system by the AOGR blower, was originating from whatever gas was leaking into the fuel system, through the stack or from other sources.

3. Results and discussion

3.1. Ex-situ reformer experiments

Fig. 4 illustrates the different qualitative results obtained in the ex-situ experiments. In Fig. 4(a), it can be seen that the catalyst exhibits some activity in steam reforming at temperature as low as 235 °C with test gas of run 1. The conversion of methane increases gradually with the inlet temperature. The inlet temperature at which the methane conversion by steam reforming starts is further referred to as the reformer light-off temperature. In Fig. 4(b), air is added to the test gas, simulating the effect of air leakage to fuel system. The catalyst behaviour is qualitatively very different compared to test gas of run 1, as no methane is reformed before ca. 390 °C. At ca. 390 °C, methane conversion starts abruptly, in other words, reformer light-off occurs.

Apparently, the presence of oxygen in air has an inhibitive effect on the steam reforming reactions at low temperature on this catalyst. In Fig. 4(c), hydrogen is added to the gas stream at stoichiometric ratio with oxygen. In this case, the catalyst exhibits some activity already at 200 °C and the conversion of methane increases gradually with the inlet temperature. This behaviour is qualitatively similar as the one obtained with the test gas of run 1 (Fig. 4(a)), performed with only natural gas and steam and in the absence of oxygen. It appears that the combustion reaction of hydrogen (Eq. (2)) takes place already at 200 °C. As a consequence, molecular oxygen and its inhibiting effect on steam reforming are removed by the reaction (Eq. (2)). Therefore, this enables methane conversion at reformer inlet temperature as low as 200 °C.

Fig. 5 illustrates the effect of the \( \frac{H_2}{O_2} \) ratio on the light-off temperature. The light-off temperature is approximately 390 °C when \( \frac{H_2}{O_2} \) ratio is zero and it decreases with increasing \( \frac{H_2}{O_2} \) ratio to fall below 200 °C at \( \frac{H_2}{O_2} \) ratio of two (corresponding to the stoichiometric ratio of \( H_2 \) and \( O_2 \)).

The results show that methane conversion can be triggered by two ways in the reformer during the heat-up of a SOFC system. Firstly, if no hydrogen is supplied, the reformer inlet gas temperature has to be ca. 400 °C because of the inhibitive effect of oxygen originating from air leakages and recycled by the AOGR loop. Alternatively, the light-off temperature can be decreased by supplying a relatively small amount of hydrogen. Thus the hydrogen production can start already at
temperature as low as 200 °C. These results suggest that during the heat-up of a SOFC system, a small amount of hydrogen can be supplied to the reformer inlet to trigger the activity of the reformer at low temperature and accomplish the light-off. This is advantageous because the hydrogen produced in the reformer protects the SOFC anode from the damaging effects of re-oxidation. These results are further exploited to design the experiments on system level presented in the next Section 3.2.

3.2. System heat-up experiments

3.2.1. Standard heat-up
A more detailed planning of the heat-up (HU) cycles was done based on results of the ex-situ experimental results presented in Chapter 3.1. At the time of the experiments, there was no possibility to pre-heat the reformer inlet gas to 400 °C in the 10 kW demo unit, since the pre-heating of the reformer inlet gas was realized only with the fuel system heat exchanger (see Fig. 1). Therefore, it was decided to accomplish the reformer light-off in HUs 2–3 with short-term hydrogen pulse of ca. 1 NLPM during the heat-up cycle.

Firstly, the characteristics of the stack and the reformer during a standard heat-up cycle are depicted in Fig. 6. Before the heat-up is commenced, the hydrogen-containing reducing safety gas supply and AOGRE are activated. This is evident at test time ca. 1 h in Fig. 6(c), where the fraction of oxygen is decreased from 21 vol-% to zero and replaced by hydrogen (and nitrogen). Interestingly, the introduction of hydrogen containing safety gas can be observed also by an increase of the reformer T_{outlet} (Fig. 6(b)). This can be explained by the high activity of the precious-metal catalyst used in the pre-reformer. The reaction (Eq. (2)) between the oxygen, leaking into the fuel system (through stack or otherwise), and hydrogen in the safety gas is occurring already at room temperature. Thus the pre-reformer is disposing all oxygen from the anode inlet gas (Fig. 6(c)).

In a standard heat-up, the voltage of the stack starts to increase already at ca. 150 °C stack T_{max} (Fig. 6(a), t = 3 h). Significant and faster increase in the stack voltage is present between 250 and 300 °C stack T_{max} (Fig. 6(a), t = 4–5 h). The increase of the stack voltage can be interpreted as the start and progression of the reduction process. Additionally, the difference between the reformer outlet and inlet temperature diminishes to zero once the stack temperature reaches 400 °C (Fig. 6(b), t = 5 h), and no oxygen is detected anymore in the anode outlet gas, which indicates that oxygen is reacting with hydrogen already in the stack.

