Innovative system designs for DMFC

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Abstract

Bipolar designs for a direct methanol fuel cell (DMFC) with liquid electrolyte have been investigated, aiming at a reduction of methanol crossover. A "spacer" (separator) material has to be applied which is inert in a sulphuric acid/methanol surrounding. This material has to be porous so that the liquid electrolyte can be pumped through. Swelling characteristics as well as variation of material properties with temperature and pressure have been investigated with several materials. It is essential to minimize the internal cell resistance in order to achieve a good performance of the DMFC.

Due to the importance of electrolyte canal thickness with respect to ohmic resistance of the cell assembly, the variation of cell power output with electrolyte canal thickness was investigated.

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1. Introduction

Direct methanol fuel cells (DMFCs) are attractive candidates for portable and mobile applications, considering their low weight and volume.

This project applies a circulating liquid electrolyte to reduce permeation of methanol from anode to cathode, which causes polarization losses at the cathode and conversion losses in lost fuel. The main advantage of a circulating electrolyte is the possibility to remove the methanol before it reaches the cathode [1–3]. It is the aim of this specific research activity to realize a bipolar cell design (Fig. 1). Therefore, a spacer has to be used in the electrolyte canal. The electrolyte is pumped through the spacer, for example a polymer cloth or a sintered porous material. Electrodes are pressed onto the membrane by gold-coated bipolar plates, the fuel and the oxidant are pumped through meanders machined into the plates [4,5].

Due to the fact that standard gas diffusion electrodes were used without adapting them to the operation with liquid electrolyte, the power densities achieved were quite poor but nevertheless enabled to verify the investigated system designs.

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Further development of electrodes will be necessary in order to achieve higher power levels.

2. System designs

The approach in designing a bipolar fuel cell design with a solution of sulphuric acid as liquid electrolyte was to introduce a material as so called "spacer" in the electrolyte canal. The bipolar plates were manufactured out of high resistant stainless steel (quality 1.4571) coated with a gold layer of $10\,\mu m$ thickness.

The fuel cell system consists of two separately pumped circles, where the electrolyte and the 2 M methanol solution are pumped through a heat exchanger to control the operating temperature. The concentration of the liquid electrolyte was 1 M sulphuric acid with an operating temperature between 45 and 70 °C.

The anodic catalyst loading of platinum/ruthenium is $4\,mg\,cm^{-2}$, the gas diffusion layer consists of Toray paper and the anode is pressed on a Nafion® membrane to decrease methanol permeation through the electrolyte. The cathode is a gas diffusion electrode with a catalyst loading of $4\,mg\,cm^{-2}$ platinum, with a Toray paper gas diffusion layer. Both electrodes were manufactured at QuinTech according to our
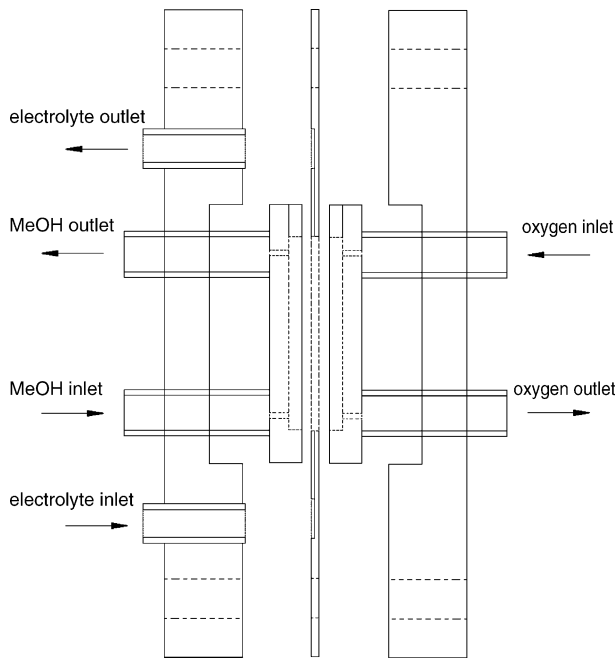
Fig. 1. Schematic view of the used system design for DMFC with liquid electrolytes and spacers.

specifications. The active electrode area is $9\,cm^2$ in square size. The operating temperature of the DMFC is set to $60\,°C$ in all cases.

The reactant at the cathodic side is pure oxygen at atmospheric pressure and the fuel cell body consists of three parts fabricated out of Lexan®. This material is transparent, which gives the opportunity to observe the proper operation of the fuel cell. Thus, an easy observation of potential operating problems such as oxygen permeation through the gas diffusion electrode or a leakage of electrolyte into the meanders of the bipolar plate, for instance, is possible.

The middle part with the spacer in it consists of three thin cemented polypropylene foils, where the middle foil varies the thickness of the electrolyte canal.

The measurements are carried out with a computer-based measurement system using a modified Bank HP 96-20 high power potentiostat/galvanostat to control a current flow up to 20 A. With this equipment it is possible to measure the polarization curves of the anode and the cathode simultaneously in a three-electrode system. The Hg/HgSO$_4$ reference electrode ($E = 650\,mV$ versus NHE) is attached to the electrolyte canal. In addition, a voltmeter is fixed to the cell to measure the total cell voltage.

