

Pressurized Solid Oxide Fuel Cells with Reformate as Fuel

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In this contribution the influence of pressure on an SOFC is studied with steam-reformed methane as a fuel. Experiments were performed with a reformat containing 58.4% H₂, 20% H₂O, 12.2% CO, 5.5% CO₂ and 3.9% CH₄ and another mixture containing 18% H₂, 34% H₂O, 2% CO, 27% CO₂ and 19% CH₄ as well as a hydrogen/nitrogen mixture. The influence of pressure on OCV, power density at constant voltage and constant current as well as on gas composition was examined for the different fuels. Power density increases of up to 70% were found.

Introduction

The demand for electrical energy increases and will continue to increase. Therefore new power plants with high efficiencies and low emissions have to be developed. A hybrid power plant consisting of a pressurized solid oxide fuel cell (SOFC) system coupled with a gas turbine is seen to fulfill both requirements because such a power plant may reach electrical efficiencies above 60% with low emissions (1). This kind of hybrid power plant also has the advantage of being suitable for a wide range of applications ranging from several 10 kW to the MW class. The German Aerospace Center (DLR) aims at setting up a hybrid power plant in the 50 kW class starting in 2013. For developing this power plant the Institute of Technical Thermodynamics (TT) and the Institute of Combustion Technology (VT) at DLR combine their expertise in fuel cells and gas turbine technology. The SOFC system is developed at the Institute of Technical Thermodynamics while the Institute of Combustion Technology focuses on the gas turbine. A schematic of the hybrid power plant is shown in Figure 1. Highest efficiencies and power are to be expected when the SOFC is operated at elevated pressures (2). In the context of the hybrid power plant the fuel cell will be operated at elevated pressures up to 8 bar. During operation of the hybrid power plant air is compressed in the compressor of the gas turbine. It is then preheated and fed to the SOFC system. The off-gases of the SOFC system are used in the combustion chamber of the gas turbine where additional fuel may be added for example for starting the system. After expansion of the gas in the gas turbine the off-gas is used to preheat the air for the fuel cell system.

For the realization of the power plant it is necessary to understand the behavior of each subsystem as well as their interactions. The pressurized solid oxide fuel cell is an essential part of the system but there is still little data available from literature concerning the behavior of SOFC at elevated pressures. Since it cannot quantitatively be derived from measurements at ambient pressure because of complex and interdependent

mechanisms taking place at the cell, a test rig for the characterization of SOFC stacks exposed to pressures up to 8 bar has been built at DLR (3).

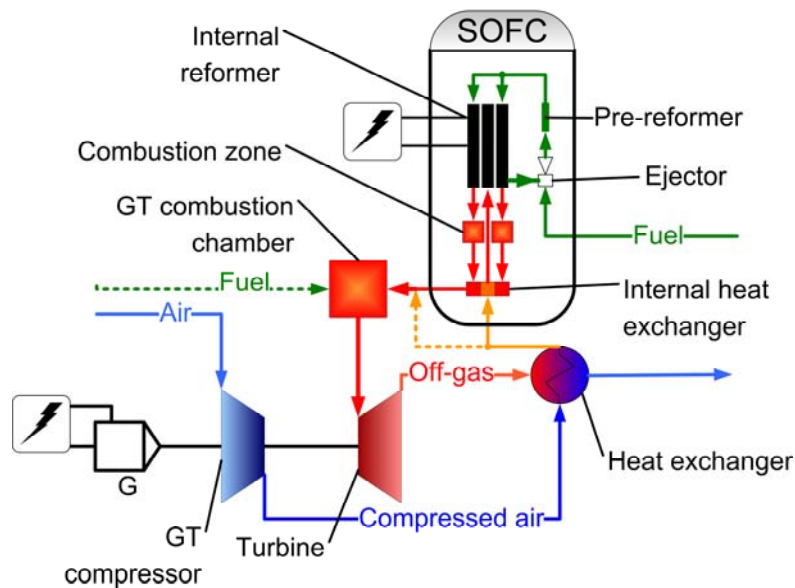


Figure 1: Schema of a hybrid power plant consisting of an SOFC system and a gas turbine.

