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Operation of a planar free-breathing PEMFC in a dead-end mode

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Abstract

Operation of a planar free-breathing PEMFC with pressurized anode was studied by constant current and polarization curve measurements. The anode outlet was equipped with a purge valve, whose duty cycle was varied. The results indicate that the cell is able to operate with 0.1 and 0.25 barg hydrogen pressures, with both dry and humid hydrogen. There were no significant differences in cell performance at different purge valve duty cycles. When the purge valve was completely closed signs of flooding were observed. Anode side flooding was reduced at higher hydrogen overpressure due to increased hydraulic permeation of water through the membrane.

Keywords: PEMFC; Free-breathing; Dead-end; Purge valve; Pressurized; Flooding

1. Introduction

Small PEMFCs are potential power sources for portable electronic devices. In such applications, the energy density of the power source should be as high as possible. This requires minimization of the power consumption of auxiliary devices, such as air pumps. One possible way to achieve this is to use the so called free-breathing cells, i.e. cells which take the oxygen passively from the surrounding air. Also fuel utilization should be as high as possible. This can be accomplished by operating the cell in dead-end mode. In dead-end mode, the hydrogen outlet is blocked and thus the anode is pressurized. Complete blocking of the hydrogen outlet may cause serious flooding problems in long term operation due to water accumulation in the anode compartment, see e.g. [1]. It may also cause increase in nitrogen concentration in the anode, see for example [2]. Dead-end operation also affects the water balance of the cathode due to decreased total water removal from the cell. Therefore, the anode outlet should be equipped with a purge valve to remove excess water. In this work, the operation of a planar free-breathing PEMFC in dead-end mode is studied. The cell was tested both with dry and humid hydrogen and with different purge valve duty cycles.

2. Experimental

The cell used in this work was a planar free-breathing PEMFC introduced and used in [3–5] and its active area was 6 cm^2. Cathode side gas diffusion backing was open to ambient air and the cell took the oxygen needed in the cell reactions directly from the surroundings. The MEA used in this work was GORE^{TM} PRIMEA$^{®}$ Series 58, with the membrane thickness of 18 μm. Ambient temperature and relative humidity were approximately 22 °C and 50%, respectively. The cell was separated from the laboratory space by partition walls to minimize the effects of air and people movements in the laboratory. The cell was not heated externally and its temperature was not controlled.

The measurement system is illustrated in Fig. 1. It was fundamentally similar to that described in [3–5] with the exception that the hydrogen outlet was equipped with a Bürkert 6013 solenoid valve. The valve was controlled with an Agilent 34970A Data Acquisition/Switch Unit connected to a computer. Hydrogen pressure was controlled

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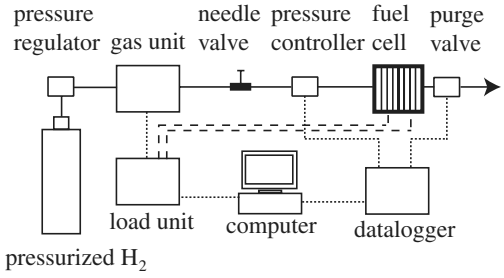

Fig. 1. Measurement system.

with Brooks 5866 pressure controller, which was also connected to the Agilent 34970A. A needle valve was installed between the gas handling unit and pressure controller to limit the hydrogen flow and pressure peaks during the purge.

Two different hydrogen pressure levels, 0.1 and 0.25 barg, were used in these measurements. The selection was based on the unpublished test measurements done with the same cell. In those test measurements, it was noticed that 0.25 barg is the maximum pressure for this cell. With larger pressures the performance decreased due to larger mechanical stresses, and the hydrogen also leaked to the surroundings from the anode compartment.

Dry hydrogen and humidified hydrogen with dew-point temperature of 30 °C were used in these measurements. These were selected to simulate different possible hydrogen storage methods. Dry hydrogen corresponds to either metal hydride storages or pressurized gas vessels. Humidified hydrogen corresponds to hydrogen produced from $NaBH_4$ solution with room temperature micro-hydrogen-generator, as reported e.g. in [6]. Needle valve, pressure controller and gas pipes between gas unit and fuel cell were heated to 35 °C to avoid condensation of water in these components.

