Diesel CPO for SOFC

Development of a cold-flame assisted CPO reactor coupled to a SOFC

H.A.J. van Dijk

J.P. Ouweltjes

R.G. Nyqvist

Version: Public Report

ECN-E--09-031 July 2009

Acknowledgement/Preface

For the coupling of the reformer to the SOFC set-up and testing of the SOFC the support of Hans van Wees and Danny Mahieu are gratefully acknowledged.

Abstract

This report describes the experimental results on the development of a diesel CPO reactor feeding a SOFC system. The goal of the project is to develop the technology required to transform a liquid logistic fuel into a reformat suitable for the operation of a SOFC. The application in mind is a small scale (5kW$_e$) diesel fed auxiliary power unit (APU).

To reform liquid fuel, the fuel must be evaporated and mixed with air before it is catalytically transformed into a $CO+H_2$ rich gas which can be fed to the SOFC. To this extent, a cold-flame assisted fuel evaporator/mixer was developed and coupled to a catalytic CPO reformer reactor. Part of the reformat is fed to a single cell SOFC, which basically serves as an analytical tool to verify the quality of the reformat.

Although the feasibility of cold-flame technology for the evaporation of the fuel was demonstrated, fouling of the reformer system by C-depositions prevented long-term operation of the reformer - SOFC combination. Different nozzle concepts have been tested. An air assisted swirler nozzle was fouled by C-deposition upon the nozzle itself, leading to a progressing decrease in spray quality. Using a capillary nozzle, fouling of the nozzle itself was suppressed. Its inherent lower spray quality, however, caused fouling of the catalyst structure by C-buildup.

Accordingly, fouling by C-deposition is identified as the bottleneck for the application of cold-flame technology for fuel evaporation and mixing.

Contents

List of tables

List of figures

List of abbreviations

ATR	autothermal reforming
CPO	catalytic partial oxidation
HEX	heat exchanger
PI	pressure indicator
SOFC	solid oxide fuel cell
TI	temperature indicator
TPR	temperature programmed reduction

Summary

Within the research program *Reforming of liquid fuels for fuel-cells*, ECN started a project on the development of a diesel CPO reformer for SOFC in 2005. The application in mind is a small scale (5kW$_e$) diesel fed auxiliary power unit (APU). The goal of the project is to develop the technology required to transform a liquid logistic fuel into a reformat suitable for the operation of a SOFC.

The emphasis of this work is on the development of a cold-flame assisted evaporator/mixer coupled to a catalytic CPO reformer. The application of cold-flame evaporation and mixing allows the reformat to be directly fed to the SOFC without further heating or cooling. Moreover, once cold-flames are ignited and stabilized, pre-heating of the air and fuel becomes obsolete. These aspects justify the development described in this report.

In the cold-flame evaporator/mixer, the cold-flames are stabilized by means of a recirculation tube. The momentum of the fuel spray of the nozzle induces the required recirculation. The cold flame evaporator/mixer was coupled to a catalytic reformer reactor, transforming the hydrocarbon+air feed into a $CO+H_2$ rich reformate.

The reformer was coupled to a SOFC to be able to verify the quality of the reformat obtained with this reformer. The SOFC therefore served as an analysis tool. Characteristically, the reformat was held at 800°C all the way towards the SOFC. For this, high temperature flange connections and steel-ceramic expansion connections were successfully applied.

It is demonstrated that that cold-flame evaporation of liquid fuels is a feasible means of feed preparation for a catalytic reforming reactor. The quality of the resulting reformat is adequate to be fed to the SOFC. The reformat quality, however, decreased with time-on-stream due to fouling of the reformer by carbon-depositions. These carbon-depositions were essentially located on the fuel injector, which is the coldest part of the reformer. The depositions were initiated by condensation of hydrocarbons. Although different nozzle configurations were tested, the depositions could not be suppressed sufficiently.

It was shown that the performance of the cold-flame evaporator strongly depends on the characteristics of the diesel spray feeding this evaporator. For a further development of the cold-flame evaporator, the spray characteristics in combination with the cold-flame reactions and the fluid recirculation within the evaporator should be modelled via computational fluid dynamics.

The second most important recommendation would be to test commercial diesels. In this study a fully paraffinic model diesel was used. The aromatics present in commercial diesel are known to significantly influence the cold-flame characteristics of the fuel since the aromatics are relatively unreactive at cold-flame conditions.

1. Introduction

In the last quarter of 2004, a project was started at ECN to develop a diesel fuel reformer to generate a reformat suitable for a solid oxide fuel cell. From a system-study [1], it appeared that diesel reforming by partial oxidation was the most promising route due to its simplicity:

1. no need for a recycle of anode off-gas or large cooling system to be able to feed water
2. the reformat of 800°C can direct be fed to the solid oxide fuel cell (SOFC)

Moreover, the efficiency was only significantly enhanced when recycling the anode off-gas. Recycling hot anode gas is technically very challenging.

The exothermal partial oxidation of a liquid hydrocarbon fuel is represented by:

$$C_nH_m + \frac{n}{2}O_2 \rightarrow n\,CO + \frac{m}{2}H_2$$

The stoichiometric O_2/C ratio is therefore 0.5. Thermodynamic calculations indicate that the syngas at 800°C mainly consists of CO + H_2 in N_2 with low amounts of CO_2, H_2O, and CH_4, see Figure 1.1. Using air as oxidant, the syngas composition is roughly represented by 50% N_2, 25% CO and 25% H_2. Both CO and H_2 are fuels for the SOFC.

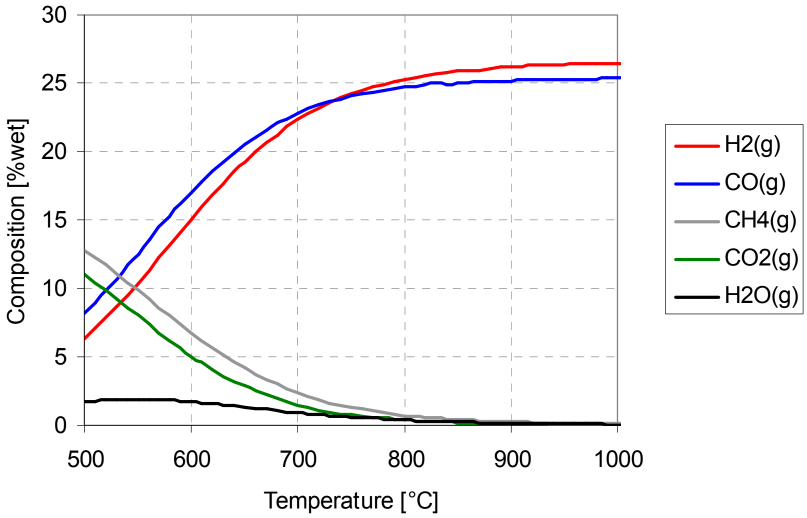

Figure 1.1 *Thermodynamic composition of the syngas as a function of temperature resulting from the CPO conversion of a diesel + air feed at 1 bara pressure (“diesel”=$CH_{2.1}$ (tetradecane), O_2/C=0.5)*

In 2005, a catalytic partial oxidation (CPO) reactor was developed using cold-flame technology to evaporate and mix the fuel and the air. Firstly, the stability of the cold-flame evaporation was studied. The cold-flames are stabilized by means of a self-induced recirculation flow, aided by an inner tube in the evaporator. Stable mixing temperatures of 400-500°C could be obtained at virtually no preheating of the air feed. Later in 2005, it was demonstrated that the cold-flame evaporator could successfully be connected to a catalytic CPO reactor. It did not appeared necessary to thermally disconnect the hot CPO reactor from the colder cold-flame evaporator. No ignition of the cold-flames into hot-flames was observed upon the coupling of the catalytic CPO reactor to the evaporator. Since 2006, the diesel reformer of the miniflow-3 test-rig has been connected to a single-cell SOFC test-rig.

In this note, the experiments with the reformer - SOFC combination are described. First, the experimental set-up will be described in detail. Some special features of the test-rig are given extra attention because of their uniqueness. Then the commissioning of the test-rig will be described. In the experimental section, three experiments with different configurations of the cold-flame assisted reformer are presented. For each experiment, the reformer is connected to a 10x10 cm^2 electrolyte supported SOFC-cell.

2. Experimental set-up

The experiments are conducted on the miniflow-3 test-rig, located in the Jules-Verne building. This set-up is designed for the processing of gaseous and liquid fuels on a 2kW$_{th}$ scale. The system consists of a catalytic partial oxidation reactor converting the diesel fuel and air into a reformat containing mainly CO, H_2, and N_2. Part of this reformat is fed to a single cell SOFC. The set-up is schematically represented in Figure 2.1. All components will be discussed in more detail below.

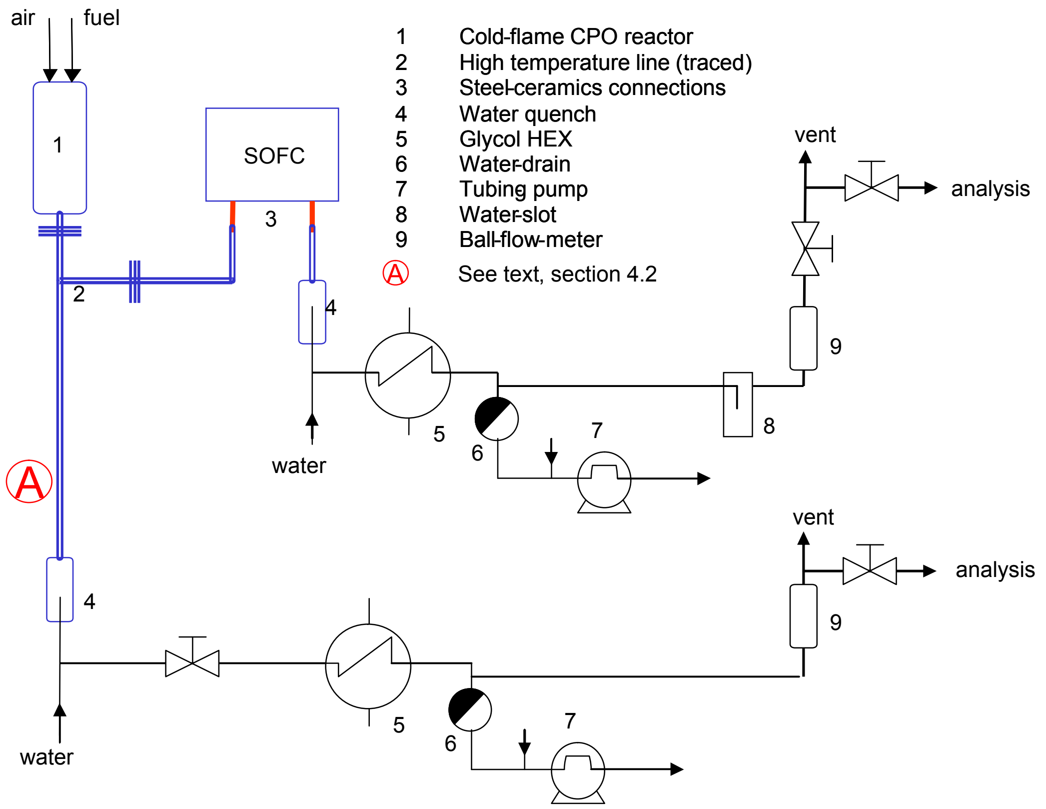

Figure 2.1 *Schematic representation of the CPO reformer - SOFC test-rig. Blue lines represent high-temperature components, red lines represent ceramic lines.*

2.1 CPO reformer

The CPO reformer consists of:

1. a diesel injection system
2. a cold-flame evaporator zone
3. a catalytic reforming zone.

It is schematically represented in Figure 2.2. The system components are discussed in more detail in the paragraphs below.