The cell temperature is controlled by heating and cooling the liquid electrolyte and the water/methanol feed. This is done by a thermostat and flasks containing the two liquids and a thermostat-controlled water circulation in an outer double-layer. It is necessary to have reflux condensers where the water and methanol condenses back in the flasks in order to keep the concentrations of the water/methanol solution and sulphuric acid constant.

2.1. Porous spacers

Several different materials have been investigated as possible spacer materials. Initially, SiC-foams have been tested, due to their high temperature resistance and the high chemical stability. The structure is too weak to withstand the mechanical stress at levels within a fuel cell assembly, though. Then, some sintered glass elements made of DURAN® (Schott Glas) have been tested with outstanding stability performance regarding mechanical stress (up to $1100\,N\,cm^{-2}$). In this configuration, the flow rate through the spacer at atmospheric pressure has been determined. A value of $1\,ml\,s^{-1}$ has been obtained as mean value which is two to three times the minimum required.
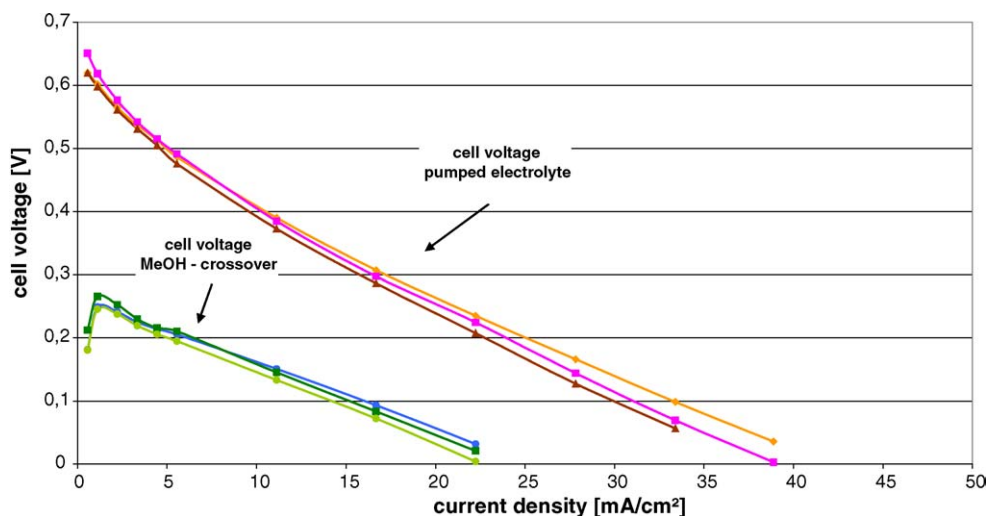

Fig. 2. Measured cell voltage at a DMFC with porous spacer (spacer layer 4.6 mm).

In Fig. 2 the real-measured cell voltage is shown for a cell with a 4.6 mm thick porous spacer of sintered DURAN®. The decrease in cell voltage associated with methanol crossover is shown for comparison. The electrolyte pump has been stopped for some time and the methanol concentration has been obtained using special measurement equipment. A gas chromatograph has been modified using a headspace to achieve the methanol concentration in sulphuric acid [6,7]. At a determined concentration of 1 vol.% MeOH in the electrolyte, the cell voltage drops roughly 30% from the initial value, from OCV over the whole range of currents.

The first system has been built with this porous spacer material. The main disadvantage is that the thickness of the DURAN® spacer was limited due to the manufacturing process of the sintered material. Thus, it is necessary to move one step forward to compressible spacers.

2.2. Compressible spacers

A polypropylene fleece of FOAMAX®, a fabric of woven PTFE, a polypropylene grid, and a grid of polyvinylidenedi-flouride (PVdF) from Junker Filters were tested. All materials have been tested due to their good behavior in the sulphuric acid/methanol surrounding as well as the good temperature resistance proposed. Problems with the fleece and woven PTFE materials occured, since after some hours of swelling time the material gets too dense and the required circulation rate of electrolyte could not be maintained anymore.

