Effect of Anode off-gas Recycling on Reforming of Natural Gas for Solid Oxide Fuel Cell Systems

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Effect of Anode off-gas Recycling on Reforming of Natural Gas for Solid Oxide Fuel Cell Systems

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Abstract

The effect of anode off-gas recycling (AOGR) on the characteristic performance of a natural gas reformer equipped with a precious metal catalyst is investigated experimentally. The reformer is operated both with synthetic AOGR gas and in steam reforming (SR) conditions. The characteristic performance in SR and AOGR mode are compared with equilibrium, and it is found that equilibrium is more readily achieved in AOGR mode. The reformer is used for extended periods of time (100–1,000 h) in conditions where carbon formation is thermodynamically possible to measure any changes in characteristic performance. No significant change in the performance is observed due to carbon formation or catalyst deactivation. The reformer could be successfully implemented in a 10 kW SOFC system with an anode off-gas recycling loop.

Keywords: Anode Off-gas Recycling, Natural Gas, Precious Metal Catalyst, Reforming, Solid Oxide Fuel Cell, Supported Catalyst

1 Introduction

Solid oxide fuel cells (SOFCs) are considered as a very promising technology in the future of energy production due to their high electrical efficiency. Additionally, SOFCs offer fuel flexibility and the fuel processing is simpler compared to fuel cells operating at lower temperature [1–3]. Fuel processing is simplified by the possibility to use hydrogen, carbon monoxide, and methane as a fuel and by the availability of recoverable heat for steam reforming (SR).

It is well known that SR of hydrocarbon fuel, typically natural gas, can be done internally in the SOFC stack [3]. This approach is advantageous due to the highly endothermal reforming reactions with hydrocarbon fuel which reduce the need for stack cooling with excess cathode air, decreases the parasitic loss caused by air blowers and can thus increase the electrical efficiency of the system. However, the temperature gradient caused by internal reforming can lead to excessive thermal stress which is detrimental for the lifetime of the stack components [4]. Moreover, there is a risk of carbon formation at the anode which can lead to a loss of performance and ultimately destruction of the stack [5, 6]. Lastly, internal reforming can decrease locally stack temperature and thus voltage resulting in sub-optimal operation. Therefore, pre-reforming of the hydrocarbon fuels is typically required in SOFC systems to mitigate these effects. The fuel is partially

converted to syngas composed of methane, hydrogen, steam, carbon monoxide, and carbon dioxide in a reformer upstream of the stack. The optimum ratio between pre-reforming and internal reforming is dependent on the SOFC stack and system design, and selected operating parameters.

Recycling the hot anode off-gas to the reformer inlet is desirable in SOFC systems to provide steam for fuel reforming, since this can simplify the system design by eliminating the need of external water supply and steam generator during operation [7]. Additionally, recycling unused fuel back to the SOFC inlet can increase the electrical efficiency, since the system inlet fuel flow rate can be decreased and the system fuel utilization increased [8, 9]. Concurrently, the stack fuel utilization remains low, which has been shown to be beneficial for the lifetime of the stack [10].

Sufficient recycling ratio of anode off-gas is required to keep the SOFC, reformer, and other fuel system components free of carbon formation. It is a common engineering practice in SOFC system design to predict the gas composition, temperature, and possibility of carbon formation in a fuel reformer using thermodynamic equilibrium calculation. However, the activity of the reforming catalyst dictates both the charac-

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teristic performance of the catalyst, and if carbon formation actually occurs to the extent that would threaten the system operation. Therefore, experimental investigation of the catalyst, reformer, and the whole fuel processing system at SOFC system relevant conditions is needed to assess the characteristic performance, measure possible deviations from the equilibrium, and to map the safe operating region without carbon formation.