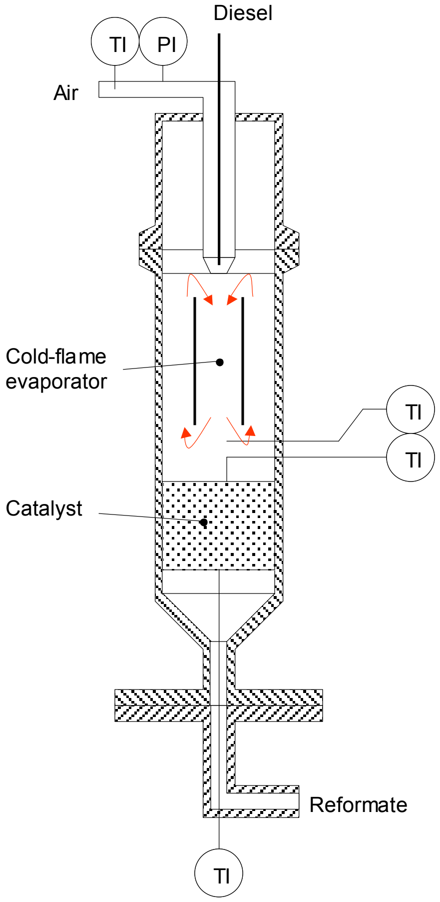

Figure 2.2 *Schematic representation of the CPO reactor*

2.1.1 Diesel injection system

Diesel is injected into the reactor by means of a nozzle. The initial experiments are conducted using a commercial Delavan air atomizing nozzle (SNA type), see drawings A 1 and A 2 in Figure 2.3. The nozzle produces a full-cone spray. The cold diesel is fed through a capillary attached to the swirler of the nozzle. Preheated air is fed to the nozzle. Overheating of the diesel feed in the capillary is prevented by a thermal barrier in the form of a stagnant air layer. Typically, all air needed for the process is fed through the nozzle and thus used for fuel atomization.

Because preheating of the air is not required (see below in paragraph 2.1.2), the nozzle is much colder than the recirculation flow in the evaporator. Hydrocarbons easily condense on the cold nozzle leading to C-deposition and negatively affecting the quality of the spray. Shielding the nozzle is required and can be realized by a cap and/or shroud air. The shield in drawing A 1 has a large hole for the spray, while the shield in drawing A 2 has a small hole. Both shields are not connected to the nozzle so they will not be excessively cooled by the cold nozzle.

In an attempt to further suppress C-deposition on the nozzle, the nozzle concept was changed from air-assisted atomization to capillary injection and atomization of the diesel. This home-made nozzle is schematically represented by drawing B in Figure 2.3. An air-jet is created by the annulus and the diesel is fed via 4 capillary holes in the central tube, perpendicular to the air-flow. Accordingly, a liquid film is produced on the tip of the central diesel tube, which transforms into a spray at the tip of this diesel tube. This nozzle was applied in combination of the same shield as in drawing A 2.

The advantage of this nozzle is that the outer parts of the nozzle are not contacted with the diesel because they are shielded by the annular air flow. Only the central tube is wetted. Note that this is not the case for the air-assisted nozzle, where the body of the nozzle can be wetted by the full cone spray leaving the nozzle, see lower right hand scheme in Figure 2.3.

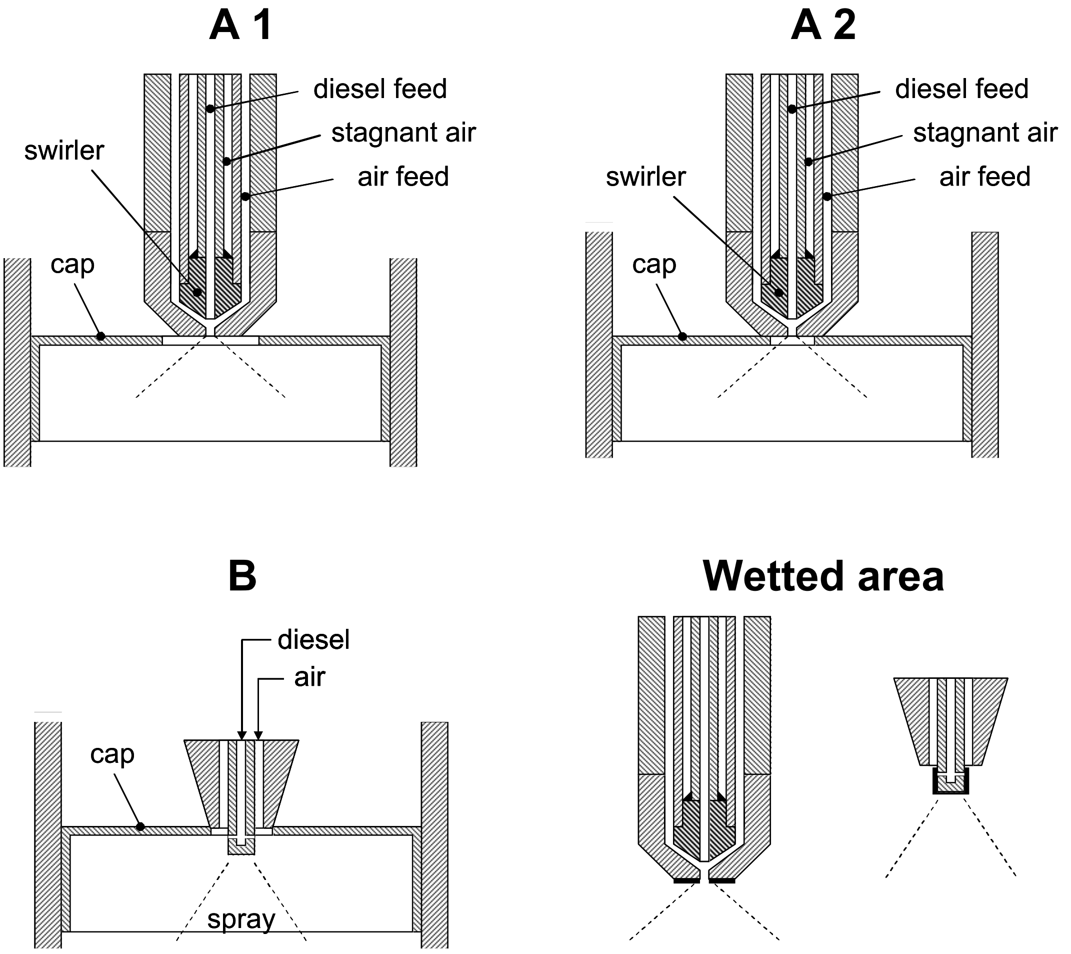

Figure 2.3 *Schematic representations of the nozzle concepts used. A1) commercial air-assisted nozzle with large-hole shield, A2) commercial air-assisted nozzle with small-hole shield, B) home-made capillary injection nozzle with loose shield, wetted area) thick lines represent the wetted area for the 2 nozzle types*

The experiments have been done using Hydroseal G232H to represent a clean diesel fuel. This is a commercial paraffinic solvent having a relatively narrow boiling range of 235°C-265°C, which is typically at the 50% boiling point for commercial diesels. It does not contain sulphur and is low in aromatics (<100weightppm). Moreover, it does not contain any additives that commercial diesels have. The average chemical composition of Hydroseal G232H is represented by tetradecane, *i.e.* $C_{14}H_{30}$.

2.1.2 Cold-flame evaporator

For stable catalytic reforming of liquid hydrocarbon fuels, it is essential that the feed is uniform in composition [2,3]. This means that the fuel must be fully evaporated and mixed with the air feed before the catalyst zone is entered. This is the prime function of the cold-flame evaporator described below.

Using CPO reforming without any pre-heating of air and fuel, the thermodynamic exit temperature at $O_2/C=0.53$ is in the order of 800°C. This reformat can thus directly be fed to the SOFC. However, reliable CPO reactor operation requires a fully evaporated fuel which is perfectly mixed with the air. This can only be realized if heat is added to this process of mixture formation. Pre-heating of the air is not an option because the reformat outlet temperature will be too high. Therefore, heat production during mixing by using cold-flames is an ideal choice.

The cold-flame evaporator consists of a mixing chamber in which a recirculation tube is placed. The momentum of the centrally injected spay induces a recirculation flow. At a sufficiently high temperature, homogeneous gas-phase combustion reactions are ignited in the diesel-air mixture. At carefully chosen conditions, these oxidation reactions are in the cold-flame regime. Characteristic for this regime is that the oxygen consumption is limited and, accordingly, the heat-production is limited. The cold-flame regime can be considered as a pre-stage for complete combustion, *i.e.* the hot-flame regime. In the cold-flame regime, the major reaction products are oxygenated hydrocarbons and olefins instead of CO_2 and H_2O for complete combustion. The reactive intermediate is believed to be a hydroperoxide radical (•ROOH) [4,5,6]. The abundance of this intermediate strongly decreases with increasing temperature. This characteristic prevents the cold-flame regime to automatically transform into the unwanted hot-flame regime. As such, the cold-flame regime stabilizes itself. Depending on the inlet conditions and fuel characteristics, typical stable cold-flame reaction temperatures are between 300°C and 500°C. With Hydroseal G232H, reaction temperatures between 400°C-450°C are typically observed. At these temperatures, the evaporation of the diesel is complete and the mixing is good. The cold-flame regime in the reactor is stabilized by the self-induced recirculation flow of hot gas. Because of the heat-production in the cold-flame regime, preheating of the diesel and/or air is obsolete. Typically, the diesel is not preheated while the air is preheated to 100°C only.

With an $O_2/C=0.53$ ratio of the feed, the cold-flame evaporator typically has an O_2 conversion of 30% at a cold-flame temperature of 400°C, while the conversion of diesel into CO and CO_2 (typical combustion products) is only 10%. The O-selectivity towards the combustion products CO, CO_2, and H_2O is only about 20%. These results illustrate the most characteristic features of the cold-flame regime:

- i) the O_2-consumption is limited;
- ii) only a limited amount of diesel is converted into CO and CO_2;
- iii) oxygenated and unsaturated hydrocarbons are important reaction products.

Due to the chemical reactions in the cold-flame evaporator, the effective O_2/C ratio of the feed is reduced from 0.53 to typically 0.40. The S/C ratio is increased from 0.0 to 0.10.

2.1.3 Catalytic reforming zone

For stable catalytic reforming of liquid hydrocarbon fuels, it is required that the feed is uniform in composition. If this is met, it is known from previous projects that a commercial reforming catalyst can process liquid fuels to a reformat essentially free of hydrocarbon slip.

It has been demonstrated that the downstream catalytic reactor does not influence the performance of the cold-flame evaporator. Apparently, no significant thermal interaction of the hot catalyst top surface (typically 800-900°C) with the cold-flame recirculation flow exists (typically 400-500°C).

The temperatures of the catalyst top and bottom are measured using thermocouples. They are contacted with the catalyst as good as possible. Especially for the catalyst top, this is troublesome and the absolute value of the measured temperature is not reliable. It may be expected that the maximum catalyst temperature is higher than measured with this thermocouple. Contacting the bottom thermocouple with the catalyst is much easier. This measured temperature is therefore expected to be representative.

Because of the relatively small scale of the reactor and its high temperature, heat losses of the reactor are considerable. The heat-loss of the catalyst section is compensated by placing a high temperature heating tape having a temperature just below the catalyst exit temperature. Illustrative, without heat-compensation a reactor outlet temperature of 650°C is observed, while applying heat compensation 780°C was obtained (maintaining the heating tape at 775°C).

2.2 The SOFC

The ECN electrolyte supported SOFC membranes are tested in a ceramic cell housing, Figure 2.4, with corrugated alumina flanges for gas distribution, platinum mesh for cathode current collection, and nickel mesh for anode current collection. The anode chamber is sealed. The current leads consist of a bundle of sixteen 0.5 mm thick platinum wires. These wires are spot-welded onto the current collecting gauzes at regular distances over the entire surface. The voltage terminals are single platinum wires, spot-welded 1 cm from the outer rim on the current collecting meshes. Air is available as oxidant flow. Hydrogen, nitrogen, carbon monoxide, carbon dioxide and methane are available for reference measurements of the electrochemical performance and to keep the cell in operation during the periods that no reformat fuel is available.

The membranes are characterized by measuring the so-called I-V behavior. The I-V characteristics are taken with upgoing current in steps of 1 A, and stabilization time at each step of approximately 20 seconds, by using a Kikusui electronic load (Kikusui Electronics Corp, Japan) in conjunction with an additional power supply in current-following mode (Delta Elektronica, Zierikzee, Netherlands). This additional power supply is needed because the electronic load is not able to control the low voltage output of the fuel cell alone. The electrical connections of the test-rig are shown in Figure 2.5.

For anode sealing of electrolyte supported cells, a gold seal is used which is placed along the sides where it is directly in contact with electrolyte. This gold seal has a width of 5 mm. The thickness is chosen in such a way that good electrical contacting between the cell and the anode current collecting mesh is obtained.

