



Efficiency gain of solid oxide fuel cell systems by using anode offgas recycle – Results for a small scale propane driven unit

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ABSTRACT

The transfer of high electrical efficiencies of solid oxide fuel cells (SOFC) into praxis requires appropriate system concepts. One option is the anode-offgas recycling (AOGR) approach, which is based on the integration of waste heat using the principle of a chemical heat pump.

The AOGR concept allows a combined steam- and dry-reforming of hydrocarbon fuel using the fuel cell products steam and carbon dioxide. SOFC fuel gas of higher quantity and quality results. In combination with internal reuse of waste heat the system efficiency increases compared to the usual path of partial oxidation (POX).

The demonstration of the AOGR concept with a 300 W_{el}-SOFC stack running on propane required: a combined reformer/burner-reactor operating in POX (start-up) and AOGR modus; a hotgas-injector for anode-offgas recycling to the reformer; a dynamic process model; a multi-variable process controller; full system operation for experimental proof of the efficiency gain.

Experimental results proof an efficiency gain of 18 percentage points (η -POX = 23%, η -AOGR = 41%) under idealized lab conditions. Nevertheless, further improvements of injector performance, stack fuel utilization and additional reduction of reformer reformer O/C ratio and system pressure drop are required to bring this approach into self-sustaining operation.

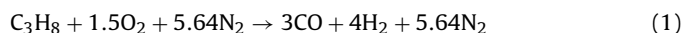
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1. Introduction

In common small-scale SOFC systems like micro combined heat and power units (μ -CHPs) for domestic applications or auxiliary power units (APU) for vehicles the production of fuel gas for electrochemical oxidation is normally accomplished by catalytic partial oxidation (POX) with air or steam reforming (SR) using water as oxidant. The heat of the exothermic POX reaction decreases the chemical energy input for the SOFC followed by lower electrical efficiency of the system. In addition, the partial oxidation of hydrocarbons demands extensive reactor temperature control due to the two stage mechanism that is presumed to consist of an exothermic total oxidation of the hydrocarbons to steam and carbon dioxide and successive reforming of the fuel to hydrogen and carbon monoxide [1,2]. The latter endothermic step results in distinct tem-

perature gradients along the catalyst, demanding a tailored reactor design and operation regime to avoid overheating of the catalyst entry, carbon formation and to reach sufficient fuel conversion. The SR process yields high partial pressures of fuel gas, but system complexity increases due to the need for an additional water supply.

The AOGR approach as another way of producing fuel gas combines the advantages of both methods, the high fuel gas concentration of the SR process and the simple system design of POX reforming by recycling a part of the anode offgas to the reformer. Both electrochemical reaction products H₂O and CO₂ from anode offgas are used for the reforming of the fuel into new fuel gas, substantially increasing its yield compared to POX mode. Eq. (1) shows the stoichiometric limit for the fuel gas yield in POX mode of 7 moles per mole of propane:



If anode offgas with a CO₂:H₂O ratio of 3:4 (corresponding to the composition of completely oxidized propane) is used for the

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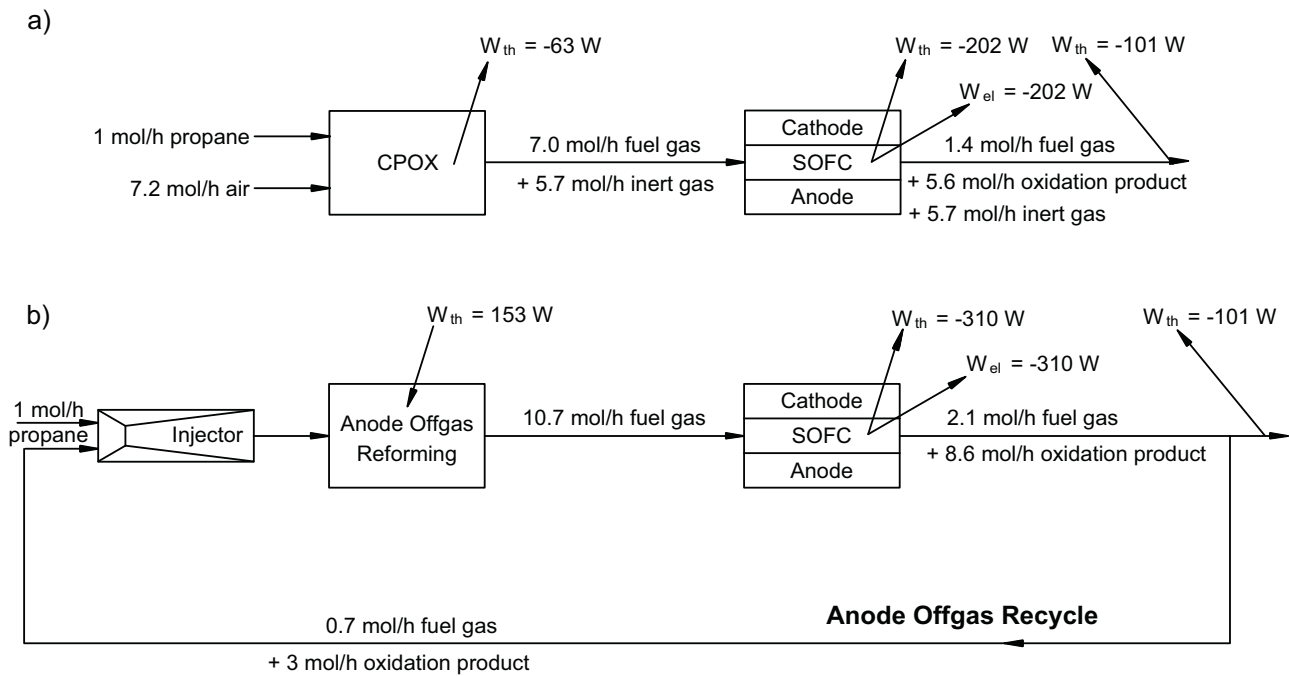
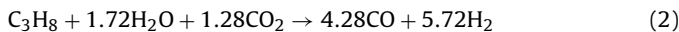


Fig. 1. SOFC system using stoichiometric reformer conversion and usual stack performance ($FU = 80\%$, $\eta_{\text{Stack}} = 50\%$). (a) Propane POX reforming, (b) propane AOGR reforming.

propane reforming the maximum amount of fuel gas production per mole of propane is 10 moles according to Eq. (2):



Additionally, partial pressure of the fuel gases at the SOFC anode is higher without nitrogen. Fig. 1 shows the principles with estimated parameters based on idealized calculations for SOFC systems with (a) propane POX and (b) AOGR reforming.