After the heat-up, the transition from safety gas to fuel gas and the load-up procedure are observed as an increase of both hydrogen and methane fractions at the anode inlet (Fig. 6(c), t = 10 h), and as a decrease in stack voltage (Fig. 6(a)).

![Fig. 6](image_url) Standard heat-up cycle with premixed safety gas (a) stack temperature and average cell voltage, (b) inlet and outlet temperature of the reformer (c) fraction of methane, hydrogen and oxygen in the anode inlet gas on dry basis.

![Fig. 7](image_url) Heat-up cycle 1 (a) stack temperature and average cell voltage, (b) inlet and outlet temperature of the reformer (c) fraction of methane and hydrogen in the anode inlet/outlet gas on dry basis.

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Concurrently, the endothermic steam reforming reactions cause that the $T_{\text{outlet}}$ of the pre-reformer decreases ca. 80 °C below the $T_{\text{inlet}}$ (Fig. 6(b)).

3.2.2. Heat-up experiment 1
The experimental heat-up cycle 1 (HU1) is depicted in Fig. 7. In HU1 the premixed safety gas was still used during heat-up phase 1 (see Table 2) and transition to fuel was done with the stack $T_{\text{max}}$ of 320 °C by decreasing the premixed safety gas flow from 70 NLPM to zero and increasing the natural gas and steam flow rates to 5 and 20 NLPM, respectively. The transition to fuel is evident as a drop in the stack voltage (Fig. 7(a), $t = 3$ h), increase in reformer $T_{\text{outlet}}$ (Fig. 7(b), $t = 3$ h) and increase in the CH$_4$ fraction of the fuel system gases (Fig. 7(c), $t = 3$ h). Lower voltage in HU1 compared to standard heat-up can be explained by the higher amount of steam in the fuel gas which decreases the Nernst potential of the cell. The stack voltage increases with the stack temperature as the H$_2$ fraction of the fuel gas increases ($t = 3$–$5$ h).

It should be noted that the steam reforming reactions and therefore the majority of the hydrogen production occurs in the SOFC stack throughout the heat-up cycle, since the temperature of the pre-reformer remains lower than the stack. Nearly all methane is converted to hydrogen in the stack once the stack $T_{\text{max}}$ reaches 650 °C (Fig. 7(c), $t > 7$ h) and the resulting hydrogen-rich gas is fed back to reformer inlet with AOGR. Concurrently, the reformer inlet temperature is still at ca. 400 °C at that time (Fig. 7(b), $t = 7$ h). The combination of hydrogen-rich inlet gas and low temperature causes that exothermic methanation reaction (reverse to Eq. (1)) takes place in the pre-reformer instead of steam reforming. This can be observed (Fig. 7(b), $t = 6$–$9$ h) as a second increase of the reformer $T_{\text{outlet}}$ above $T_{\text{inlet}}$ before the load-up ($t = 8.5$ h) after the first increase caused by oxidation of hydrogen in the reformer (Fig. 7(b), $t = 3$–$5$ h).

Similarly to the standard heat-up, steam reforming in the pre-reformer starts during the load-up, once more fuel is supplied to the system, and the reformer $T_{\text{inlet}}$ increases above 500 °C (Fig. 7(b)). Even though the Ni-cermet of the SOFC stack makes it a very efficient steam reformer during the heat-up process, the amount of hydrogen remains relatively low, below 10 vol-% (dry basis) at the beginning of the heat-up cycle. Marked increase of hydrogen starts to occurs only at higher temperatures, when the stack $T_{\text{max}}$ is above 400 °C (Fig. 7(c), $t = 4$ h). Since the pre-reformer has the capability for steam reforming as well, it would be beneficial to operate the reformer at higher temperature during that time i.e. when relatively little methane is reformed in the stack. Therefore, when the fuel supply is started, the reformer $T_{\text{inlet}}$ should preferably be above 550 °C to accomplish both reformer light-off and immediate production of H$_2$-rich gas. However, a pre-reformer is required and very useful also when it is used at lower temperature than the stack, since it removes any oxygen from the anode inlet gas.

3.2.3. Heat-up experiments 2 and 3
The experimental heat-up cycle 2 (HU2) is depicted in Fig. 8. It was observed that the system characteristics were similar to HU1 soon after the transition to fuel was done, thus the measurements depicted in Fig. 8 are shown only for this transition phase. In HU2, the stack $T_{\text{max}}$ was ca. 350 °C when the transition to fuel gas was done ($t = 4$–$5.5$ h) and, additionally, no premixed safety gas was supplied to system at all. The reformer light-off was accomplished by a 10 min duration H$_2$ pulse. The transition to fuel was initiated by starting the steam supply at $t = 4$ h. At $t = 5$ h natural gas supply was started, and at $t = 5.5$ h the hydrogen pulse was done (see Fig. 8 for annotations).