Figure 2.4 *Ceramic cell housing used for the SOFC tests. The anode flange and current collecting mesh are shown on the left hand side, and the total set-up on the right hand side.*

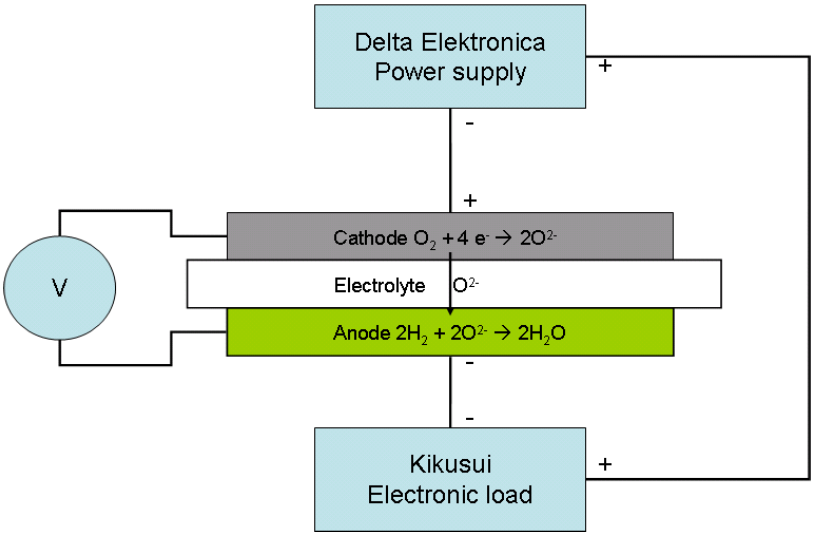

Figure 2.5 *Electrical connections for the SOFC*

2.3 The reformer - SOFC connection

The reformat produced in the reformer typically has a temperature of 800°C. At C=0.53 and S/C=0, the analysed composition of the reformat is 24% H_2, 25% CO, 1% CO_2, 1% H_2O and 0.5% CH_4 with balance N_2. This composition corresponds to thermodynamic equilibrium, see Figure 1.1, except for the slightly higher CH_4 content. The total flow is about 12 $Nl.min^{-1}$. The SOFC test-rig is equipped with a single 10x10 cm^2 electrolyte supported cell, needing an anode feed of up to 1 $Nl.min^{-1}$. Splitting of the reformat flow coming from the reformer is mandatory. Both the main-flow as the flow coming from the SOFC pass ball-flow meters, allowing a sufficient accurate monitoring of the flow through the SOFC.

The cathode of the SOFC cell is continuously fed with a dry air-flow of 1.5 $Nl.min^{-1}$.

Since the reformat has a high tendency towards C-deposition it should not be allowed to cool. Accordingly, all piping containing this reformat is maintained at 800°C. All connections in this hot section are realized by flanges (packing material=thermiculite). Critical points in this hot section are the SOFC in- and outlets, where the steel tubes need to be connected to the ceramic tubes entering the SOFC compartment. These couplings are realized via a thermal expansion connection: the steel tube is placed into the ceramic tube and the diameters are chosen such that due to the difference in thermal expansion the fit is tight at 800°C (linear thermal expansion coefficient for the steel=1.25E-05 $m.m^{-1}.K^{-1}$ for 25°C-800°C, linear thermal expansion coefficient for the ceramic=7.73E-06 $m.m^{-1}.K^{-1}$ for 25°C-800°C).

Care is taken to avoid stresses from the tubing on the ceramic parts via:

i) a thermal expansion U-turn at the inlet, which has been annealed after welding
ii) a bulge in the outlet at the cold part downstream the water-quench

The outlet of the SOFC and the main flow downstream the splitting point are instantly cooled using a water quench. Water is injected into a metal wire structure (material=FeCrAlloy), assuring homogeneous evaporation. Rapid cooling and the generation of steam avoid C-deposition.

3. Commissioning of the test-rig

The most critical mechanical point in the whole experimental set-up are the steel-ceramics expansion connection. The system leak was determined by using the water-slot (8 in Figure 2.1): the N_2 flow was lowered until bubbles ceased to occur. This flow was taken as the total leak of the system. At 800°C, the leak for the whole system (=reformer+SOFC, including 2 flange connections and 2 steel-ceramics connections at 800°C) at a slight overpressure of 5 mbarg was in the order of 10 $ml.min^{-1}$. At a working pressure of 30 mbarg, the leak was in the order of 100 $Nml.min^{-1}$. These leak-rates are considered acceptable and it was concluded that the expansion connections worked properly.

The control software of the miniflow-3 test-rig controls all safety actions, except for the temperature of the SOFC furnace, which is controlled in the SOFC test-rig. The most important safety actions were checked during commissioning. At emergency, the whole system is instantaneously flushed with N_2, while all temperatures are set to 25°C. The accompanying pressure-pulse of 80 mbarg does not influence the leak-tightness of the system.

During start-up, the flow towards the SOFC set-up would be cut for a few minutes due to the relatively poor reformat quality during start-up (high hydrocarbon slip). The start-up protocol is represented in Appendix A.

4. Experimental results using nozzle A1

4.1 General description

For the tests an electrolyte supported SOFC-cell was used. The cell was operated for some 1000 hrs in total. The cell was fed three times with reformat from the reformer: 1st run for 5 hrs, 2nd run for 7 hrs, and 3rd run for 35 hrs. In between, the cell was operated with H_2. The performance of the cell was frequently characterized with IV-curves, both in operation with H_2 as with reformat. All experimental runs are discussed in chronological order.

4.2 Experimental results

During commissioning, the control of the power of the wire-element of the SOFC inlet pipe was too rough (on/off) and it failed. Since replacement of this element requires an almost complete dismantling of the gas-inlet system, it was decided to continue the experiments at a risk of line blockage by C-deposition at cold-spots.

For the first run with reformat, the temperatures of the reformer are shown in Figure 4.1. At about t=2 hrs, the system was started-up. Immediately after start-up, the gas-inlet temperature was lowered to 100°C. At this temperature, the cold-flame evaporator produced a mixture at 425°C. The catalyst top was 725°C, while the catalyst bottom was 800°C. This catalyst bottom temperature is considered typical for the reformer. The catalyst top temperature was lower than expected, probably due to imperfect contact of the thermocouple with the catalyst.

The corresponding dry composition of the reformat is represented in Figure 4.2. During the experiment, the gas sampling alternated between the reformer and the SOFC. The composition of the reformat entering the SOFC unit is roughly indicated in Table 4.1. Note that the composition is given on a dry basis and that the reformat has a low water content of 0.41%.

Table 4.1 *Composition of the reformat at the reformer and SOFC outlet for the 1st run. The SOFC was operated at 60% utilization.*

component		reformer outlet	SOFC outlet
H_2	%dry	24.9	8.7
CO	%dry	24.0	10.5
CO_2	%dry	1.22	20.6
H_2O	%wet	0.41	n.d.
CH_4	ppmdry	3150	0
$C_2H_6/C_2H_4/C_2H_2$	ppmdry	130/675/6	0/0/0
C_3H_8/C_3H_6	ppmdry	15/200	0/0
C_4H_{10}/C_4H_8	ppmdry	5/0	0/0
$C_5H_{10(+2)}/C_6H_{12(+2)}$	ppmdry	0/0	0/0
Backflush (C_6+)	Ppmdry	900 (as CH_2)	220 (as CH_2)

The reformer had a C-based conversion of the diesel to $CO+CO_2$ of 97.5%, meaning that 2.5%C was in the form of hydrocarbon slip. Of this slip, CH_4 was the main component, accounting for 1.2%C. The C-based conversion to $CO+CO_2+CH_4$ was thus 98.7%.

The utilization of the reformat by the SOFC is defined as:

$$Utilization = 1 - \frac{\left(x_{CO} + x_{H_2}\right)_{SOFC,outlet}}{\left(x_{CO} + x_{H_2}\right)_{SOFC,inlet}} \tag{1}$$

where x_i represents the molefraction on dry basis of component i. Note that the hydrocarbons in the reformat are consumed but are not considered in equation (1).

The SOFC was operated at 60% utilization and converted practically all hydrocarbons present in the reformat as is observed in Table 4.1. This holds for both the saturated hydrocarbons as the unsaturated hydrocarbons. Only a C_6+ slip was maintained at 220 ppmdry (expressed as CH_2 equivalent) in the SOFC outlet.

The performance of the cell is represented in Figure 4.3. Here, the cell-voltage, cell-current, and SOFC operating temperature are shown. The system pressure was constant at typically 22 mbarg. It was higher during start-up because the system is heated using 15 $Nl.min^{-1}$ N_2.

For the first hours, the cell was operated at a load of 30 A, but this was increased to 40 A at t=3.9 hrs. In order not to have a too high utilization at this point, the dry SOFC anode outlet flow was increased from 0.42 $Nl.min^{-1}$ to 0.63 $Nl.min^{-1}$. At 40 A load, the cell voltage was 623 mV.

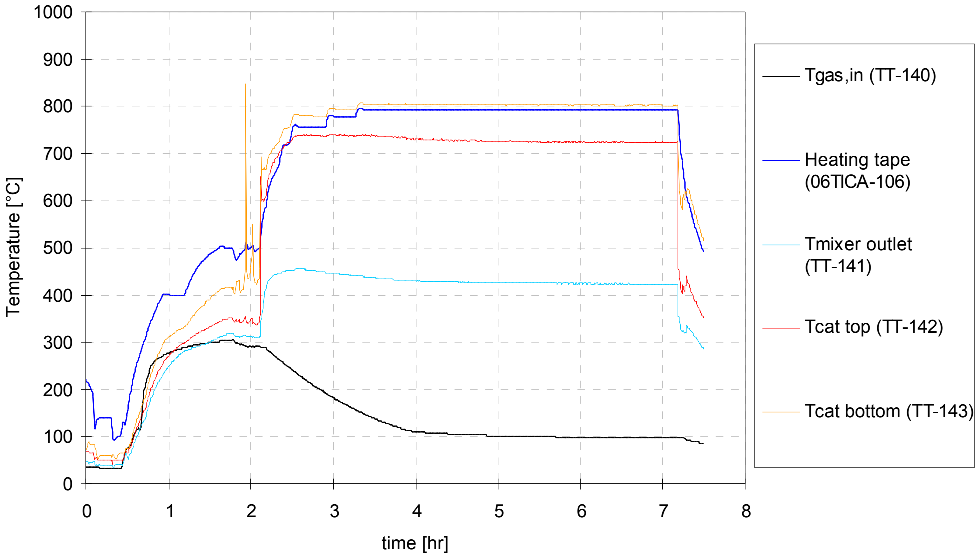

Figure 4.1 *Temperatures of the gas inlet, cold-flame mixer, catalyst top, and catalyst bottom during the 1st run*