Assuming an efficiency of state-of-the-art SOFC stacks of 40% (considering fuel utilization $FU^1 = 80\%$ and electrochemical efficiency of the stack $\eta_{\text{Stack}} = 50\%$) the electrical energy output increases from POX to AOGR mode from 202 W to 310 W and the gross electrical system efficiency (based on $\text{LHV}_{\text{C}_3\text{H}_8} = 567 \text{ W h/mol}$ input, see chapter 2 for more details) increases from $\eta_{\text{el,POX}} = 36\%$ to $\eta_{\text{el,AOGR}} = 55\%$.

Heat is recycled into the system from both the anode offgas directly and from the burner-unit that oxidizes the non-recycled anode offgas in tight thermal contact to the reformer catalyst.

In summary, the AOGR concept is characterized by the following advantages:

- Increase of the fuel gas production per mole of propane.
- Internal usage of waste heat for endothermic reforming processes.
- Higher partial pressures of fuel gas at the SOFC.
- No hot-spots inside the reforming catalyst.
- More compact and simple system design.

At start-up the system has to be operated in POX mode to heat-up the SOFC stack to its minimum temperature for electricity production, generating the required amount of H_2O and CO_2 for propane reforming.

2. Objective

The aim was to demonstrate the feasibility of the AOGR concept using anode offgas recycling with a $300 \text{ W}_{\text{el}}$ SOFC system and the proof of higher efficiency compared to a POX system, including the determination of the

- conversion rate of fuel and anode offgas depending on operation parameters of the SOFC stack and the reformer,
- reformer configuration for three operation modes: POX mode during start-up, autothermal mode for the intermediate phase and anode offgas mode during steady-state operation,
- hotgas-injector design for anode offgas recycling operating at 800 to 850°C ,
- dynamic system behavior by simulation for the development of control strategies,
- confirmation of the overall system efficiency with a system containing reformer, SOFC stack, anode recycle and burner.

Additional work concerning modeling and simulation of the complete system under stationary and dynamic operation and the development of proper control systems by hardware-in-the-loop simulation was required [3].

3. Experiments

3.1. Hardware development

3.1.1. Reformer/burner-reactor

Due to the advantages of catalytic combustion compared to conventional flame combustion, e.g. low peak temperatures, low emission levels in the exhaust gas, high fuel tolerance and high fuel utilization [4,5] a catalytic burner was designed to provide the required heat for reforming. The reformer/burner reactor is based on metallic structures with high surface-to-volume-ratios. Large surface, high heat conductivity and low thermal inertia of the metallic structure result in an excellent heat transfer from the inner burner unit to the reforming zone, located concentrically around

¹ Fuel utilization FU is defined as relation between converted fuel gas and fuel gas feed.

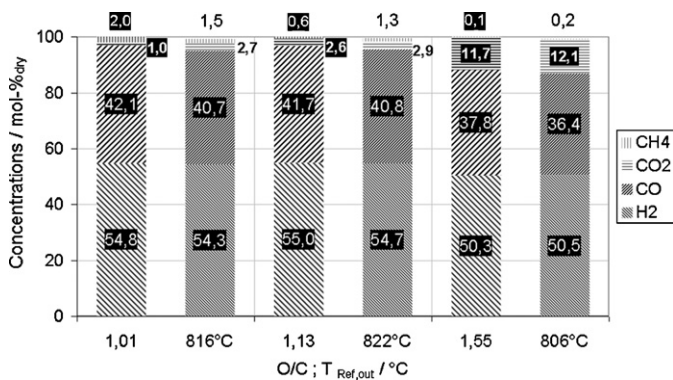


Fig. 2. Comparison of experimental results (fine lining, right) and thermodynamic equilibrium (coarse lining, left) in AOGR mode.

the burner [6] and thus preventing an overheating of the burner and assuring proper reaction conditions for the endothermic reactions. The reformer and the burner reactor are coated with precious metal catalysts leading to reduced reactor size, greater structural stability and an improved durability, when coupled with a fuel cell [7]. Furthermore, the affinity of precious metal catalysts to carbon formation is less than for nickel based catalysts [8].

The characterization of the reformer/burner reactor was conducted with focus on the performance of the reformer catalyst. Therefore system operation parameters like fuel utilization of the SOFC and the ratio of recycled anode offgas gas to propane in AOGR mode have been varied. In Fig. 2 the experimentally achieved reformer product compositions and the corresponding thermodynamic equilibriums are compared for different O/C-ratios (Eq. (3)) and reformer outlet temperatures.

$$\frac{O}{C} = \frac{\dot{n}_{H_2O} + 2 \cdot \dot{n}_{CO_2} + \dot{n}_{CO}}{3 \cdot \dot{n}_{C_3H_8} + \dot{n}_{CO_2} + \dot{n}_{CO}} \quad (3)$$

Parameter variation tests have been performed at different O/C-ratios leading to reformer outlet temperatures between 806 and 822 °C. The experimental reformer product compositions show a high conformity with the thermodynamic equilibrium.

For the proof of long term stability of the reactor and both the reformer and the burner catalysts and to define characteristic parameter for the carbon formation at different operations conditions in the AOGR mode long term tests have been made. Carbon formation was detected by measuring the corresponding increase of the pressure drop across the reformer reactor. In Fig. 3 the pressure drop of the reformer as well as the CH₄ concentration at the reformer outlet of two tests are shown.

Although the O/C-ratio is comparable for both tests the pressure drop and the analogous rate of carbon formation is different. Another definition of the O/C-ratio (referred to as $(O/C)_{Ref}$) was found as a more characteristic parameter to indicate carbon formation (Eq. (4)), corresponding to the steam/carbon-ratio for the steam reforming.

$$\left(\frac{O}{C}\right)_{Ref} = \frac{\dot{n}_{H_2O} + \dot{n}_{CO_2}}{3 \cdot \dot{n}_{C_3H_8}} \quad (4)$$

No increase of the pressure drop across the reformer reactor and therefore no carbon formation was detected within 24 h of operation at an $(O/C)_{Ref}$ -ratio of 2.5 or higher. The measured CO concentration in the exhaust gas of the burner unit was below 10 ppm at any time.

