Pressurized Solid Oxide Fuel Cells: Operational Behavior

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Abstract

The increasing demand of electrical energy requires power plants with high efficiencies and low emissions. Hybrid power plants consisting of an SOFC system coupled with a gas turbine fulfill these requirements and have the advantage of a large scope of applications (several 10 kW to multiple MW). The hybrid power plant project at DLR aims at investigating the fundamentals and requirements of a combined fuel cell and gas turbine power plant. A specific aim is to demonstrate stable operation of a plant in the 50 kW class in the next phase of the project. Building of the system will start in 2013. Prerequisite for the power plant realization is the detailed characterization of each subsystem and their interactions. The pressurized solid oxide fuel cell (SOFC) is an essential part of the system. In the context of the hybrid power plant the fuel cell will be operated in a pressure range from 1 to 8 bar.

Due to complex and interdependent mechanisms inside a SOFC the behavior at elevated pressures cannot be derived from measurements at ambient pressure. In addition, no sufficient literature data is available. Therefore, a test rig for the characterization of SOFC at pressures up to 8 bar has been built to examine the behavior of SOFC at elevated pressures with regard to two different aspects. On the one hand the effect of the elevated pressure on the electrochemical behavior has to be understood. On the other hand, on account of the system focus, the steady state and transient operational behavior is an important research area.

For this contribution the operational behavior of SOFC short stacks at elevated pressures up to 7 bar was examined. The experiments were performed on planar, anode-supported 5-cell short stacks. First, the pressure-dependency of performance at steady state at different relevant operating conditions is shown, and then temperature variations and gas composition change as well as their effects on pressurized SOFC are presented.

Introduction

The increasing demand for electrical energy requires the development of power plants with high efficiencies and low emissions. Hybrid power plants consisting of an SOFC system coupled with a gas turbine promise to fulfill both requirements reaching electrical efficiencies above 60% with low emissions. They also have the advantage of being usable for a large range of applications from several 10 kW to multiple MW.

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DLR aims at setting up a hybrid power plant in the 50 kW class starting in 2013. To achieve this goal, the Institutes of Technical Thermodynamics and Combustion Technology cooperate, combining their expertise in fuel cell and gas turbine technology. A schematic of the hybrid power plant is shown in Figure 1.
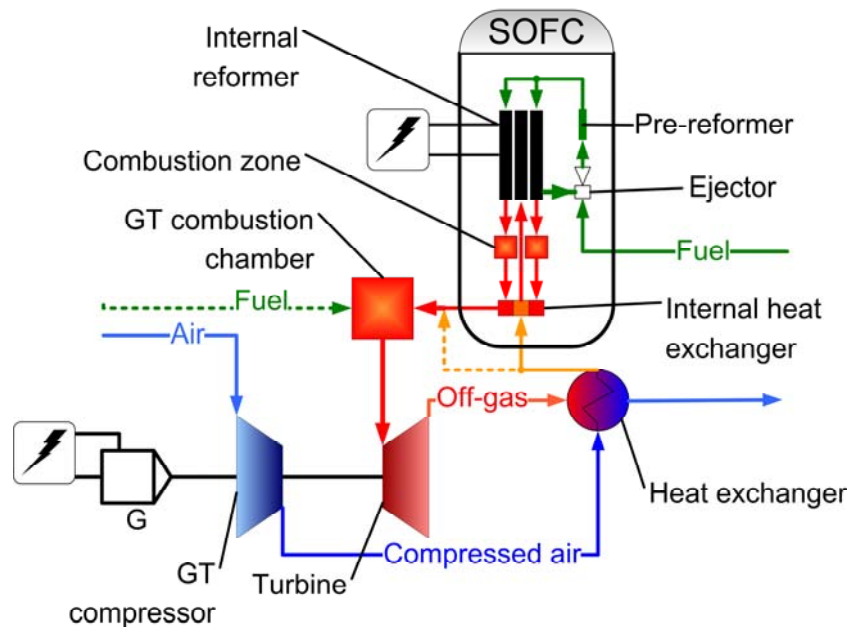

Figure 1: Schematic of the hybrid power plant with gas turbine and pressurized SOFC

For the realization of the power plant the behavior of each subsystem and their interactions have to be understood. The pressurized solid oxide fuel cell (SOFC) is an essential part of the system. In the context of the hybrid power plant the fuel cell will be operated in a pressure range from 1 to 8 bar. There is little or no data available from literature and the behavior of the SOFC at elevated pressures cannot be derived from measurements at ambient pressure due to complex, interdependent mechanisms. Therefore a test rig for the characterization of SOFC at pressures up to 8 bar has been built [1]. Of special interest is on the one hand the effect of elevated pressure on the electrochemical behavior of the cells. On the other hand the knowledge of steady state and transient operational behavior is essential for the integration in the hybrid system.