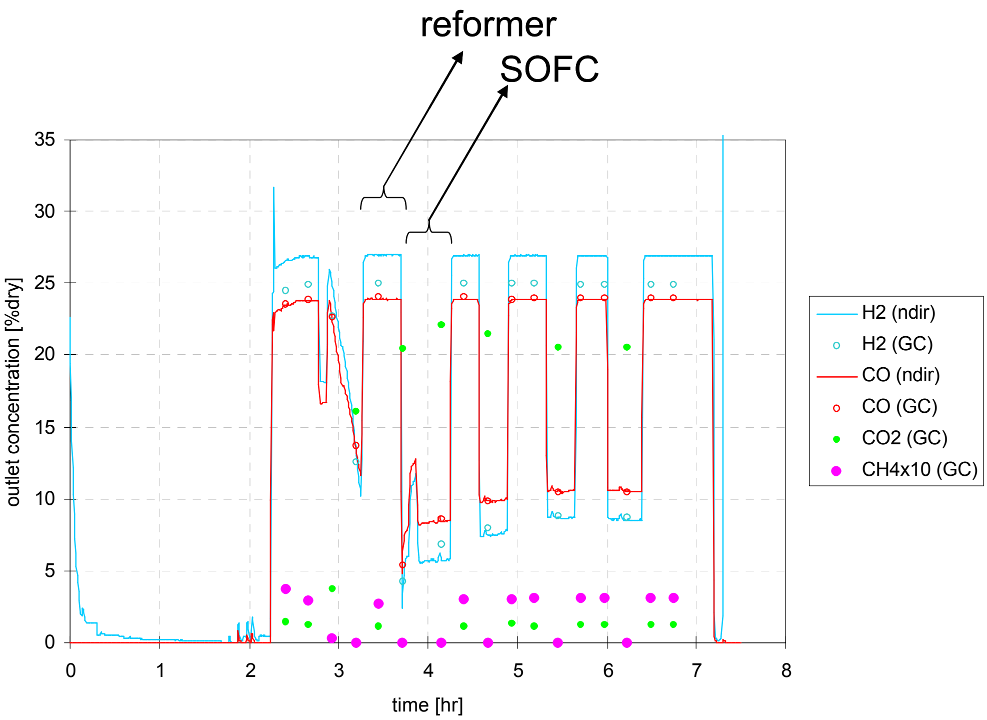

Figure 4.2 *Composition of the reformat alternating between reformer and SOFC*

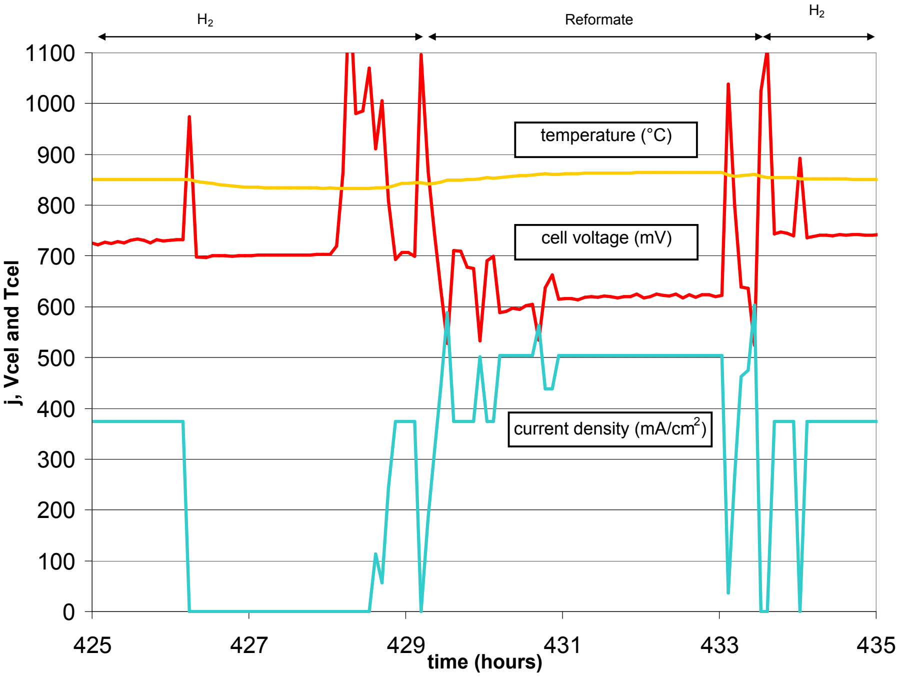

Figure 4.3 *SOFC performance and operating temperature during the 1st run with reformat*

In the 2nd test with reformat, the cell was operated with reformat for 7 hrs. The current was held at 40 A and the SOFC outlet flow at 0.83 Nl.min^{-1} to obtain a fuel utilization of about 50%. The performance of the reformer was comparable to the performance observed in the previous experiment: temperature levels were similar and the C-based conversion was similar. The total hydrocarbon slip was similar, with the only difference that the C_2+C_3 slip was somewhat higher and the C_4+ slip somewhat lower, see Table 4.2. There is no explanation why. Again, the SOFC consumed all hydrocarbons, except for the heavier C_6+ fraction of which only about half was consumed. At 40 A, a cell voltage of 620 mV was obtained, which is comparable to the previous test.

Table 4.2 *Composition of the reformat at the reformer and SOFC outlets for the 2nd run. During the gas analysis, the SOFC was operated at 50% utilization (40 A).*

Component		reformer outlet	SOFC outlet
H_2	%dry	24.7	11.4
CO	%dry	23.9	13.0
CO_2	%dry	1.27	17.3
H_2O	%wet	0.41	n.d.
CH_4	ppmdry	3500	0
$C_2H_6/C_2H_4/C_2H_2$	ppmdry	130/700/15	0/0/0
C_3H_8/C_3H_6	ppmdry	17/240	0/0
C_4H_{10}/C_4H_8	ppmdry	8/0	0/0
$C_5H_{10(+2)}/C_6H_{12(+2)}$	ppmdry	0/0	0/0
Backflush (C_6+)	ppmdry	360 (as CH_2)	200 (as CH_2)

In the 3rd run, the system was operated for a longer time at 50% utilization. During this test, the cell voltage gradually decreased, see Figure 4.4. The hydrocarbon slip, together with the dry concentrations of H_2 and CO, are represented in Figure 4.5 for the three experimental runs together. It is observed that the initial performance of the third run is in line with the performance observed in the two previous runs. Similar hydrocarbon slips were observed initially. Gradually, the hydrocarbon slip increases. Note that the H_2 and CO concentrations remain fairly constant over the whole period. They are therefore no good indicators for the performance of the reformer, while the hydrocarbon slip is.

The temperature levels of the reformer and system pressure are represented in Figure 4.6 for the three experimental runs together. Although initially the reformer behaved as observed in the former two runs, the system pressure and the cold-flame mixing temperature gradually change in time: the cold-flame mixing temperature decreased and the system pressure increased.

A decrease of the mixing temperature indicates a worsening of the performance of the evaporator, probably caused by fouling of the nozzle. From previous experiments it is known that fouling of the nozzle by C-deposition leads to poorer spray quality. An increase in the droplet size together with a lower degree of recirculation in the mixer leads to a poorer mixing/evaporation quality. At a decreasing homogeneity of the feed entering the catalyst zone, the catalyst looses activity and selectivity, leading to an increase in the hydrocarbon slip. Following this test, the diesel injection system was dismantled and the nozzle indeed displayed severe C-deposition, see Figure 4.7.

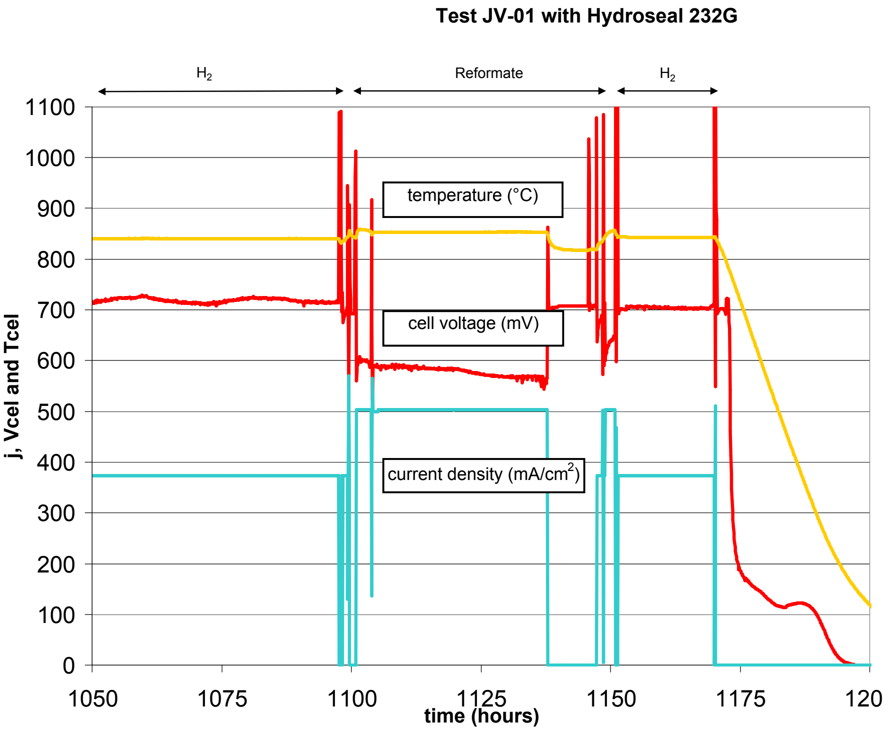

Figure 4.4 *SOFC performance and system pressure during the 3rd run with reformat*

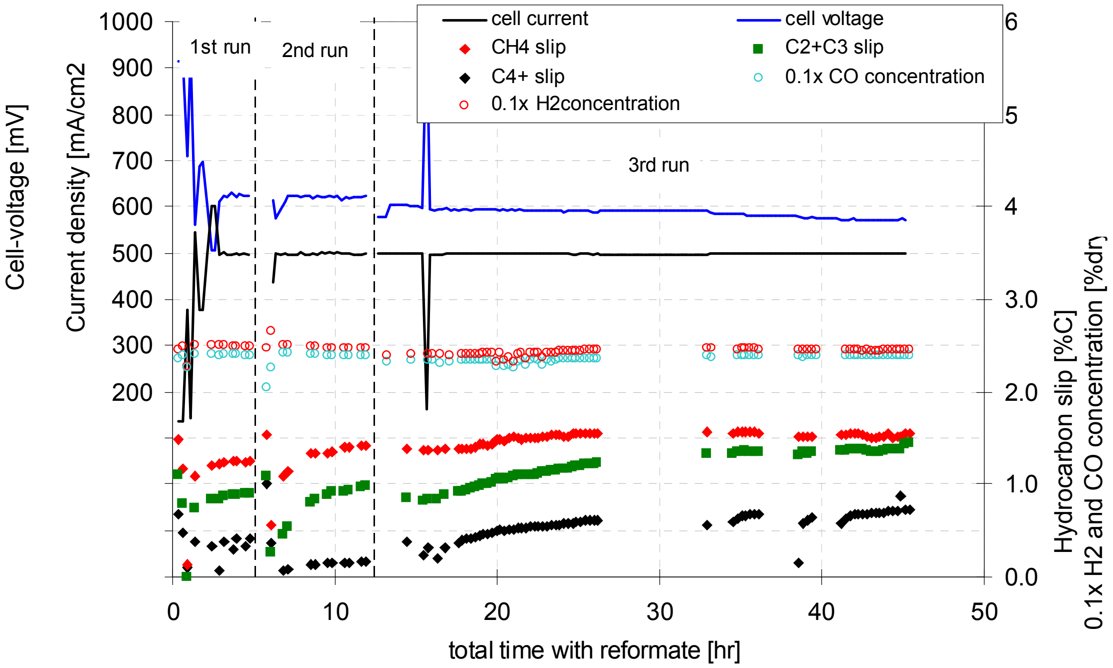

Figure 4.5 *Cell and reformer performance in terms of cell current and voltage (left scale) and H_2 and CO concentrations and hydrocarbon slip for the three experimental runs together(right scale)*

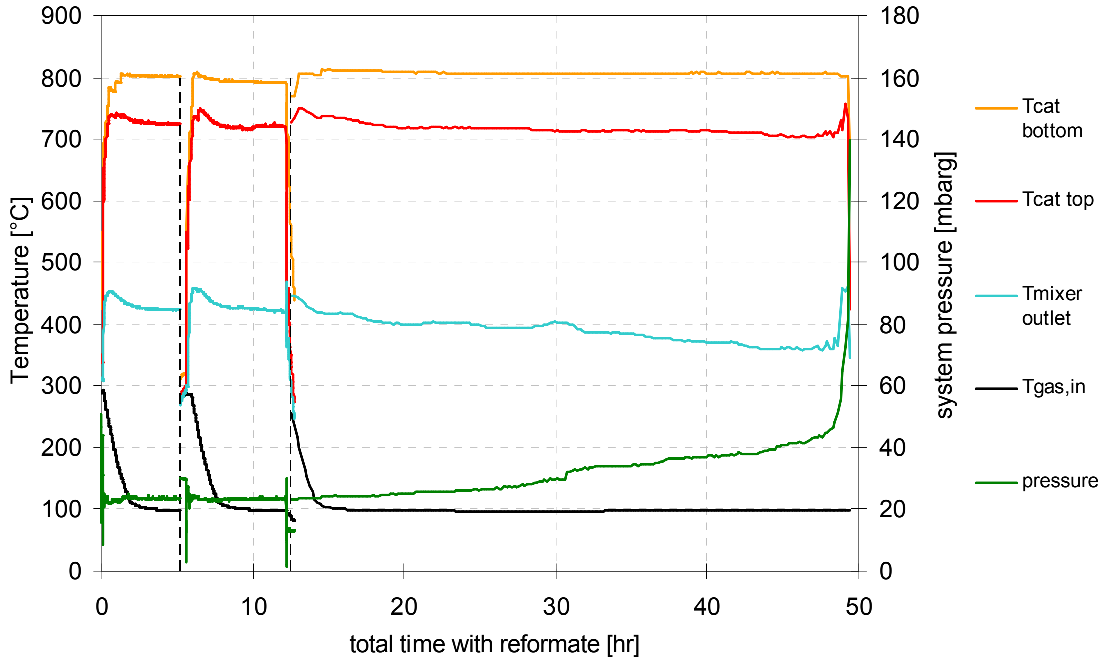

Figure 4.6 *Reformer temperatures for the three experimental runs with reformat put together*

Figure 4.7 *Carbon deposition on the nozzle*

It is believed that C-deposition on the nozzle is the limiting factor for long-term operation. In previous experiments, this C-deposition was already suppressed by adapting the geometry of the injection system. However, the problem has not been solved yet.