3.1.2. SOFC stack characterization

The AOGR system concept is in general stack independent, but sets specific requirements for the SOFC stack operation. Within this project the concept was analyzed using the Mk100 stack of Staxera

Table 1

Range of expected reformate composition for POX (at start-up) and AOGR mode (final operating point).

Operation mode	Anode gas inlet concentration [vol.%]					
	H ₂	CO	H ₂ O	CO ₂	CH ₄	N ₂
POX	22–25	17–20	3–4	2–3	<0.2	45–55
AOGR	50–55	37–40	4–5	3–4	<1	0

GmbH, Germany, further details about the stack features and performance results are available in [9,10]. The SOFC stack should be able to achieve acceptable performance with two different reformate compositions depending on the propane-reforming mode, shown in Table 1:

During AOGR mode the SOFC performance defines the system performance via

- Maximum electrical power output: system gross efficiency is calculated by electrical power output of the stack versus energy input of propane.
- Production rate of oxidants: the AOGR concept requires maximum water and carbon dioxide content in the anode offgas to reduce the amount of recycled offgas. Unconverted hydrogen and carbon monoxide increases the recycle ratio² *R* of the injector. A characteristic value for the oxidant production rate of the stack is the fuel utilization FU.

Fig. 4 shows the effect of reformate throughput on both of these parameters. Higher gas throughput results in higher power output but reduces fuel utilization.

Electrical stack power of 474 W is achieved at high anode gas throughput and a single cell voltage $U_{Cell} = U_{Stack}/30 \text{ cells} = 0.716 \text{ V}$. At this operation point the resulting fuel utilization of $FU = 0.4$ is much too low for the suggested AOGR concept. The best compromise between high power output and good fuel utilization was found at $6.34 \text{ l}_N \text{ min}^{-1}$ AOGR reformate, where an electrical power of $P_{el} = 370 \text{ W}$ was produced with a fuel utilization of $FU = 0.64$ at $U_{Cell} = 0.706 \text{ V}$.

Subsequent to the characterization of the reformer/burner-unit and the SOFC stack, steady-state simulations with AspenPlus[®] were conducted to fix the requirements for the hotgas-injector and estimate the theoretical system efficiency. These calculations predict a system efficiency of $\eta_{el} = 51.8\%$ at $P_{el} = 370 \text{ W}$, using the experimentally validated parameters for the reformer/burner-unit and the SOFC stack illustrated above, based on a propane flow rate of $\dot{V}_{C_3H_8} = 0.46 \text{ l}_N/\text{min}$.

3.1.3. Hotgas-injector

Small-scale and high-temperature feeding devices for the recycling of the anode offgas at the operation temperature of 850 °C are not available. A hotgas-injector had to be developed for propane as motive gas to drive the anode offgas partially back to the reformer inlet. The unit needs to recycle offgas in the desired amount at different operation conditions and gas compositions. Further on, carbon formation had to be considered, because of propane decomposition at high temperatures. The following parameters were predetermined by the system units:

- Propane flow used as motive gas: $\dot{V}_{C_3H_8} = 0.46 \text{ l}_N/\text{min}$.
- Recycle ratio: $R > 10$.

² Recycle ratio *R* is defined as relation between recycled anode offgas (suction) flow rate and propane (motive) flow rate.

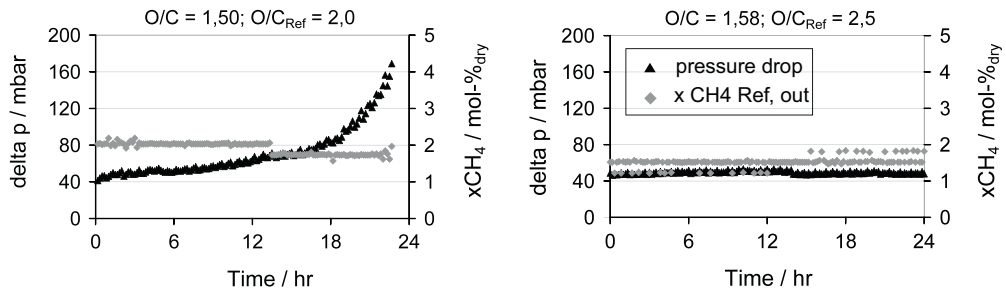


Fig. 3. Long term tests of the reformer/burner-reactor.

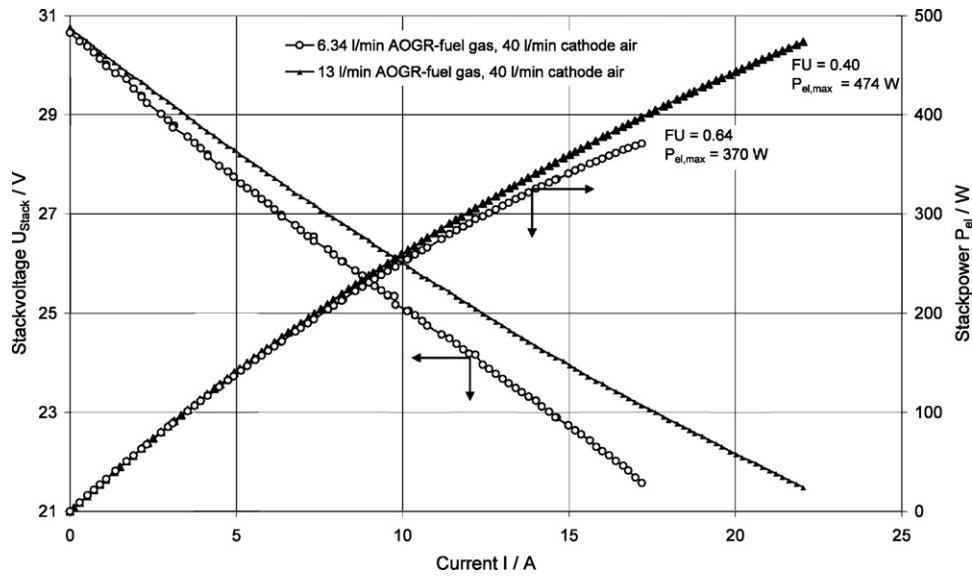


Fig. 4. SOFC stack characteristic in AOGR mode, maximal fuel utilization (FU) and power ($P_{el,max}$) for different flow rates, Staxera Mk100 stack at 850 °C. Fuel gas composition: H₂:CO:CH₄:CO₂:H₂O = 51.6:39.0:0.9:3.8:4.7 mol.%.