The hybrid power plant will eventually run on natural gas, therefore the SOFC stack will be operated with prereformed reformat gases. The effect of elevated pressure on reformat gas composition, reforming reactions, electrochemical processes and the general behavior of the cells are of great interest. The knowledge of steady state as well as transient operational behavior and of course of operational limits is essential for the integration of the SOFC into the hybrid power plant system.

Experimental setup

In the pressurized SOFC test rig SOFC short stacks can be characterized at pressures of 1 to 8 bar. Pressure difference between anode and cathode gas compartments and the furnace can be controlled by a pressure control system up to 500 mbar. This pressure control is important to keep pressure differences low since a large pressure difference may lead to the destruction of the cells or stack. To control the pressure difference between anode, cathode and the furnace two equalizing tanks of 400 l each are used balancing the small volumes of the anode and cathode gas compartment against the far greater volume of the furnace.

The maximum temperature for testing is 950°C and the stack in the test rig can be supplied with mixtures of hydrogen, nitrogen, methane, carbon monoxide, carbon dioxide and steam on the anode side that can be mixed to represent reformat gases. At the cathode air, oxygen, nitrogen and helium are available. The test rig offers the possibility

to measure current-voltage characteristics of the stack and its individual cells as well as performing impedance spectroscopy on the cells. The gas composition at the in- and outlet of the anode and cathode can be measured by means of a gas chromatograph (3).

For the results presented here anode-supported 5-cell short stacks provided by ElringKlinger AG with an active area of 84 cm² per cell were used. They consist of sintered cells which are integrated into stamped metal sheet bipolar plates as shown in Figure 2. These are referred to as cassettes. The cells consist of an anode substrate (Ni/YSZ) and functional layer. The YSZ electrolyte is 10µm thick and the cathode consists of two layers, a functional layer made of LSM/YSZ and a current collector made of LSM.

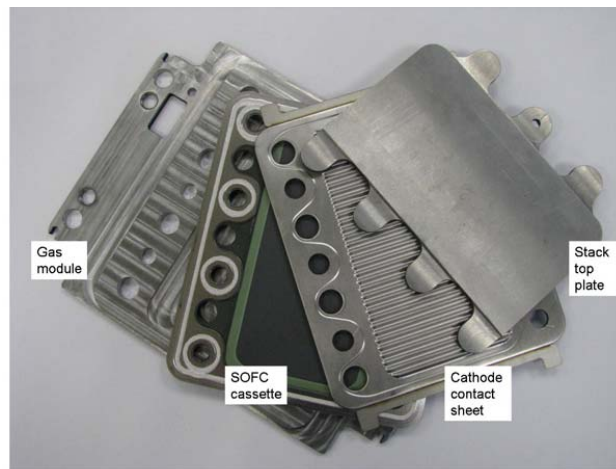


Figure 2: Cell integrated into metal bipolar plates.

Measurements were done with a 1/1 hydrogen/nitrogen mixture with a water content of 3%, a partially reformed reformat containing 18% H₂, 34% H₂O, 2% CO, 27% CO₂ and 19% CH₄ (reformat 1) as well as a steam-reformed reformat containing 58.4% H₂, 20% H₂O, 12.2% CO, 5.5% CO₂ and 3.9% CH₄ (reformat 2). The temperature was varied between 700°C and 800°C and pressure variations were done ranging from 1.35 bar up to 8 bar. The flow rate for the hydrogen/nitrogen mixture was 5 l/min of hydrogen. The flow rate for the reformates was chosen to obtain the same theoretical current as for H₂/N₂ resulting in a total flow rate of 5.63 l/min for the first reformat and 5.06 l/min for the second. The results shown in this contribution are for one of the cells from the middle of the stack since outer cells often show a deviation in performance due to temperature effects (4).

