

Short communication

Utilization of mine gas with a high-temperature SOFC fuel cell

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Abstract

SaarEnergie (SE) GmbH, Forschungszentrum Jülich, and Institut für ZukunftsEnergie-Systeme are partners in a project titled ‘Pilot operation of a high-temperature solid oxide fuel cell (SOFC) using mine gas,’ which was launched in November 2003.

As a first step in this project, the quality of the mine gas was analysed at the intended installation site. These first analyses were performed to obtain information on the fluctuations in the methane concentration in the mine gas as a function of time. The composition of the gas was determined by means of micro gas chromatography. The results were used to design the test stand suitable for operating an SOFC rated at 1–2 kW in combination with a pre-reformer. The system layout finally selected from a number of possible options was a partly integrated design with pre-reformer and fuel cell with combined heat system. The pre-reformer was optimized on the basis of laboratory tests using synthetic mine gas. Additional preliminary tests using synthetic mine gas were also performed on single cells and laboratory scale short-stacks.

The paper presents the results of the mine gas analyses and their effect on the pre-reformer and the fuel cell. It goes on to discuss the results obtained from the preliminary tests using synthetic mine gas on the pre-reformer and on the fuel cell. Finally, an outlook is given, taking a closer look at the results expected for the second project year.

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1. Introduction

SaarEnergie (SE) as well as Forschungszentrum Jülich and the Institut für ZukunftsEnergieSysteme (IZES) are partners in the project ‘‘Pilot operation of a high-temperature solid oxide fuel cell (SOFC) using mine gas,’’ which is based in the SE Innovationszentrum including the IZES Technikzentrum in Luisenthal [1]. The strategic targets of the project partners and their motivation behind this research programme as well as the technical and scientific elements and objectives of the project were already presented at the 10th REGWA symposium on the use of renewable energy sources and hydrogen technology in November 2003 in Stralsund, Germany [2]. At that time, details were presented on the integrated mine

gas grid of SaarEnergie, the medium mine gas, the SOFC technology using the Jülich substrate concept, as well as first results from tests and investigations. The following section will now report on the progress that has been made since the last symposium.

2. Mine gas analyses at the Luisenthal site

One of the major characteristics of mine gas as an energy source are the limits within which it varies both in terms of the methane content and the production volume. Important for the operation of the fuel cell and the pre-reformer is also the amount of oxygen, which is often found in the mine gas. The mine gas for the project comes from an interconnected mine gas grid in the federal state of Saarland. At a total length of 110 km, this regional grid is unique in Europe and offers an excellent basis for decentralized power generation, using

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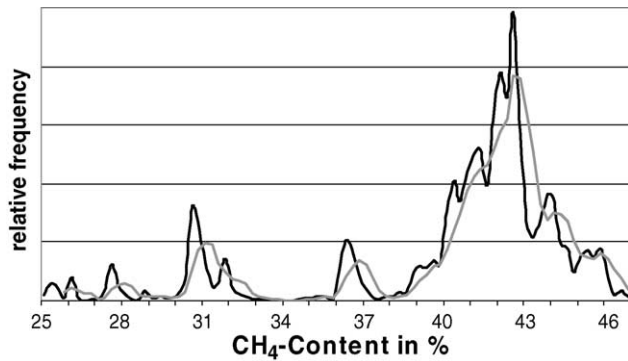


Fig. 1. Methane concentration at the Luisenthal site in 2004.

for instance fuel cell technology. The mine gas grid, owned by SaarEnergie, has 12 points at which it is fed with mine gas, partly from disused coal mines and partly from active mining operations. This is why the methane concentration in the mine gas may vary between 30 and 90% [3]. Fig. 1 shows the methane concentrations and their frequency in the course of a half-year for the Luisenthal site.