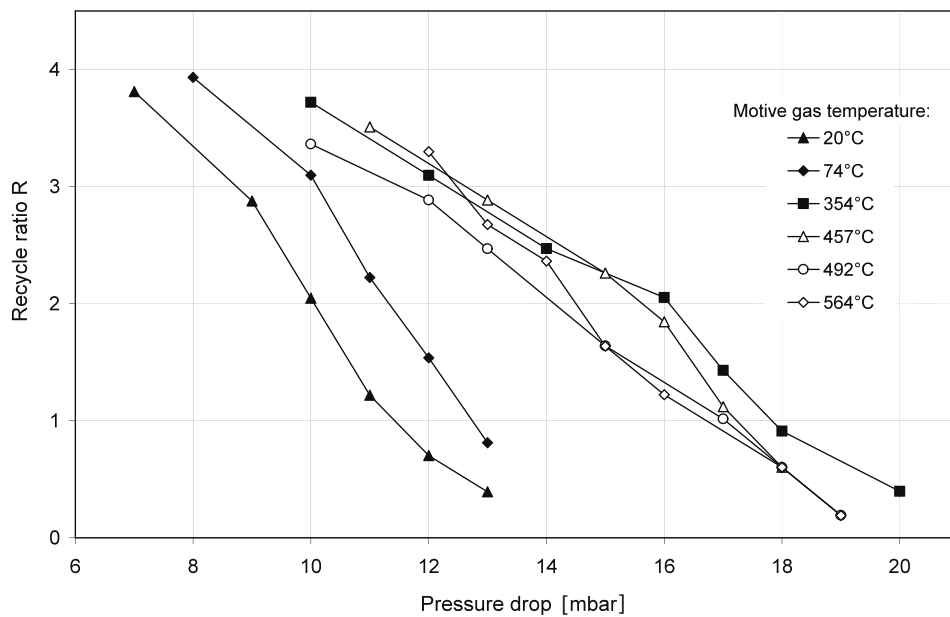


Fig. 5. Recycle ratios for propane as motive gas ($0.46 \text{ l}_N \text{ min}^{-1}$), nitrogen as suction gas and different gas temperatures (nozzle diameter 236 μm).

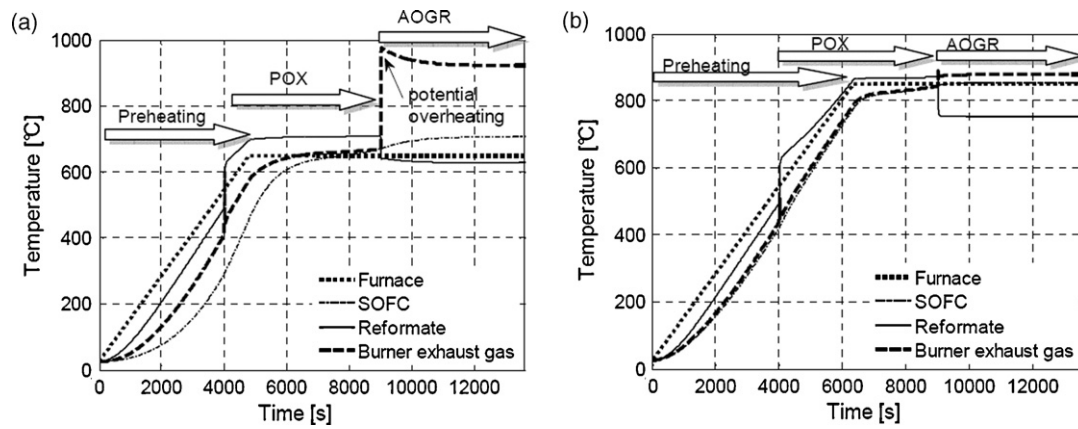


Fig. 6. Temperature response of startup simulation. (a) Furnace temperature up to 650 °C, (b) furnace temperature up to 850 °C.

- Back pressure at injector outlet (lump sum pressure drop of reformer, anode and recycle pipe): $\Delta p = 30$ mbar.
- Operation temperature: $T \leq 850$ °C.

A prototype of a hotgas-injector was manufactured from Thermax®4828 steel. It employs a commercial injection nozzle body, intended for fuel injection into combustion engines.

Fig. 5 shows the resulting recycle ratios R for a propane flow rate of $0.46 \text{ l}_N \text{ min}^{-1}$ and a nozzle diameter of $236 \mu\text{m}$ at different motive gas temperatures. As expected, the hotgas-injector performance declines with higher pressure drops. This emphasizes the need to reduce the pressure drop of the downstream components and the piping.

The injector performance initially increases with higher temperatures, above 350 °C there is no further improvement. The effect was confirmed in additional measurements using different motive gases (N_2 , CO_2) and a larger nozzle diameter ($d = 260 \mu\text{m}$). The increase of gas temperature increases the nozzle outlet velocity of the motive gas reaching sonic velocity at about 230 °C. A further rise would require Laval nozzles with supersonic flow at the nozzle exit.

Although the hotgas-injector shows noteworthy recycle ratios at the desired propane flow and operation temperature, the system requirements are not fulfilled yet. Due to backflow risk in the test rig, for the subsequent system tests CO_2 was used instead of propane as injector motive gas, H_2O and additional CO_2 are added to the propane feed to enable stable system operation and to compensate the lack of reforming agent.

3.2. Dynamic simulation

Although a higher system efficiency can be achieved using the proposed AOGR concept, the system cannot be started directly in AOGR mode due to the required high operating temperature and the lack of available heat, steam and CO_2 for the reformation at start-up. Partial oxidation of propane followed by a switching procedure into the nominal AOGR mode is the preferred start-up operating mode, thus avoiding any auxiliary hydrogen or initial water evaporation. The dynamic simulation shall identify potential critical states during the switching procedure and shall support the development of a suitable control strategy. A detailed model permits complete start-up simulations with all necessary gas and wall temperatures and substantial concentrations as state variables. Modeling formulations and assumptions are briefly introduced in [11]. The model is implemented with the simulation tool Matlab/Simulink.

The startup of the SOFC stack is a crucial step, as the solid electrolyte has to be sufficiently preheated to gain sufficient ionic

conductance to draw current, thus providing steam and CO_2 in the downstream of SOFC to recycle. One option could be electrical preheating until 650 °C to ignite partial oxidation of propane with air in the reformer unit to overcome both the thermal and substantial deficiency at the startup. Hot reformat will provide the SOFC with heat and fuel gas, so that current can be collected already in the POX operating mode. As the SOFC approaches steady fuel utilization, the supply of POX air is successively replaced with recycled anode off-gas by injecting propane into the hotgas-injector, thus gradually switching the operation mode from partial oxidation to endothermic reformation of propane.