Experimental setup

In the pressurized SOFC test rig SOFC short stacks can be characterized at pressures of 1 to 8 bar. The pressure difference between the anode and cathode gas compartment as well as the furnace can be controlled by an accurate pressure control system to be between 10 and 500 mbar. This accurate pressure control is essential to keep the pressure differences low since too large a pressure difference may lead to the destruction of the cells or stack and the electrochemical activity may be influenced. To control the pressure two equalizing tanks of 400 l each are used to balance the small volume 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, argon, methane, carbon monoxide, carbon dioxide and steam on the anode side. 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 cells as well as performing

impedance spectroscopy. The gas composition at the in- and outlet of the anode and cathode can be measured by means of a gas chromatograph [1].

Anode-supported 5-cell short stacks with an active area of 84 cm² per cell were used. The stacks were kindly provided by ElringKlinger AG. The stacks consist of sintered cells which are integrated into stamped metal sheet bipolar plates ("cassettes"). The cells consist of an anode substrate (Ni/YSZ) and a 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.

The short stacks have been characterized so far at pressures ranging from 1.4 to 7 bar. In the experiments the pressure was adjusted at the anode outlet. The pressure differences between anode and cathode as well as between the anode and the pressure vessel and between the cathode and the vessel were beneath 20 mbar at all times to avoid damage to the cells. Variations of temperature and gas composition were done for the various pressure levels. The temperature was varied from 750°C to 800°C. Measurements shown in this paper were done with a 1/1 mixture of hydrogen and nitrogen as well as with pure hydrogen. The flow rate on the anode side was 10 l/min for the whole stack while the cathode was supplied with 15 l/min of air.

Modeling

Modeling is done on cell as well as on system level. The results in this paper are done on cell level and are based on a model previously validated on anode-supported cells [2]. The framework for the physically-based SOFC modeling and simulation has been presented previously [3]. A detailed 1D + 1D elementary kinetic electrochemical model was applied that represents one single channel of the experimental setup. One-dimensional channel flow (x dimension) is described using the Navier-Stokes conservation equations (continuity, species, momentum). One-dimensional mass transport through the MEA (y dimension) is described by coupled Fickian/Knudsen diffusion and Darcy flow. Charge transport in the solid electrolyte and the electrolyte phase of the composite electrodes is described in two dimensions using Ohm's law. Anode electrochemistry is described using previously validated elementary kinetics for surface reactions on Ni and YSZ, and for charge transfer (hydrogen spillover) [4]. Cathode electrochemistry is described using a modified Butler-Volmer equation given in [3]. Current-voltage relationships are modeled by directly solving for the electric-potential distribution in the electrodes and electrolytes without using the Nernst equation.

Even though the model does not exactly represent the experimentally examined cells, the model still provides sufficient accuracy to qualitatively show and explain the pressure-dependent mechanisms. The model will be adapted to the examined cells in the near future. All simulations are isothermal. The operation parameters of the simulations (pressure, temperature, gas composition) are the same as in the experiments.

Results

Variations of temperature and gas composition were done for the various pressure levels. The temperature was varied from 750°C to 800°C. Measurements shown here were done with a 1/1 mixture of hydrogen and nitrogen as well as with pure hydrogen. The flow rate on the anode side was 10 l/min for the whole stack while the cathode was supplied with 15 l/min of air.