During the phase 1 of the HU2, prior to fuel transition, the oxygen fraction in the fuel system gas is measured to be ca. 23 vol-%, which clearly shows that air is circulating in the fuel system and through the stack (Fig. 8(c), $t = 3$ h). The oxygen concentration is observed to decrease by ca. 1 vol-% before fuel transition at stack $T_{\text{max}} > 200$ °C ($t = 3$–$4$ h), which indicates that oxidation of the Ni-cermet starts to occur. Additionally, the cell voltage decreases once steam supply of 20 NLPM is started (Fig. 8(a), $t = 4$ h). The O$_2$ fraction decreases significantly, from 18 to 7.5 vol-%, upon introduction of 4 NLPM of natural gas (Fig. 8(c), $t = 5$ h) and the CH$_4$ fraction in the fuel system gas increases to nearly 50 vol-%, a sign that the flow rate of the air leaking into the fuel system is of the same magnitude i.e. 4 NLPM.

Similarly to the ex-situ reformer experiments no light-off occurred in the pre-reformer even at 250 °C reformer $T_{\text{inlet}}$ due to oxygen present in the fuel system (Fig. 8(b), $t = 3$–$5.5$ h). The reformer light-off and production of H$_2$ is commenced...
3.2.4. Reduction and reforming activity of the anode during heat-up

There are specific differences between the HU1 (safety gas used) and HU2-3 (no safety gas used) with respect to (i) reduction/oxidation behaviour of the stack and (ii) the activity of the Ni-cermet to catalyse steam reforming reactions. This phenomenon is illustrated with Fig. 9, where the flow of fuel and hydrogen, as well as the average cell voltage and the \( H_2 \) fraction at anode outlet, are presented for HU1-3. The measurements are plotted as a function of stack \( T_{\text{max}} \), a common denominator for the phenomenon under discussion. It should be noted that the stack \( T_{\text{max}} \) is relative to test time as well, since heating of the stack occurred at relatively steady rate of ca. 2 °C min\(^{-1}\) from 300 to 500 °C.

Qualitatively, it is evident that in HU1 the stack is already more reduced (stack voltage is higher) and also catalytically active with respect to steam reforming. In HU1, the \( H_2 \) fraction at the anode outlet as well as voltage increases steadily with the stack temperature (Fig. 9(c–d)), occurring immediately when the \( H_2 \) supply is stopped and fuel supply started (Fig. 9(a–b)). Moreover, the results show that the steam reforming reactions and \( H_2 \) production in the stack can start already at 300–350 °C.

In HU2, the short-term \( H_2 \) pulse of 10 min duration is triggering both reduction and reforming activity in the stack, observed as a stepwise transition for both \( H_2 \) and stack voltage (Fig. 9(c–d)). However, the stack has to heat up ca. 70 °C more to 420 °C (in 1 h, see also Fig. 8) until the reduction of the stack has proceeded to a level where a notable recovery of the stack voltage, as well as in increased reforming activity is observed.

In HU3, however, the recovery of stack voltage as well as reforming activity is occurring nearly simultaneously with the introduction of the natural gas. Faster recovery can be related to longer duration of the \( H_2 \) pulse. The \( H_2 \) flow is started once the stack temperature reached 350 °C, and the reduction process of the stack can proceed while the stack heats up to 400 °C (Fig. 9(b)). Thus the reduction is completed faster in HU3 once the natural gas supply is initiated. However, the 1 NLM of \( H_2 \) in HU3 is insufficient to reduce the entire active cell area since no \( H_2 \) is detected in the anode outlet gas at first. The \( H_2 \) is present in anode outlet gas only after transition to fuel is complete.

Based on the results it is clear that in HU2-3 both the electrochemical, as well as steam reforming activity, are first inhibited by the oxidation of the Ni-cermet already at lower temperature than 350 °C for stack \( T_{\text{max}} \). Additionally, to realize the reduction of the Ni-cermet after oxidation has occurred at low temperature, all oxygen has be removed from the anode inlet gas (see Fig. 8) and replaced with high enough amount of hydrogen, so that there is hydrogen present at the anode outlet gas as well. Otherwise, it appears that the Ni-cermet of the stack will remain in oxidized state and will not start the steam reforming reactions, and the accompanied production of reducing hydrogen gas.

3.3. Effect of the heat-up experiments on the SOFC performance

Voltage characteristics of the SOFC stack is commonly used as a performance indicator. Thus the effects of the different heat-up cycles on the SOFC can be assessed by observing changes in the stack or individual cell voltages [6]. If the experiments cause permanent damage to the cells e.g. due to re-oxidation, it would be recorded as a stack voltage decrease.