Duty cycle of the purge valve was varied from completely closed to 1/60 (seconds open/seconds closed), 1/120, 1/300, 1/600, and 1/1200. In dead-end measurements, the hydrogen flow rate was only measured but not controlled. Reference measurements were also conducted in flow-through mode. In these measurements the hydrogen flow rate was controlled, and the stoichiometric factor was kept at 1.5. Dew-point temperature of hydrogen in the reference measurements was 30 °C.

At each humidity and pressure level, and purge valve duty cycle, polarization and constant current measurements were performed. To minimize the effects of load history, the following measurement sequence was applied. First the purge valve and pressure controller were turned on and the current was increased to 0.6 A (100 mA cm^{-2}) in 0.1 A/30 s steps. The cell was operated 15 min at 0.6 A current, after which the polarization curve was measured. During polarization measurements, the current was changed in 0.1 A steps with 30 s intervals. The scan was reversed when the cell voltage decreased under 0.4 V or 0.5 V, depending on the conditions (see Section 3). After the scan the cell was operated in an open-circuit mode for 3 h. This procedure was repeated three times and the third scan was used in the results. Typically the second and third scans were already identical, so it could be concluded that with this procedure the results are not affected by the load history. The constant current measurement was started after the third scan. The cell current was kept at 1.5 A (250 mA cm^{-2} for 8 h and the cell voltage was recorded during that period.

3. Results and discussion

Polarization curves measured with purge valve closed and with 1/60 and 1/1200 duty cycles are illustrated in Figs. 2 (0.1 barg) and 3 (0.25 barg). The polarization curves measured with other three duty cycles were between these extreme cases and they are left out for clarity. The performance of the cell was slightly better than in [4,5] where only dry hydrogen was used in a flow-through mode. Hence, the slightly better performance observed here was most probably caused by better conductivity of the membrane due to higher water content.

Polarization curves measured with 0.1 barg hydrogen pressure show that with periodically opened purge valve, the performance of the cell was similar to reference measurements and practically not dependent on the duty cycle. When the purge valve was completely closed, the performance of the cell slightly decreased. With completely closed purge valve, the polarization scan had to be reversed already at 0.5 V, because the voltage typically collapsed suddenly from 0.4 V to under 0.2 V, which was the shutdown limit of the measurement system.

The humidity of the hydrogen had no effect on the polarization curves when the anode side was purged periodically. When the purge valve was closed, the performance of the cell was only slightly decreased with humidified hydrogen, probably due to water accumulation

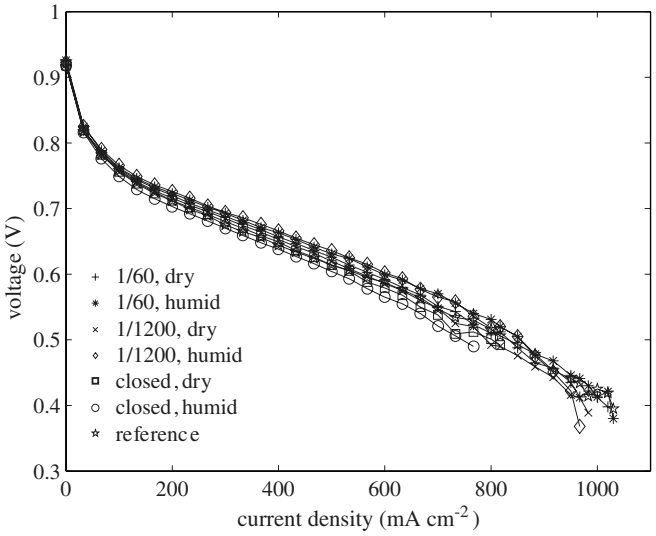

Fig. 2. Polarization curves measured with 0.1 barg hydrogen pressure.

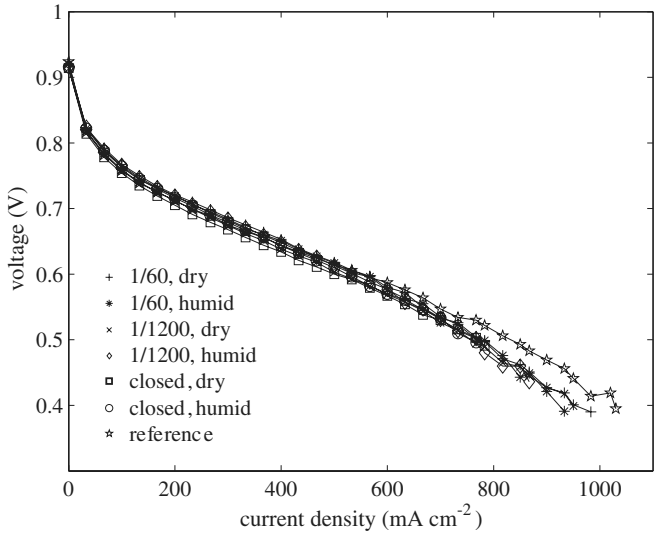

Fig. 3. Polarization curves measured with 0.25 barg hydrogen pressure.