Figure 2 shows the current voltage curves of cassette 3, which is located in the middle of the stack, at different pressures ranging from 1.4 bar to 7 bar at 750°C. It can be observed that the performance of the cell rises with higher pressures. At a cell voltage of 0.9 V a power density of

154 mW/cm² is reached for a pressure of 1.4 bar. At 3 bar the power density is 176 mW/cm² which is a gain of 22 mW/cm² or an increase of 14 %. At 7 bar the power density reaches 203 mW/cm², which is an increase of 32%.
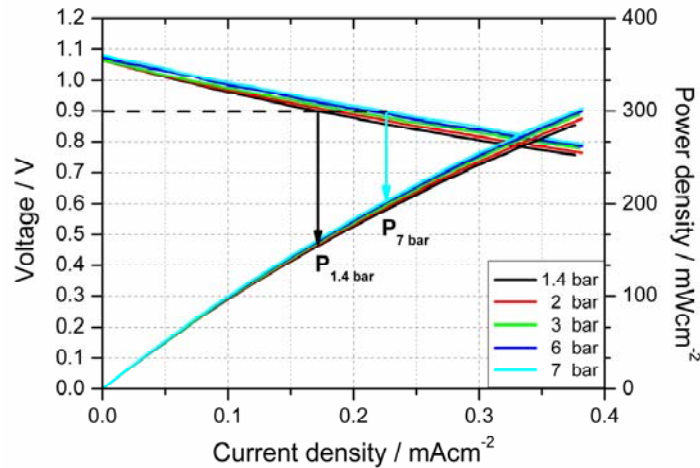

Figure 2: Current voltage curves for pressures between 1.4 bar and 7 bar at 750°C

Figure 3 shows the power density gain for different pressure levels measured between 1.4 to 7 bar over cell voltage. The lower the cell voltage and consequently the higher the current density the greater is the benefit of the pressure increase. At a voltage of 1 V the performance gain due to a pressure rise from 1.4 to 2 bar is about 3mW/cm² while at a voltage of 0.8 V the gain is 14 mW/cm². If the operating pressure is raised from 1.4 bar to 7 bar 30 mW/cm² are gained at a voltage of 1 V while at a voltage of 0.8 V the performance gain is 50 mW/cm².
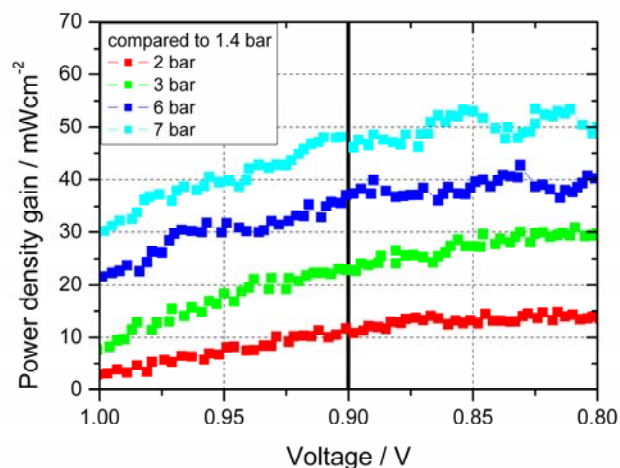

Figure 3: Power density gain for different pressures at voltage decrease at 750°C

The results obtained from simulation correspond qualitatively with the experimental ones. Figure 4 shows the simulated current voltage curves for various pressure levels. The pressure increase leads to a higher OCV, a lower gradient at intermediate current densities and a higher limiting current density. Figure 5 shows the simulated power density at 0.7 V for pressures from 1 to 8 bar. It can be seen that the benefit of a pressure increase is higher at low pressures. The power density gained through augmenting the pressure by 1 bar gets smaller the higher the initial pressure is.
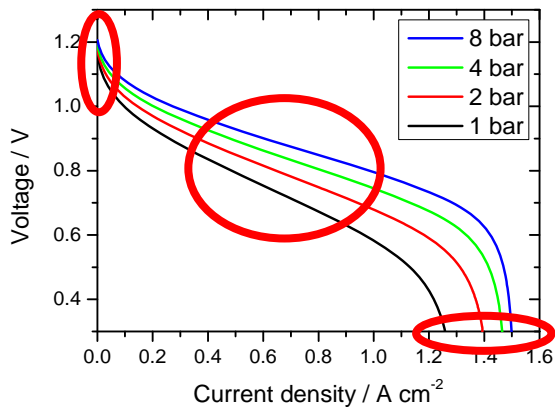
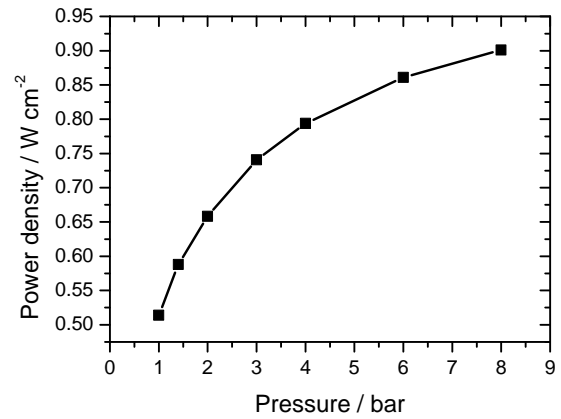**Figure 4: Simulated current voltage curves for pressures between 1.4 bar and 8 bar**