To ensure the safety of the testing rig, the inlet valve introducing anode offgas to the offgas burner should be closed at the POX mode and successively opened in the AOGR mode. This valve is simulated with a proportional lag element of the second order (PT_2). Other simulation settings are shown in a separate publication of the authors in [12]. The results of the startup simulation are shown in Fig. 6.

The simulation with 650 °C furnace temperature shows a potential overheating in the offgas burner, which could be explained through the following correlation diagram (see Fig. 7).

The simulation shows an insufficient preheating of the SOFC, resulting in low SOFC fuel utilization. Fuel rich anode offgas must be burned in the offgas burner, causing potential overheating if not sufficiently cooled down by cathode offgas. Without recuperating the heat from burner to cathode air within the furnace environment the low air inlet temperature would lead to an even lower SOFC temperature but overheating in the offgas burner. The cooling effect gets enhanced by the endothermic internal reforming of methane,

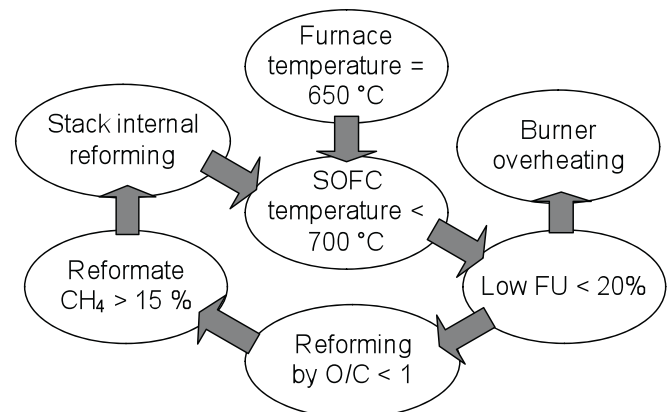


Fig. 7. Correlations of furnace temperature, burner temperature, fuel utilization and stack temperature.

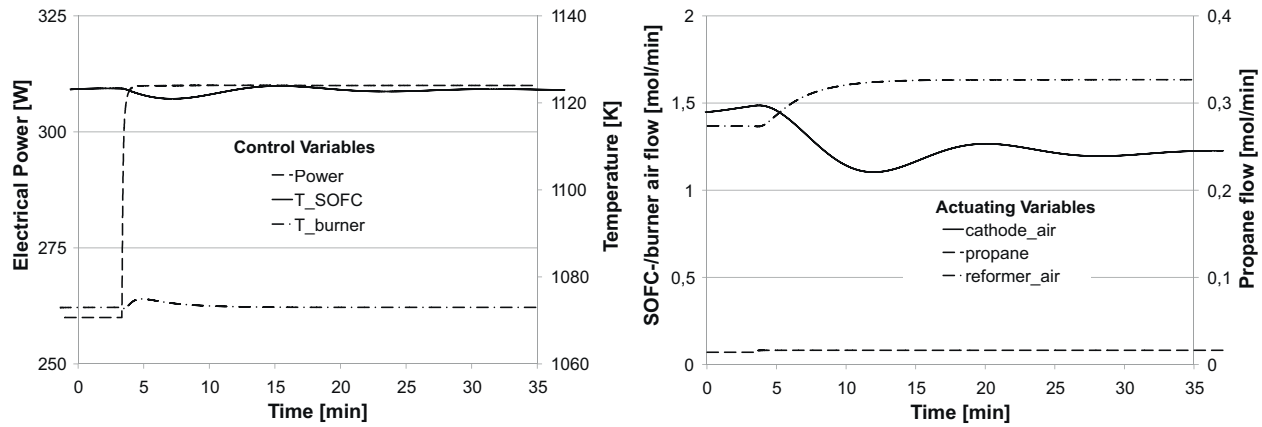


Fig. 8. Controlled variables response (left) and actuating variables response (right) after set point raising from 260 to 310 W power at $t=4$ min.

which is not fully converted into H_2 and CO in the reformer and remains as methane due to the low O/C-ratio and reformer temperature caused by radiant heat loss from the non-isolated reformer surface to the furnace. The result of this simulation shows the impact of the furnace temperature and lack of system isolation upon the startup behavior of the system. To avoid overheating during the switching, the following countermeasures should be considered in the future:

- Higher furnace temperature or
- Higher heat integration through thermal isolation of the SOFC and reformer and
- Control of offgas burner temperature through separate input of fresh air.

Based on the analysis above and available conditions at the testing rig, another simulation with a furnace temperature of 850°C was evaluated and no overheating was identified. Further simulations showed, that a minimal furnace temperature of 750°C is required to maintain the offgas burner under 950°C with the minimal requirement of cathode air input of $20\text{ l}_N\text{ min}^{-1}$ during the switching.

Besides the potential burner overheating caused by insufficient heat integration, the soot formation in the reformer is another critical issue during the switching procedure, which can be qualitatively represented by the O/C_{Ref} -ratio at the reformer inlet. Experimental investigations of the reformer showed an $O/C_{\text{Ref}} > 2.5$ as sufficient condition to avoid soot formation in the reformer. Based on this knowledge, a case study of three different rates of POX air switching-off aiming at short switching time and rapid increase of O/C_{Ref} was evaluated in a separate publication of the authors [13]. The furnace temperature was set to 850°C . Study results show an optimal increase of O/C_{Ref} by maintaining the excess POX air ratio at 0.3.

Future work of the dynamic simulation will focus on the development of a startup strategy, which ensures a self-sustaining startup of the system with enhanced heat integration. The simplified injector model should be refined to study the impact of the dynamic behavior of the recycle ratio on the system. Based on the existing dynamic model, a control concept was developed and will be discussed in the following chapter.

3.3. Controls

The AOGR-mode is a challenge for the control design as the SOFC exhaust gas is fed via the reformer to the stack inlet, thus creating a loop. Therefore, the actual state of the fuel cell stack not only depends on the input, but time-delayed on the output as well.

Both the cathode air inlet temperature and the air flow rate are options for the fuel cell temperature control. The air flow rate proved to be sufficient to keep the fuel cell temperatures within the working range during the tests, saving power consumption of the air heater. Propane flow to the reformer was used as actuating variable for stack power or voltage control. Contrary to most papers [14] the current draw was set to a constant rate, ensuring a stable conversion of fuel gas to oxidation products for the AOGR mode. Furthermore and regarding the composite design of the reformer/burner-reactor, it was possible to control both parameters reformer temperature and burner temperature by a single actuating variable, the burner airflow rate.