Since the volumes too, have to be expected to vary as a function of gas emissions, face (phase?) advance rate and air pressure conditions, the mine gas available at the Luisenthal site, which has been selected for the project, have been subjected to constant measurements since the beginning of the project. The method used for this purpose is the gas chromatography. Fig. 2 shows the variations in the methane concentration, plotted against a period of several hours. For these variations, see also Fig. 3, which can be explained as follows: the local grid segment at the Luisenthal site is mainly fed from two different mines. In this segment, there are different mine gas consumers. Caused by shutdown of one connected gas consumer near the Luisenthal site, the flow direction in the local gas grid changed and in order to that the main mine gas source, responsible for supplying the Luisenthal site changed too.

It is evident from this example that the methane concentration in mine gas changes within narrow limits. On the other hand, sudden changes of up to 15% may occur within periods

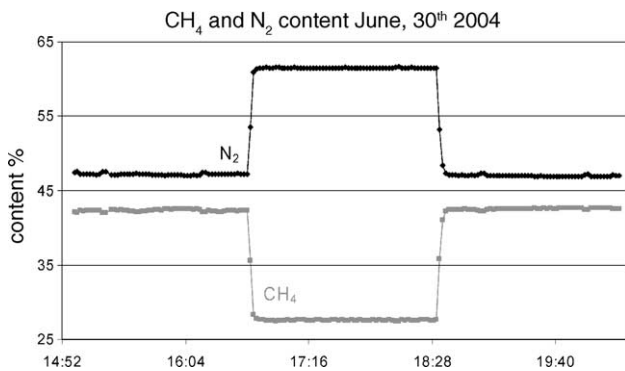


Fig. 2. Methane and nitrogen readings for mine gas at the Luisenthal site.

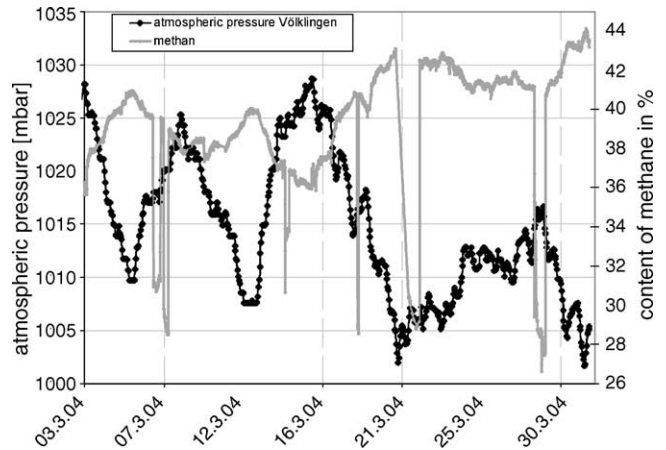


Fig. 3. Methane concentration in mine gas as a function of air pressure.

of less than 10 min, which has to be attributed to the needs of other users in the grid/1/.

Such jumps in the concentration graph are primarily recorded whenever gas from another tapping point reaches the research platform. This will be the case when users between tapping point and research centre are connected to or disconnected from the system.

There are other factors too, that affect the quality of mine gas and the methane concentration. In Fig. 3 below, the methane concentration has been plotted against the air pressure. It should be noted in this context that a distinct relationship will be evident only for aerated mine sections.

3. Test set-up

One of the objectives of the research project is to design a pre-reformer in such a way that the reformate obtained from the mine gas can be used in the SOFC, and to determine how far variations in the methane and oxygen concentrations may have an effect on the pre-reformer and the performance of the fuel cell. The test stand set-up for the required tests, hence had to meet a number of requirements, in particular concerning measuring and control instrumentation. The designs considered and subjected to intensive pre-testing included separate pre-reformer/SOFC test stands as well as combined test stands. Having carefully weighed the pros and cons of either concept, the project group decided in favour of the combined system, which is schematically shown in Fig. 4.

