Reforming of natural gas in solid oxide fuel cell systems

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Abstract

Internal steam reforming is an attractive option offering a significant cost reduction and higher system efficiencies of a solid oxide fuel cell (SOFC) power plant. Furthermore, faster load response may characterise systems with internal reforming. However, complete internal reforming can lead to several problems, which can be avoided with partial pre-reforming of natural gas. For SOFC systems the ratio between internal and pre-reforming has to be optimised on the basis of experimental performance data. A detailed study concerning the pre-reforming in a reformer of considerable size (10 kW) is carried out. The influence of operating temperature and mass flow variations on conversion of methane and ethane is analysed. During internal reforming of methane with substrate anodes, large temperature gradients were detected. Substrate samples with low catalytic activity show large response times with respect to parameter variations. © 1998 Elsevier Science S.A.

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1. Introduction

Solid oxide fuel cells (SOFCs) operate at temperatures between 800 and 1000°C. The most interesting fuel for SOFC systems used for stationary applications is natural gas consisting mainly of methane. One main target of further process development is to reduce the large amount of air supply to the fuel cell stacks, which is necessary to remove the electrochemical waste heat. Alternative stack cooling concepts are necessary to improve plant operation. The endothermal steam reforming of natural gas within the anode chamber of the SOFC stack (internal reforming) is favourably applied to reduce the expenses of a pre-reformer and to provide additional cooling of the cell. Internal steam reforming is an attractive option offering a significant cost reduction and higher system efficiencies of a SOFC power plant. Furthermore, faster load response may characterise systems with internal reforming.

However, complete internal reforming can lead to several problems: (i) carbon formation in the anode chamber; (ii) the endothermal reforming reaction is very fast and influences the temperature distribution in the stack considerably. In the fuel inlet area of the stacks a strong cooling can occur

and therefore, large temperature gradients appear [1]. With partial pre-reforming of natural gas these problems can be avoided. For SOFC systems the ratio between internal and pre-reforming has to be optimised on basis of experimental performance data. Because of higher hydrocarbons in natural gas pre-reforming – at least to some extent – has to be provided in future SOFC-plant concept development. This should be realised with a compact pre-reformer (small, low investment cost). Instead of a fuel preheater and a conventional reformer, which would be relatively large, only one apparatus for simultaneous fuel preheating and natural gas reforming is used in the compact pre-reformer concept. Conventional reformers are optimised for high methane conversions and consist of reformer tubes, which are about 10 m long [2]. Under such reaction conditions the synthesis gas compositions are close to equilibrium [3]. In SOFC systems fuel gases with more or less lower methane conversions are sufficient. Therefore, the length of the reforming reaction path is restricted to about 1 m in our pre-reformer concepts.

In a first approach, the influence of process parameters (process gas temperature, educt mass flow) on product stream composition of pre-reforming will be examined under practically relevant conditions with such a compact pre-reformer.

An anode-supported planar SOFC concept has been developed and tested at the Forschungszentrum Jülich.

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The specific behaviour of substrate anodes with respect to the reforming reaction was studied. At the Forschungszentrum Jülich, Ni supported on yttrium stabilized zirconia (YSZ) is used for substrate anodes. They are about 2 mm thick, in order to serve as supporting anodes. This concept allows the application of a very thin electrolyte film and thus lower working temperatures (about 750°C) at a high power density are possible [4]. It was shown previously [5,6] how mass transfer in the anode can influence the rate of steam reforming. The interference of mass transfer and reaction rate should affect the temperature gradients and the load response behaviour during internal reforming. Therefore, the second part of the study focuses on the experimental estimation of both phenomena.

2. Experimental

2.1. Test facility for peripheral components

A test facility for peripheral components is operating with natural gas (87 mol% CH_4, 6 mol% C_2H_6, 2 mol% higher hydrocarbons) to simulate selected critical gas processing steps of a SOFC plant under real operating conditions. Components like pre-reformers, injectors and heat exchangers are developed and investigated. The capacity of the test facility corresponds to a 10 kW SOFC plant (feedstock pre-reformer up to 2 m^3(STP) natural gas).