The control setup was tested with PID-controller in both a time-discrete simulation and the more detailed dynamical simulation. Stable control behavior was achieved in both simulations while reducing the remaining offset to zero.

In Fig. 8(left) trends of the controlled process variables resulting from a power change from 260 W to 310 W in the dynamical simulation is shown. Fuel cell and offgas burner temperatures were set to 1123 K and 1073 K respectively. The power meets the new target within less than a minute, followed by both temperatures which deviated only 5 K from the set point at most.

The corresponding trends of the actuating variables are shown in Fig. 8(right). Similar to the controlled process variables their behavior is stable.

In addition to the one-variable control shown here, a multi-variable controller was designed based on a mathematical description of the time-discrete simulation [15]. This controller especially reduced the overshoot of the fuel cell temperature by the factor two, in half the time of the one-variable derivative. Transferred to the dynamic simulation this controller configuration shows a remaining offset compared to the target value for both temperatures. Further studies regarding the optimization of the multi-variable control will be conducted.

4. Results

All process units were assembled inside a furnace, Fig. 9 shows the system set-up. CO_2 was used as injector motive gas because of insufficient hotgas-injector performance at the given propane flow rate. Thus, higher flow rates for the motive gas can be used resulting in an increased pressure level for the mixed gas stream and enabling the operation of the system including the injector. Propane, steam and additional CO_2 were fed directly to the reformer.

Modification in the welding execution of the reformer/burner-reactor led to a significant reduction of the pressure drop of the reformer from 40 to <10 mbar. Overall pressure drop of reformer,

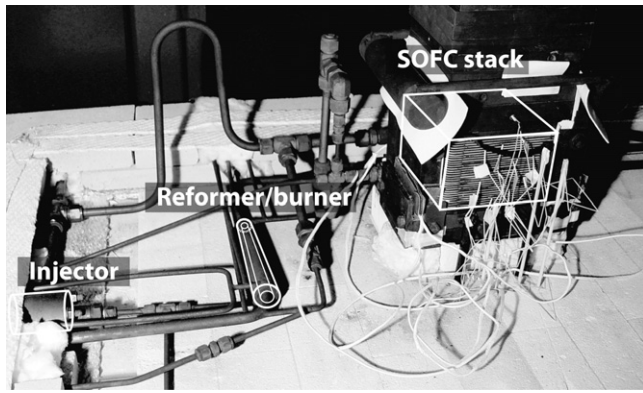


Fig. 9. Overall system assembled inside the furnace, white contours from left to right: hotgas-injector, reformer/burner-reactor, SOFC stack.

stack and recycle pipe was in the range between 24 and 31 mbar, enabling noticeable recycle ratios of hot anode offgas.

The system was heated up in the furnace to 850 °C under forming gas (5 mol.% H₂ in N₂) and switched into stationary AOGR mode. Continuous gas analytics were conducted to measure gas composition of reformer inlet, anode inlet and anode outlet and to calculate the received injector recycle ratio. It was detected, that the hotgas-injector recycles noteworthy and stable amounts of anode offgas for CO₂ motive gas flow rates above 0.8 l_N min⁻¹. Injector recycle ratios for these operation conditions were in the range of $R \approx 2$, corresponding to the values measured during the injector characterization.

Fig. 10 shows characteristic system performance values for a steady-state AOGR-experiment. Propane feed was set to 0.44 l_N min⁻¹, a chemical power input (LHV) of 640 W accordingly. The hotgas-injector was operated with a CO₂ motive gas stream of 0.8 l_N min⁻¹, additional steam was fed to adjust an (O/C)_{Ref} = 2.5 at the reformer inlet. System temperature was 850 °C. The fluctuation of stack current (and thus, stack power and efficiency) is due to the change of the gas analytics between reformer inlet, reformer outlet and stack outlet. Gas analytics at reformer outlet with a sample gas

consumption of 0.5 l_N min⁻¹ reduces the reformat gas at the stack inlet, decreasing stack current at fixed stack voltage of 21 V.

The resulting electrical stack power of $P_{el} = 270$ W was below the expectation from the stack characterization measurements (see Fig. 4), presumably due to degradation of the stack and the reformer catalyst during the measurements and the low recycle ratio of $R (\approx 2)$, which introduces less unused CO and H₂ from the offgas back to the stack.

In addition, the primary pressure for the injector motive gas continuously increases with ongoing measuring time. Upon completion of the tests the injector was dismantled and the nozzle diameter was measured, showing a decrease from initially 260 μm to 210 μm. Microscopic inspection does not indicate any depositions within the nozzle, so change in nozzle diameter seems to be caused by material changes during high temperatures, requiring further investigations.

Besides AOGR operation the system was also tested in POX-mode for comparison and proof of efficiency gain (Fig. 11) with a propane feed flow rate of 0.475 l_N min⁻¹ and O/C = 1. Start-up procedure was analogous to the AOGR experiments with the exception that the offgas burner was cooled with air and the anode offgas was removed from the system by a burner bypass line. Overheating of reformer and burner due to the exothermal reactions was avoided.

It is obvious that system efficiency in AOGR exceeds system performance in POX mode. For POX, $P_{el} = 200$ W and $\eta_{el} = 28\%$ results compared to $P_{el} = 270$ W and $\eta_{el} = 41\%$ for AOGR operation with comparable amounts of propane. With higher propane throughput, efficiency for POX even decreases (23% for a propane feed of 0.88 l_N min⁻¹).