Results

In Figure 3 to Figure 4 current voltage characteristics for one cell from the middle of the stack at different pressures can be seen for the three gas compositions at 700°C and 800°C. Each diagram shows the current-voltage curves for one gas composition and one temperature at different pressures. It can be seen in these diagrams that elevated pressure leads not only to a higher OCV but also affects the gradient of the curve under load. This

can be seen for all gas compositions and temperatures. The higher the current density the greater is the difference between the i-V curves for the different pressures. In the following chapters the behaviour shown in the characteristic curves is examined more closely.

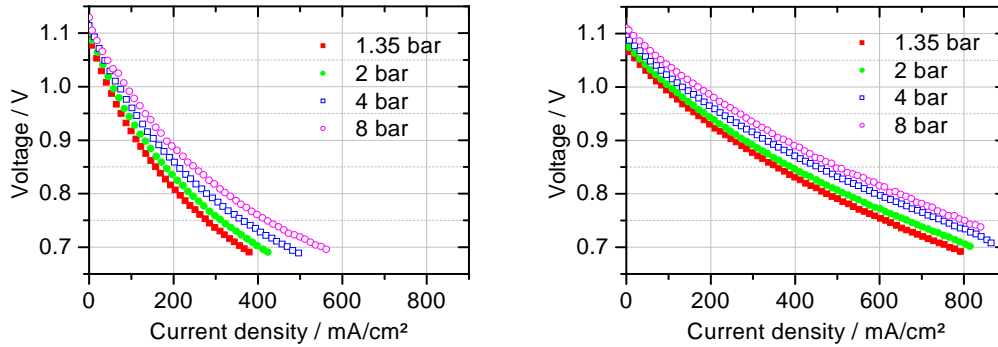


Figure 3: Pressure dependent current voltage curves for H₂/N₂ at 700°C (left) and 800°C (right).

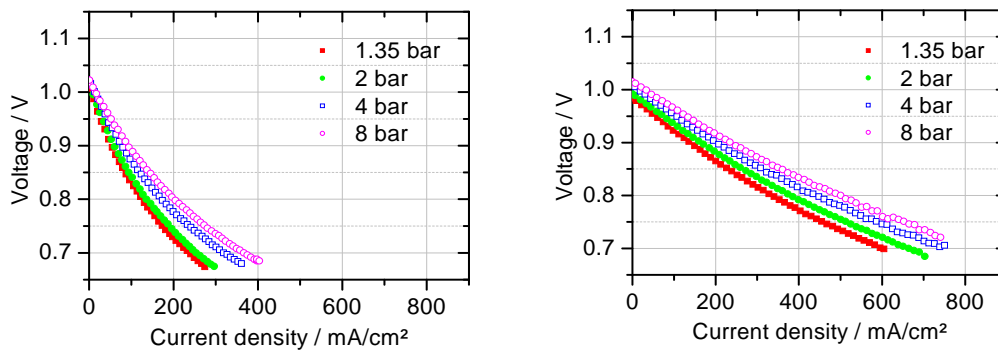


Figure 4: Pressure dependent current voltage curves for reformat 1 at 700°C (left) and 800°C (right).

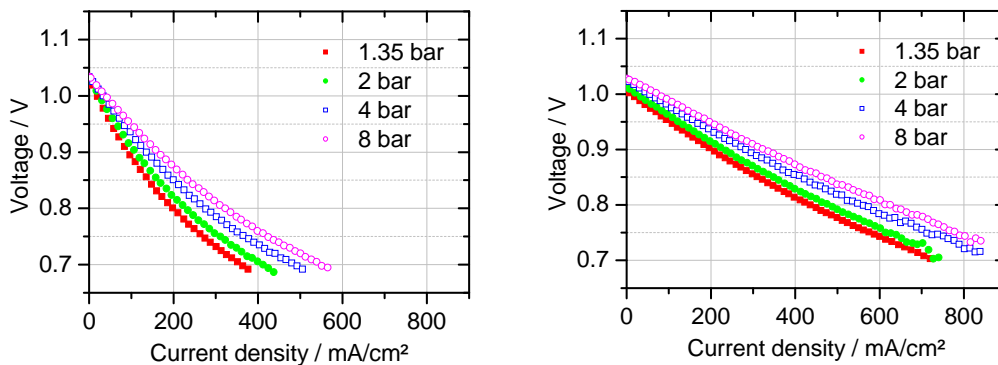


Figure 5: Pressure dependent current voltage curves for reformat 2 at 700°C (left) and 800°C (right).