Desulfurization takes place in an active carbon bed. The pre-reformer and other peripheral components are located in a pressure vessel (Fig. 1). As heat source a natural gas burner is mounted on top of the pressure vessel. The test facility is designed for system pressures up to 14 bar and burner temperatures up to 1000°C. The product gas of the pre-reformer is cooled down. The composition of the gas is analysed by means of gas chromatography. For the detection of ethane contents of the order of 1 mol% (ethane content in the natural gas 6 mol%) the gas chromatograph was adjusted with a special calibration gas. The main components are checked by an IR Binos Analyzer system.

2.2. Test rig for internal reforming

In the test equipment for internal reforming, a mixture of pure methane with steam flows at 1.5 bar and 1 m/s over one side of a flat piece of the substrate anode. At the sample side not exposed to the gas phase, the cermet temperature can be measured at different positions via thermocouples. The temperature of the bulk gas phase prior the reforming zone is set to 915°C during all experiments. This experimental set-up serves for the investigations of the dependence of methane reforming rate on steam-to-methane ratios (3–6 mol/mol), on space velocities (80–120 m^3(STP)/h/m^2) and thicknesses (0.3–1.2 mm) of the anode under conditions similar to the ones for operating SOFCs. The dry product gas stream was analysed continuously by a Binos IR-adsorption-detector
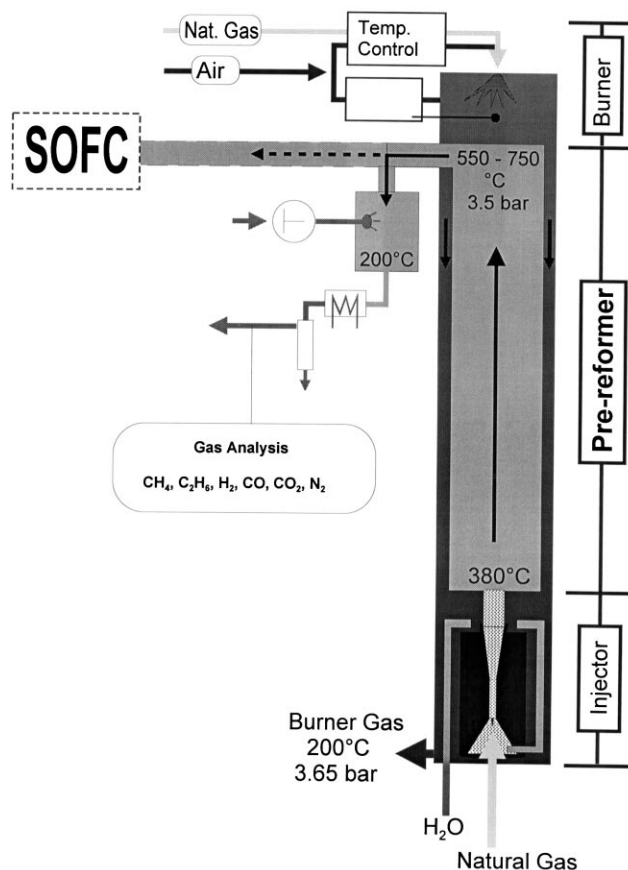

Fig. 1. Test facility for peripheral components.

for CO, CO_2 and CH_4. Hydrogen was detected by a thermal conductivity detector (TCD). A detailed description of the experimental set-up is published elsewhere [7].