Additional tests were performed to clarify the reason for the poor stack performance in AOGR operation compared to the preliminary measurements shown in Fig. 4 and to estimate the feasible efficiency gain for AOGR systems. Stack performance decline was confirmed as primary source for the efficiency discrepancy: Initially a stack power of 370 W resulted for an operation with a simulated reformat according to AOGR composition (see Fig. 4). The same operation point yielded only 308 W in this system. This stack degradation was attributed to the dismantling and interim storage of the stack after the preliminary tests and the subsequent re-mounting

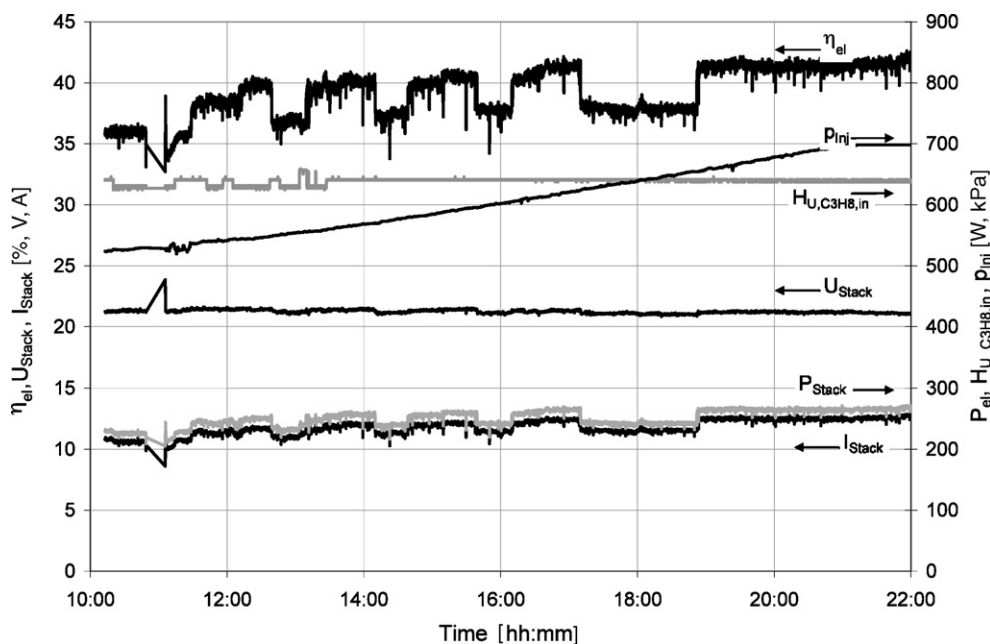


Fig. 10. System performance for stationary AOGR-operation for 0.44 l_N min⁻¹ propane + 0.8 l_N min⁻¹ CO₂ injector motive gas stream.

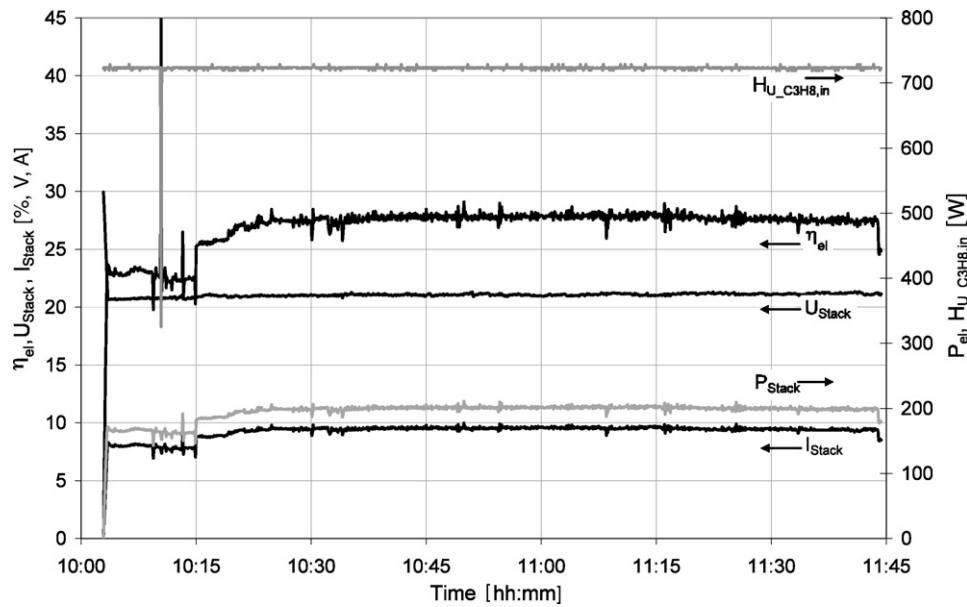


Fig. 11. System performance for stationary POX-operation using $0.475 \text{ l}_N \text{ min}^{-1}$ propane + $3.4 \text{ l}_N \text{ min}^{-1}$ POX air.

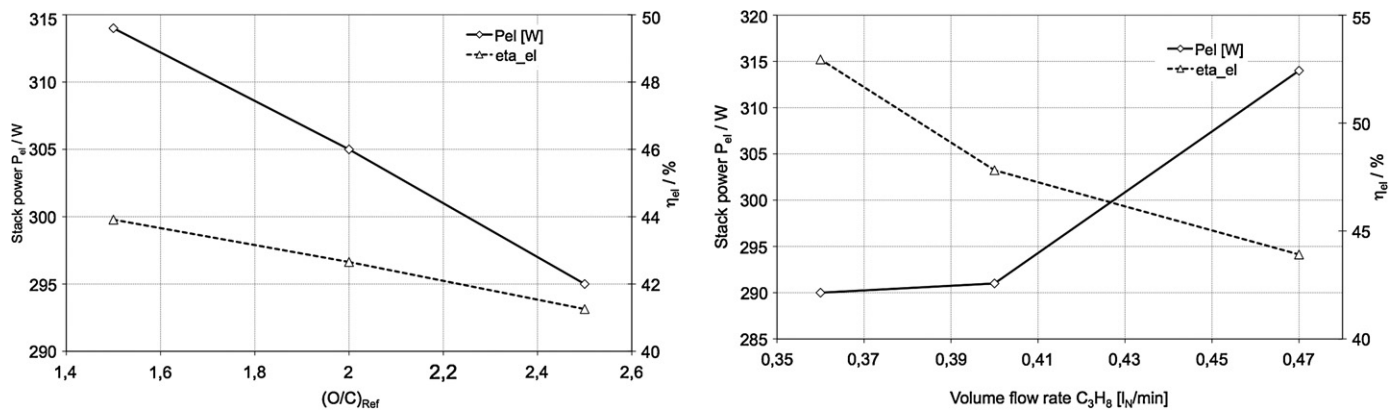


Fig. 12. Stack performance in different AOG modes. Left: lowered $(O/C)_{\text{Ref}}$, simulated reformat from $0.47 \text{ l}_N \text{ min}^{-1}$ C_3H_8 . Right: reduced propane flow rate, simulated reformat based on $(O/C)_{\text{Ref}} = 1.5$.

in the furnace for the overall system measurements. Because of the temporary and potentially inhomogeneous tensioning of the stack during the storage, degradation seems to be plausible.