4. Laboratory tests at Forschungszentrum Jülich

4.1. Pre-reformer experiments

An extensive test programme was performed at Forschungszentrum Jülich to be able to decide on the pre-reformer design and on the suitability of the reformate for use in the SOFC. The experiments were performed using

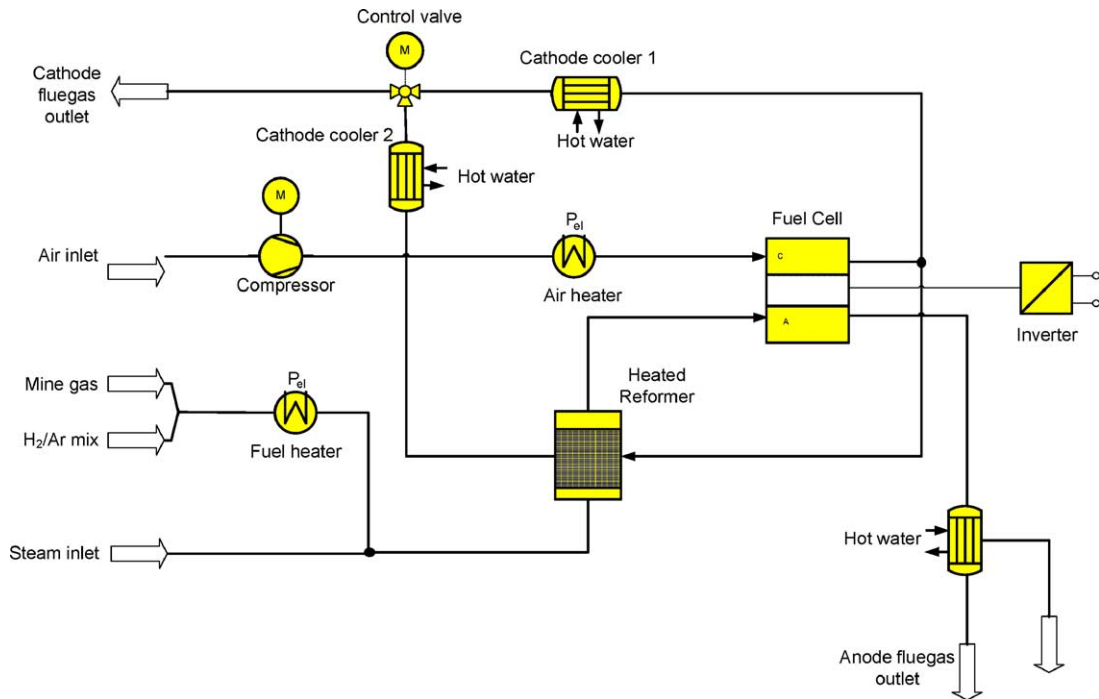


Fig. 4. Schematic representation of the test stand.

synthetically composed mine gas. Fig. 5 shows the temperature profile in the pre-reformer operated on different mine gas compositions, with and without certain amounts of oxygen.

As soon as the fuel gas reaches the catalyst, the methane/steam reforming process commences, and hydrogen and CO are produced. Since the reformer uses the counter-flow principle, heating of the fuel gas mixture continues, and the reforming reaction is accelerated. This goes along with a cooling effect, due to the endothermic nature of the reforming process, which slows down the speed at which the temperature rises. The presence of oxygen favours the superimposed process of partial oxidation of methane and hydrogen. Because of this exothermal reaction, the fuel gas mixture is heated more intensively above all at the fuel feed side than is the case for operation with pure methane. When analysing the composition of the reformer products it was found that

under the given operation conditions the oxygen is converted completely (below the detection limit). The gas compositions upstream and downstream of the reformer are shown in Fig. 6.

Fig. 7 illustrates the effect the hot-air mass flow rate has on the temperatures and the conversion rate in the pre-reformer. Changes in the air flow rate used for heating the reformer have a clear influence on the temperature at which the reformed gas exits from the reformer. This effect is shown in Fig. 7 for air flow rates from 13.1 to 9.3 and 6.3 kg h⁻¹. Lowering the air flow rate to 6.3 kg h⁻¹, the fuel outlet temperature is close to the value measured for the mine gas composition without oxygen, but with the higher air flow rate (cf. Figs. 5 and 7). The air flow rate can thus be used to control the fuel exhaust temperature in dependence of the mine gas composition.