The porosities of the grid materials are comparable. The flow rate has been determined at three levels of compression, 0, 5.5 and 12.5% of the fabric diameter (see Fig. 3). Polyvinylidenediflouride fabric achieves the highest flow rates and it is therefore selected to be used as spacer material.
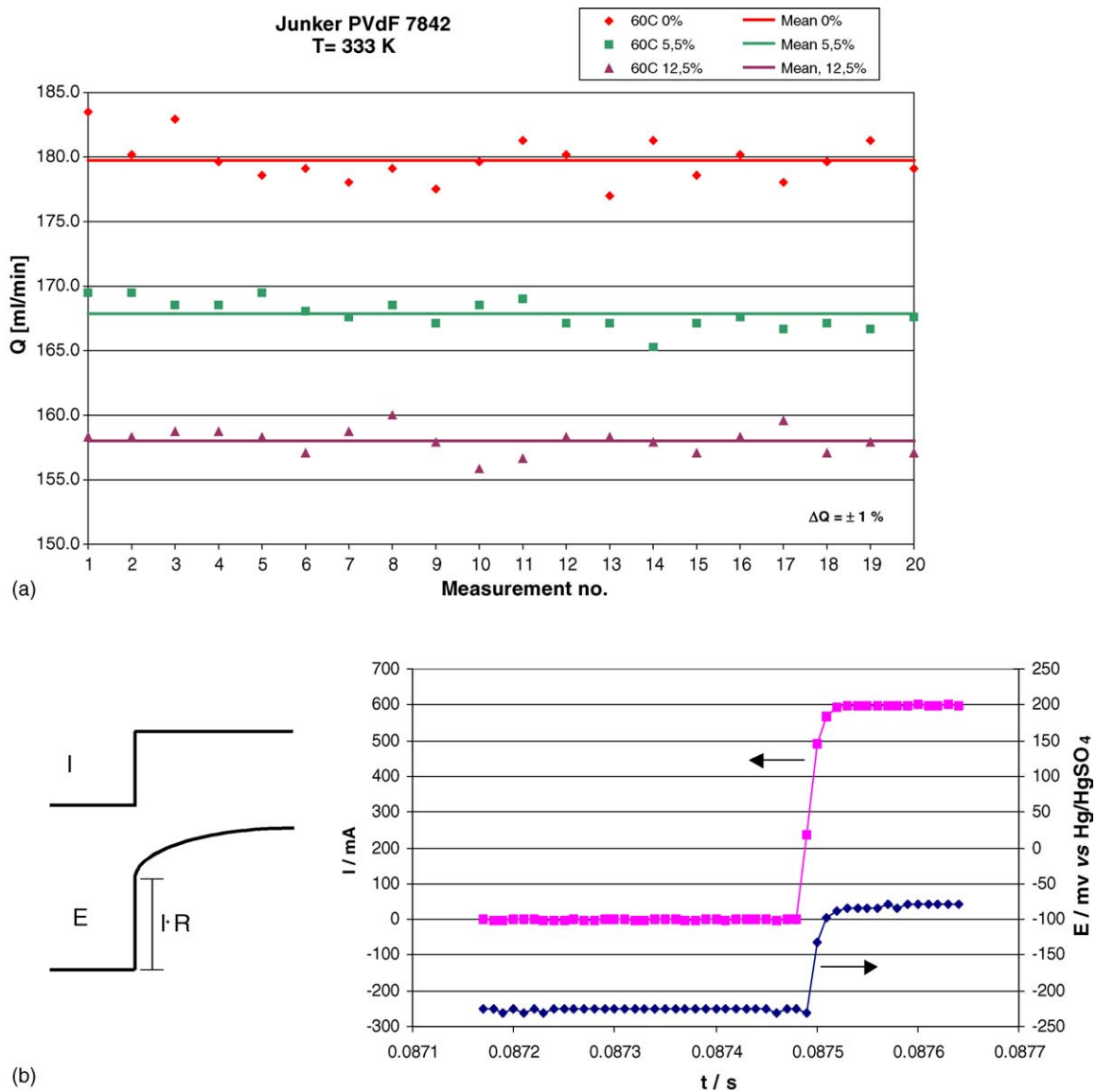

Fig. 3. Flow rate of electrolyte through a (multilayer) 3 mm PVdF grid used as spacer at 333 K and different compression levels ($\Delta Q = \pm 1\%$). (a) Resulting voltage signal with an ideal current pulse, (b) resulting voltage signal (lower curve) with a real current pulse of 600 mA.

With PVdF the width of the electrolyte canal could be reduced to 0.5 mm. Thereby the performance of the fuel cell is substantially improved due to reduction in ohmic losses. The measurements to determine the flow rate are performed at 25 and 60 °C with a multilayer canal thickness of 3 mm (single grid layer 0.55 mm). Each value is measured 35 times, that leads to a statistical error below 1%.

3. Measurement methods

For each current density, a certain number of measurements are performed and the mean values are determined. The current density is then increased, and the next measurements are performed. After each step, the resulting voltage is measured until equilibrium is reached and a stable voltage is established. This value does, however, not really show the true electrode potential, due to the ohmic losses within the fuel cell, especially at thicker canal diameters.

In order to prove the performance of the electrodes at different temperatures and different cell assemblies, it is necessary to eliminate the influence of the ohmic losses due to the thickness of the electrolyte canal (IR correction), which causes the main potential drop between the electrodes of the three-electrode system. A fast galvanostatic pulse is used to obtain the resistance values.

