PEFC Stack for Operating Temperatures up to 130 °C

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Abstract: *At the DLR Institute of Technical Thermodynamics new concepts for fuel cell stacks are being developed for various applications and load profiles. Thereby, the main focus lies on the simplification of the stacks for reaching a cost reduction as well as an increase of the power density.*
Today's polymer electrolyte fuel cells (PEFCs) are applicable only within a limited range of the operating temperature. This limitation restricts the spectrum of possible applications and hinders their flexibility during operation. Therefore, the continuous operation at elevated temperatures or in an extended temperature range for a limited time offers the opportunity to overcome these restrictions.
Unfortunately, higher operating temperatures lead to new challenges, especially when conventional materials for the membrane electrode assemblies (MEAs) are used: In order to avoid critical operating conditions and to ascertain a sufficient durability and performance of a fuel cell stack, special concepts regarding the bipolar plates, the cooling strategy, the MEAs themselves as well as a closer look on the water management are essential. Furthermore, the operating strategy of the stack has to be adapted with respect to all of the stack components.
The status of the development work, the definition of problems as well as the approaches to overcome them will be presented.

Keywords: PEFC, bipolar plate, endplate, segmented cell, diagnostic methods, current density distribution, light-weight stack, deformation and stress analysis

Introduction

At present-day polymer electrolyte fuel cells suffer from a limited range of the operating temperature, because it restricts the spectrum of possible applications and hinders their flexibility during operation.

Hence, one of the most important targets in fuel cell research is to increase the operating temperature for a PEFC. Higher operating temperatures (up to 130 °C) accelerate the kinetics of the fuel cell reactions and improve the CO-tolerance of the PEFC. Furthermore, the efficiency of the cooling system increases due to the lower surface demand and the operating strategies can be simplified.

Unfortunately, the performance and applications of PEFC systems are limited by the cooling requirements when "standard"-MEAs with PFSA-membranes are used. These membrane materials need a sufficient humidification for operation and consequently a low operating temperature ($T \leq 80$ °C). Therefore, higher levels of the operating temperature lead to new challenges, especially if neither the humidification nor the pressure nor the stoichiometry shall be increased.

For these reasons, the DLR has embarked on a double tracked strategy: On the hand MEAs with standard-PFSA-membranes shall be used for transient operation at higher temperatures for a limited time (e.g. 130 °C for about 45 minutes). On the other hand the DLR will take advantages of novel membrane materials to develop a concept for extended temperature fuel cell operation involving adapted electrode structures.

In order to avoid critical operating conditions and to ascertain a sufficient durability and performance of a fuel cell stack, special concepts regarding the bipolar plates, the cooling strategy as well as a closer look on the water management are essential. Furthermore, the operating strategy of the stack has to be adapted with respect to all stack components.

For the implementing of some of these requirements the DLR has developed a measurement technique for the determination of local current density and temperature distributions. This sensor technology can be applied in each cell of the stack and helps to investigate and to assess any operating state. Consequently, this monitoring tool can be used in a controlling system for optimizing the performance, the durability and the reliability of a stack.

Experimental set-up: Current stack configuration

The current DLR-stack consists of two endplates, which are made of stainless steel. Each endplate is covered with a gold layer of 3 µm thickness and can be equipped with connections for the supply with the reactant gases and the cooling media. In this way, different flow and circulation strategies can be realized. For the assembly of the stack both endplates can be connected by at least eight screws. Thereby, the bipolar plates and the MEAs are sandwiched between them. An exploded assembly view of the DLR-stack is shown in figure 1.

In contrast to many other bipolar plates, the bipolar plates of the DLR stack are divided into two pieces. In this way, an internal cooling circuit within the bipolar plates is realized. Each plate is made of a mixture of graphite and a

phenolic resin- (SGL Sigracet®-BBP4) and can be used in a temperature range up to 180 °C. The flow field area of the bipolar plates is 11.9 x 11.9 cm^2.

For avoiding leakages within the cooling circuit, a sealing made of Fluororubber (FKM) is used between the two halves of a bipolar plate. Fluororubber resists elevated temperatures up to 200 °C. Hence, this material is also used for sealing the gas compartments on both sides of the MEAs.