Voltage characteristics of the SOFC stack were investigated by conducting a load-up cycle to 150 A (0.273 A cm\(^{-2}\)) after each heat-up experiment and allowing the system to stabilize for 20 h (Fig. 10(a–c)). After the stabilization, the individual

**Fig. 9** - Reduction and reforming in the stack for HU1-3 (a) fuel flow, (b) hydrogen flow, (c) fraction of \( H_2 \) in anode outlet gas, and (d) average cell voltage.

![Image](image-url)
voltage measurements from all 64 cells of the stack were averaged for a period of 1 h. Then, a difference was calculated to the measurements at 150 A prior to performing any of the experiments HU1-3 (Fig. 10(d)). The average cell voltage prior to HU1-3 is also shown in Fig. 10(a–c).

The majority of the cells in the stack do not show any performance deterioration after the HU1-2 compared to the values recorded at 150 A prior to experiments (Fig. 10(a),(b) and (d)). However, after the HU3 the average cell voltage is ca. 6 mV lower at the end of the stabilization period (Fig. 10(c)), and nearly all cells exhibit voltage decrease (Fig. 10(d)). In the HU3 the stack maximum temperature was allowed to increase up to 400 °C before the supply of fuel gas was started. Thus it is possible that the higher temperatures used in HU3 may have caused too severe oxidation of the anode, thus damaging the stack.

However, the differences of the cell voltages compared to prior measurements in Fig. 10(d) are small and within 10 mV for the majority of the cells. Moreover, some of the cells exhibit increased voltage compared to prior measurement. This indicates that the resulting differences in the voltage between the heat-up cycles can be partly explained by other effects as well e.g. by the variation of the in-stack temperature distribution due to small hysteresis of the plant controllers. Additionally, deep thermal cycling of a SOFC stack down to room temperature can cause damage and performance loss of the stack even with premixed reducing gas, and this phenomena can also contribute to the apparent lower cell voltage with increased number of heat-up cycles.

Therefore, this comparison of the cell voltage distribution with respect to the effect of the heat-up cycles should be treated as indicative rather than conclusive since there are other mechanisms which can affect the performance of cells. However, the results show that the stack can withstand a heat-up cycle with fuel reformate and AOR without any significant performance deterioration. Moreover, stack temperatures below 350 °C appears to be a more beneficial region to introduce the fuel gas and trigger the reforming reactions to produce hydrogen-rich reducing gas because (i) performance loss was measured after HU3 when the stack was heated up to 400 °C before starting the fuel supply and (ii) the Ni-cermet is oxidized already below 350 °C which prevents steam reforming reactions.

4. Conclusions

The results of this study clearly show that it is essential to investigate the characteristic operation of the system pre-reformer to accomplish a safe heat-up cycle. Furthermore, the interactions with other system components e.g. air leakages and the choice for system layout, such as the use of AOR, will affect the feasibility of any heat-up strategy and have to be taken into account.

The light-off temperature, i.e. start of the reforming reactions in a pre-reformer, is significantly affected by the use of AOR and any leakages of air to the fuel system, through stack or otherwise. The light-off temperature is increased by ca. 200 °C when oxygen is present in the reformer inlet gas. However, it is possible to accomplish lower reformer light-off temperatures by adding hydrogen to the reformer inlet.

SOFC stack is an efficient steam reformer due to high amount of catalytically active nickel in the anode cermet, and thus is an obvious solution to produce the hydrogen-rich reducing gas from the fuel during system heat-up. It is observed, that the SOFC stack can start sufficient steam reforming and production of hydrogen-rich reducing gas at temperatures above 400 °C. However, oxidation of the anode Ni-cermet in system conditions can proceed already below 350 °C, which inhibits the reforming activity of the anode. Thus, the usage of a pre-reformer to remove trace oxygen from the anode inlet gas is required with AOR, since any air
leakages to fuel system will retain the anode in oxidized state. Moreover, some performance loss was measured when the stack was heated to 400°C before fuel supply was started. Therefore, it is recommended that the supply of hydrogen-rich reducing gas is started already below 350°C, or as low temperature as possible, to prevent oxidation of the Ni-cermet.

During the system experiments it was noted that sufficient temperatures for pre-reformer light-off were not possible by relying only on the heat recuperated from the fuel system heat exchanger. Thus electrically or otherwise assisted heating of the pre-reformer (i) to 400°C enables reformer light-off without the short-term hydrogen pulse, thus simplifying the system layout even further and (ii) above 500°C can potentially be lower than 300°C when the fuel is introduced to the system. This would significantly decrease the risk of oxidizing the Ni-cermet anode.

The results show that a heat-up from room temperature to the operating temperature of SOFC stack is possible without premixed gas and without significant loss of stack performance. This finding allows reducing the premixed gas storage capacity in a SOFC system and thus the physical size of the system as well capital and servicing costs.

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