Figure 5: Simulated power density at 0.7 V for pressures between 1 bar and 8 bar

Simulation allows to interpret data and to understand effects that cannot be observed experimentally. Figure 6 shows the simulated contributions of the different overpotentials to the current-voltage curve at ambient pressure. Since the cells are anode-supported the main losses occur at the anode. In Figure 7 the pressure dependence of theses overpotentials is shown. The concentration overpotential at the anode decreases with pressure. So does the activation overvoltage at the anode and cathode. A pressure increase enhances diffusion and therefore augments the surface coverage of intermediates [5]. The concentration overvoltage at the cathode does not change significantly because the cathode is thin and diffusion is not a dominant effect.
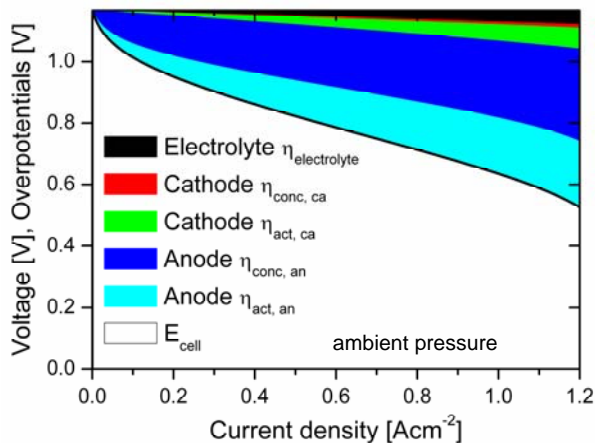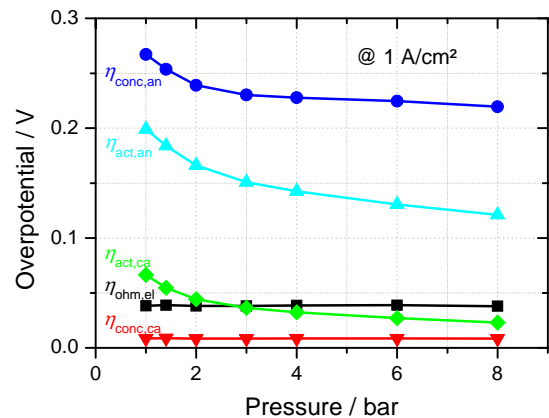

Figure 6: Simulated overvoltages at ambient pressure

Figure 7: Simulated pressure-dependancy of overvoltages

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The effect of pressure variation on cell voltage at different temperatures can be seen in Figure 8. Here experimental current voltage curves can be seen for 1.4 bar at 750°C and at 800°C. In green the current voltage characteristics at 3 bar and 750°C as well as 800°C are shown. It can be seen that the change in temperature at constant pressure has a greater effect than the increase of pressure at constant temperature. The temperature increase from 750°C to 800°C at 1.4 bar causes an increase of power of 30.9% or 45.6% at 3 bar while the pressure increase at constant temperature only produces an increase of power of 2.3% or 13.8% respectively.

The higher the pressure level at which the stack is operated the higher is the benefit of a temperature increase as well as the other way round: a higher temperature results in a higher benefit from pressure increase.
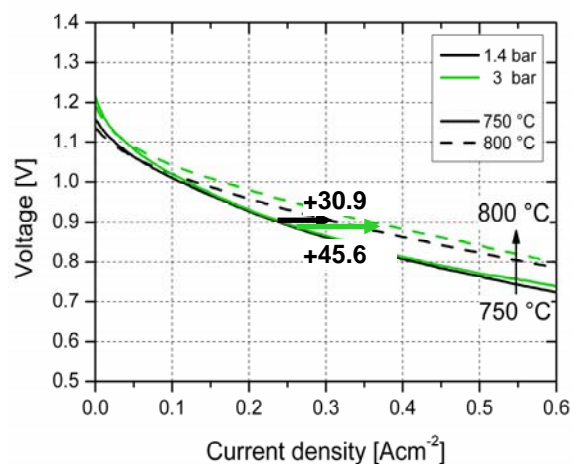