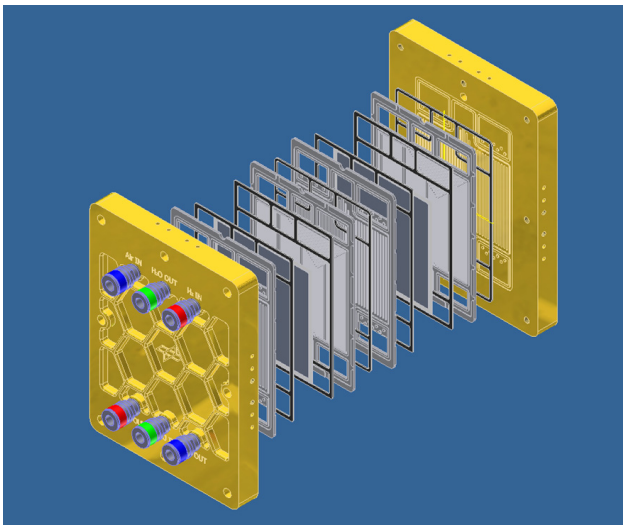

Figure 1. Exploded assembly view of the current configuration of the DLR-stack.

The sealing concept that is realized in the stack leads to a large number of single gaskets (e.g. 31 gaskets inside a stack with 10 cells). Such a large number of sealings may cause problems concerning the gas tightness. After an optimization of the sealings' thickness the pressure drop of the gas compartments was around 5 mbar/min (measured with nitrogen at an overpressure of 500 mbar in a stack configuration with 10 cells). These are excellent values, even compared to a commercial stack.

Experimental Investigations

For the investigation of the transient behavior at higher temperatures for a limited time, the fuel cell was operated at a temperature of 90 °C and ambient pressure with full humidification of the gases (λ_{H2} = 1.5, λ_{AIR} = 2). After reaching steady state, the temperature was increased to 100, 110 or 120 °C. In contrast to the temperature all other operation parameters were kept constant.

For a Nafion® type membrane with a catalyst loading of 0.3 mg Pt/(cm^2·electrode) the measured characteristic of the current is shown in figure 2 as a function of time for a raise of the temperature from 90 to 100 °C. Thereby, the voltage was kept constant at 500 mV.

While the temperature was increased from 90 to 100 °C the relative humidity declined from φ = 1.0 to 0.69. As a consequence, the current dropped from 100.6 to 75.2 A. Unfortunately, the heating rate of the used thermostat was too low for the high thermal mass of the cell. Hence, it took nearly 1.5 h for reaching the higher temperature level. After reaching 100 °C the electrical current stays constant. According to this, the fuel cell remains in a quasi-stationary state during the entire heat-up phase. For higher temperature levels, even much longer heating-up periods were necessary. In figure 3 the results for the corresponding measurements at 100, 110 or 120 °C as well as the initial values are compared.

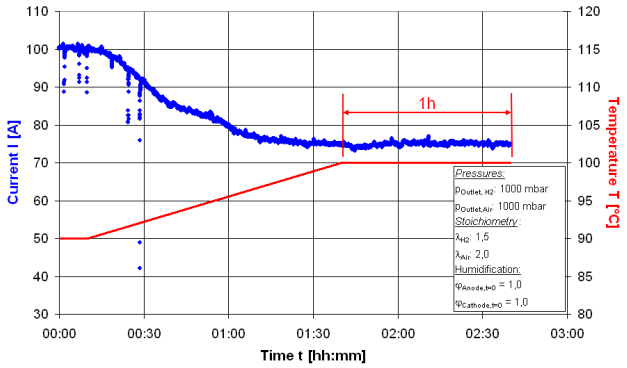

Figure 2. Behavior of the current when increasing the cell temperature from 90 to 100 °C (V = 500 mV).