Typically, C-deposition in the cold-flame mixing chamber is observed on parts that are relatively cold during operation. For example, the recirculation tube is hot and normally free of any C-deposition. In this tube C-deposition is only observed in case the spray is affected to such a large extent that droplets directly incline with the tube wall. The nozzle, however, is generally cold and displays severe C-deposition. The first generation caps intended to shield the nozzle from the mixing-zone were thermally connected to the nozzle and displayed C-deposition as well. Later generations are thermally uncoupled and are normally free of C-deposition. C-deposition on the nozzle tip, however, has not been prevented successfully yet. The tip is always exposed in the mixing chamber and wetting is difficult to prevent. Using shroud air (also known as secondary air), C-deposition was suppressed in previous experiments, but not prevented.

The increase in system pressure is due to C-deposition in the pipe just upstream the water quench of the miniflow-3 test-rig, position (A) in Figure 2.1. This piece of pipe was not actively heated because of heater failure and apparently the temperature was too low to prevent C-deposition. Just before the experiment was terminated (emergency shut-down), the pressure suddenly increased rapidly, see Figure 4.6. At that moment, the temperature of the cold-flame evaporator also increases and the cold-flame transforms into hot-flame. Typically, the temperature of the catalyst top becomes instable when this happens.

The conversions of CO, H_2, and CH_4 by the SOFC are given in Figure 4.8. It is observed that all conversions decreased in time. In principle, this was caused by the C-deposition described above causes an increase in gas flow towards the SOFC test-rig, decreasing the utilization of the reformat. However, deterioration of the cell performance could also contribute to the drop in conversion by i) deactivation of sites which are catalytically active for steam reforming or water gas shift, and ii) changes in microstructure. From I-V measurements with hydrogen before and after the third reformer test, shown in Figure 4.9, and the stable performance with hydrogen after the third reformer test, it can be said that permanent deactivation of the cell had occurred during the third test with reformat.

The composition of the reformat at t=28 hrs for ther 23rd run is given in Table 4.3 (28 hrs for the 3rd run corresponds to a total accumulated time of 39 hrs in Figure 4.5). At this point, the utilization is low at 36% and the SOFC displays quite some hydrocarbon slip. It is, however, remarkable that the C_6+ slip of the SOFC hardly changes while it drastically increased for the reformat leaving the reformer. Typically, the C_6+ hydrocarbon slip leaving the SOFC remains at the 200 ppmdry level observed in Table 4.2 and Table 4.3. Apparently, the higher hydrocarbons are converted in the SOFC (in analogy with steam-reforming).

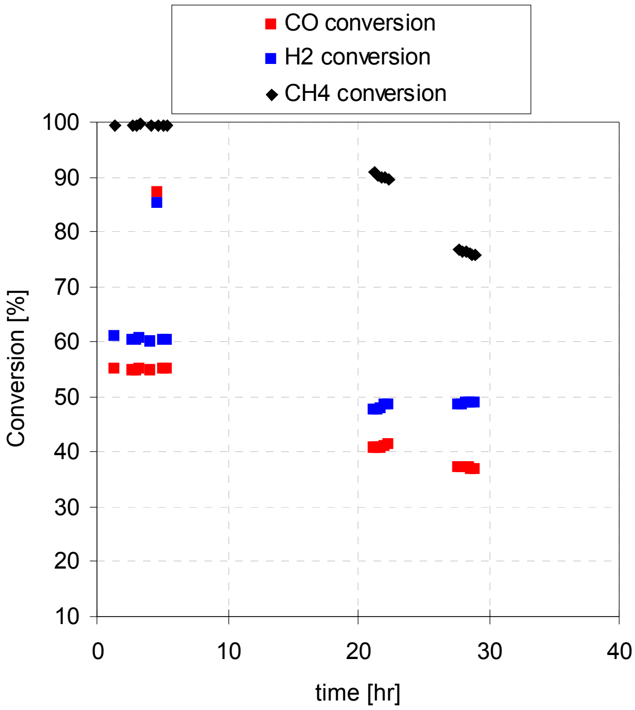

Figure 4.8 *Conversion of CO, H_2, and CH_4 by the SOFC for experimental run 07-08-2006*

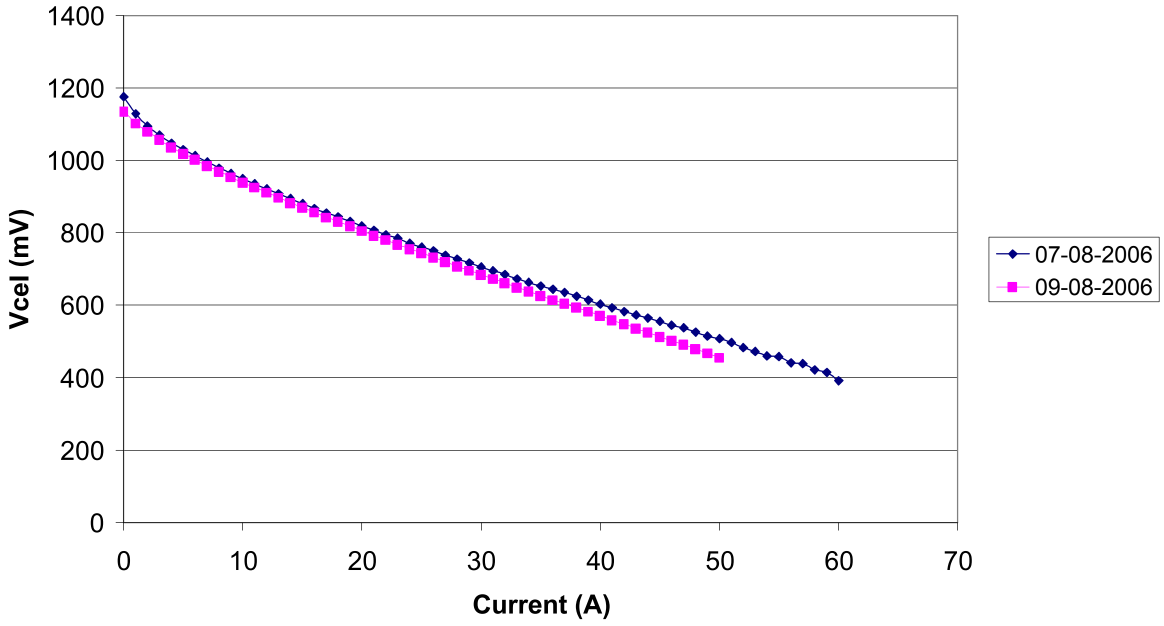

Figure 4.9 *I-V measurements with 500 Nml.min*$^{-1}$ *H_2 at 850°C, before and after the third reformer test*

Table 4.3 *Composition of the reformat at the reformer and SOFC outlets for the 3rd run at t=28hrs. The SOFC is operated at 36% utilization.*

component		reformer outlet	SOFC outlet
H_2	%dry	25	14.2
CO	%dry	24	17.0
CO_2	%dry	1.2	12.5
H_2O	%wet	0.41	n.d.
CH_4	ppmdry	3900	1050
$C_2H_6/C_2H_4/C_2H_2$	ppmdry	240/1040/26	6/3/0
C_3H_8/C_3H_6	ppmdry	23/260	0/0
C_4H_{10}/C_4H_8	ppmdry	8/5	0/0
$C_5H_{10(+2)}/C_6H_{12(+2)}$	ppmdry	0/0	0/0
Backflush (C_6+)	ppmdry	1700 (as CH_2)	190 (as CH_2)

Figure 4.10 shows the anode surface of the cell after testing, from which it can be seen that the anode retained its greyish colour due to the presence of nickel. Darker lines were visible at the anode outlet. This is normal for tested anodes. In Figure 4.11, cross sections of reduced anode before and after the test are shown, from which it can be seen that delamination of the nickel contact layer occurred. It can also be seen that agglomeration of nickel occurred the most at the anode inlet. Most likely, the electrochemical degradation that was observed during the test is related to the sintering of nickel and possibly also delamination of the anode contact layer. TPR measurements (100-1000ºC) revealed that 3.2 w% carbon had deposited in the anode during the test. This is less than the total amount of C_6+ hydrocarbons that passed the fuel cell. It is therefore assumed that C_6+ the hydrocarbons were mainly reformed by the anode.

Figure 4.10 *Anode surface after the test*

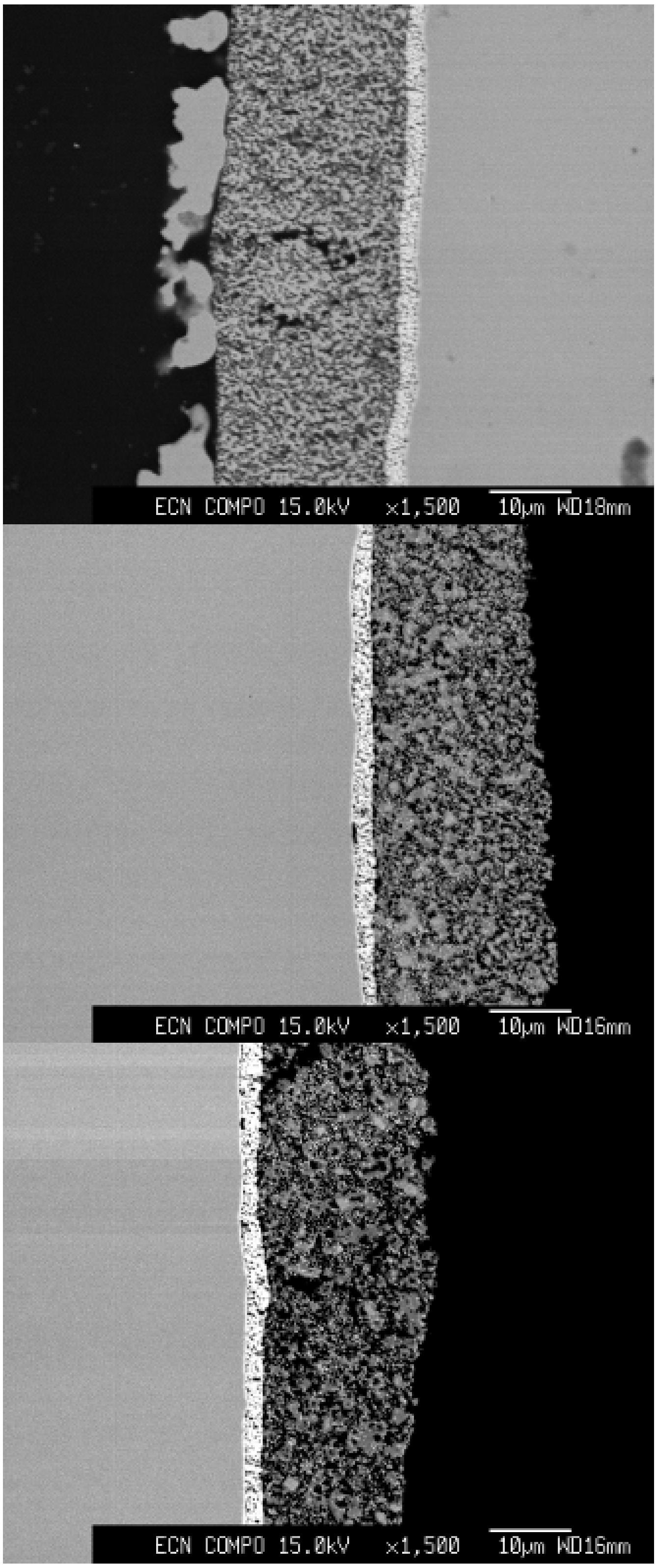

Figure 4.11 *Anode cross section directly after reduction (top), after testing at the anode inlet (middle), and at the anode outlet (bottom)*

5. Experimental results using nozzle A2

5.1 General description

For this test a fresh catalyst was used for the CPO reactor. Moreover, a fresh electrolyte supported SOFC-cell was installed. The cell was operated for 350 hrs in total. The cell was once fed with reformat from the reformer for 65 hrs. Before and after, the cell was operated with H_2.