Pressure influence on gas composition and open circuit voltage

Figure 6 shows the development of OCV of one cell from the middle of the stack with increasing pressure for the three different gas compositions that were examined. The squares show the experimentally obtained values. The lines show the theoretical OCV that was calculated using equation [1] and assuming equilibrium composition of the fuel at the cell. For determining equilibrium composition and OCV the open-source software CANTERA (5) was used.

$$\text{OCV} = -\frac{RT}{2F} \ln \frac{\sqrt{p_{\text{O}_2, \text{cathode}}}}{\sqrt{p_{\text{O}_2, \text{anode}}}} \quad [1]$$

Filled symbols are experimental values at 800°C while open symbols represent measurements at 700°C. The continuous lines are calculated for 800°C and the dotted lines for 700°C. Colour and symbol shape stand for the three different gas compositions measured. Calculated and experimental values show similar tendencies. For all gas compositions OCV increases with pressure but not to the same extent. Temperature has an influence on the OCV and its increase through pressure. The hydrogen/nitrogen mixture shows a greater increase in OCV than the reformat gases. For the following comparisons theoretical OCV values are taken. For a pressure increase from 1.35 bar to 8 bar the OCV of the hydrogen/nitrogen mixture rises by 40 mV (3.7 %) at 800°C while for reformat 1 it rises only 30 mV (3.1%) and for reformat 2 by 23 mV (2.3%). The increase in OCV through pressure at different temperatures varies only slightly for the H₂/N₂ mixture. At 700°C the increase is 36 mV (3.3%) compared to the 40 mV (3.7 %) at 800°C mentioned above. For the reformat gases temperature has a stronger influence on OCV increase through pressure. For both reformates the increase in OCV remains below 10 mV for a temperature of 700°C (9 mV or 0.9% for reformat 1 and 4 mV or 0.4% for reformat 2). In the case of the reformates the lower temperature leads to a higher OCV at low pressures, but at high pressures the difference in OCV because of temperature gets smaller. For reformat 2 the OCV at 8 bar is almost the same for both temperatures.

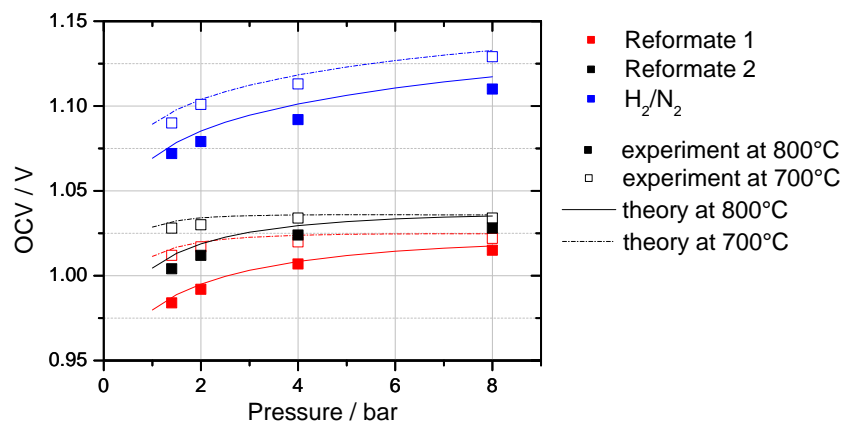


Figure 6: Pressure and temperature dependence of OCV for three different gas compositions

This can be explained by looking at the pressure dependency of the equilibrium compositions of the reformat gases at different temperatures. The lines in Figure 7 show the calculated equilibrium compositions for reformat 1 that were determined using CANTERA for pressures ranging from 1 to 8 bar for 700°C and for 800°C. The symbols are the gas compositions that were measured at OCV after the stack for the different conditions using a gas chromatograph. The measured values match well with the theoretical equilibrium composition, although there is a discrepancy especially for the water content.