3. Results and discussion

3.1. Pre-reforming of natural gas

Two types of pre-reformer concepts were investigated. The type I pre-reformer is based on a hybrid heat exchanger with catalytic active wall. The small reforming activity of stainless steel can be increased by nickel coating [8]. In cooperation with the Bavaria Company, about 100 plate elements of the heat exchanger were separately coated with carbonyl–nickel by a galvanic method. Small samples (10 × 200 mm) were investigated in a tubular reactor [9]. The reforming rates were relatively low. It could be calculated that the catalytic active surface area of the pre-reformer, which is identical to the designed heat exchange area, is not sufficient for typical operation conditions designed for SOFC systems. As a consequence a very high reformer temperature of about 900°C or a much larger pre-reformer would be necessary to reach sufficient methane conversions for a system pressure of about 2 bar. Additionally, problems caused by the complicated hybrid-type construction of the
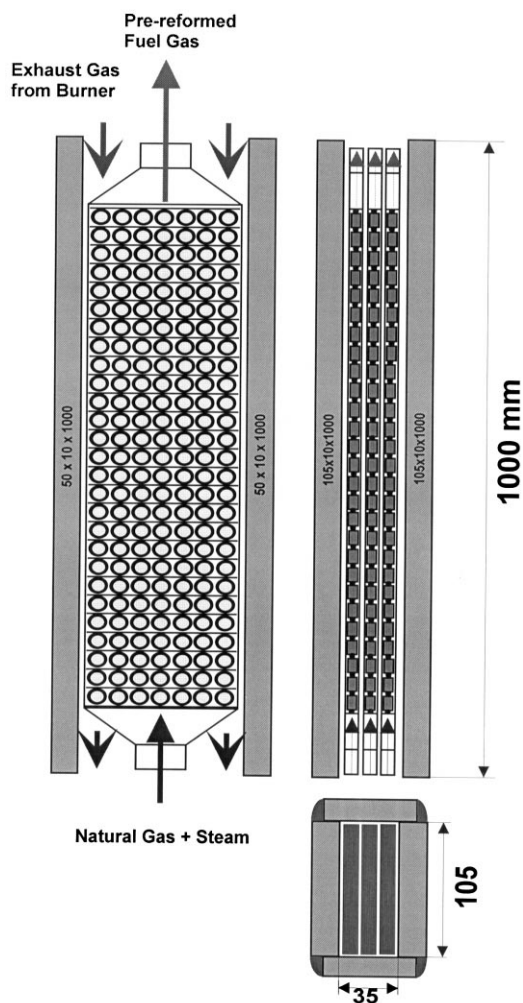
Fig. 2. Compact pre-reformer with Rasching rings (type II).

Table 1

Experimental data of the pre-reformer

Reformer geometry	
Reformer space	7.5 l
Reaction space	1.5 l
Wall area	0.6 m^2
Geometric catalyst area	0.6 m^2
Data of experiment	
Pressure	3.5 bar
Temperature burner gas	780°C
Natural gas flow	1.6 m^3(STP)/h
H$_2$O/CH$_4$ (inlet)	3 mol/mol
Space velocity (reaction space)	1070 m^3(STP) natural gas/m^3/h
Catalyst load (geom. catalyst area)	2.7 m^3(STP) natural gas/m^2/h
Gas velocity	About 2 m/s
Temperature of pre-reformed gas	690°C
Ethane conversion	73%
Methane conversion	41%
Pressure drop in catalyst zone	40 mbar
$(p_{H_2}^2/p_{CH_4})/K_p$ (CH$_4$ cracking)	1.1
(i.e. the composition of the pre-reformed gas is not critical to carbon formation)	

heat exchanger were observed during the start-up phase. After detection of leakage between the hot and the cold side, the experiments were stopped.

Another pre-reformer (type II) was constructed by using a simple plate heat exchanger. As shown in Fig. 2, the space between adjacent walls is filled with one layer of a conventional Raschig ring steam reforming catalyst (Südchemie G-90 B, 12 × 6 × 6 mm). First experiments were carried out at a pressure of 3.5 bar.