Anode off-gas recycling (AOGR) has proven to be challenging to implement in actual systems due to various technical challenges, e.g., providing the motive force for recycling gas at high temperature, and identifying the suitable reforming catalyst with reliable and durable performance. Recycling blowers and ejectors suitable for SOFC system use cannot be found off-the-shelf and are still in the development phase [8]. SR of natural gas is traditionally performed with nickel-based catalyst and the effect of AOGR on such a catalyst has been previously reported in the literature. Peters et al. reported that AOGR caused a decrease of activity of a nickel-based catalyst which resulted in a decreased conversion of hydrocarbons [11]. On the other hand, Nummela and Noponen reported that AOGR had no negative effect on the performance of another pre-reformer nickel catalyst [12].

Little experimental data can be found in the literature on the effects of AOGR on a precious metal catalyst using natural gas as a fuel. Precious metal catalysts have been less investigated due to their higher price, despite having potential for higher resistance against sulfur poisoning, carbon formation, and ageing [13]. Powell et al. reported using a precious metal catalyst with natural gas in an SOFC system containing a recycling loop, but the study did not include the evaluation of the reformer performance with different operating conditions [14]. Precious metal catalyst was also used by Dietrich et al. who implemented successfully an anode off-gas recycling loop in an SOFC test setup using propane [8]. The reformer was used at high temperature (>800 °C) and at such high temperatures almost all hydrocarbons are reformed to syngas, and little is left for internal reforming reactions in the SOFC stack. In order to maintain the benefits of internal reforming in an SOFC system, it is relevant to strive for lower operating temperature for the reformer, where the conversion of methane is not complete, i.e., at temperatures between 500 and 700 °C.

This study contributes to the field of fuel processing in SOFC systems by assessing the characteristic performance of a precious metal-based reformer using natural gas in AOGR mode. Performance of the reformer in AOGR conditions is compared against SR conditions at an inlet temperature of 600 °C. Additionally, the effect of varying the recycling ratio is evaluated to determine its effect on the characteristic performance, and to identify the minimum recycling ratio that can be used safely in an SOFC system, i.e., corresponding to carbon formation-free operation. Results of this work led to the successful implementation of an anode off-gas recycling loop in a 10 kW SOFC demonstration unit, where the system is operated at nominal conditions without external water supply, and the motive force for AOGR is achieved by a recycling blower [15].

2 Experimental

2.1 Experiment Setup

The experimental setup includes a natural gas reformer and a gas analysis system. The reformer unit consists of mass flow controllers for natural gas ($0–10.0 \pm 0.2$ L$_N$ min^{-1}), carbon monoxide ($0–1.50 \pm 0.03$ L$_N$ min^{-1}), carbon dioxide ($0–10.0 \pm 0.2$ L$_N$ min^{-1}), hydrogen ($0–5.0 \pm 0.1$ L$_N$ min^{-1}), water ($0–10.0 \pm 0.1$ g min^{-1}), nitrogen ($0–10.0 \pm 0.2$ L$_N$ min^{-1}), and air ($0–10.0 \pm 0.2$ L$_N$ min^{-1}), sulfur removal reactor filled with sulfur adsorbent (Süd-Chemie), water evaporator and mixer (CEM-303, Bronkhorst), superheater, reactor chamber equipped with a commercially available precious metal monolithic catalyst (Süd-Chemie), a particle filter and an heat exchanger (Alfa-Laval) to condense water in the exhaust gas (Figure 1). Similar reformer catalyst has been used previously at VTT in a 5 kW SOFC demonstration unit [16]. Temperature of the process gas was measured after the evaporator (TI1 in Figure 1), at the reactor inlet (TI2), from the leading surface of the catalyst (TI3), at the center of the catalyst (TI4), from the trailing surface of the catalyst (TI5), at the reactor outlet (TI6), and after the filter (TI7). Pressure was measured before the evaporator unit (PI1), before the reactor (PI2), after the reactor (PI3), and after the particle filter (PI4). Reformer exhaust gas was analyzed with an online gas analyzer (Sick S710 series) and with gas chromatographs (Agilent 6890 N, Agilent 6850, and HP 5890 Series II).
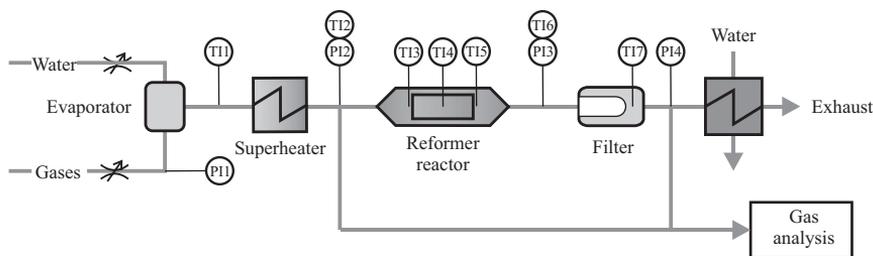