At 700°C the gas composition varies far more with pressure than at 800°C. The higher the pressure the smaller is the hydrogen and CO content of the equilibrium fuel gas. While at 800°C the hydrogen content decreases from 46% to 41% for the theoretical equilibrium and stays constant in the measurements, it decreases at 700°C from 46% to 32% for the theoretical equilibrium and from 48% to 36% for the measured values. The pressure increase leads to an increase in OCV of the cell but it also leads to a less favourable gas composition with smaller fuel content which is decreasing this OCV gain through pressurization.

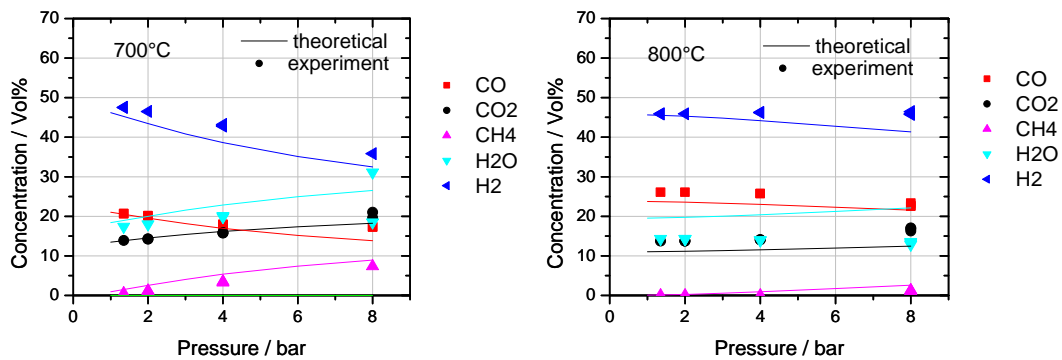


Figure 7: Calculated equilibrium gas composition and measured values over pressure for reformat 1 at 700°C and 800°C.

A similar tendency is seen for reformat 2 in Figure 8. The H₂ content is higher than for reformat 1 but the decrease in hydrogen content for the theoretical equilibrium is similar to that of reformat 1.

The calculated H₂ content of the H₂/N₂ mixture hardly varies with pressure for either temperature as can be seen in Figure 9 which is why OCV rises more strongly with pressure for this fuel.

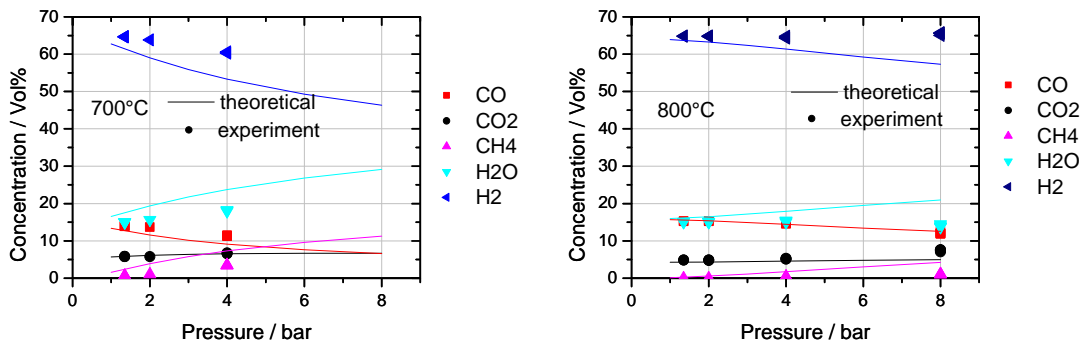


Figure 8: Calculated equilibrium gas composition and measured values over pressure for reformat 2 at 700°C and 800°C.