In Table 1, a typical result for a maximum process gas temperature of about 700°C (catalyst outlet) is given. This pre-reformer shows a good characteristic behaviour. Methane conversions up to about 40% and ethane conversions up to about 80% are reached. Measurements of the pressure drop are carried out at room temperature with air. Extrapolation to operation conditions gives a relatively low pressure drop of 40 mbar.

The variation of temperature (Fig. 3) results in an increase of about 10–15% methane conversion per 100 K temperature increase. The ethane conversion in general is about a factor of 2 higher than the methane conversion. It can be assumed that the propane conversion (not measured) is even

higher than the ethane conversion. The low conversion of ethane observed at 660°C may be a result of some catalyst degradation.

The methane conversions are also very sensitive to the variation of mass flow. In the measured range, where the mass flow is increased by nearly a factor of 2, the conversions are practically inverse proportional to the mass flow or, in other words, the conversions are proportional to the residence time in the catalyst zone. Thus it is possible to calculate the methane conversion rate for different mass flows (Fig. 4). At a given temperature the rate does not depend on the chosen mass flow. Within the ranges of the investigated parameter (low and medium methane conver-
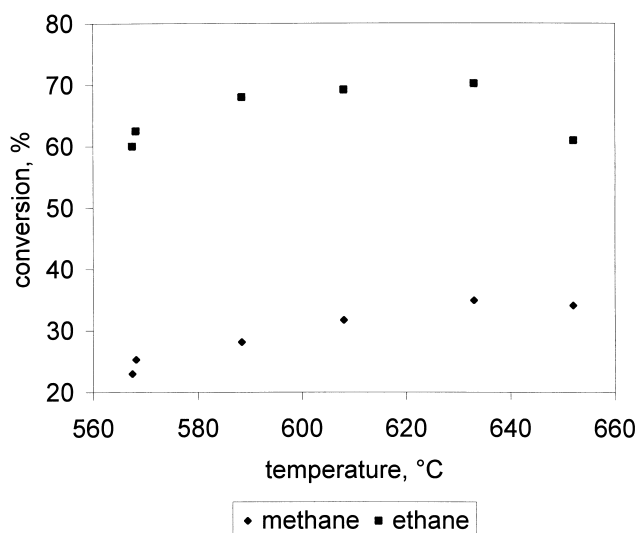

Fig. 3. Pre-reforming of natural gas in type II pre-reformer. Conversion of methane and ethane vs. reaction temperature.
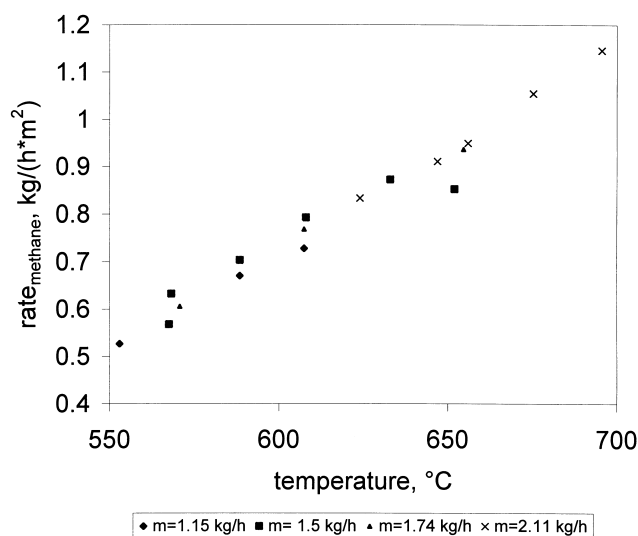
Fig. 4. Pre-reforming of natural gas in type II pre-reformer. Conversion rate of methane at different mass flows vs. reaction temperature.

sions), the reforming process is completely kinetically controlled.