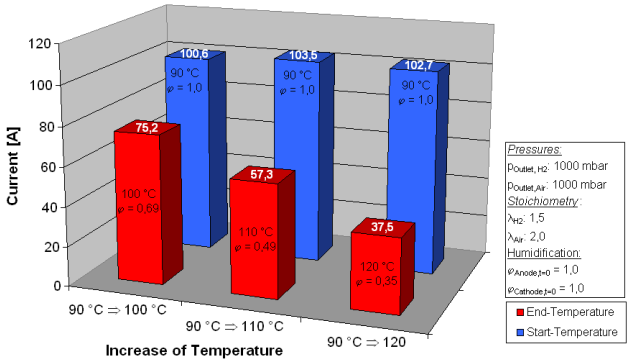

Figure 3. Current reduction at a temperature rise from 90 to 100, 110 and 120 °C (V = 500 mV).

As it can be seen in figure 3 a rise of the temperature from 90 to 120 °C leads to a reduction of the current to 37.5 A. For a steady state with a relative humidity of 0.35 the reduction of around 62.5 % for the current is quite acceptable, because it is measured for steady state and not for a real transient. Furthermore, the MEAs did not suffer from a loss of the performance, because the initial current can be restored after cooling the cell down to 90 °C.

Another important aspect for a fuel cell is the long-term stability of the MEA. For this reason the MEAs used before were investigated over a longer period. Thereby, the temperature was kept constant at 80 °C. The gases were fully humidified at ambient pressure (λ_{H2} = 1.5, λ_{AIR} = 2). The stack was assembled with two cells, whereby the voltage remains constant at 800 mV. In figure 4 the current density of the cell is shown as a function of time.

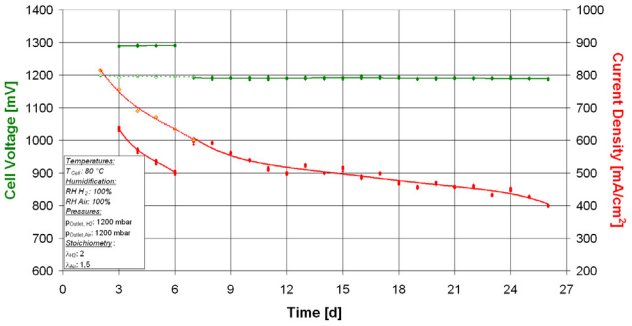

Figure 4. Long-term behavior of a two-cell stack.

During a period of 26 days the current density of a MEA containing a membrane of the Nafion® type is reduced to less than 50 % of the initial value. This corresponds to a degradation rate of around 16 mA/(cm^2·d).

A degradation rate in this range is not acceptable for commercial applications. Hence, further MEAs with new membrane materials have been tested for long-term operation. For these purposes experimental membranes –a PFSA membrane with short side chains and a non fluorinated one– were coated with platinum by using the DLR dry spraying technique [1]. The catalyst loading of the MEAs was adjusted to 0.3 mg Pt/(cm^2·electrode). All experiments were performed at temperature of 85 °C and ambient pressure. The stoichiometry was 1.5 on the anode and 2.0 on the cathode. In contrast to the experiments described above, these were performed galvanostically in a single cell with an active area of 25 cm^2 and at a current density of around 1 A/cm^2. In figure 5 the results of these measurements are shown. For comparison, the corresponding results with the MEA containing the Nafion® type membrane are also depicted in this figure.

As it can be seen in figure 5 the MEAs with the experimental membranes have a significantly better long-term behavior. In contrast to the commercial MEA with the Nafion® type membrane, the performance of the non-fluorinated one rises up (during the first 100 h) before it slightly decreases. Less distinctive but similar is the behavior of the PFSA membrane with short side chains.

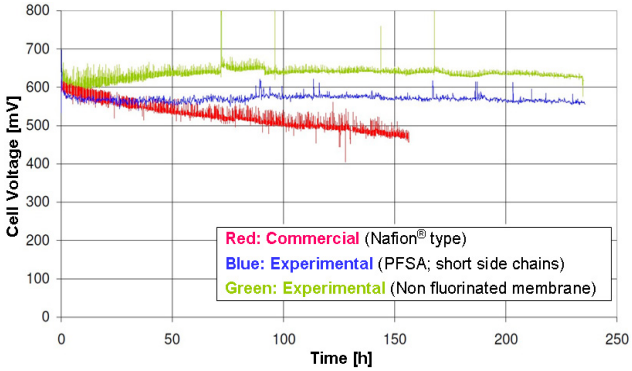

Figure 5. Long-term behavior of MEAs with different membranes.

