

Innovative concepts for the coproduction of electricity and syngas with solid oxide fuel cells

H.-E. Vollmar ^{a,*}, C.-U. Maier ^b, C. Nölscher ^c, T. Merklein ^d, M. Poppinger ^e

^a Siemens, ZT IF E, PO Box 3220, D-91050 Erlangen, Germany

^b Siemens, ZT IF IU, PO Box 111809, D-81730 Munich, Germany

^c Siemens, KWU I-E5, PO Box 3220, D-91050 Erlangen, Germany

^d Siemens, KWU LZM Ref E, PO Box 3180, D-91050 Erlangen, Germany

^e Siemens, ZT EN 1, PO Box 3220, D-91050 Erlangen, Germany

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Abstract

Design of an SOFC for both high internal heat and high electrical power generation at reduced electrical efficiency results in a SOFCR, solid oxide fuel cell reformer. The high-temperature heat is used mainly for internal reforming of natural gas. This new combined production of electrical energy and hydrogen-rich syngas is much more efficient than separate production. The most important applications are the supply of the chemical industry with electricity and hydrogen, and the use for on-site power generation in conjunction with PEM fuel cells. The results of thermodynamic calculations, particularly in the range of low cell voltages, are confirmed by experimental studies and modeling calculations. © 2000 Elsevier Science S.A. All rights reserved.

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1. Scenario of a distributed energy supply system using fuel cells

If the high-temperature heat of the SOFC is utilized to produce hydrogen-rich synthesis gas, the range of application of fuel cells for distributed energy supply is significantly extended. For example, in addition to the envisaged supply to the processing industry of electricity and process heat, of power generation using combined SOFC/gas turbine plants, and of supplying households with electricity and heat using PEM fuel cells, the following applications are also feasible (Fig. 1).

The chemical industry could be supplied with electricity and syngas or hydrogen. This combined process yields a significant increase in efficiency levels.

On-site production of hydrogen in future hydrogen filling stations is also feasible and has the advantage that the filling station only requires a connection to the natural gas supply network. Then the transport of cryogenic or compressed hydrogen would be unnecessary.

Electricity for compression or refrigeration is generated on-site and enhances the efficiency for the energy supply chain.

Hydrogen from the filling station can be distributed via a local supply network to PEM fuel cells in dwellings. In this way, PEM fuel cells can be operated more flexibly and efficiently than in the case of hydrogen production using small reformers.

The direct coupling of larger SOFCs and PEMFCs for the provision of electrical energy and space heat is also feasible for buildings.

2. Thermodynamic design calculations

SOFC plants for the generation of electricity and possibly heat at a high cell voltage in the range from 0.75 to 0.8

* Corresponding author. Fax: +49-91-31-72-02-40; e-mail: horst.vollmar@erls.siemens.de

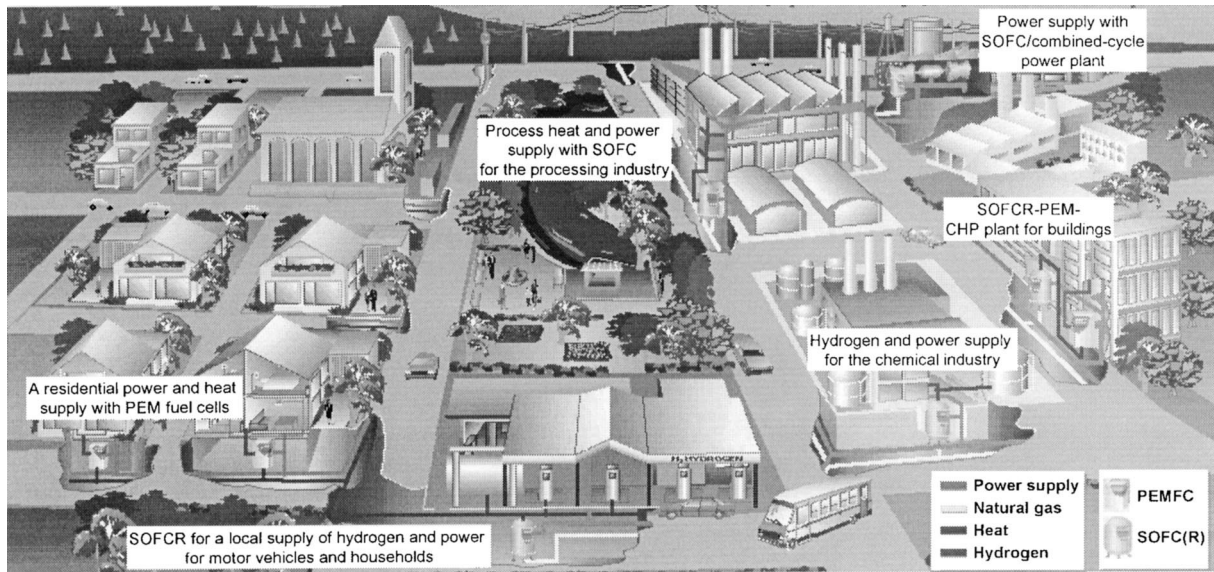


Fig. 1. Scenario of future distributed generation using fuel cells.