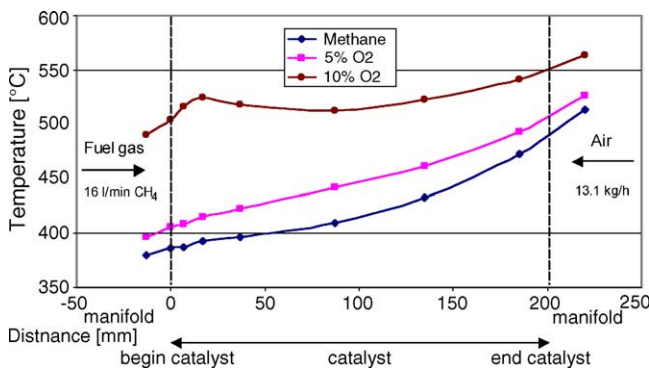


Fig. 5. Temperatures in the reformer operated with different types of mine gas.

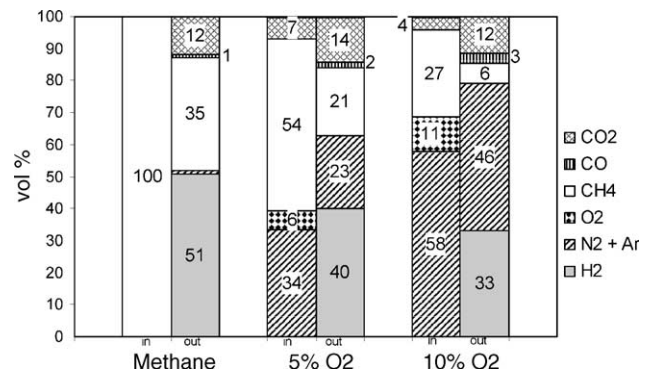


Fig. 6. Gas compositions upstream and downstream of the reformer.

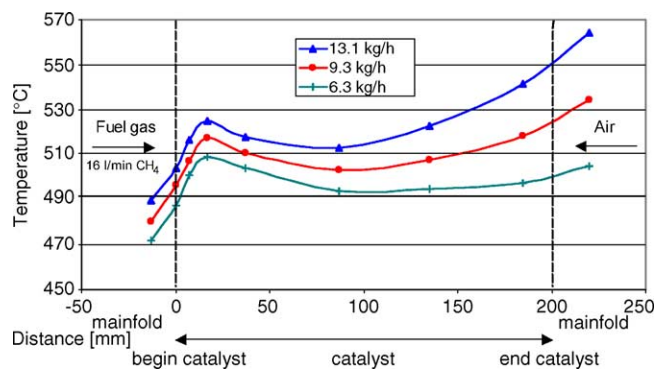


Fig. 7. Effect of hot-air mass flow rate on the temperature profile and conversion rate in the pre-reformer.

4.2. Short-stack electrochemical measurements

A currently standard F-design SOFC stack, in detail described in ref. [4], was used for laboratory experiments using synthetic mine gas. Two anode substrate type cells were stacked between metallic interconnect plates. The short-stack F1002-43 (test no. SK184) was started using standard procedures for joining and reducing. The first characteristic current–voltage measurement was made under standard conditions (800 °C, H₂ + 10 vol% H₂O, air). The stack was then loaded under these standard conditions with a constant-current of 0.3 A cm⁻². It was not supplied with different compositions of simulated reformed mine gas until it had operated for a period of 1000 h without any major voltage dips and/or degradation rates. The simulated reformed mine gas compositions used in the measurements are listed in Table 1. All measurements were made at a stack temperature of 800 °C.

Fig. 8 shows the current–voltage curves for the three mine gas compositions, including for comparison, the initial and a final measurement with hydrogen (and low fuel gas utilization).

In Fig. 8, it can be seen that for the same volumetric flow rates of the fuel gas, the three different mine gas compositions do not give any significant differences in performance. At a voltage of 0.7 V per cell, a current density of approximately 0.44 A cm⁻², i.e. a power density of 0.31 W cm⁻² is achieved. Neither are there any significant differences between operation with mine gas and hydrogen, although a slight loss in performance resulting from carbon deposition (see below) cannot be excluded entirely.