Fig. 1 Principle layout of the test equipment.

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The natural gas used in Finland is of Russian origin and contains a high content of methane (ca. 98%) and low amount of higher hydrocarbon (typically 7,000 ppm of ethane, 2,000 ppm of propane, 680 ppm of butane, and trace amounts of pentane and hexane). Carbon monoxide (>99% purity), carbon dioxide (>99.7% purity), and hydrogen (>99.5% purity) were supplied from gas bottles and purified water (Millipore Elix system) was used to create the synthetic recycling gas mixture needed in the experiments.

Electric trace heating elements were used before and after the reactor to prevent cooling of the gas. The heat used in the SR reaction was provided by superheating the inlet gases with electric heaters. In order to achieve operation conditions as close to adiabatic as possible, the reactor was carefully insulated and an electric heater was enclosed around the insulation layer. The reactor and the catalyst were kept close to adiabatic conditions during the experiments, and the heating element around the reactor insulation was used only to minimize the heat losses through the inner insulation layer.

A filter thimble made of micro-quartz was installed in a metallic casing after the reactor. The filter was used to increase the probability to identify carbon formation in the reformer during the experiment. Although carbon can deposit at the surface of the catalyst, part of the carbon containing particles may be carried from the reactor downstream. The particles can be accumulated in the filter thimble gradually obstructing the gas flow. This would result as a measurable pressure increase before the filter and could be used to identify carbon formation in the reformer.

2.2 Experiment Conditions

In order to assess how the use of AOGR affects the performance of the reformer, the reformer was used both in AOGR mode and SR mode with an inlet temperature of 600 °C. The experiments with recycling gas were conducted by supplying a synthetic gas mixture. The AOGR gas mixture corresponds to the composition of a reformer inlet gas, when a varying fraction of the anode exhaust gases are recycled back to the inlet of the reformer and mixed with natural gas. The inlet gas composition and the gas hourly space velocity (GHSV) of the catalyst at different experimental conditions are given in Table 1.

The gas composition given in Table 1 was calculated prior to the experiments on the basis of equilibrated gas with an in-house developed code [9]. Since the results of this study were meant to be used to build a fuel processing unit of an SOFC demonstration unit [15], the experimental conditions given in Table 1 were constrained by a set of pre-defined boundary conditions for that specific system at nominal operating conditions. The reformer inlet temperature was defined to be ca. 600 °C due to heat exchanger present in the fuel system to pre-heat the inlet gas. Constant stack fuel utilization ($FU_{SOFC} = 0.6$), stack outlet temperature ($T = 700$ °C) and electric current for the SOFC were used in the calculations.

In an SOFC system, the reformer GHSV should be as high as possible to decrease the size of the reformer reactor, the catalyst and by that the amount of expensive catalytic material. Concurrently, the GHSV should be limited to a value where there is still sufficient catalytic activity to achieve equilibrium for the reformer outlet gas and the pressure drop at the reformer is limited. A GHSV value of ca. 20,000 h^{-1} with recycling ratio of 0.5 was selected as a reference condition for this study. GHSV was allowed to vary according to recycling ratio and other parameters to observe the effect on the reformer performance. The GHSV of the reformer catalyst increases with the recycling ratio which means that the residence time of the gas in the reformer reactor becomes shorter (Figure 2, left). Moreover, since the stack fuel utilization is kept constant in the calculations, less fuel is fed to the reformer when the recycling ratio is increased (Figure 2, right).