V and high fuel gas utilization are customarily designed to exploit the high electrical efficiency potential of the SOFC.

In markets where hydrogen and syngas are considered more important than high-temperature heat, operation at a low cell voltage with correspondingly high heat generation and conversion of this heat into chemically bound energy in the form of CO and hydrogen can be advantageous (Fig. 2). For hydrogen users, the CO can be converted in the established fashion into CO₂ and H₂ using a shift reactor followed by CO₂ separation.

Reduction of the cell voltage (to 0.5 V for example), and simultaneously, of the fuel utilization more than doubles the electrical power density and increases the heat generated. With an adequate additional amount of methane-containing fuel gas and water vapour available, the heat is then converted into chemical energy by the reformatting of CH₄ to CO and H₂.

If, after conversion of the CO in a shift reactor and CO₂ separation, the syngas or the hydrogen is used, for example, in a PEM fuel cell, this represents an operating point

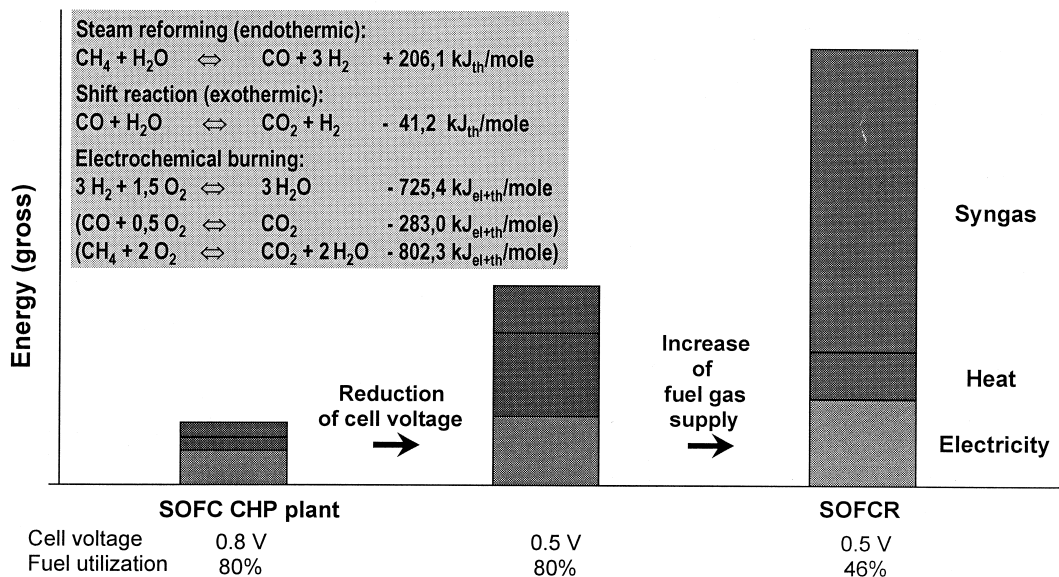


Fig. 2. Utilization of high-temperature heat for the production of syngas. Chemical and electrochemical processes.

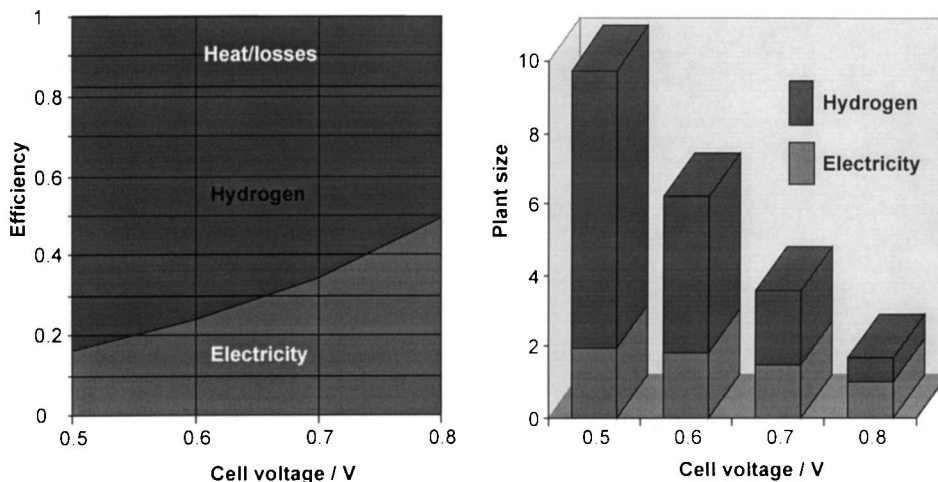


Fig. 3. Efficiency of electricity and hydrogen generation. Flexibility in design for a given stack.

for the SOFC at which more electrical energy is produced per cell surface area and, in addition, a high-grade chemical is produced.