Table 1
Compositions of simulated mine gas

	Before reforming ^a				After reforming used in electrochemical measurements ^b				
	CH ₄	CO ₂	N ₂	O ₂	H ₂	CH ₄	H ₂ O	Ar	
MG1 (in vol%)	90	7	3	0	29.0	19.5	44.8	6.7	
MG2 (in vol%)	60	8	27	5	26.6	13.3	36.6	23.4	
MG3 (in vol%)	30	5	55	10	26.7	4.5	24.9	44.0	

^a Steam reforming with S/C = 2.2.

^b CO in the reformat is replaced by H₂ for the electrochemical measurements CO₂ and N₂ are replaced by Ar.

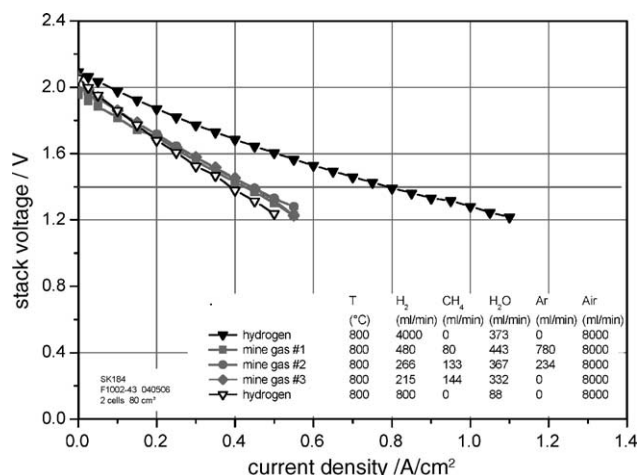


Fig. 8. Current–voltage characteristics for the F1002-43 stack, with different simulated reformed mine gas compositions.

The *I*–*V* measurements were followed by constant-current operation using the three gas compositions (initially at 24-h intervals), starting with 50% fuel utilization, and subsequently 70% fuel utilization. Finally, a current–voltage curve was recorded for hydrogen under comparable conditions.

Fig. 9a and b show the cell voltages during constant-current operation as a function of time. The period under hydrogen operation commences with the normal voltage drop of about 30 mV at both cells during the first 450–480 h of operation. After this period, the cell voltages level off to degradation behaviour, which is linear in time. The degradation rates are 2.0 and 2.9%/1000 h for the first and second cell in the stack, respectively. These values reflect the materials selected in the stack, i.e. the CroFer22APU-1st interconnect material in combination with a MnOx/LCC10 contact layer on the cathode side of the cell [4].

The bottom part of Fig. 9 shows enlarged periods at constant-current operation under mine gas. Unlike the results obtained with the *I*–*V* measurements, this presentation does show some minor differences in the cell voltages. Since the current was increased every second minute during the *I*–*V* measurements, the stack was hardly allowed to stabilize. Such an *I*–*V* characteristic always reflects a momentary situation. When considering constant-current conditions with periods in this case of no less than 23 h, slight differences still may appear. Starting from MG1 to MG2 and MG3, the partial pressure of the methane is found to decrease significantly, while

Table 2
Performance data for the short-stack F1002-43 (SK184) on mine gas

Mine gas composition	Fuel utilization (%)	Cell 1		Cell 2	
		Voltage at 0.3 A cm^{-2} (V)	Power density (W cm^{-2})	Voltage at 0.3 A cm^{-2} (V)	Power density (W cm^{-2})
MG1	50	0.773	0.23	0.784	0.24
	70	Not determined	Not determined	Not determined	Not determined
MG2	50	0.764	0.23	0.774	0.23
	70	Not determined	Not determined	Not determined	Not determined
MG3	50	0.745	0.22	0.757	0.23
	70	0.715	0.21	0.730	0.22

the partial pressure of the inert component (Ar) increases, and the partial pressure of the hydrogen remains almost constant. By analogy, the stack performance decreases slightly and in the same order. The performance also decreases when the fuel utilization is increased. Table 2 summarizes the performance data.