3.2. Internal reforming

Experiments concerning internal reforming were carried out with two samples. Both of them consist of Ni-8YSZ (8 mol% Y_2O_3–stabilised ZrO_2) substrate with a standard composition of 51 wt.% Ni, and were manufactured by the Coat Mix process starting with a powder mixture of NiO and 8YSZ together with a resin [4]. The preparation of sample A was finished after a pre-sintering step at 1285°C. On sample B, after the pre-sintering an anode functional layer was deposited on one side of the substrate [4] followed by a further sintering step. Sample B is characterised by larger surface areas and better electrochemical performance.

In Fig. 5 the temperature gradients measured in flow direction at the down-side of the substrate cermet (sample A) are visualised. The data correspond to steady-state conditions, e.g. after reaching constant values in methane conversion with three different steam-to-methane molar ratios (Table 2). At a constant mass flow of 100 m^3(STP)methane/m^2/h but with an increasing amount of steam, the conversion drops. In the steam reforming literature, kinetic expressions with partial pressure dependencies of zero order in steam [10] as well as expressions with negative reaction orders with respect to steam [2] have been reported, largely dependent on the type of catalyst and its microstructure. The temperature gradient along the substrate increases with increasing methane conversion (Table 2). The minimum cermet temperature is 20 K lower than at the beginning of the cermet, with a total methane conversion of 9.5%. This temperature minimum occurs at 5 mm cermet length, e.g. 50% of the total length (a gradient of around 4 K/mm). Under milder process conditions and lower conversion degrees not only the temperature gradient declines, but in
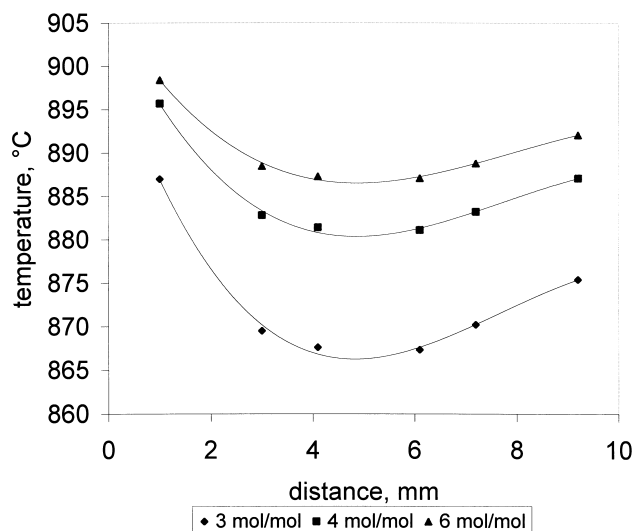

Fig. 5. Internal reforming of methane with substrate anodes. Cermet temperature in flow direction for different molar ratios H_2O/CH_4. T_{oven}: 915°C; b: 100 m^3(STP)/m^2/h; VCH_4: 32.4 m^3(STP)/m^2/h; p: 1.5 bar; sample A.

addition the position of minimum is shifted to shorter distances. This is the expected behaviour for a strongly endothermic reaction performed in a polytropic reactor. In future, with these temperature profiles and the measured conversions, detailed modelling of the internal reforming will be carried out. Shut-down procedures for SOFC with internal reforming must prevent fuel being provided to the stacks without electrochemical power generation.

The complete run of the above-mentioned experiment (methane conversion versus time on stream) is shown in Fig. 6. In the plot, the time zero is defined by first contacting the reduced sample with methane at operation conditions. It is remarkable that after starting the experiment a period of more than 15 h is necessary until constant conversion is reached (Fig. 6, part I). In a blind control experiment (with no cermet sample in the reactor), after less than 5 min methane was detected at the reactor outlet. So it seems that the delay time observed is related to the reaction and/or cermet material properties. Under identical conditions the start-up behaviour is completely different with sample B (Fig. 7, part I). Within a few minutes the conversion is stabilised. Practically no differences in response times between sample B and the blind experiment exist. Furthermore, with sample B the level of methane conver-