In the cell voltage range between 0.5 and 0.8 V, the thermodynamic plant calculations show a net utilization factor for the generation of electrical energy and hydrogen slightly higher than 0.8, with this factor being almost independent of the cell voltage (Fig. 3). The plant design and operating point for each cell voltage has been chosen for maximum syngas production (Fig. 3). Because of the major dependence on cell voltage of current density and heat generation, in turn linked to electricity generation, we obtain high flexibility in terms of stack design, ranging from primary electricity generation at high cell voltage to predominantly hydrogen generation at high electrical power in the lower cell voltage range.

If the hydrogen produced is used in a PEMFC downstream of the SOFC reformer (SOFCR) for further electricity generation, the net electrical efficiencies are between 53 and 68% in the cell voltage range of the SOFCR between 0.5 and 0.8 V (Fig. 4). The design of SOFC reformer and its operating point can be set designed depending on the cost ratios of SOFCR and PEMFC, and of electricity and natural gas, respectively. The highest electrical efficiencies are achieved with a combination in which the electrical power produced by the SOFC is significantly higher than that of the PEMFC. On the other hand, operation with a relatively small SOFCR at a low cell voltage and appropriately high heat and hydrogen production can also be advantageous.

The SOFCR used to produce hydrogen for the chemical industry or for PEMFCs, comprises the following compo-

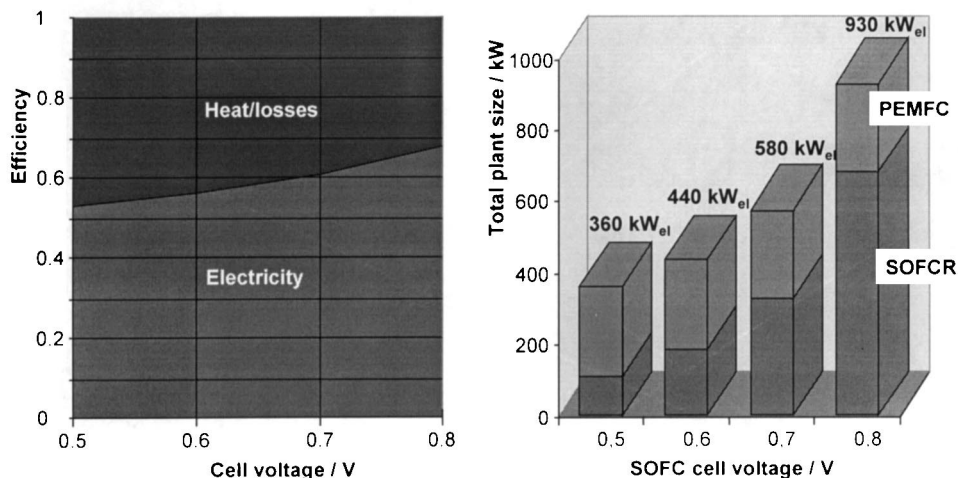


Fig. 4. Net electrical efficiency for a combination of SOFCR and PEMFC. Flexibility in design at a given PEMFC plant size (250 kW_{el}).