The heating element of the SOFC inlet pipe was fixed and the controls were tuned. This mitigates the risk of C-deposition at the SOFC inlet pipe.

5.2 Experimental results

The performance of the reformer in terms of hydrocarbon slip, together with the performance of the SOFC cell in terms of cell voltage and current, are represented in Figure 5.1. The temperatures of the reformer together with the system pressure are represented in Figure 5.2.

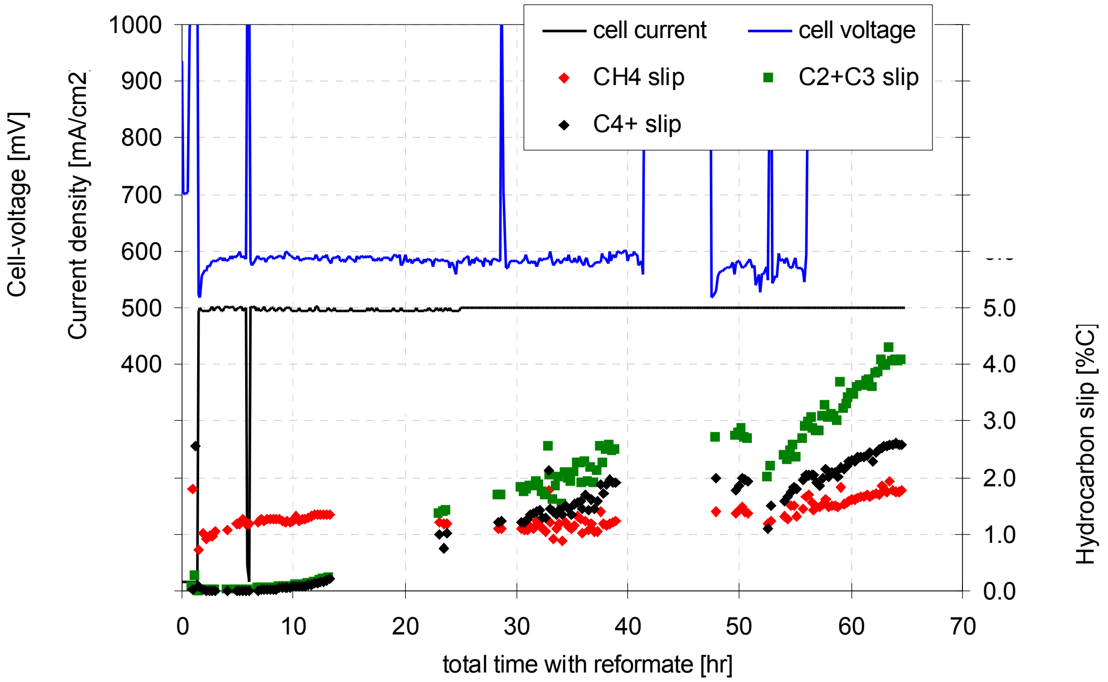

Figure 5.1 *Performance of the reformer in terms of hydrocarbon slip (right scale), and SOFC cell in terms of cell current and voltage (left scale)*

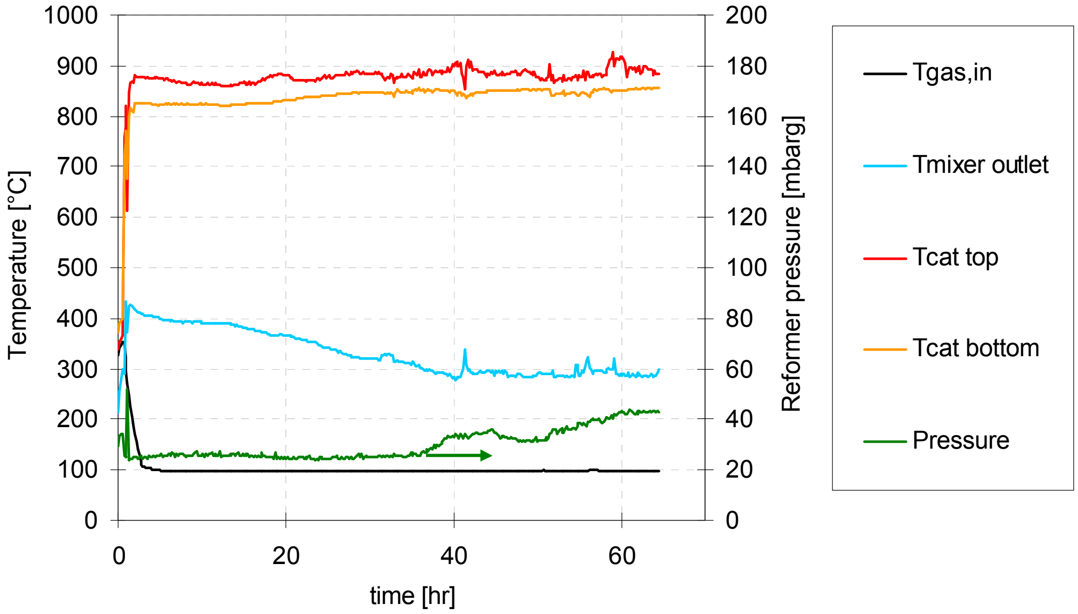

Figure 5.2 *Temperatures and pressure of the reformer*

The performance of the reformer during the first 10 hrs of operation is good: the evaporator temperature is stable at about 400°C and the hydrocarbon slip is low for the non-methane hydrocarbons. A 10-times lower concentration is observed for the C_2-C_3 hydrocarbons compared to the initial performance during the previous experiment mentioned in paragraph 4.2 (see Figure 4.5), while no C_4, C_5, or C_6 were detected. The C_6+ hydrocarbon concentration was only 100 ppm (as CH_2). The SOFC completely converts all non-methane hydrocarbons, while the conversion of methane was about 90%.

During this 10 hrs period, the evaporator temperature as well as the catalyst temperatures are as expected. Starting at 15 hrs runtime, the temperature of the evaporator starts to decrease. Simultaneously, the hydrocarbon slip starts to increase. As time progresses, the hydrocarbon slip of the reformer increases, the mixture temperature leaving the evaporator decreases, the pressure drop increases and the catalyst temperatures become unstable. These are all symptoms of a worsening of the quality of the mixture entering the catalyst zone due to fouling of the diesel injection system. The initial positive effect of decreasing the exposed surface area of the nozzle by applying a shield with a smaller hole quickly diminishes due to an increased rate of fouling of the nozzle.

It should be noted that during the time that the cell was operated with reformat, the cell voltage was fairly stable. I-V curves that were taking during operation with reformat are shown in Figure 5.3, which makes clear that the opencircuit voltage of the SOFC was more or less constant, indicating that the nominal gas quality was constant, despite the fact that the hydrocarbon slip increased. I-V curves that were measured with hydrogen before and after the operation with reformate show the same picture, Figure 5.4. Comparison between Figure 4.9 and Figure 5.4 made clear that the electrochemical performance under hydrogen is fairly reproducible.

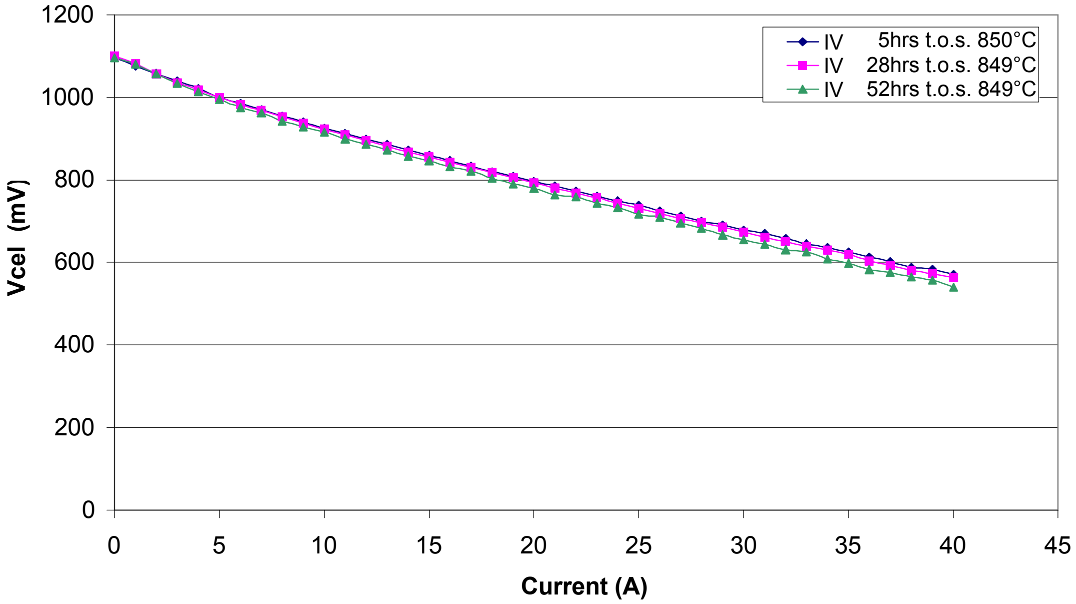

Figure 5.3 *I-V curves taken after 5, 28, and 52 hrs operation under reformat at appr. 850°C*

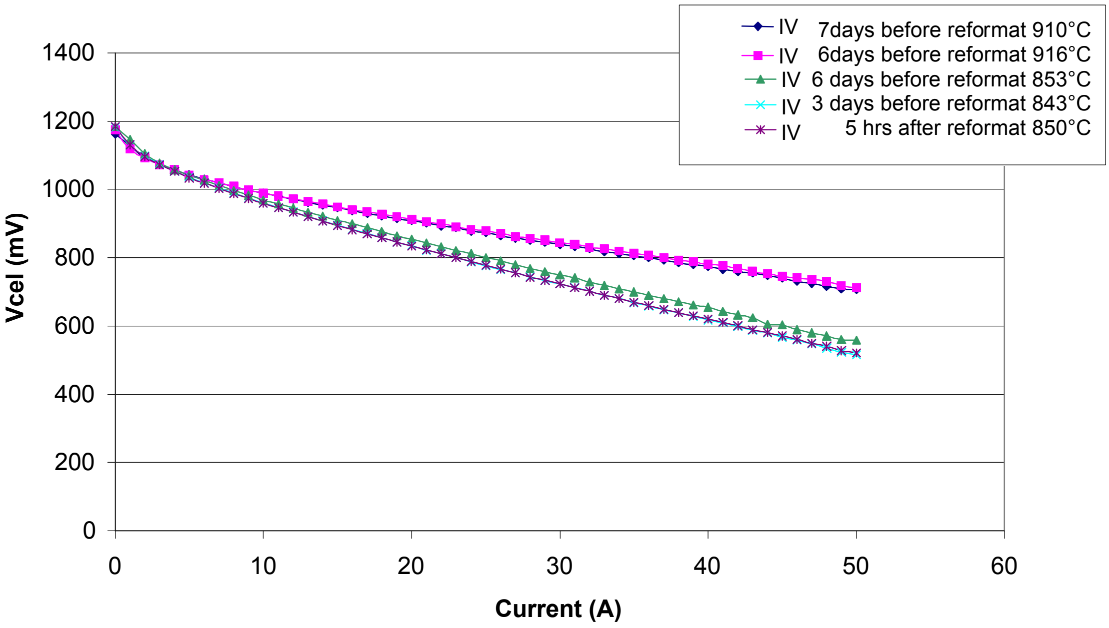

Figure 5.4 *I-V curves taken at appr. 920 and 850°C during operation with hydrogen both before and after operation with reformat*

6. Experimental results using nozzle B

6.1 General description

For this test a fresh catalyst was used for the CPO reactor. Moreover, a fresh electrolyte supported SOFC-cell was installed. The cell was operated for 400 hrs in total. The cell was once fed with reformat from the reformer for 30 hrs.

6.2 Experimental results

The performance of the reformer in terms of hydrocarbon slip, together with the performance of the SOFC cell, are represented in Figure 6.1. The temperatures of the reformer together with the system pressure are represented in Figure 6.2.