Additionally, the atomic oxygen-to-carbon ratio (O/C) of the gas and the conversion of methane at equilibrium are provided in Table 1. In AOGR mode, the O/C increases with the recycling ratio since more oxygen containing species of the anode off-gas are fed back to the reformer inlet. The conversion of methane at equilibrium is calculated for an adiabatic reactor with an inlet temperature of 600 °C. It should be noted that in AOGR mode equilibrium conversion of methane is generally lower compared to SR mode. However,

Table 1 Experimental conditions in SR and AOGR modes.

| | H₂O/C | Recycling ratio | GHSV (h^{-1}) | Inlet gas composition (vol%) | | | | | O/C | Methane conversion (%) |
				Natural gas	CO	CO_2	H_2	H_2O		
SR	2.5	–	21,896	28.6	0.0	0.0	0.0	71.4	2.50	17
	2	–	18,781	33.3	0.0	0.0	0.0	66.7	2.00	15
	1.5	–	15,676	40.0	0.0	0.0	0.0	60.0	1.50	13
AOGR	0.2	0.2	10,209	56.7	5.5	8.8	14.1	14.8	0.53	5
		0.28	12,118	46.0	6.4	11.6	16.5	19.5	0.77	5
		0.36	14,470	37.1	6.9	14.0	17.9	24.0	1.02	6
		0.4	15,760	33.3	6.8	15.3	18.1	26.4	1.15	7
		0.5	19,974	25.0	6.7	18.3	17.9	32.2	1.51	9
		0.55	22,707	21.5	6.4	19.8	17.4	35.0	1.70	11
		0.6	26,053	18.2	6.0	21.2	16.5	38.0	1.90	13
		0.65	30,286	15.3	5.5	22.7	15.4	41.1	2.12	16
		0.7	35,833	12.5	5.0	24.1	14.1	44.3	2.34	19

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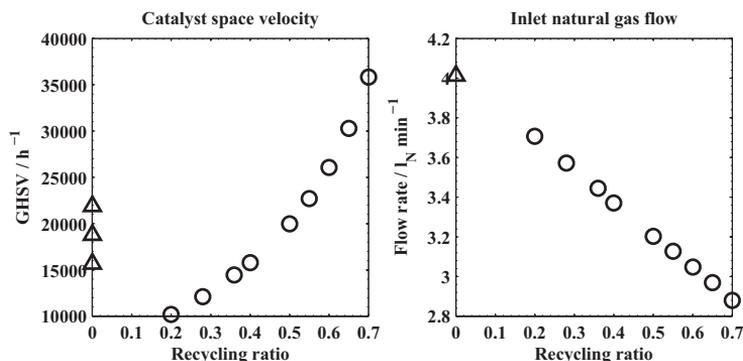
Fig. 2 The gas hourly space velocity (GHSV) of the reformer catalyst and the inlet natural gas flow rate in SR ($\triangle$) and AOGR ($\bigcirc$) modes.

above recycling ratio of ca. 0.30 the amount of methane in the reformer outlet gas becomes lower in AOGR mode than SR mode since the inlet natural gas flow rate decreases with recycling ratio (Figure 2, right). Thus, with recycling ratio above 0.30, less internal reforming would occur in the SOFC stack in AOGR than in SR mode.