Figure 8: Current voltage curves for 1.4 bar and 3 bar at 750°C and 800°C

If the power density at 0.4A/cm² is regarded the benefit of a temperature increase is also greater at elevated pressures and the benefit of a pressure increase is higher at elevated temperatures. This is illustrated in Figure 9. At 1.4 bar power density increases by 22 mW/cm², if temperature is raised from 750°C to 800°C. At 3 bar the same temperature rise increases power density by 28 mW/cm². A pressure rise from 1.4 bar to 3 bar causes power density to rise by 2 mW/cm² at 750°C, while at 800°C it rises by 8mW/cm². If both parameters are changed, pressure from 1.4 bar to 3 bar and temperature from 750°C to 800°C, the gain in power density is 30 mW/cm².
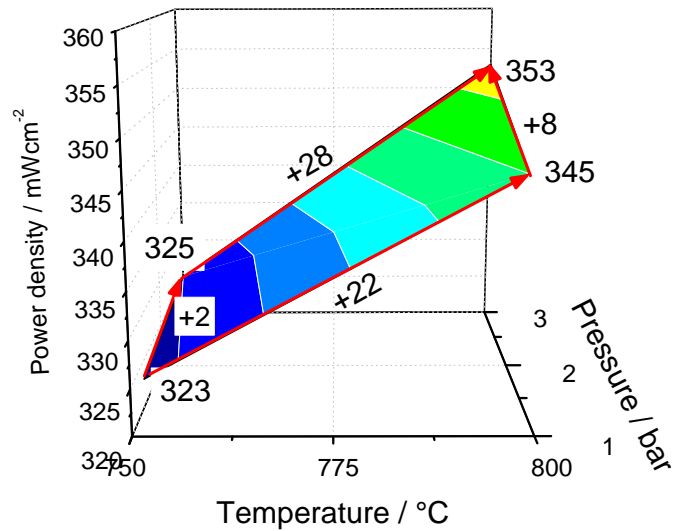
Figure 9: Performance gain through temperature and pressure rise at 0.4 A/cm²

Figure 10 shows the simulated overpotentials over pressure for two different temperatures, 750°C and 800°C. The contribution of the activation overpotentials at anode and cathode are lower at 800°C. Also, the gradients with which the activation overpotential changes with pressure are lower at higher temperatures. The concentration overpotential at the anode is slightly higher at 800°C but the temperature does not affect the influence an increase in pressure has. The slope is similar for both temperatures.
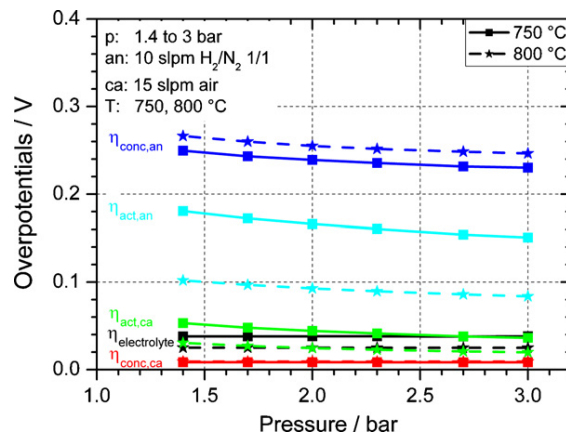

Figure 10: Overpotentials for 1.4 bar and 3 bar at 750°C and 800°C

Figure 11 shows the current voltage curves at 750°C and two different gas compositions at the anode (pure hydrogen and a 1/1 mixture of hydrogen and nitrogen) for pressures of 1.4 bar and 3 bar. Similar trends as for the temperature change are seen. At 1.4 bar the measured power density at a voltage of 0.9V and 750 °C increases from 217mWcm⁻² with the H_2/N_2 mixture to 276mWcm⁻² with pure H_2 on the anode. This is an increase of 27.5%. The pressure increase from 1.4 bar to 3 bar with the H_2/N_2 mixture only gives an increase of 2.3 %. This means that the change in gas composition at one pressure has a greater effect than the increase of pressure at constant gas composition. Still, the performance gain of the gas change increases if pressure