This method enables to obtain the answer in the voltage due to a fast current pulse. The first part of the signal shows the ohmic resistance of the overall cell resistance. It is possible to obtain the real electrode potential with this correction
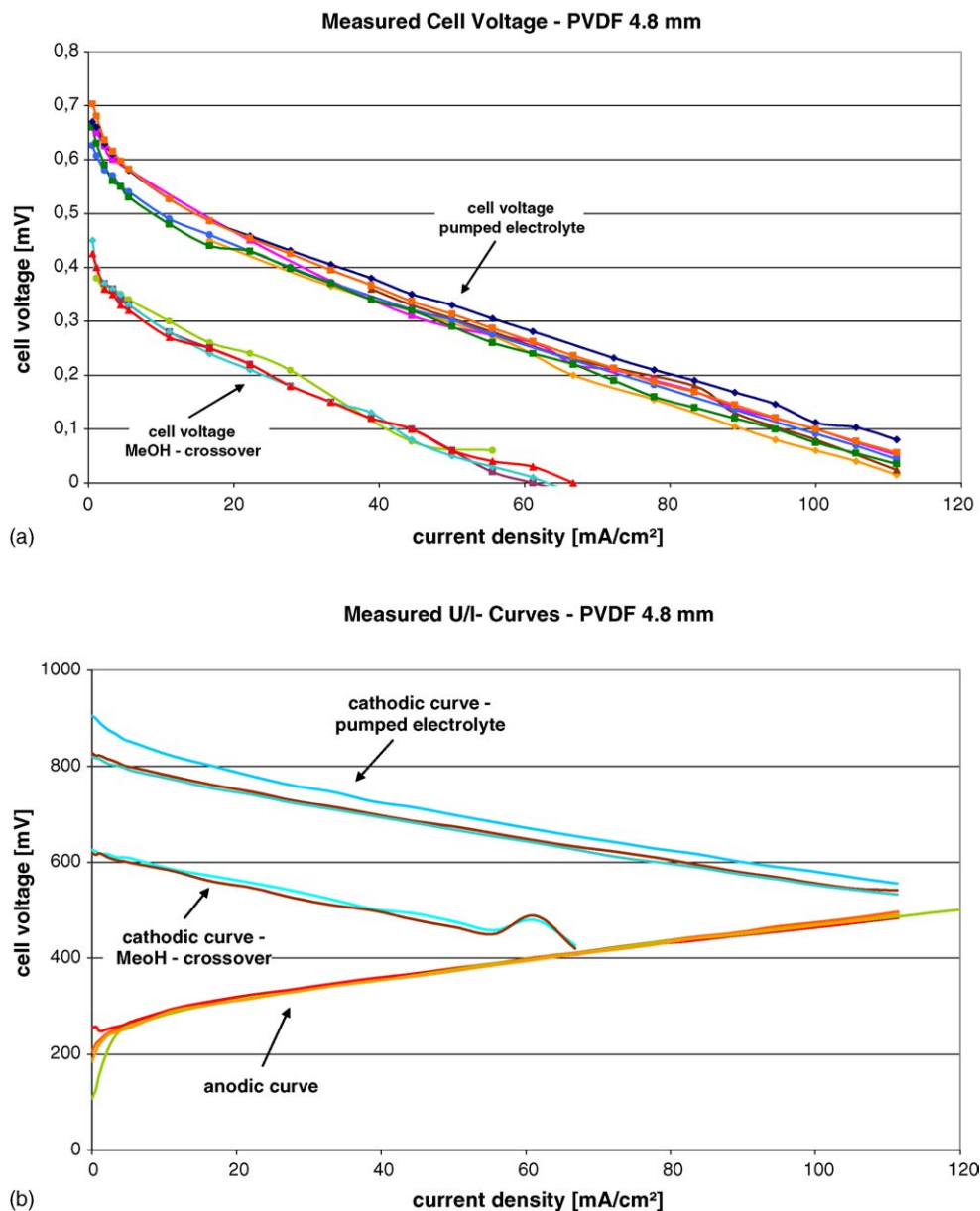

Fig. 4. (a) Measured total cell voltage curves (spacer layer 4.8 mm), (b) measured polarization curves of cathodes and anodes (spacer layer 4.8 mm).

method. Assuming that the other parts of the whole cell resistance do not depend on the current, it is possible to obtain the true electrode potential with just one pulse experiment [8]. This was proven at different current levels and found to be valid within our measurements.

The I/U correction method is used to measure ohmic losses in the fuel cell for evaluation of cell designs and the spacer materials, to obtain the electrode potential, and to correct the measured values in order to determine the effect of polarization loss caused by methanol crossover.

This correction method is only used to obtain the true electrode potential curves and not utilized to correct the obtained values of the measured power output and cell voltages of the different designs, as well as in the long-term measurements of the cells running on constant load.

4. Performance increase with decreasing spacer layer diameter

The ohmic losses within the electrolyte can be minimized using a smaller electrolyte canal thickness. It had to be proven that the given pumping velocity of the electrolyte is sufficient to suppress the methanol crossover to the cathodic side and also does not affect the stability of the electrodes.