The temperature limit of carbon formation in AOGR mode was calculated using HSC 6.1 [17] software to assess which experimental conditions could potentially lead to carbon formation in the reformer. According to the equilibrium calculations, the risk of carbon formation becomes more severe with lower recycling ratios (Figure 3). This is due to the lower oxygen-to-carbon ratio of the inlet gas, i.e., with lower recycling ratios, less steam and other oxygen containing species are recycled back to the system inlet. With recycling ratio below 0.5, the temperature limit of carbon formation is already above the typical operating temperatures of anode supported SOFCs (above 700 °C). On the other hand, reformer can be operated at lower temperatures, e.g., 500–600 °C depending on the system design, and therefore is more prone to carbon formation since thermodynamics predict an increased risk of carbon formation for decreasing temperature.
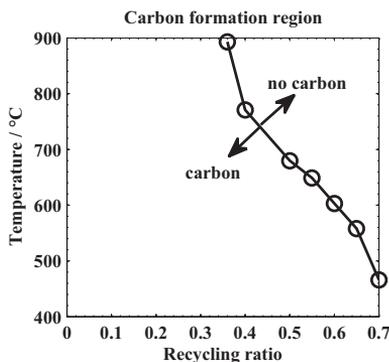

Fig. 3 Calculated temperature limit of carbon formation in AOGR mode.

To assess the characteristic performance of the reformer in AORG and SR modes the experimental results from gas analysis and the temperature measurement at the trailing edge of the catalyst were compared to the thermodynamic equilibrium at corresponding conditions. The equilibrium temperature and the composition of the reformate gas was calculated with Cantera toolbox [18] using GRI-Mech 3.0 reactions developed for natural gas combustion [19]. Equilibrium was solved for an adiabatic system, where the total enthalpy and pressure between reactants and products was kept constant, i.e., the total enthalpy of the inlet gases equals to the total enthalpy of the outlet gases and the sum of reaction enthalpies. Temperature measurement at the reactor inlet and measurements from mass flow controllers were used to define the inlet gas mixture temperature and composition for the calculations.

3 Results and Discussion

3.1 Performance of the Reformer in SR and AOGR Modes

The total duration of the experiment was over 2,500 h. During that time the reformer was used with a set of predefined operating conditions in SR and AOGR modes (Table 1). In order to achieve steady-state results, the reformer was left to stabilize for at least 24 h before each measurement. The measured inlet and outlet temperature, and the calculated reformer outlet temperature at equilibrium with different operating conditions are depicted in Figure 4. It can be seen that higher reformer outlet temperature can be achieved in AOGR mode than in SR mode. The measured and calculated equilibrium temperatures at reformer outlet correspond well in AOGR mode, where the difference between measured and calculated temperature is below 13 °C with every condition. However, in SR mode larger deviation exists between the measured and equilibrium outlet temperature, where the difference is 30–43 °C.

The measured and calculated molar fractions of methane and hydrogen in the reformer outlet gas are presented in Figure 5. The molar fractions are given on dry basis. Similarly to the reformer outlet temperature (Figure 4), there is a larger deviation between the measured and calculated values in SR than in AOGR mode. The difference between the values in SR mode cannot be explained only by the uncertainty related to the gas analysis (ca. 4% of the measured value).