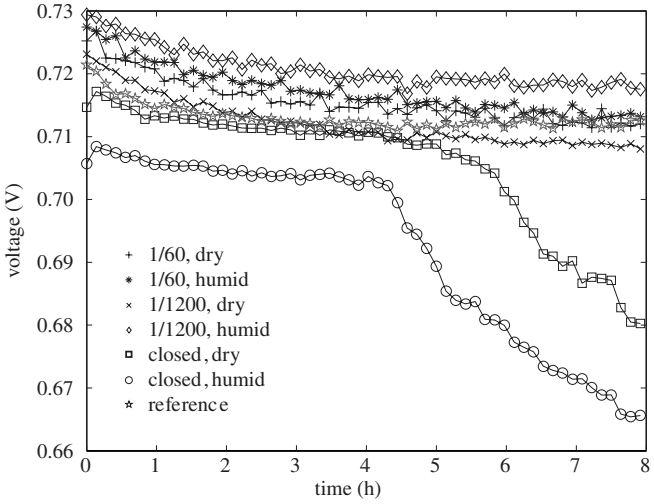

Fig. 4. 8 h measurement with 0.1 barg hydrogen pressure.

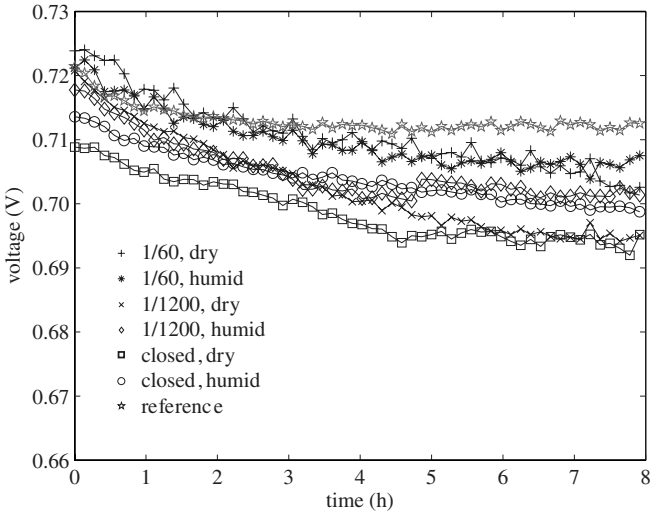

Fig. 5. 8 h measurement with 0.25 barg hydrogen pressure.

on the anode side of the cell. This small dependency on the humidity can be explained with the low amount of water in the inlet hydrogen compared to the water produced in the cell reactions. For example, if half of the reaction product water is assumed to be transferred to the anode, the inlet humidification causes less than 10% of the total amount of water at the anode. Therefore, a variation in the inlet gas humidification does not affect the amount of water at the anode significantly, and causes only slight changes in the cell water balance.

Polarization curves measured with 0.25 barg hydrogen pressure show that the duty cycle of the purge valve practically does not affect the operation of the cell. With purge valve closed the scan had to be reversed again at 0.5 V due to instable operation of the cell. This instability was similar to the 0.1 barg case and probably caused by the water accumulation in the anode side at high current densities. The humidity of the inlet hydrogen had no effect on the performance of the cell. At current densities higher than 500 mA cm^{-2}, the voltage of the cell was lower than in the reference measurement or in the measurements conducted with 0.1 barg pressure. This can be explained with increased water transport from the anode to the cathode by hydraulic permeation. Water transport by hydraulic permeation is dependent on the pressure difference over the membrane, see e.g. [7] and therefore it is approximately 150% larger with 0.25 barg pressure than with 0.1 barg. This leads to excess water at the cathode, which decreases the performance of the cell.