Segmented Cell Technology

For the development and the improvement of fuel cells, fuel cell stacks and their operating strategies a detailed understanding of the processes within the cell(s) and the local operation conditions is necessary.

While most of the existing current density measuring systems are focused on measurements in single fuel cells, the DLR has developed special bipolar plates with segmented flow fields and integrated current sensors for adoption in fuel cell stacks. Current density distribution measurements in stacks are helpful to optimize the stack design and the operating parameters, to identify malfunctions, to investigate interactions between adjacent cells (leading to thermal, electrical and mass transfer gradients), and to control the operating state of the stack.

The segmented bipolar plates of the DLR are built up in printed circuit board (PCB) technology. This allows a flexible design of the separate current collector segments, which are placed within the epoxy-glass resin matrix. The current collector segments are gold plated to decrease the contact resistance and to avoid corrosion. Because of the moderate electric conductivity of the gas diffusion layer the interference between neighboring segments is relatively low and the gas diffusion layer as well as the reaction layer are not segmented. A detailed description of the assembly can be found in [2]. The measurement principle and an image of the latest development of the segmented bipolar plate are shown in figure 6.

The resistor array for the current measurement is integrated in the PCB using a multi-layer assembly. The flow field channels can be machined directly into the board. The overall thickness of the plate is 3 mm, which corresponds to the thickness of the regular bipolar plates within the stack. In this way –and due to the fact that between the segmented cell and the bipolar plate the same sealing concept is used as between the regular bipolar plates– each bipolar plate can be replaced easily by this measurement tool.

In the latest stage of development 90 segments for a flow field area of 11.9 x 11.9 cm² were chosen, whereby the bipolar plate is segmented on both sides. Moreover the segmented bipolar plates can be used at temperatures up to 200 °C. This allows the use for diagnostic, monitoring and controlling tasks in 130 °C-stacks or High Temperature (HT-)PEFCs that are currently favored in the automotive industry. Furthermore, the segmented bipolar plates can be used for locally resolved, electrochemical impedance spectroscopy. This promises to get additional information about the processes within the fuel cell.

The measurement setup works independently from the electric load unit and the control system of the fuel cell. The sense wire connectors on the segmented bipolar plate are connected to a data acquisition unit consisting of a multiplexer and a digital multimeter.

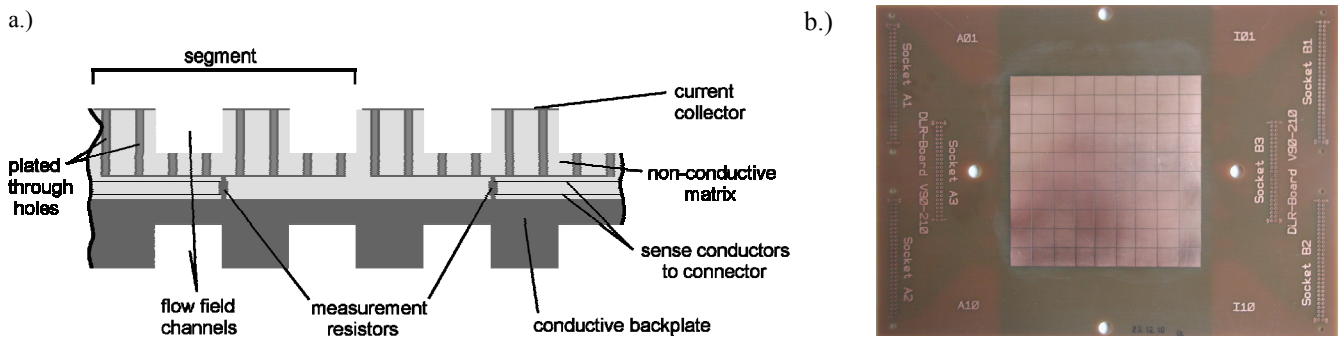

Figure 6. Measurement principle (a.) and image (b.) of the segmented bipolar plate for stack application.