Since both the outlet temperature and mole fraction of methane are higher than corresponding equilibrium values, kinetics are limiting the extent of the SR reaction. This indicates that either the space velocity should be decreased or the inlet temperature should be increased to achieve thermodynamic equilibrium. In AOGR mode and the same reactor inlet
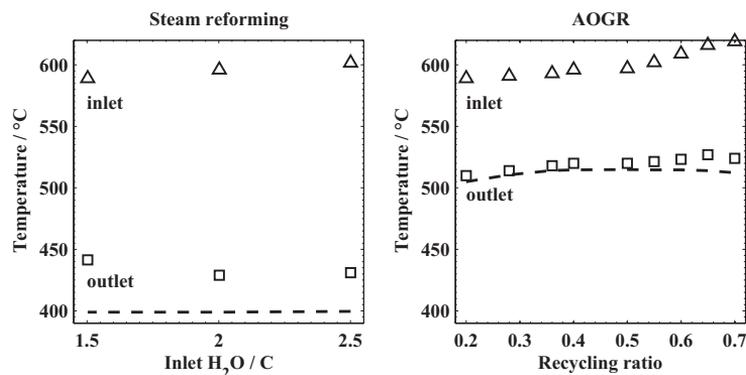
Fig. 4 Inlet and outlet temperature of the reformer in SR and AOGR modes. △: measured inlet temperature, □: measured outlet temperature, dashed line: calculated equilibrium outlet temperature.
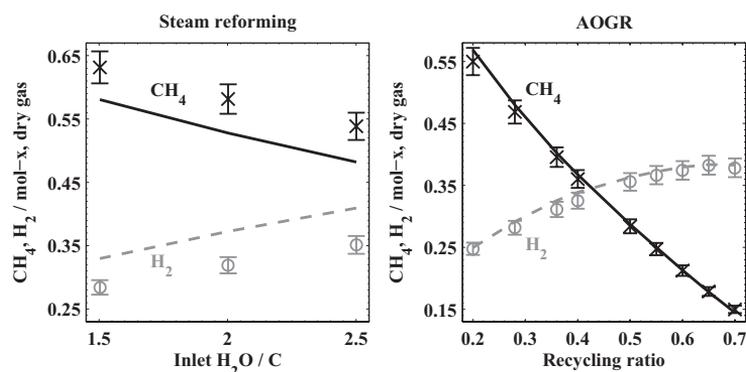

Fig. 5 Molar fraction of methane and hydrogen at reformer outlet with varying SR and AOGR conditions. Measured values are x: methane and ○: hydrogen. Calculated equilibrium values are solid line: methane and dashed line: hydrogen.
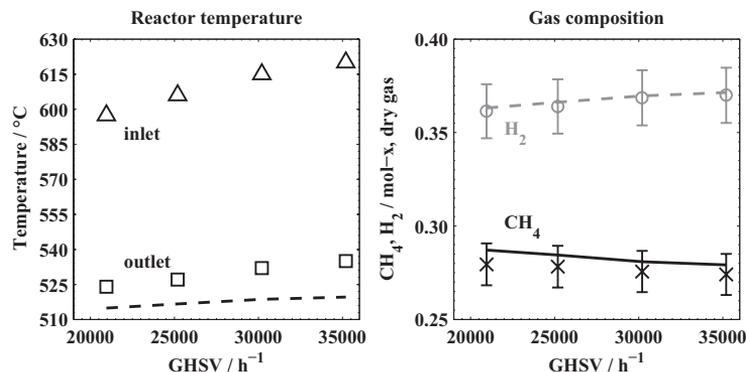

Fig. 6 Inlet and outlet temperature of the reformer operating in AOGR mode (left) and molar fraction of methane and hydrogen at the reformer outlet (right) with varying GHSV at recycling ratio of 0.5. Measured values are △: inlet temperature, □: outlet temperature, x: methane, and ○: hydrogen. Calculated equilibrium values are presented with lines.

The difference in behavior of the reformer in SR and AOGR mode with respect to achieving equilibrium could be explained by the lower fuel inlet flow rate in recycling condition (e.g., 3.2 L_N min^{-1} of natural gas for a recycling ratio of 0.5) compared to SR condition (4 L_N min^{-1}, see Figure 2). In order to investigate this reason, experiments were conducted in AOGR mode (recycling ratio 0.5) with varying space velocity and thus fuel inlet flow rate. The flow rate of gases was increased to the maximum that was possible with the test equipment. The space velocity and the natural gas flow rate were increased up to 35,000 h^{-1} and 5.4 L_N min^{-1}, respectively. The results depicted in Figure 6 show that there is no increasing deviation between experimental and equilibrium values for temperatures and gas composition. Therefore, it can be concluded that some other rate limiting phenomena are preventing the achievement of equilibrium condition in the SR conditions tested. Additionally, these results show that relatively high space velocity can be achieved using this type of precious metal based catalyst in AOGR mode. As a comparison, nickel-based catalyst have been used at much lower space velocity in the range of 2,000–6,000 h^{-1} [12].