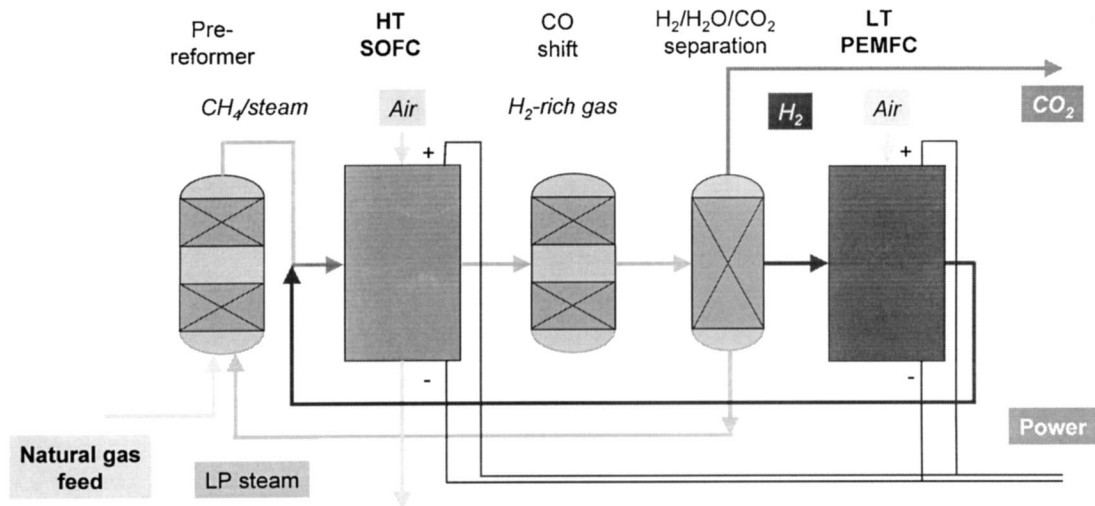


Fig. 5. Schematic of an SOFCR-PEMFC power plant. CO₂ removal and high efficiency.

nents: a pre-reformer for splitting higher molecular weight hydrocarbons, an SOFC designed for reformer operation, a shift reactor and a gas separator for the separation of water and CO₂ (Fig. 5).

The separated water is used advantageously together with the natural gas and returned to the process via a pre-reformer. When coupled with a PEMFC it is likewise beneficial to route the hydrogen which was not oxidized in the PEMFC to the SOFC.

The CO₂ produced by gas separation can be retained and utilized or sequestered by injecting it into tertiary oil deposits, for example.

3. Experimental results

The objective of the experimental investigations was to demonstrate reformer operation of the SOFC with the MEAs (membrane electrode assemblies) developed at

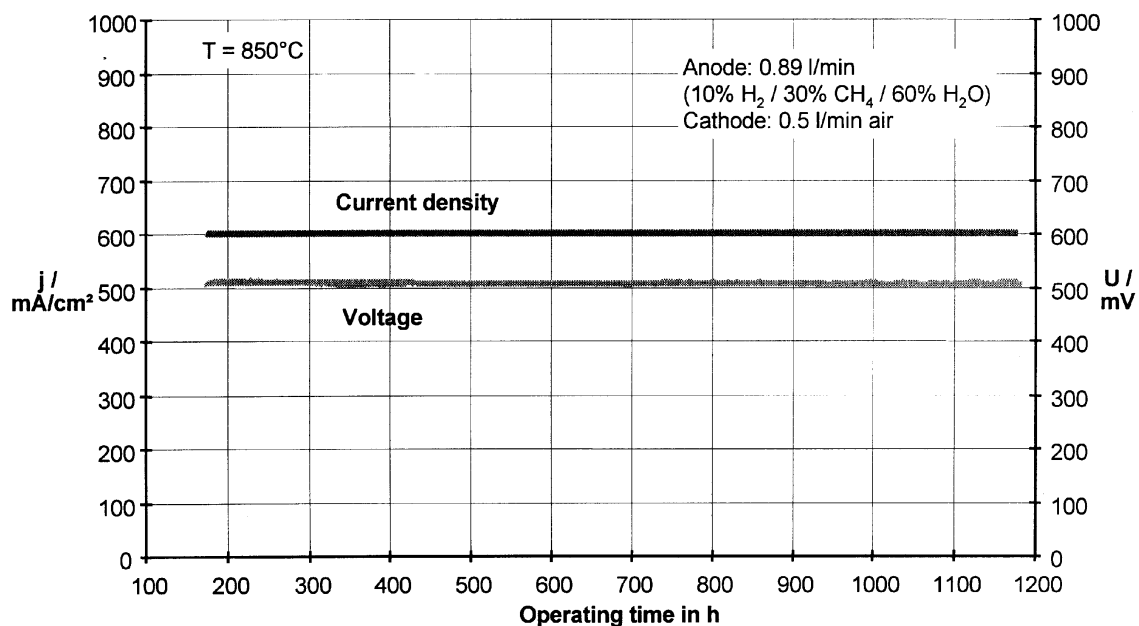


Fig. 6. Endurance test of a single cell with pre-reformed fuel gas. No excessive aging in reformer operation over a period of 1000 h.

Siemens as part of the development of the planar SOFC and to provide physical parameters for modeling. The aspects of particular interest here were the long-term load behavior of MEAs in reformer operation, the electrochemical conversion of CO, the kinetics of the shift reaction in a ceramic housing and in “short stacks”, as well as the suitability of the anode used for the reforming reaction.

All the tests were conducted at gas flow rates and fuel gas compositions matched to the conditions in the stack. The fuel gas composition of 10% H₂, 30% CH₄ and 60% H₂O is roughly equivalent to the composition downstream of a pre-reformer operated at about 500°C.