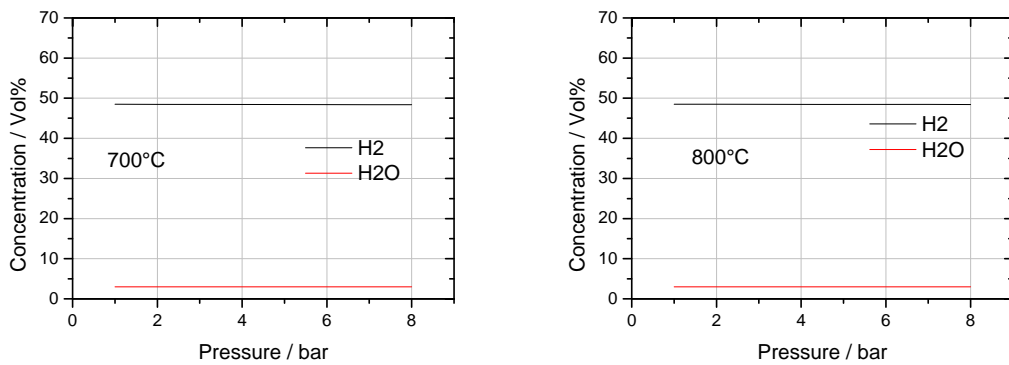


Figure 9: Calculated equilibrium gas composition over pressure for H₂/N₂ mixture at 700°C and 800°C.

Performance gain under pressure at constant voltage

In Figure 10 the influence of pressure on performance at a constant voltage of 750 mV can be seen for the different fuels. The filled symbols are the measured values at 800°C, the open symbols at 700°C. The pressure dependency shows a logarithmic behavior for all fuels increasing more strongly at low pressures and leveling out at elevated pressures. At 800°C power density is highest for H₂/N₂ but the relative as well as the absolute power density gain through pressurization is slightly greater for the reformates. At a pressure rise from 1.35 bar to 8 bar power density at 750 mV rises by 138 mW/cm² or 30% for the H₂/N₂ mixture, while it rises by 146 mW/cm² (42%) for reformat 1 and by 154 mW/cm² (35%) for reformat 2. Here the reformat gas with the greater methane content (reformat 1) shows a smaller absolute increase but a higher relative increase than the almost entirely reformed reformat 2. It can be seen from Figure 10 that at a constant cell voltage of 0.75 V the curves for 700°C have a smaller gradient than those for 800°C. A lower temperature leads to a smaller increase in power density while a higher temperature leads to a stronger increase in performance with rising pressure for all fuels measured. At 700°C the increase with pressure for reformat 1 is

smaller than for both the other fuels. The increase is only 78 mW/cm² if pressure is increased from 1.35 bar to 8 bar while for H₂/N₂ the increase is 106 mW/cm². Nevertheless the relative gain is highest (60%) for reformat 1 in comparison to 51% for H₂/N₂. At 700°C reformat 2 and the H₂/N₂ mixture hardly differ from each other although the absolute power density increase through pressurization at 700°C as well as at 800°C was highest for reformat 2 (115 mW/cm² or 57 % at 700°C). For clarity the power density gains in comparison to 1.35 bar are shown also in table I.