To illustrate the value of locally resolved current density measurements in figure 7 the behavior of a fuel cell after switching off humidification is displayed.

In the corresponding experiment a 25 cm^2 single cell was operated in the galvanostatic mode at 80 °C and at a pressure of 1.5 bar fully humidified (λ_{H2} = 1.5, λ_{AIR} = 2). The current was set to 10, 15 and 20 A. After reaching the steady state for these conditions the humidification was switched off by bypassing the humidifiers.

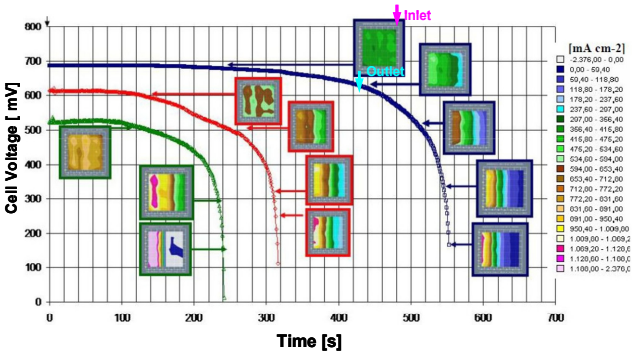

Figure 7. Time depending cell voltage after switching off the humidification (Flow field: Vertical meander).

For each of the three adjusted currents the missing humidification leads to a continuous reduction of the cell voltage. Thereby, the descent of the voltage accelerates with time. Due to the larger water demand at higher currents the voltage reduces faster from 10 A to 20 A. As it can be seen in the current density distributions (inserted in this diagram) the drying of the membrane results in an inhomogenization of the current density distributions: Starting with a very uniform current density distribution in the beginning the drying process leads to the formation of a maximum, that is shifted continuously from the inlet to the outlet.

Development of light-weight endplates

In addition to an increase of the power density by increasing the performance of the stack a weight reduction of distinctive components can cause the same. In particular, this approach is successful when a single component is responsible for a huge part of the total weight e.g. like the endplates in a short stack.

For this reason the DLR also works on the optimization of different stack components by using light-weight materials and structures. As a result of these development processes in figure 8 the design for a new endplate of the DLR stack is depicted. This endplate was analyzed by using finite elements methods (FEM) for optimizing the structure for different materials. In contrast to the current endplates (Weight: 8.5 kg) a weight reduction of 83 % can be achieved, if aluminum is used. In addition, the production costs may be reduced significantly, because it can be manufactured by injection molding.

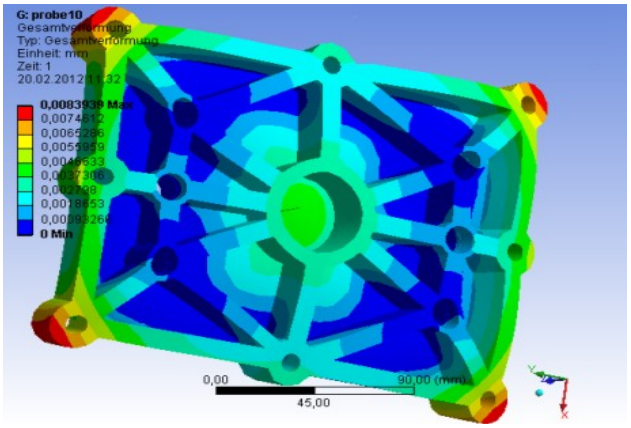

Figure 8. Optimized endplate (Stress analysis).

Acknowledgements

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References

1. Gülzow, E., Schulze, M., Wagner, N., Kaz, T., Reissner, R., Steinhilber, G. and Schneider, A., "Dry layer preparation and characterisation of polymer electrolyte fuel cell components" Journal of Power Sources, Vol. 86, pp. 352-362, 2000.
2. Schulze, M., Gülzow, E., Schönbauer, S., Knöri, T. and Reissner, R. "Segmented cells as tool for development of fuel cells and error prevention/ prediagnostic in fuel cell stacks" Journal of Power Sources, Vol. 173 (1), pp. 19-27, 2007.