For qualification of the MEA employed, the cell was measured after installation and conditioning according to a standard procedure, initially with 50% H₂ and 50% H₂O in air operation at temperatures of 950, 850 and 750°C. The MEA yielded the customary curves and is thus representative of MEAs produced by Siemens. It could be loaded up to 0.5 V, a feature that had not previously been tested in SOFC development.

A long-term test was subsequently performed for a period of 1000 h at 850°C with a terminal voltage of 0.5 V at a current density of 600 mA/cm² (Fig. 6). Aging of the order of $-5 \mu\text{V/h}$ was established. Compared to experience gained in H₂/H₂O operation this can be considered an acceptable value. There is thus no indication that aging would be increased by internal methane reforming. After long-term testing, methane and hydrogen curves were measured as a means to check the eventually changes performance of the MEA. They are practically identical with those prior to the long-term test.

The CO produced during reforming can either be converted by the shift reaction or by way of electrochemical oxidation into CO₂. The entire cell current would then

comprise two components on the anode side, one component from the oxidation of H₂ and one from the oxidation of CO. The polarization losses of the two processes would influence the curve. In order to clarify whether the anode catalyzes the CO oxidation, it was attempted to run a curve in CO/CO₂/air operation. The experimental problem here is that there is no practical CO/CO₂ ratio below around 400°C which is thermodynamically stable. The CO will be disproportionately converted into CO₂ and soot. Since the anode gas flows through cold pipe sections up to the cell, soot formation is to be avoided at any CO/CO₂ composition. It was, however, apparent that this reaction is kinetically inhibited.

Curve analyses were conducted with CO/CO₂ mixtures with 4, 8, 12 and 25% CO. The open circuit voltages agreed well with the theoretical data. The cell could not be measurably loaded until the CO content was 25%. Fig. 7 shows the curve for an anode gas flow of 0.5 l/min of 25% CO and 75% CO₂ at 850°C. This composition is not thermodynamically stable below a temperature around 600°C. The test was completed successfully, without problems caused by soot formation, over the entire CO/CO₂ operating time of about 19 h. The current densities achievable are very low. In the range of the curve between 0 and 4 mA/cm², a rough estimation is a kinetic resistance is around 50 Ω cm². In H₂/air operation this value is typically about 0.4 Ω cm², i.e., around two orders of magnitude lower (Fig. 7).

These measurements indicate that, in the presence of H₂ and H₂O, almost no CO is electrochemically oxidized. In the cell, the CO can only be removed via the shift reaction. This result is of importance for modeling. Since the polarization losses for oxidation of CO are high, the only possible practical path is via H₂ oxidation in the case of

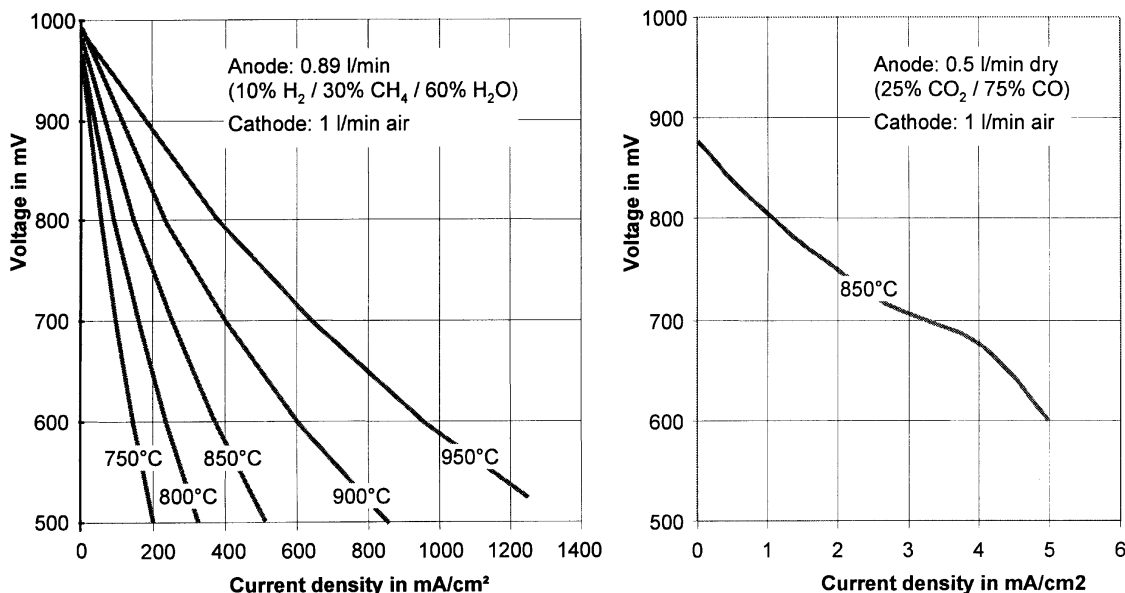


Fig. 7. Steady-state current–voltage curves of a single SOFC cell. CO oxidation about 100 times less than H₂ oxidation.