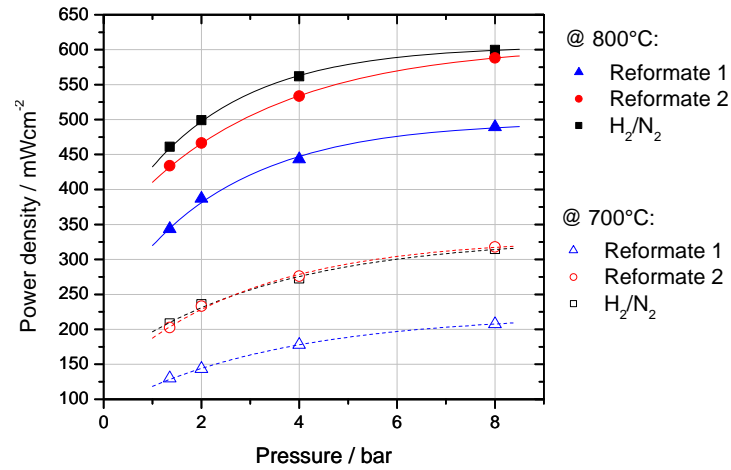


Figure 10: Power density at 750mV cell voltage at different pressures

TABLE I: Power density gain through pressurization at 750 mV compared to 1.35 bar.						
700°C	→ 2 bar		→ 4 bar		→ 8 bar	
	mW/cm²	%	mW/cm²	%	mW/cm²	%
H ₂ /N ₂	28	13	65	31	106	51
Reformat 1	14	11	48	37	78	60
Reformat 2	30	15	73	36	115	57

800°C	→ 2 bar		→ 4 bar		→ 8 bar	
	mW/cm²	%	mW/cm²	%	mW/cm²	%
H ₂ /N ₂	38	8	101	22	138	30
Reformat 1	43	13	99	29	146	42
Reformat 2	33	8	100	23	154	35

At a higher cell voltage tendencies are similar with only minor differences. In Figure 11 power densities for different pressures at a cell voltage of 850 mV are shown. At 850 mV the absolute power density level is lower for all fuels compared to 750 mV. The absolute power density gain through pressurization is also lower although the relative increase in performance is greater. At this voltage the absolute power density gain for reformat 1 which contains a greater part of methane shows a smaller gradient than the

other fuels for both temperatures (51 mW/cm² at 700°C and 108 mW/cm² at 800°C) while relative power density gain is highest (70% and 55%). Although the hydrogen/nitrogen mixture shows the highest performance for both temperatures, reformat 2 shows the greatest increase in absolute power density gain of the examined fuels (80 mW/cm² at 700°C and 134 mW/cm² at 800°C) while the hydrogen/nitrogen mixture gains 77 mW/cm² at 700°C and 118 mW/cm² at 800°C. For clarity the values are shown again in table II.

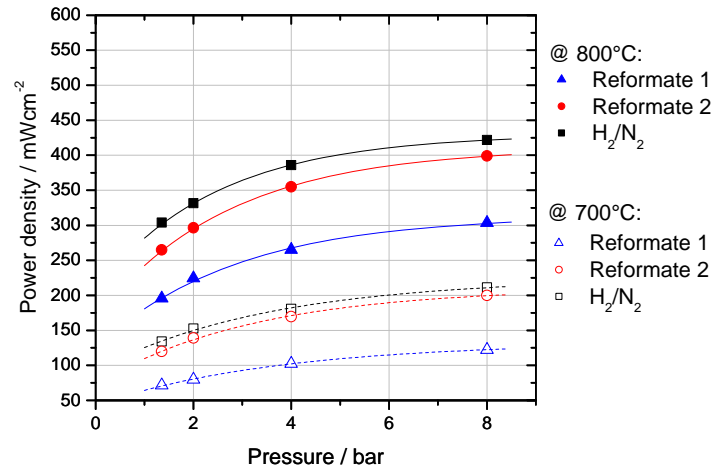


Figure 11: Power density at 850mV cell voltage at different pressures.

700°C	→ 2 bar		→ 4 bar		→ 8 bar	
	mW/cm ²	%	mW/cm ²	%	mW/cm ²	%
H ₂ /N ₂	18	14	46	35	77	57
Reformat 1	8	4	31	43	51	70
Reformat 2	19	16	50	41	80	67

800°C	→ 2 bar		→ 4 bar		→ 8 bar	
	mW/cm ²	%	mW/cm ²	%	mW/cm ²	%
H ₂ /N ₂	28	9	82	27	118	39
Reformat 1	29	15	69	35	108	55
Reformat 2	31	12	90	34	134	51

Performance gain under pressure at constant current density

If power density is regarded at constant current density instead of constant voltage the power density increase through pressurization is smaller. Figure 12 shows the development of power density under pressure at a constant current density of 0.4 A/cm². As in Figure 10 the full symbols are the measured values at 800°C, the open symbols at

700°C. At 700°C the curve for reformat 1 fuel is missing since for that condition 0.4 A/cm² were only reached at 8 bar.