4.1. Cell voltage and methanol crossover with 4.8 mm PVdF spacer

The fuel cell is mounted as discussed before, the diameter of the spacer layer consisting of several sheets of polyvinylidenediflouride grid was 4.8 mm. In order to achieve an
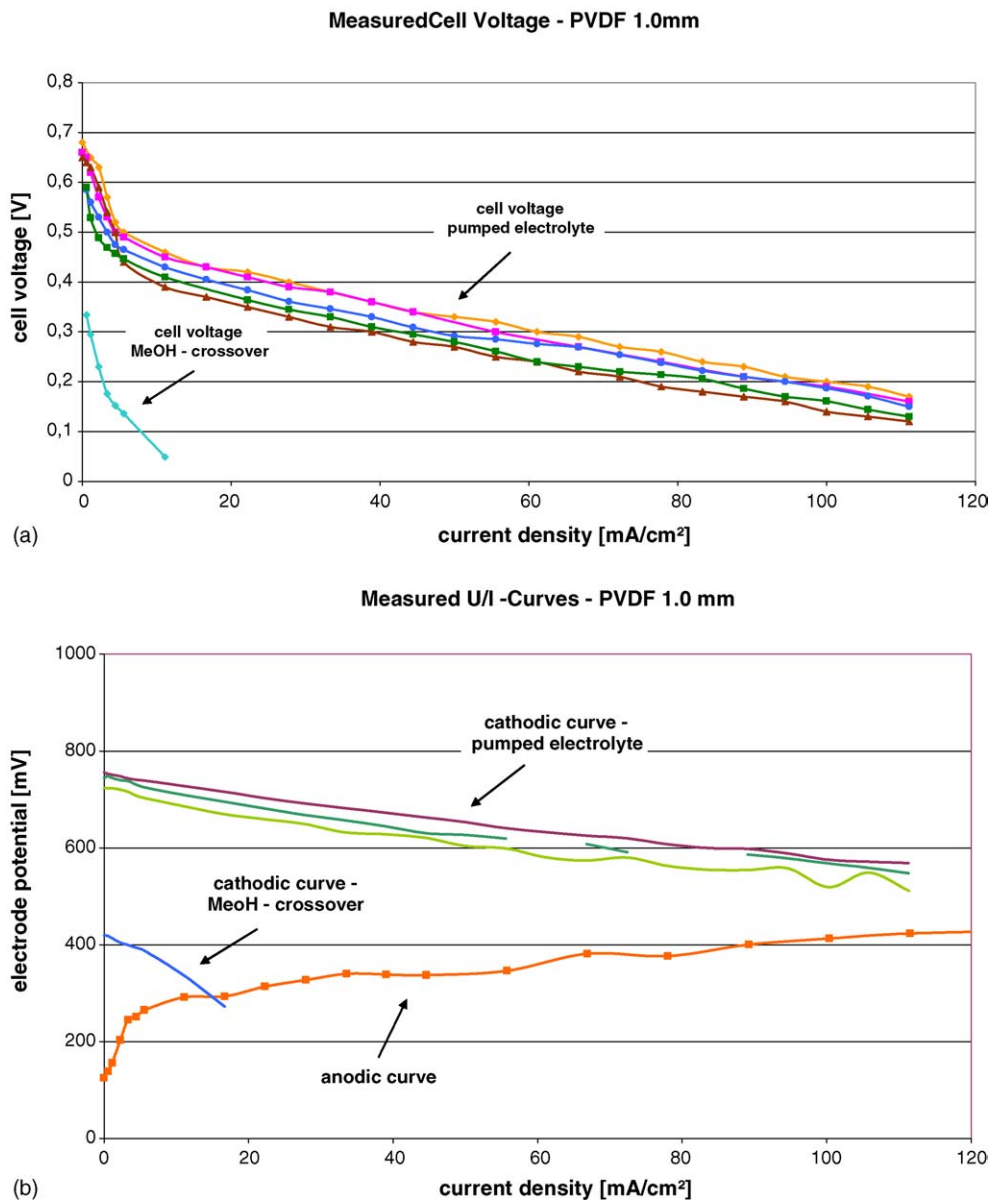
Fig. 5. (a) Measured total cell voltage curves (spacer layer 1.0 mm), (b) measured polarization curves of cathodes and anodes (spacer layer 1.0 mm).

exchange of the total electrolyte volume before the diffusing methanol reaches the cathode, the pumping velocity of the electrolyte is set to 14.5 ml min^{-1}, the pumping velocity of the 2 M methanol feed is set to 10 ml min^{-1}.

Low performance curves shown in Fig. 4a are due to methanol crossover in the fuel cell. The electrolyte pump is stopped for 20 min, and thus a methanol crossover is allowed. A mixing potential is established at the cathode electrode due to the presence of methanol in the electrolyte. This causes a decrease in the cathodic potential, resulting in a loss of cell voltage. The presence of a mixing potential is observed at the cathodic side, whereas the anodic electrode showed no performance loss, as expected. The measured methanol concentration in the electrolyte is determined during these measurements by a custom-developed gas chromatographic

method, enabling measurements of the methanol content in sulphuric acid using a headspace technology [4]. The methanol concentration obtained is 0.8 vol.% using a 4.8 mm PVdF spacer.

The cathodic potential decreases from the OCV level on and lies stable approximately 30% below the normal cathodic potential. The effect of methanol crossover on the cell voltage can be seen in Fig. 4a. The substantially lower voltage curve is the result of the poorer performance of the cathode.