Table 2

Internal reforming of methane with substrate anodes: maximum temperature gradients for different molar ratios H_2O/CH_4

Molar ratio H_2O/CH_4 (mol/mol)	$t_{at\ 1\ mm} - t_{minimum}$ (K)	Conversion (%)
3	20	9.5
4	14	6.8
6	11	5.0

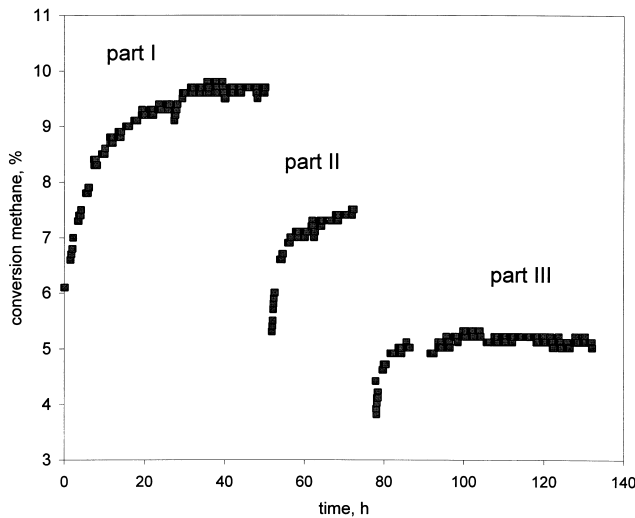T_{oven}: 915°C; b: 100 m^3(STP)/m^2/h; VCH_4: 32.4 m^3(STP)/m^2/h; p: 1.5 bar; sample A.

Fig. 6. Internal reforming of methane with substrate anodes. Methane conversion for different molar ratios H_2O/CH_4 vs. time on stream. T_{oven}: 915°C; *b*: 100 m^3(STP)/m^2/h; VCH$_4$: 32.4 m^3(STP)/m^2/h; *p*: 1.5 bar; sample A.

sion is higher than with sample A. It seems that the more active the cermet material, the shorter is the start-up time. This observation was confirmed by additional experiments. After 50 h time on stream with sample A, the steam/methane ratio was increased from 3 to 4, and after 75 h from 4 to 6 (Fig. 6, parts II and III). In each case of load change, the system needs more than 2 h to achieve around 90% of the final conversion level. With sample B, after 21 h time on stream the mass flow was decreased from 100 to 80 m^3(STP)/m^2/h, and after 43 h on stream increased to 120 m^3(STP)/m^2/h (Fig. 7 part II and III). As expected, the conversion increases after 21 h on stream. The response of the system is nearly a perfect step function. Otherwise, at 43 h conversion drops rapidly due to the diminished residence time. Similar to the observations with sample A, more than
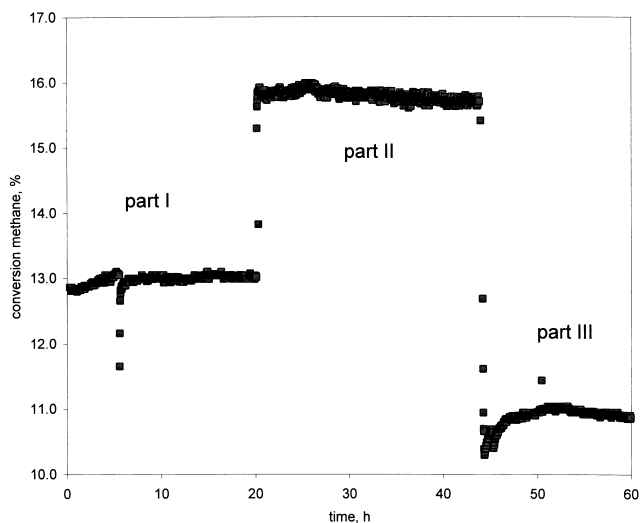

Fig. 7. Internal reforming of methane with substrate anodes. Methane conversion for different space velocities vs. time on stream. T_{oven}: 915°C; molar ratio H_2O/CH_4: 3; *p*: 1.5 bar; sample B.