The results from the long-term measurements are illustrated in Fig. 4 for 0.1 barg and in Fig. 5 for 0.25 barg. Again, only the results obtained with purge valve closed and at duty cycles of 1/60 and 1/1200 are illustrated. With a pressure of 0.1 barg, the cell voltage was practically independent of the duty cycle, when the valve was periodically opened. They were within 10 mV and there was no clear order between different conditions. Thus, the slight differences were most probably caused by arbitrary changes in operational conditions such as the laboratory temperature and humidity. With purge valve closed the cell voltage started to decrease significantly after 6 h with dry hydrogen and 4 h with humid hydrogen. This implies that the anode compartment was eventually flooded by the accumulated water.

The results for the 0.25 barg measurements were very similar with the exception that there was no clear drop in the cell voltage when the purge valve was closed. The larger pressure difference increased hydraulic permeation of water from the anode to the cathode, and a more favorable water balance was achieved. It seems that with the rather low current density used in the measurements, the water removal from the cathode side was efficient enough to avoid flooding of the cathode.

Hydrogen consumption of the system was measured to see how much hydrogen is consumed in the purge. The

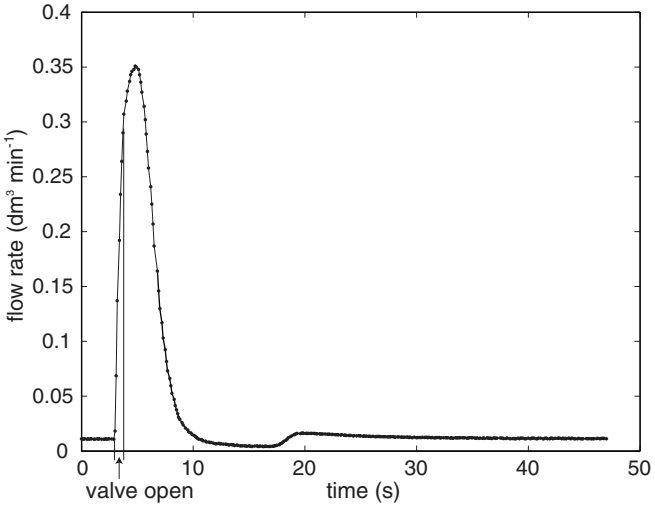

Fig. 6. Hydrogen flow rate during purge.

measured hydrogen flow rate and opening time of the purge valve are illustrated in Fig. 6. Duty cycle was 1/1200, hydrogen was dry, and pressure was 0.1 barg. During normal operation in a dead-end mode, the hydrogen stoichiometry is close to unity. The maximum flow rate during the purge is 350 ml min^{-1} and the duration of the flow pulse is approximately 10 s. Extra hydrogen consumption of the purge was calculated from the measurement data and it was approximately 19 ml. Total stoichiometry over 1200 s period can be calculated to be 1.05. This 1 s / 1200 s duty cycle was chosen for the stoichiometry calculation, because it is the most suitable for real applications. The performance of the cell is similar to other cases where the purge valve is periodically opened, but the amount of flushed hydrogen is smaller. With a completely closed purge valve, the stoichiometry is even better, but the performance of the cell is weaker.

4. Summary and conclusion

A free-breathing PEMFC in a dead-end mode was studied at two different hydrogen pressure and humidification levels and by varying the duty cycle of the purge valve. It was observed that the cell is capable of operating with the anode outlet blocked with both dry and humid hydrogen.

A slight decrease in cell performance was observed with closed purge valve compared to periodically opened valve. This was most probably due to the increased amount of water in the anode compartment. With increased hydrogen pressure the difference was negligible due to increased water transport from the anode to the cathode caused by hydraulic permeation. However, with increased hydrogen pressure the overall performance was slightly decreased, and this was most probably caused by changed water balance which in this case led to cathode flooding.

With long-term measurements there was a clear drop in the cell voltages with closed purge valve at the lower hydrogen pressure, and the drop started earlier with humid hydrogen. This implies that the anode eventually flooded due to insufficient water removal. At higher hydrogen pressure, there was no clear drop in the cell voltage observed supporting the conclusion of changed water balance caused by increased hydraulic permeation.

The achieved results are promising for practical power source use of free-breathing PEM fuel cells. The cell is able to operate in dead-end mode making high fuel utilization rates possible, and thus also high overall system efficiency. However, in long-term operation the cell has to be equipped with a purge valve in order to ensure the removal of excess water in case of flooding. The purge valve is also needed to flush the anode during the start-up. This is especially important if the cell has not been operated for a long time because air may replace hydrogen in the anode compartment.

Acknowledgement

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