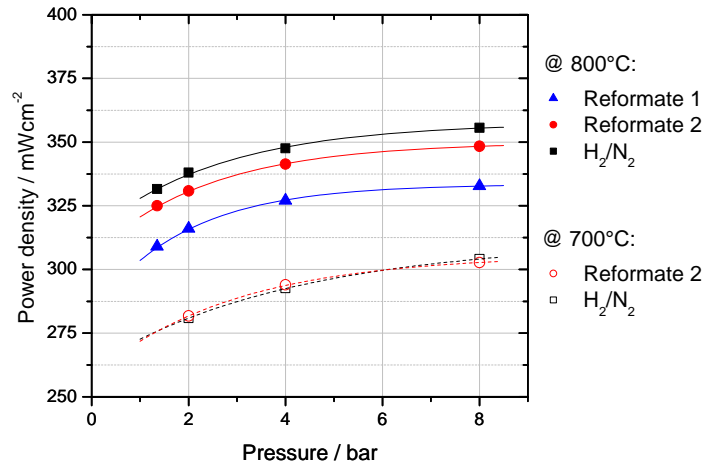


Figure 12: Power density at constant current density of 0.4 A/cm².

Power density increase through pressurization is similar for all fuels as can be seen also from table III. A pressure increase from 1.35 to 8 bar at 800°C leads to an increase of 24 mW/cm² for the H₂/N₂ mixture and reformat 1. For reformat 2 the increase is 23 mW/cm². The relative increase in power density is 7% for H₂/N₂ and reformat 2 and 8 % for reformat 1. At 700°C there is hardly any difference in performance for the H₂/N₂ mixture and reformat 2.

800°C	→ 2 bar		→ 4 bar		→ 8 bar	
	mW/cm ²	%	mW/cm ²	%	mW/cm ²	%
H ₂ /N ₂	6	2	16	5	24	7
Reformat 1	7	2	18	6	24	8
Reformat 2	6	2	16	5	23	7

At 700°C the increase in power density is slightly higher than at 800°C. For the hydrogen/nitrogen mixture and reformat 2 power density increases by 23 mW/cm² and 21 mW/cm² respectively when increasing pressure from 2 bar to 8 bar at 700°C while at 800°C the increase is 18 mW/cm².

Summary

The behavior of pressurized solid oxide fuel cells was examined using reformates as fuel. Two different reformat gases were used as well as a hydrogen/nitrogen mixture with 3% of water. Reformat 1 contained 18% H₂, 34% H₂O, 2% CO, 27% CO₂ and

19% CH₄ while reformat 2 contained 58.4% H₂, 20% H₂O, 12.2% CO, 5.5% CO₂ and 3.9% CH₄. Measurements were done at 700°C and 800°C at pressures ranging from 1.35 bar to 8 bar.

Pressure dependency of OCV was found to be highest for the hydrogen/nitrogen mixture. The pressure increase of OCV through pressurization for reformates showed a strong dependency on temperature. At lower temperatures the increase in OCV with pressure was found to be considerably smaller than for higher temperatures. This was explained by considering the gas compositions in equilibrium for the different temperatures as well as measurements of the gas composition after the stack. Measurements and calculated equilibrium compositions showed a good agreement. At lower temperatures gas composition varied strongly with pressure resulting in smaller hydrogen content at high pressures, which explains the smaller gain in OCV.

Under load pressurization showed a positive effect on performance for all fuels. At constant voltage a higher temperature led to a higher increase in power density for all fuels. The absolute increase in power density was found to be greatest for reformat 2 where up to 154 mW/cm² were gained at a voltage of 750 mV while the relative increase was greatest for reformat 1 which contained the greater part of methane and for which up to 70% of power increase was measured. The lower the voltage the greater was the absolute increase in power density through pressure while the relative increase got smaller. At constant current density the increase in power density because of pressure was similar for all fuels. At a current density of 0.4 A/cm² an increase of 24 mW/cm² or 8% was obtained.

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