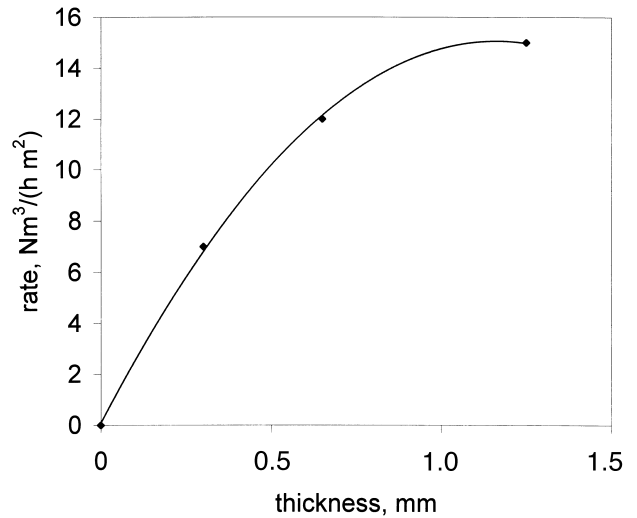Fig. 8. Internal reforming of methane with substrate anodes. Reaction flux density vs. anode thickness. T_{oven}: 915°C; molar ratio H_2O/CH_4: 3; *b*: 100 m^3(STP)/m^2/h; *p*: 1.5 bar; sample A.

2 h are necessary to stabilise the system at a low level of conversion. The response time for internal reforming depends on process parameters and material properties. The delay times observed may result from interference of reaction and mass transfer phenomena which are related to structural properties of the cermet material. Therefore, with materials of sample A type, the influence of anode thickness on reactivity was studied. The rate of the reforming reaction was measured as a function of the thickness of the anode (variation between 0.36 and 1.9 mm). The aim of these experiments was to determine the depths of the reaction zone in the anode. In Fig. 8 the reactivity related to the surface of the sample is plotted versus the anode thickness. At a reaction temperature of 915°C the reactivity increases linearly with the anode thickness up to a thickness of 0.6 mm. In the range of 1.2–0.6 mm, no significant difference in methane conversion could be observed. This result leads to the conclusion that for these anodes with defined structural properties, the depth of the methane reforming reaction zone is larger than 0.15 mm but smaller than 0.3 mm [7]. Based on these experiments it was shown previously [5,6] by computer simulations how mass transfer in the anode can influence the rate of steam reforming. Samples of type B are characterised by higher activity. This can be the result of almost no transport limitation due to higher porosity.

4. Summary

A compact pre-reformer (10 kW) with Raschig ring layers was constructed and operated with natural gas. At 650°C 30% of the methane was reformed. Under these conditions ethane conversion reaches 70% and no higher hydrocarbons have been detected in the product stream. The product quality, e.g. methane and ethane conversion

degrees, can be controlled by the temperature and the variation of the mass flow. Future experiments should clarify whether SOFC stacks can be operated with this pre-reformed natural gas.

During reforming of methane with substrate anodes, large temperature gradients were detected. At a total level of 9.5% methane conversion, a maximum temperature gradient of 4 K/mm at the substrate anode was observed. Samples with low catalytic (and electro-catalytic) activity show remarkable start-up and response times with respect to process parameter variations. The low activity of these 'slow' substrate anodes can be explained by a restriction of the reaction rate by mass transfer processes, which could also be the reason for the slow response behaviour. The response of anodes can be improved via modifying the substrate with a functional layer. Adopting substrate anodes for internal reforming purposes needs further material optimisation. In particular, the necessary dynamics of a SOFC system demands defined structural properties of substrate anodes.

Acknowledgements

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