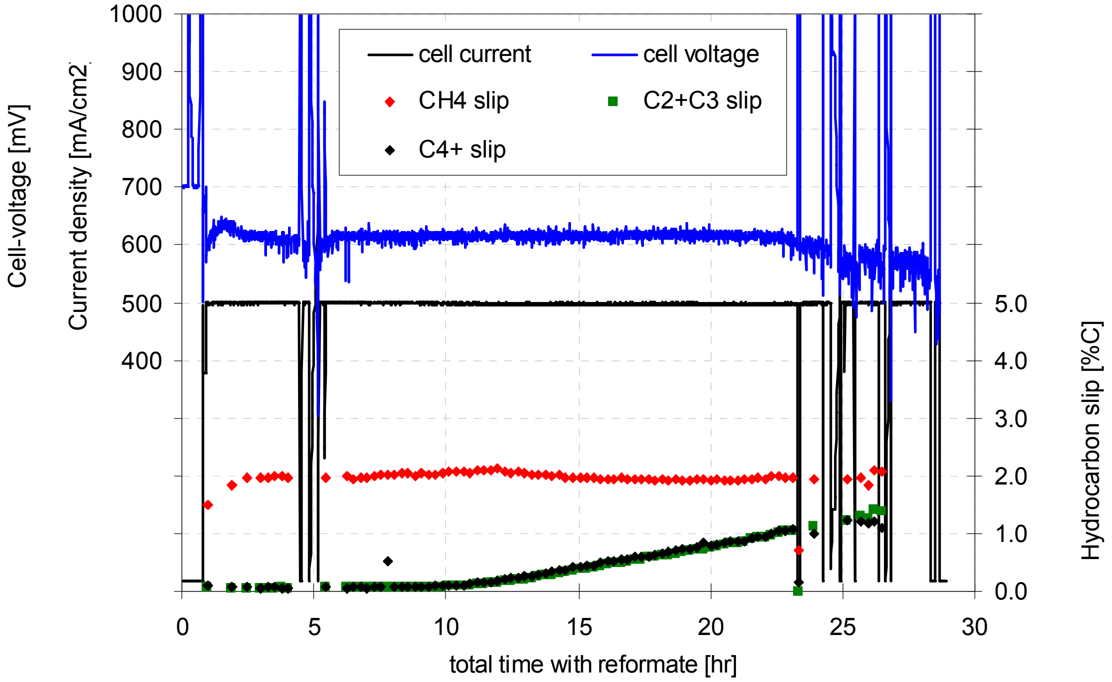

Figure 6.1 *Performance of the reformer in terms of hydrocarbon slip (right scale), and SOFC cell in terms of cell current and voltage (left scale)*

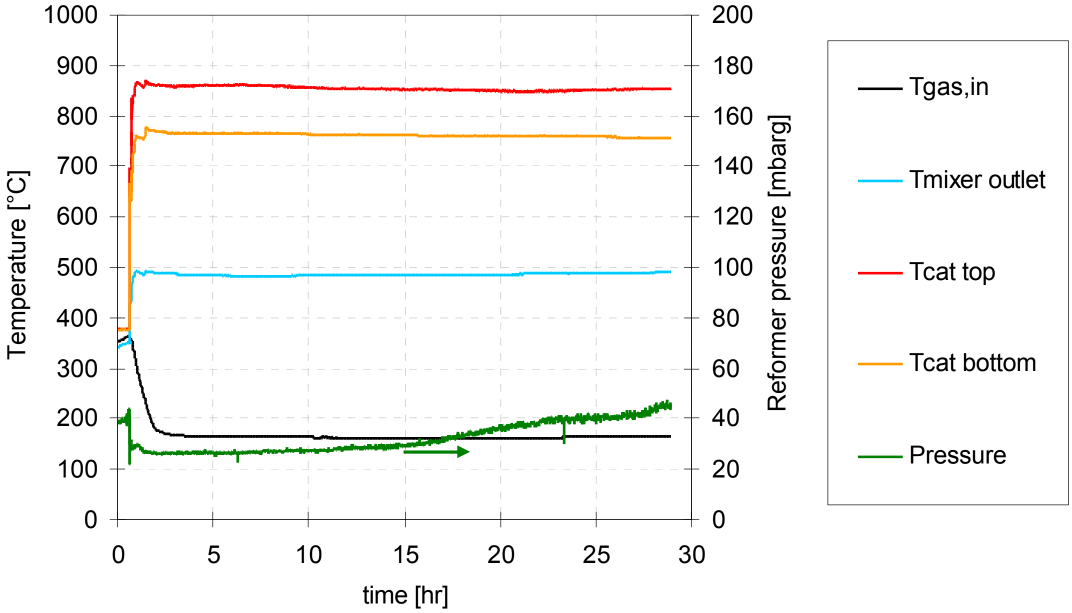

Figure 6.2 *Temperatures and pressure of the reformer*

As in the previous experiment, the initial performance of the reformer was good. The hydrocarbon slip is in the same range as for the previous experiment. Also the temperatures of the reformer are as expected with the exception of the cold-flame temperature. The cold-flame temperature is somewhat higher at 490°C with the new nozzle concept. It is nevertheless stabile and the cold-flame regime is not transferred into the hot-flame regime.

Interestingly, the initial good catalyst performance again deteriorates starting at 10 hrs operating time. The hydrocarbon slip of the non-methane hydrocarbons increases in time. The slope of the increase is much smaller than observed in the previous experiment using nozzle configuration A2 (paragraph 5) and comparable as observed using nozzle configuration A1 (paragraph 4). In contrast to previous experiments, the increase in hydrocarbon slip is not accompanied by a decrease in cold-flame temperature. Throughout the entire experiment, the cold-flame temperature is stable at 490°C, while the cell performance markedly decreases.

Although the new nozzle concept resulted in a more stable operation of the cold-flame evaporator, the hydrocarbon slip could not be prevented. During dismantling of the system, it was observed that the nozzle displayed much less fouling by C-deposition compared to the previous nozzle concepts. The catalyst structure, however, showed massive C-buildup at the monolith entrance, which was not observed in previous experiments. A picture of the monolith entrance is represented in Figure 6.3.

Figure 6.3 *Carbon build-up on the inlet side of the catalyst structure when using nozzle concept B*

The home-made nozzle B produces a spray with a larger droplet size than the commercial nozzle used in the configuration A1 and A2. Calculations show that the time needed for evaporation of 0.1mm droplets $C_{14}H_{30}$ within the reactor is in the order of 50 ms, while the mean residence time of the feed within the evaporator is in the order of 100 ms. These estimations indicate that it is very likely that a fraction of the fuel sprayed into the evaporator is not completely evaporated before the feed enters the catalyst zone. Since the catalyst structure is hot (typically 800-900°C), these droplets will evaporate upstream the catalyst structure, but mixing will be poor. The feed entering the catalyst structure consists of zones rich in hydrocarbons but poor in O_2 and zones poor in hydrocarbon but rich in O_2. Especially the hydrocarbon-rich zones will lead to C-deposition onto the catalyst structure by thermal cracking.

I-V curves that were taken during operation with reformat are shown in Figure 6.4. It illustrates that throughout this period the performance was fairly stable. From I-V curves that were taken under hydrogen before and after the experiments with reformat, shown in Figure 6.5, it can however be observed that irreversible degradation has taken place after the last I-V curve was taken under reformate. This is likely due to temporary overloading of the cell due to reduced reformat flow while the cell was still under the same electrical load. Post test inspection on the tested cell revealed that the anode was indeed severely damaged, see Figure 6.6. Parts of the anode were lost. This location where delamination occurred is at the exhaust side of the cell (bottom left) which indicates that fuel shortage occurred during the test.

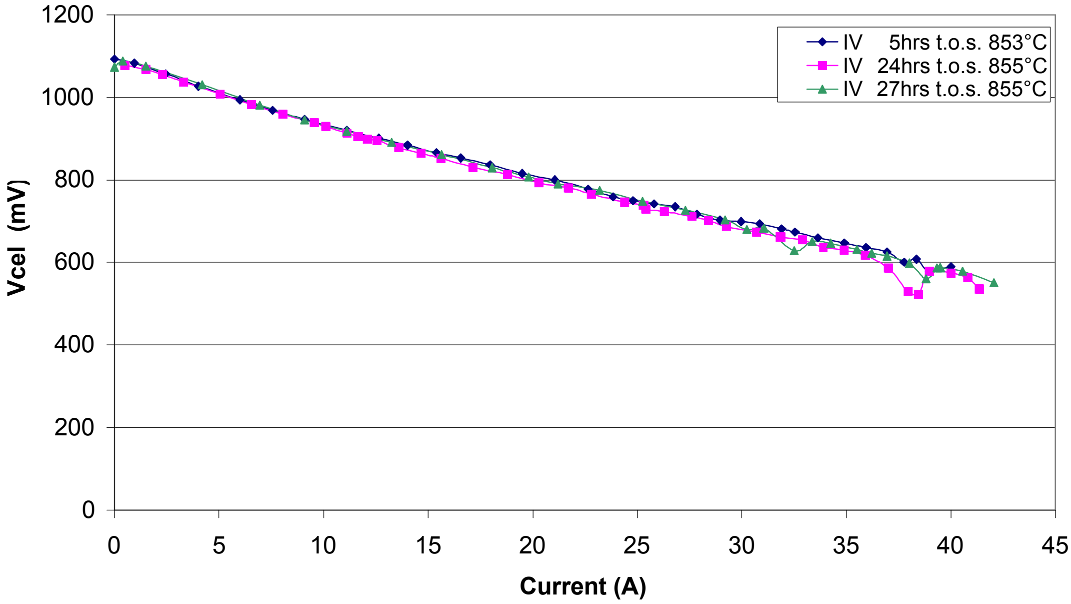

Figure 6.4 *I-V curves taken after 5, 24, and 27 hrs operation under reformat at appr. 850°C*

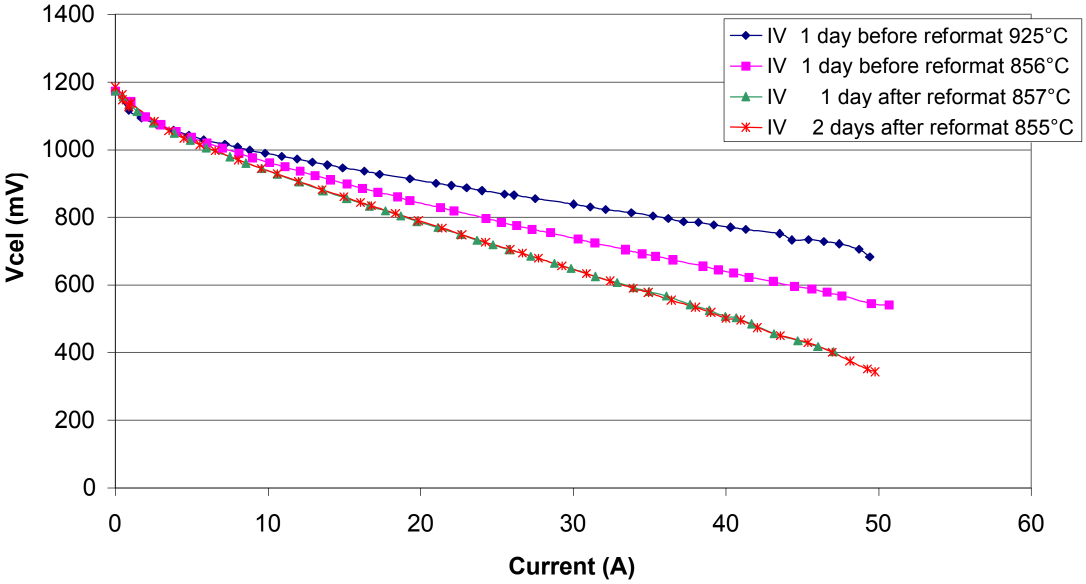

Figure 6.5 *I-V curves taken at appr. 920 and 850°C during operation with hydrogen both before and after operation with reformat*