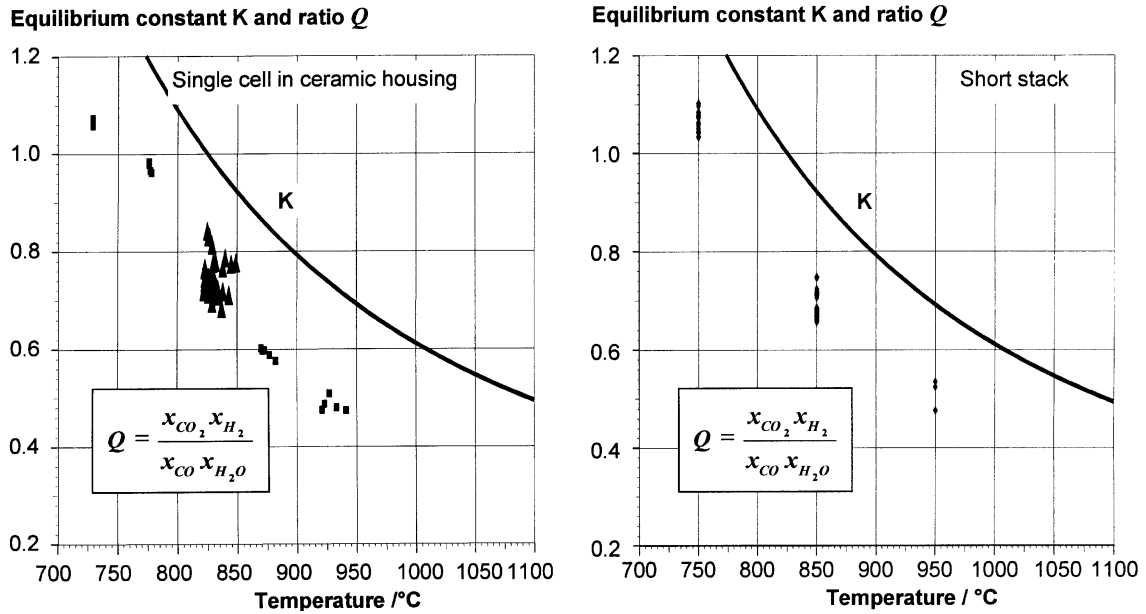


Fig. 8. Temperature dependence of the equilibrium constant *K* for the shift. Shift reaction is not in equilibrium.

current loading of the cell. The cell voltage is essentially not affected by the parallel path of CO oxidation. Electrochemical conversion can, therefore, be anticipated in methane operation just as in hydrogen operation. The kinetic data of the MEA determined for hydrogen operation can thus also be applied to methane operation. Reforming and shift reactions can merely be taken as parallel, purely chemical reactions.

A Fisher Rosemount system was used for gas analysis. It comprises three BINOS 1001 sensors for measuring the

CO, CO₂ and CH₄ gas concentrations and one HYDROS 100 sensor for measuring H₂. The water vapor is removed for the most part by cooling the gas to about 15°C prior to measurement. The residual moisture can be calculated from the measurement of the other components.

The CO and H₂ concentrations in the dry inlet gas were about 16 and 70%, respectively, figures which are equivalent to about 12.5 and 55.5% in the moist gas at the cell outlet. When calculating an effective equilibrium constant *Q* for the shift reaction (product of the CO₂ and H₂