Additionally, a loss of activity of the reformer catalyst is supposed. While first measurements deliver fuel gas fractions of reformer product in the range of 84–86 mol.% for the AOG operation, values obtained in the system test were reduced to 76–80 mol.%.

Stack tests were performed for demonstrating the efficiency gain potential of the AOG concept, feeding premixed AOG reformat that corresponds to reformer operation with lowered $(O/C)_{\text{Ref}}$ -ratio (excluding H_2 and CO that actually gets recycled due to incomplete fuel utilization in the SOFC) and with smaller propane feed gas flow rates (Fig. 12).

Stack power and thus efficiency increases, due to the higher fuel gas concentrations at the SOFC. System efficiency of 44% results for the given propane feed of $0.47 \text{ l}_N \text{ min}^{-1}$ at $(O/C)_{\text{Ref}} = 1.5$. Reformer catalysts should be aspired to get maximum efficiency enabling soot-free propane conversion at the minimized $(O/C)_{\text{Ref}}$ -ratio.

Propane feed flow reduction shows an even more pronounced effect on power output and efficiency. A replicated reformat

based on a propane feed of $0.36 \text{ l}_N \text{ min}^{-1}$ and an $(O/C)_{\text{Ref}} = 1.5$ yields a system efficiency of 53%, aiming for stacks with better fuel utilization at higher throughput. Lower values for the propane flow couldn't be examined because of mass flow controller limits.

5. Summary and outlook

A reformer/burner-reactor and a hotgas-injector were developed and characterized to demonstrate the feasibility of the AOG concept. The stack characteristic was determined and the complete AOG system was dimensioned based on the result of the component testing. The overall system was mounted inside a furnace and evaluated at different operation points to proof the possible efficiency gain. The following main results were obtained:

- The system efficiency is considerably higher for the AOG operation compared to POX. An efficiency gain of 18 percentage points ($\eta_{\text{POX}} = 23\%$, $\eta_{\text{AOG}} = 41\%$) was demonstrated experimentally.

- Start-up and steady-state operation of the overall system in POX- and AOGR-operation were realized over an operation time of several hours.
- A motive gas throughput $\geq 0.8 \text{ l}_N \text{ min}^{-1}$ allows stable hotgas-injector operation with recycle ratios of about $R \approx 2$ for a system backpressure of 24–30 mbar.
- The reformer/burner-reactor limit of $(O/C)_{\text{Ref}} = 2.5$ reduces system power output and efficiency but is essential to avoid soot formation.
- The electrical power and system efficiency achieved is lower than expected from the component characterization. Degradation effects of stack and reformer catalyst seem to be responsible for the loss.

Transferring the AOGR system concept into practice the project team stated the following main technical challenges:

- SOFC-stacks with maximum fuel utilization ($FU > 0.8$) should be deployed. This increases overall efficiency and reduces the recycle ratio requirements for the injector.
- Pressure loss of components and piping should be reduced to minimize parasitic losses and to reduce hotgas-injector performance requirements.
- Improved reformer catalyst should be investigated to reduce the $(O/C)_{\text{Ref}}$ -ratio needed for soot-free operation.
- The hotgas-injector needs substantial improvements for the usage within the overall system. CFD simulations and the deployment of Laval-nozzles are recommended to achieve recycle ratios necessary to avoid soot formation at the given pressure conditions.
- A following system should be build-up and operated in a thermal self-sustaining housing to eliminate the influence of the furnace used so far.

These topics will be addressed by the research team within a follow-up project.

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References

- [1] C.S. Chen, S.J. Feng, S. Ran, D.C. Zhu, W. Lin, H.J.M. Bouwmeester, *Angew. Chem. Int. Ed.* 42 (2003) 5196.
- [2] J. Caro, *Chemie-Ingenieur-Technik* 78 (7) (2006) 899–912.
- [3] R.-U. Dietrich, J. Oelze, A. Lindermeir, O. Carlowitz, C. Spitta, M. Steffen, B. Schönbrod, A. Heinzel, H. Stagge, H.-P. Beck, C. Schlitzberger, S. Chen, M. Mönnigmann, R. Leithner, SOFC-Brennstoffzelle mit partieller Anodenabgas-Rückführung zur Reformierung [SOFC system using partial anode offgas recycle for fuel reforming], *VDI-Berichte* (2036), 2008, pp. 217–230.
- [4] D.L. Trimm, *Appl. Catal.* 7 (1983) 249–282.
- [5] B.E. Liyan Ma, Hydrogen production from steam reforming of light hydrocarbons in an autothermic system, Ph.D. thesis, University of New South Wales, 1995.
- [6] Y. Liu, R. Farrauto, Abstracts of 2004 Fuel Cell Seminar, San Antonio, USA, 2004, pp. 46–49.
- [7] R. Farrauto, T. Poles, Abstracts of 2005 Fuel Cell Seminar, Palm Springs, USA, 2005, p. 163.
- [8] J.R. Rostrup-Nielsen, K. Aasberg-Petersen, *Handbook of Fuel Cells – Fundamentals, Technology and Applications*, vol. 3, part 1, John Wiley & Sons Ltd., West Sussex, 2003, pp. 159–176.
- [9] C. Wunderlich, Fuel Cell Seminar, Honolulu, 2006.
- [10] C. Wunderlich, Fuel Cell Seminar, San Antonio, 2007.
- [11] S. Chen, C. Schlitzberger, R. Leithner, M. Mönnigmann, Proceedings of 8th European SOFC Forum, 01.07.2008–04.07.2008, Luzern, 2008.
- [12] S. Chen, C. Schlitzberger, R. Leithner, Proceedings of 9th European SOFC Forum, 28.06.2010–02.07.2010, Luzern, 2010.
- [13] R.-U. Dietrich, J. Oelze, A. Lindermeir, O. Carlowitz, C. Spitta, M. Steffen, B. Schönbrod, A. Heinzel, H. Stagge, H.-P. Beck, C. Schlitzberger, S. Chen, Proceedings of the 7th International Conference on Fuel Cell Science, Engineering & Technology, 08.06.2009–10.06.2009, Newport Beach, 2009.
- [14] R. Gaynor, F. Mueller, F. Jabbari, J. Brouwer, *J. Power Sources* 180 (2008) 330–342.
- [15] T. Küster, H.-P. Beck, H. Stagge, Proceedings of European Fuel Cell Forum, 29.06.2009–02.07.2009, Luzern, 2009.