In the two last periods with the mine-gas compositions MG2 and MG1 and the highest fuel-gas utilization of 70%, the cell voltages show very large fluctuations. This is why it was no longer possible to determine exact performance figures. In both cases, the amount of water (steam) that has to be injected approaches the lower control limit of the mass

flow controller. At some points, the mass flow controller even closed completely, which resulted in sharp voltage drops. Another consequence of repeated short-term closing of the mass flow controller, and consequently inadequate steam content in the fuel gas mixture, was a higher risk of coking. The formation of carbon may partly deactivate the anode and/or result in faster degradation. To a very large extent, coking is however reversible as soon as adequate amounts of water vapour are available again for prolonged periods of time.

It was shown that a standard F-design short-stack of Forschungs-zentrum Jülich, a detailed description can be found in ref. [4], could be operated successfully on different qualities of simulated mine gas. The current–voltage measurements did not reveal any variations in the short-stack performance: at a temperature of 800°C and 0.7 V per cell, the current density attained was about 0.44 A cm^{-2} , which corresponds to a power density of 0.31 W cm^{-2} . When operated at a constant-current load of 0.3 A cm^{-2} , there were only minor variations of less than 10% in the performance ($0.22\text{--}0.24 \text{ W cm}^{-2}$), which was subject to the mine gas composition and a higher fuel utilization (up from 50 to 70%).

5. Outlook

Orders are now being sent out for the test stand components, and the combined test stand with pre-reformer and SO fuel cells is expected to be put into operation at the turn of the years 2004/2005. Once the test phase has been completed for the control and measuring point concept, the pre-reformer, and at a later stage, the fuel cell will be supplied with natural mine gas. This will then allow the aggregates of the system to be checked for their suitability and the hardware and/or control elements to be adjusted as and if required.

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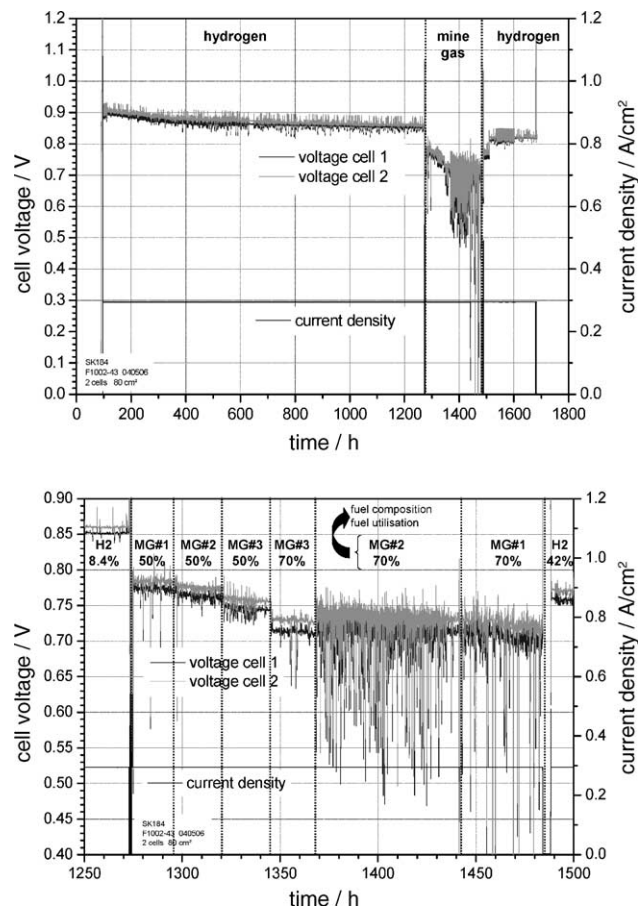


Fig. 9. (a and b) Cell voltages (short-stack F1002-43) under constant-current operation as a function of time and fuel.

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