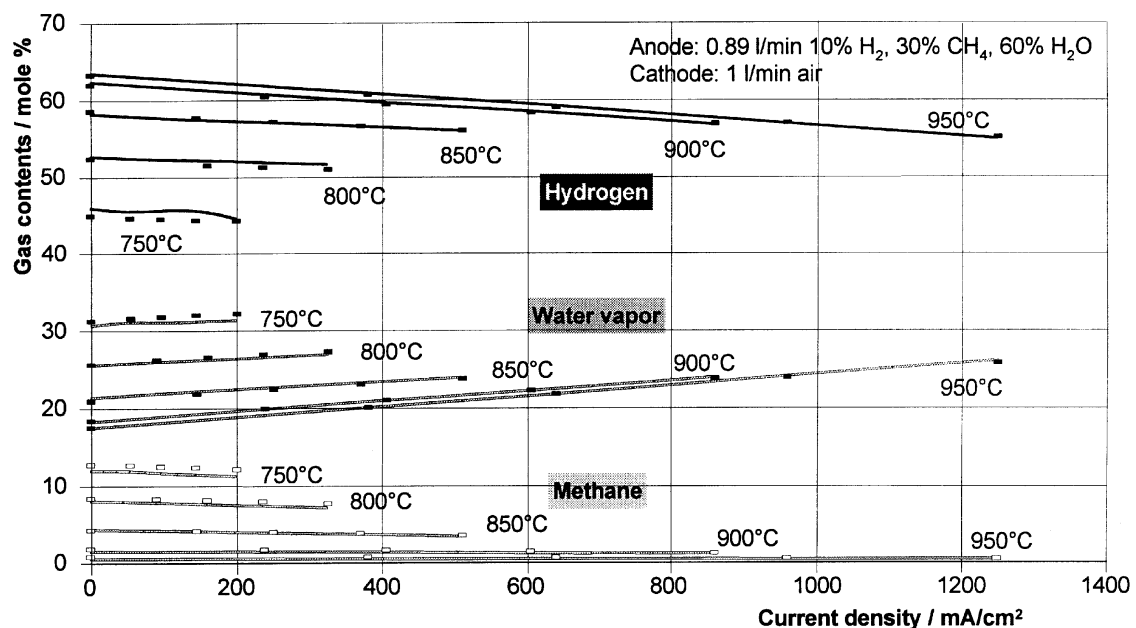


Fig. 9. Percentages of H₂, H₂O and CH₄ in the gas flow at the cell outlet. Methane is almost completely reformed in one cell.

concentrations divided by the product of the CO and H₂O concentrations) a smaller value was found in all measurements than was anticipated under the assumption of thermodynamic equilibrium for this reaction. This means that the shift reaction is kinetically inhibited and the catalyst is not suitable for achieving thermodynamic equilibrium within the dwell time of the gas (Fig. 8). To account for this experimental result in the modeling, the shift reaction is retained, but the chemical equilibrium is calculated for a higher temperature than the local temperature, according to the results in Fig. 8.

At the high fuel gas flow rate mentioned and at 850°C, between 76% (no load) and 81% (approx. 0.5 V) of the methane are converted over the length of the cell. The higher conversion rate at a lower terminal voltage, i.e., higher current density, is a result of the increased amount of reaction heat from H₂ oxidation and the higher local temperature of the cell.

Methane conversion drops significantly as temperature decreases. At 500°C, within experimental error, no more methane was converted. At 750°C, less than half of the conversion predicted occurred although, according to thermodynamic equilibrium calculations, practically all the methane should be converted at this temperature. The catalytic activity of the anode material is evidently no longer sufficient at this low temperature.

Fig. 9 shows, by way of example the agreement between measurement and model of the measured (continuous-line curves) and calculated (symbols) concentrations of the hydrogen, water vapor and methane for different temperatures as a function of current density. There is also comparatively good agreement between the modeling calculations and measurements for the other gases CO and CO₂, as well as temperature and current density.

Within the range of water vapor partial pressures emitted in the tests in the gas phase, no dependence of the reforming rate on the water vapor content was found. The

rate equation was therefore only set proportional to the methane partial pressure. The value for the rate at 950°C is about 3.3 mol/(m² s bar).

4. Modeling calculations

The parameters derived from the measurements were used to numerically simulate a model stack. The stack design is in line with the concept applied to for a 200-kW plant comprising four stacks in an insulating container. The stack is planar with metallic bipolar plates and has 150 layers each comprising nine 10 × 10 cm² MEAs. The active surface area of one MEA is 9 × 9 cm². The MEAs are arranged in three rows with three columns each.

Gas is supplied in counterflow because it is known from simulations with H₂/air operation in an SOFC that this method of supply essentially results in more uniform stack temperature distribution. Technical implementation was not considered in the model.

The stack was treated virtually adiabatically, so that heat losses across the surface play no role. The fuel gas composition at the stack inlet was assumed to be 12% H₂, 28% CH₄, 3% CO₂ and 57% H₂O and is equivalent to a methane/water vapor mixture with an S/C ratio of 2, which was pre-reformed at about 500°C. The fuel gas flow rate was 810 l/min and the layer current 400 A. On the air side, almost double the amount of stoichiometric oxygen was provided. Under these conditions, the simulated stack produces 43.6 kW of electric output at a fuel utilization of 41.5%.

Fig. 10 shows a compilation of the distribution of current density and temperature for one layer halfway up the stack, from the results of the simulation. The other layers behave in a very similar manner, which can be seen from the fact that the layer voltages only vary between 0.7612 and 0.7631 V.