4.2. Cell voltage and methanol crossover with 1 mm PVdF spacer

The same system setup is used as with the experiments presented above. The diameter of the spacer layer consisting of
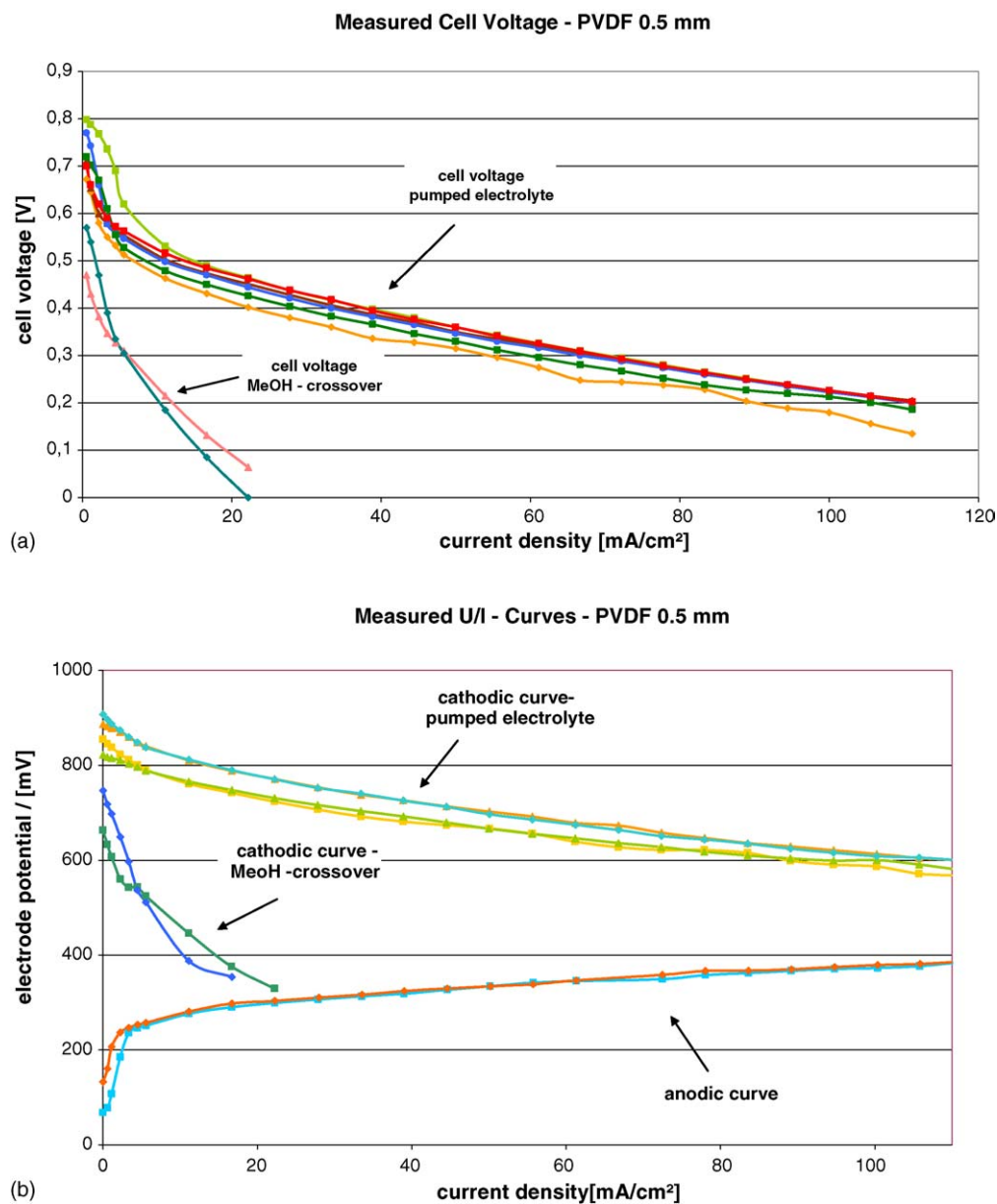

Fig. 6. (a) Measured total cell voltage curves (spacer layer 0.5 mm), (b) measured polarization curves of cathodes and anodes (spacer layer 0.5 mm).

four sheets of polyvinylidenedifluoride grid is 1 mm. A complete exchange of the electrolyte volume avoiding methanol from diffusing to the cathode electrode is already possible at a pumping rate of 5.5 ml min^{-1}. The pumping velocity of the 2 M methanol feed is set to 10 ml min^{-1}.

The loss in cathodic potential due to the allowed methanol crossover (as described in Section 4.1) was observed and is displayed as the lower curve in Fig. 5b. The measured methanol concentration in the electrolyte is in this case 1.1 vol.%.

The cathodic potential is reduced from the OCV level on for all current densities and lays approximately 50% below the normal cathodic potential. In Fig. 5a, the strong effect of the methanol crossover on cell voltage can be seen. The methanol concentration found is about 30% higher than with the 4.8 mm spacer layer.

4.3. Cell voltage and methanol crossover with 0.5 mm PVdF spacer

Finally the thickness of the spacer layer could be reduced to 0.5 mm, where a double-layer of the DVDF grid is used as matrix for the electrolyte canal to pump the sulfuric acid through.