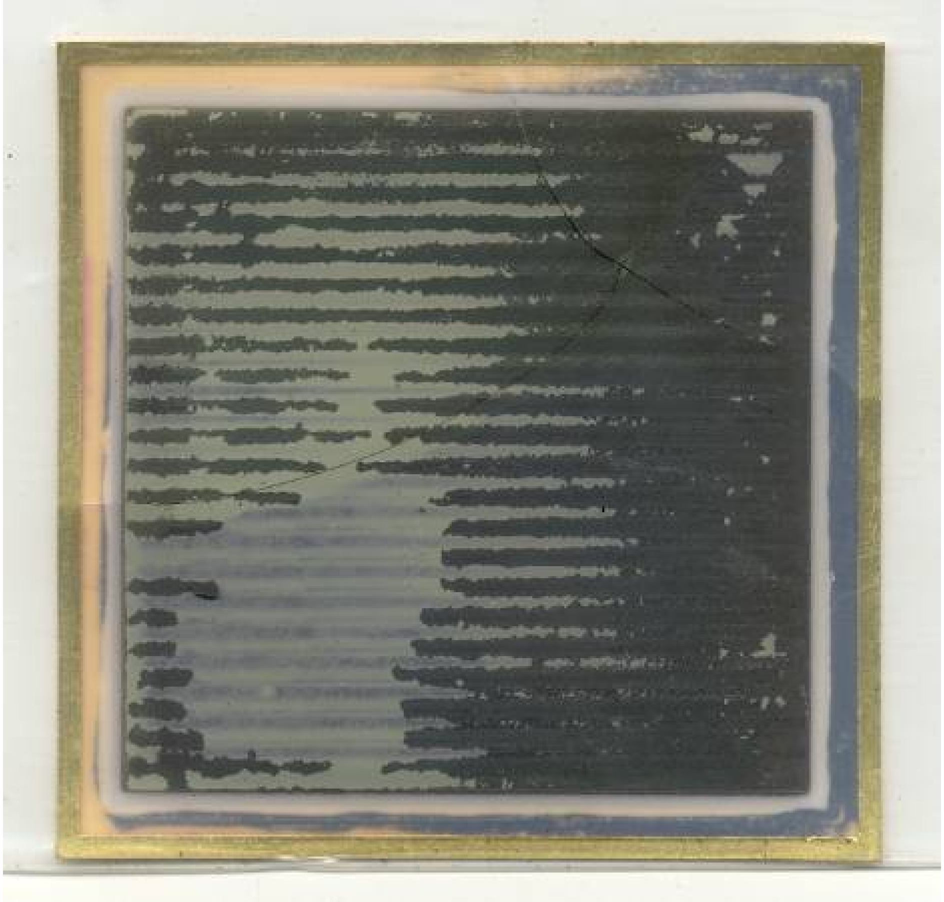

Figure 6.6 *Anode surface after the test*

In conclusion, the new nozzle concept does suppress fouling of the nozzle by C-deposition upon the nozzle. The annulus shaped air feed successfully shrouds the nozzle body from the diesel spray, preventing wetting of nozzle body. Moreover, the coldest nozzle part (i.e. the diesel capillary) cannot be contacted by the hot recirculating gasses within the cold-flame evaporator.

Unfortunately, the home-made nozzle produces a spray having a larger mean droplet size and/or droplet-size distribution, endangering the complete evaporation of every fuel droplet. The uniformity of the mixture of the evaporated fuel with the feed air is much lower, leading to C-deposition upon the catalyst. In this respect, the higher cold-flame temperature might be related to the lower degree of fuel evaporation since less heat is used for the evaporation.

7. Discussion and conclusions

The tests described in this report made clear that it is in principle possible to feed the SOFC with diesel reformed by a cold-flame assisted CPO reactor. A test-rig was constructed in which a CPO diesel reformer was coupled to a single cell SOFC. Characteristically, the reformat was held at 800°C all the way towards the SOFC. For this, high temperature flange connections and steel-ceramic expansion connections were successfully applied.

Three nozzle configurations were tested for the diesel injection into the cold-flame evaporator. In all tests, the cold-flame assisted CPO reformer was coupled to a single cell SOFC test-rig. The tests lasted for 30-65 hrs before the system was shut-down because of fouling of the cold-flame assisted catalytic reformer. For stable catalytic reforming of liquid hydrocarbon fuels, it is known that the feed of the catalyst must be uniform in composition. Moreover, from previous projects, it is known that the applied catalyst can accordingly process liquid fuels to a reformat essentially free of hydrocarbon slip. In all tests described in this report, the reformer operation was good for the first 10-15 hrs time-on-stream. The cold-flame evaporator temperatures were stable and the non-methane hydrocarbon slip was low at <0.25 %C. The SOFC cell typically converted all hydrocarbons present in the reformat, with the exception for the heavier C_6+ fraction of which about half was converted. The performance of the SOFC cell during this period was satisfactory.

With increasing time on stream, the non-methane hydrocarbon slip of the reformer increased in time. For all tests, this could be ascribed to fouling of the cold-flame assisted CPO reformer by C-deposition. The location of the C-deposition, however, was different between nozzle configurations A (A1 and A2) on the one hand and nozzle configuration B on the other hand.

For the nozzle configuration A, a commercial air-assisted nozzle was used, which was shielded from the evaporation chamber by means of a cap. This cap had a large hole for configuration A1 and a small hole for A2. In both these configurations, the diesel-spray and the circulating cold-flame gas mixture could contact the relatively cold nozzle. Condensation of hydrocarbons upon the nozzle caused fouling by C-deposition, leading to a deterioration of the spray quality and to a decrease of the CPO performance.

In configuration B, the diesel feed was shielded from the exterior of the nozzle by means of the annular air feed. Accordingly, the nozzle is less susceptible to fouling, which was experimentally demonstrated by a much more stable cold-flame temperature than with configurations A1 and A2. This home-made nozzle, however, has a poorer spray quality in terms of a larger average droplet size and/or droplet size distribution. This caused an incomplete evaporation of the fuel and mixing with the air, resulting in C-deposition upon the CPO catalyst structure.

Summarizing: whereas the nozzles in configurations A1 and A2 were readily fouled by C-deposition leading to a worsening of the spray quality and cold-flame stability, the nozzle in configuration B was less susceptible to fouling resulting in an increased stability of the cold-flame evaporator. The home-made nozzle used in configuration B, however, has a poorer initial spray quality than the commercial nozzles used in configurations A1 and A2. The C-deposition was thus shifted from the nozzle towards the catalyst structure. In other words, the cold-flame product had an initial high quality which deteriorated in time due to fouling of the nozzle for configurations A1 and A2. For configuration B, the cold-flame product had a lower initial quality that did not decrease in time.

The increased hydrocarbon slip of the reformer observed in every experiment probably caused electrochemical degradation of the cell. To this respect, further improvement is needed.

The tests were also influenced by C-deposition in the vent-lines of the reformer and the SOFC. It was demonstrated that controlled cooling by water injection is mandatory to prevent line blockage by C-deposition.

8. Recommendations

The results presented in this report indicate that cold-flame evaporation of liquid fuels is a feasible means of feed preparation for a catalytic reforming reactor. It was shown that the performance of the cold-flame evaporator strongly depends on the characteristics of the diesel spray feeding this evaporator.

By means of an experimental approach, it was shown that fouling of the nozzle can be suppressed by changing the nozzle concept. However, to further optimize the diesel injection, it is believed that a modeling based approach should be chosen. The spray characteristics in combination with the cold-flame reactions and the fluid circulation within the evaporator should be modeled via computational fluid dynamics. In advanced nozzle concepts, wetting of the nozzle by the diesel feed or by condensation of hydrocarbons from the cold-flame evaporation product should be prevented. It is believed that to that extent shrouding could be very effective.

Another important step would be to use commercial diesel instead of the Hydroseal model-fuel. The presence of typically 20wt% aromatics can severely alter the cold-flame characteristics. It is known that aromatics do not easily participate in the cold-flame reactions. The heat production of the cold-flames is therefore much less with commercial diesel, resulting in a more difficult fuel evaporation and mixing.

9. Literature

[1] Tillemans, F.W.A., *Evaluation and selection of a feasible diesel reforming option with SOFC for vehicle APU application*, 2004, 7.0238-GR-04-01

[2] Pasel, J., Meißner, J., Porš, Z., Samsun, R.C., Tschauder, A., Peters, R., *Autothermal reforming of commercial JetA-1 on a 5kWe scale*, International Journal of Hydrogen Energy 32 (2007) 4847 – 4858

[3] Sarioglana, A., Olguna, H., Baranaka, M., Ersoza, A., Atakulb, H., Ozdoganc, S., *Diesel evaporation as the first step of hydrogen production*, International Journal of Hydrogen Energy 32 (2007) 2895 – 2901

[4] Naidja, A., Krishna, C.R., Butcher, T., Mahajan, D., *Cool flame oxidation and its role in combustion and reforming of fuels for fuel cell systems*, Progress in Energy and Combustion Science 29 (2003), 155-191

[5] Matos da Silva, J., Hermann, I., Mengel, C., Lucka, K., Köhne, H., *Autothermal reforming of gasoline using a cool flame vaporizer*, AIChE Journal 50(5) (2004), 1042-1050

[6] Hartmann, L., Lucka, K., Köhne, H., *Mixture preparation by cool flames for diesel-reforming technologies*, Journal of Power Sources 118 (2003) 286-297

Appendix A: SOFC test protocol

Testprotocol voor JV-02

Cel: AS9 // 3YSZ // KS5, cofire 1250/1
Code CKS5E060320-3

Inbouwen en opwarmen

1. Celbehuizing is stofvrij, gazen zijn vlak en heel
2. Goudseal en cel plaatsen, kathodeflens plaatsen, gastoevoeren en thermokoppels positioneren en ovenstenen plaatsen
3. Gewicht op cel 9 kg
4. Rotaflow dicht, SOFC open
5. Gascondities:
    anode 2000 N_2 droog
    kathode 2000 Air
6. Opwarmprofiel: oven 30°C/hr tot 1080°C, dwell 2 uur, afkoelen naar 960°C
7. Tracing in stappen van 100°C opwarmen tot 850°C
8. Gewicht op cel 18 kg
9. Meten lekdichtheid SOFC testopstelling aan de hand van minimale N_2 flow waarbij waterslot borrelt

Reduceren / testen onder waterstof

10. Gascondities:
    anode 500 N_2 droog
    kathode 1500 Air
11. Reduceren volgens onderstaand schema, telkens temperatuur en celspanning noteren:

Stikstof	Waterstof
475 ml/min	25 ml/min
450	50
400	100
300	200
200	300
100	400
0	500

12. Cel in OCV gedurende 60 minuten
13. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
14. Belasten bij 40 A gedurende 24 uur
15. - Zonodig ovensetpoint aanpassen zodat celtemperatuur 920 ± 2°C blijft –
16. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
17. Afkoelen 30°C/uur naar 850°C onder 40 A belasting
18. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV

Testen onder reformaat

19. Cel in OCV, Rotaflow open, SOFC afvoer dicht
20. Gascondities gedurende minimaal 10 minuten:
    anode bulk flow N_2
    kathode 1500 Air
21. Zodra reformaat vrij is van hogere koolwaterstoffen: SOFC open, rotaflow knijpen met 1 l/min, waterslot borrelt nu
22. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV (ballflowmeter 37 Nl/min bij 40A), stroom schatten waarbij reformaatutilisatie ongeveer 60% is. Rotaflow zonodig bijstellen zodat 60% utilisatie bij 40 A wordt bereikt.
23. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
24. Belasten bij 40 A gedurende 100 uur, met elke dag een I-V meting tot 40 A
25. - Zonodig ovensetpoint aanpassen zodat celtemperatuur 850 ± 2°C blijft –

26. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
27. Overige testen onder reformaat in overleg met Eric en Jan Pieter

Testen / afkoelen onder waterstof

28. Cel in OCV, Rotaflow open, SOFC dicht
29. Shutdown reformer: Diesel uit, spoelen met droge N_2 gedurende 30 minuten
30. Gascondities gedurende minimaal 10 minuten:
    anode 500 N_2 droog
    kathode 1500 Air
31. Gascondities gedurende minimaal 10 minuten:
    anode 500 H_2 droog
    kathode 1500 Air
32. SOFC open, Rotaflow dicht, waterslot borrelt nu
33. Cel in OCV gedurende 60 minuten
34. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
35. Belasten bij 40 A gedurende 24 uur
36. - Zonodig ovensetpoint aanpassen zodat celtemperatuur 850 ± 2°C blijft –
37. Opnemen opgaande I-V curve tot 50 A of V_{cel}=300 mV
38. Gascondities gedurende minimaal 10 minuten:
    anode 2000 N_2 droog
    kathode 2000 Air
39. Afkoelen tracing naar RT in stappen van 100°C
40. Afkoelen cel 30°C/uur naar RT