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is higher. The performance gain at 0.9V when changing from H2/N2 at 3 bar to pure H2 is 40.3% (+89mWcm−2) contrasting to 27.5% (+60mWcm−2) if pressure is at 1.4 bar.
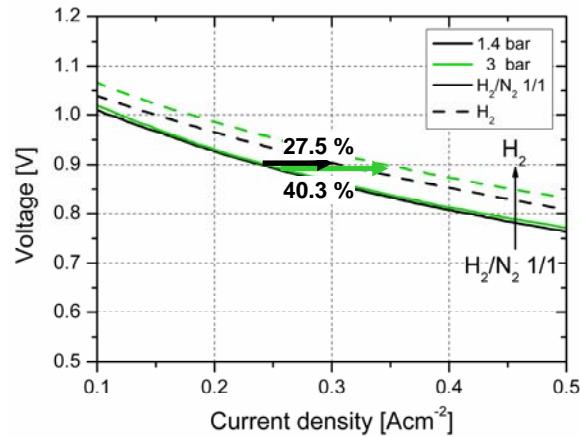

Figure 11: Current voltage curves for 1.4 bar and 3 bar with H$_2$/N$_2$=1/1 and pure hydrogen as fuel

Figure 12 shows the simulated overpotentials over pressure for two different anode gas compositions. It can be seen that the main effect is the decrease of the concentration overpotential at the anode. Due to the higher hydrogen concentration in the fuel the availability of hydrogen within the porous anode is higher for pure hydrogen.

It can also be seen that the activation overpotential of the anode increases slightly if the gas composition is changed to pure hydrogen. This is due to the increasing H$_2$/H$_2$O ratio that leads to decreased electrode kinetics [6, 7].

The gas on the cathode side does not change therefore no changes of the cathode overpotentials take place. The electrolyte overpotential is independent of gas composition at the electrodes and consequently stays constant as well.
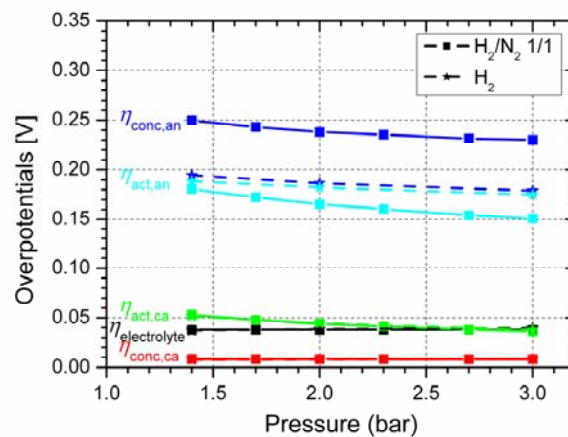

Figure 12: Overvoltages for 1.4 bar and 3 bar with H$_2$/N$_2$=1/1 and pure hydrogen as fuel

Summary and conclusion

Short stacks provided by Elring Klinger AG and consisting of 5 anode-supported SOFCs were characterized at elevated pressures between 1.4 and 7 bar. Variations of temperature and gas composition were done for the various pressure levels. The temperature was varied from 750°C to 800°C. Simulations on cell level were done to better understand the electrochemical processes at the cell and their pressure dependence.

The performance of the cell rises with higher pressures. When raising the pressure from 1.4 bar to 3 bar an increase in power density of 23 % was observed. Rising pressure from 1.4 bar to 7 bar resulted in an increase in power density of 32%. It was also found that the lower the cell voltage and consequently the higher the current density the higher is the benefit of the pressure increase.
A change in temperature at constant pressure was found to have a greater effect than the increase of pressure at constant temperature. Nevertheless, the higher the pressure level at which the stack is operated the higher is the benefit that can be obtained by a temperature increase. The same effect is true the other way round: a higher temperature results in a higher benefit from pressure increase. When the anode gas composition was changed from H_2/N_2 to pure hydrogen similar trends as for the temperature change were seen.

In future the pressure dependant behavior with reformate gases will be examined. Here gas analysis at the anode and cathode will be done. Of interest are also the operational limits as e.g. pressure differences between anode, cathode and the surroundings.

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