The rate of electrolyte exchange is slightly increased up to 7 ml min^{-1}, in order to assure that methanol could not
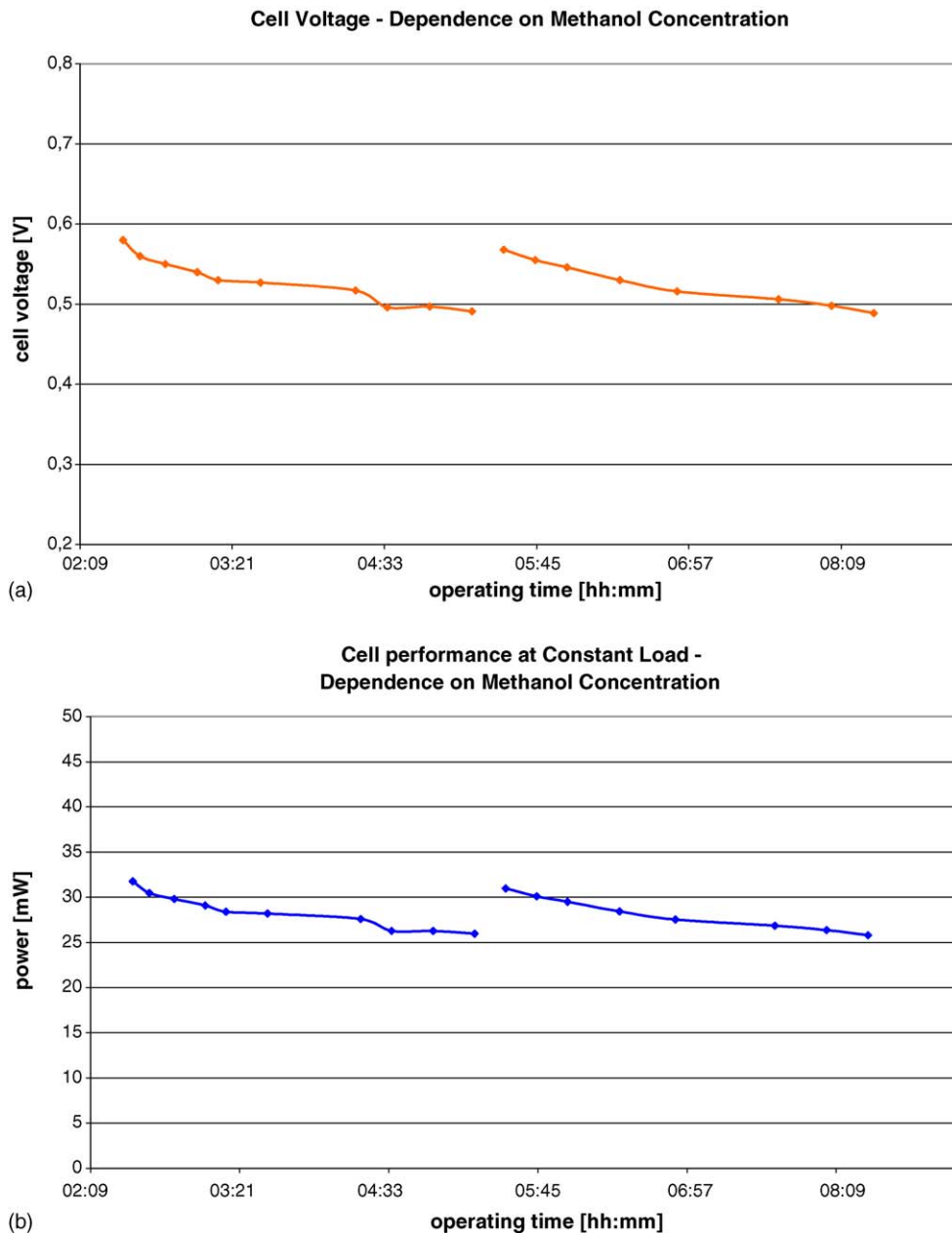

Fig. 7. (a) Time dependence of the measured total cell voltage (spacer layer 4.8 mm), (b) time dependence of the measured total cell power output (spacer layer 4.8 mm).

get to the cathode through this very small electrolyte canal diameter. The pumping velocity of the 2 M methanol feed is the same as with the investigations before and set a constant rate of $10\,ml\,min^{-1}$.

The loss in cathodic potential due to the allowed methanol crossover (as described above) is observed and displayed as the lower curve in Fig. 6b. The extent of the loss in cell voltage is comparable to the values obtained with the cell having a 1 mm spacer layer. The measured level of methanol concentration in the electrolyte is again 0.8 vol.%.

The cathodic potential at OCV level is not decreased as much as observed before, but even at small current densities the values found before are achieved. In Fig. 6a, the effect of methanol crossover on the fuel cell voltage is shown with a fuel cell featuring a 0.5 mm spacer layer. The methanol concentration due to the crossover measured is comparable to that observed under identical conditions with other cell designs.