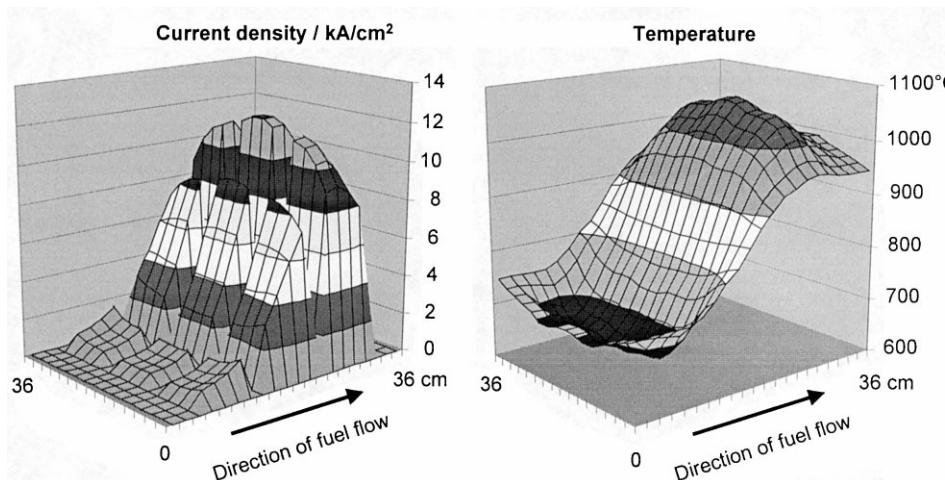


Fig. 10. Current density and temperature distribution in one stack layer. Pronounced cooling and low current density in the reforming regime.

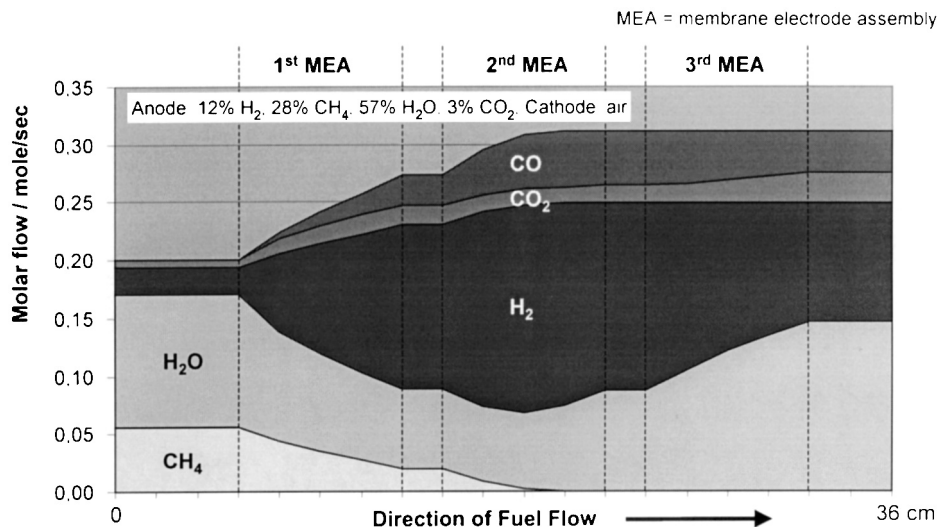


Fig. 11. Gas flow in one stack layer based on modeling calculations.

Although the gas admission temperatures of 850°C are assumed as being very high, the minimum stack temperature drops to about 620°C because of the heat required for reforming. Because of this cooling, the first MEA row contributes only very little to the total current in one layer. The maximum temperature is about 1070°C and occurs at the location of the highest current density.

Since the air leaves the stack at the side of the fuel gas inlet, it cools to about 680°C and cannot be used to heat the fresh air. In particular, the high temperature differential of 450 K rules out this operating mode for a real stack.

Under the temperature conditions described, reforming has already progressed considerably after the first MEA row and, as shown in Fig. 11, is virtually complete in the center of the second MEA row. Methane conversion is practically complete.

Pronounced conversion of CO into CO₂ via the shift reaction does not take place until the third MEA row. The syngas at the stack outlet contains around 33% H₂ and 12% CO. The remainder is water vapor (47%) and CO₂ (8%).

5. Conclusions

SOFC reformers have the potential for the development of new, highly efficient combined processes such as the

coproduction of electricity and syngas or hydrogen as well as the coupling of SOFCR and PEMFC.

The model calculations show that the stack design has to be adapted to reformer operation.

The experimental results confirm reformer operation of SOFC MEAs at low cell voltages.

The anode used is not suitable for the electrochemical oxidation of CO.

6. Further reading

[1,2]

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