3.2 Performance of the Reformer in Carbon Formation Prone Conditions

Periodically, the reformer was used in certain AOGR conditions for a much longer time to observe any changes in performance of the reformer due to carbon formation and accumulation in the catalyst, or due to other catalyst deactivation processes. The longest hold period used in this study was 1,000 h. In addition to the recycling ratio, the reformer reactor inlet temperature and/or space velocity was varied for selected experiment conditions to see any short term changes in the performance (Table 2). The primary characteristic performance measurements that were monitored during these extended holds were the reformer outlet gas composition, gas temperature, and pressure drop over the catalyst and filter. Additionally, after each extended hold period, the entire test equipment was flushed with nitrogen and air to

temperature at 600 °C, the measured values match well with the calculated values. Equilibrium is reached regardless of the recycling ratio which shows good characteristic performance of the reformer in AOGR mode.

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Table 2 Operating conditions during extended holds.

Hold no.	Recycling ratio	Inlet temperature (°C)	GHSV (h^{-1})	Hold time (h)
1	0.60	609	26,053	122
2	0.50	597	19,979	121
3	0.50	598	19,965	117
4	0.50	513	19,981	67
5	0.50	600	19,981	1,000
6	0.20	589	10,209	165
7	0.20	646	20,260	165

oxidize possible carbon deposits, and to detect any oxidized carbon as CO and CO_2 with the online gas analysis equipment. It should be noted that carbon formation is thermodynamically possible at the measured reformer reactor outlet temperature with all the conditions given in Table 2 (see Figure 3).

The reactor outlet temperature and fraction of methane at the outlet gas during the periods of extended hold, along with the corresponding equilibrium values, are depicted in Figure 7. It should be noted that no significant changes in the outlet gas composition or gas temperature occurs during the different hold periods. Concurrently, a good correspondence with equilibrium values is maintained over the hold period. Toward the end of the experiments, at low recycling ratio of 0.2, a small increase of methane fraction is observed at higher inlet temperature. However, with this low recycling ratio, carbon can already form readily at the operating temperature of the SOFC and it is very unlikely that an actual system could be operated safely with such a low recycling ratio without additional steam supply.

Similarly to the outlet temperature and methane fraction, the pressure drop over the reformer reactor and filter remained unchanged (measured changes in pressure drop <1 mbar) during the different operating conditions. Additionally, no carbon deposits were detected at the catalyst and downstream with the oxidation procedure performed at the end of each hold period. It is possible that minor carbon deposits were accumulated to the superheater located upstream to the catalyst, but the amount of carbon was very small, only a few milligrams, and did not increase during longer hold periods. These results clearly demonstrate that carbon formation is not occurring in the experimental conditions tested to an extent that would compromise the operation of this reformer in an SOFC system.

4 Conclusion and Future Work

The performance of a natural gas reformer with a precious metal catalyst was experimentally evaluated using a set of operating conditions in SR and AOGR modes. The experiments revealed that thermodynamic equilibrium was achieved in AOGR mode. On the other hand, in SR mode, equilibrium was not achieved; both outlet temperature and methane mole fraction were higher than the values at thermodynamic equilibrium. These results indicate that the SR reactions were kinetically limited and that the space velocities used in the experiments were too high to reach equilibrium.

Therefore, it is clear that equilibrium is more readily achieved in AOGR mode than SR with this precious metal catalyst. When these results are utilized for SOFC system design and operation, it can be concluded that the size of the catalyst and the reformer can be decreased when an anode off-gas recycling loop is used for fuel processing instead of SR.

The reformer unit was used for over 2,000 h with operating conditions where carbon formation is predicted at thermodynamic equilibrium. Recycling ratios as low as 0.2 were used during the experiments, which are already beyond safe operating limits in an actual SOFC system since carbon formation at Ni-YSZ anode would be expected. However, no significant changes in performance were observed based on measurements of outlet gas composition, pressure drop, and temperature. Additionally, the periodic oxidation cycles did not reveal any significant carbon deposits in the reformer. Therefore, no significant carbon formation occurred during the experiment that would change the characteristic perfor-
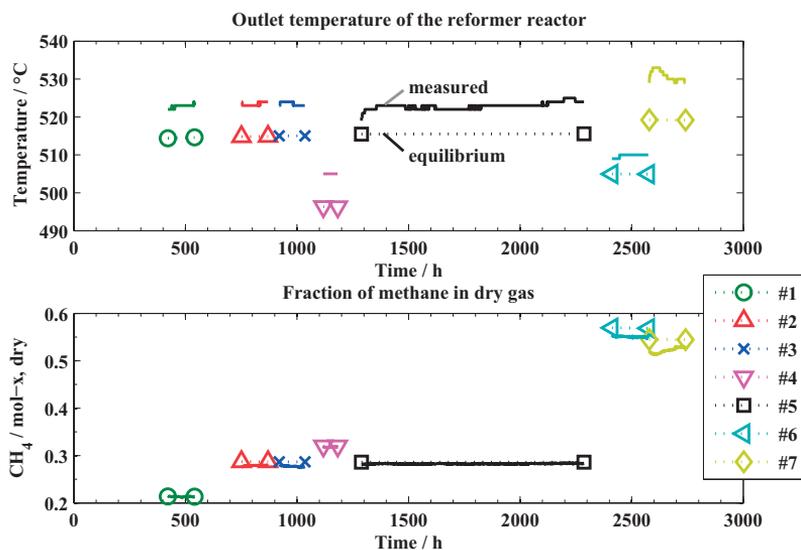
Fig. 7 Temperature (above) and mole fraction of methane (below) at reactor outlet during the experiment. The measured value is presented by a solid line and the calculated equilibrium value by a dashed line with markers at ends. Measured data in other process conditions is excluded to improve the clarity of the figure.

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mance of the reformer and compromise operation in SOFC system conditions.

According to the results presented in this study, the reformer unit is suitable to be used in an SOFC fuel processing system which includes an anode off-gas recycling loop. Since good correspondence with equilibrium was always reached when AOGR mode was used, further experiments are needed to assess the operating parameters, e.g., maximum space velocity, where equilibrium is not reached anymore. Furthermore, the natural gas used in the experiments contains less than 1% of higher hydrocarbons than methane. Sufficient conversion of C_{2+} hydrocarbons has to be addressed by conducting future experiments with a fuel gas that contains higher hydrocarbon content.

Acknowledgements

List of Symbols

$RR = \dfrac{\dot{V}^{recycled}}{\dot{V}^{out}_{SOFC}}$ Recycling ratio

$GHSV = \dfrac{\dot{V}^{in}_{reformer}}{V_{reformer}}$ GHSV of the reformer at NTP, h^{-1}

$FU_{SOFC} = \dfrac{I}{F\left(2\dot{n}^{recycled}_{H_2} + 2\dot{n}^{recycled}_{CO} + 8\dot{n}^{recycled}_{CH_4} + z_{NG}\dot{n}_{NG}\right)}$

Fuel utilization of the SOFC

$FU_{SYS} = \dfrac{I}{z_{NG}F\dot{n}_{NG}}$ Fuel utilization of the whole SOFC system

$O/C = \dfrac{\dot{n}_{CO} + 2\dot{n}_{CO_2} + \dot{n}_{H_2O}}{\dot{n}_{CH_4} + \dot{n}_{CO} + \dot{n}_{CO_2}}$ Oxygen-to-carbon ratio

F Faraday's constant, 96,485 A s mol^{-1}
I Current, A
$\dot{n}$ Molar flow, mol s^{-1}
$V_{reformer}$ Geometrical volume of the reformer
$\dot{V}$ Volume flow in NTP, m^3 s^{-1}
z_{NG} Valence number for natural gas

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