5. Long-term observation of methanol crossover influence

In order to investigate the decrease of cell performance due to the methanol crossover over time, a constant load is
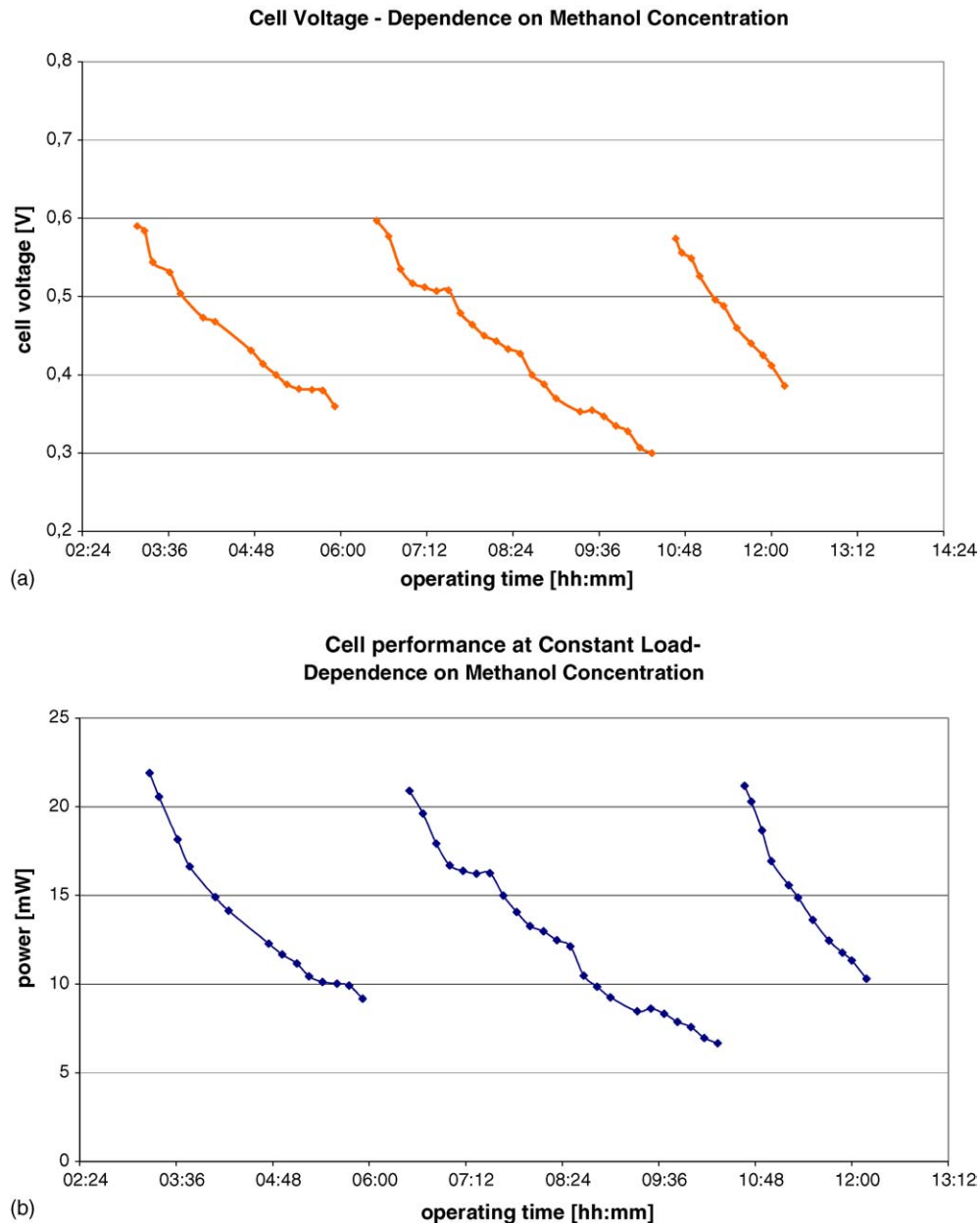

Fig. 8. (a) Time dependence of the measured total cell voltage (spacer layer 0.5 mm), (b) time dependence of the measured total cell power output (spacer layer 0.5 mm).

attached to the DMFC and the cell voltage is measured as function of time.

5.1. Fuel cell system with 4.8 mm PVdF spacer

A small bulb is attached to the DMFC serving as constant load. The methanol diffusing into the electrolyte is not removed from the pumping circle in order to evaluate the loss in cell voltage. The current delivered to the bulb and the cell voltage are monitored.

After a certain decrease in cell voltage, the methanol feed and the electrolyte circle get replaced and the methanol concentration in the liquid electrolyte is measured.

After 165 min of continuous cell operation the first probe is taken and the obtained value for the methanol concentration in the electrolyte was 0.512 vol.%. The second measurement after replacing the fluids is done after 175 min of continuous cell operation and the methanol level detected in the electrolyte was 0.617 vol.%.

The influence of the increase in methanol concentration in the electrolyte is shown in Fig. 7a and b, showing the decrease in cell voltage and cell performance when operated at a constant load.

5.2. Fuel cell system with 0.5 mm PVdF spacer

A resistor bank is used as constant load in order to obtain knowledge of the cell behavior, and to observe the level of decrease of the cell performance in time due to the methanol crossover. The permeating methanol is not removed from the electrolyte in the pumped liquid circle to evaluate the loss in cell voltage. The current delivered to the load as well as the cell voltage are monitored.

After a significant decline of cell voltage and power output, the liquid electrolyte (1 M sulphuric acid) is replaced. Concentration of methanol in the electrolyte is again measured with a gas chromatograph.

The first probe is taken after 165 min of continuous cell operation and the obtained value for methanol concentration in the electrolyte was 0.133 vol.%. After replacing the electrolyte, the second measurement is done after 230 min of continuous cell operation, and the methanol level detected in the electrolyte was 0.176 vol.%. After the measurement, the electrolyte is replaced again. The third probe is taken after an operation time of 135 min, showing a methanol concentration level of 0.112 vol.%.

In Fig. 8a and b the influence of the increase in methanol concentration in the electrolyte is shown with respect to the decrease in cell voltage and cell performance at the operation point of the constant load. It has been taken into account that the operating point of the constant load (approximately $3.3 \, mA \, cm^{-2}$) is far from the power maximum of the fuel cell (at approximately $106 \, mA \, cm^{-2}$—see section below), so that little changes in current flow cause significant changes in cell voltage.

6. Dependence of cell power and methanol crossover on diameter of spacer layer

Comparing the measured power densities of the different cell designs with spacer layers of different thickness show a shift in the power maximum from a current density of about $50 \, mA \, cm^{-2}$ to a current density of approximately $105 \, mA \, cm^{-2}$.

An increase in maximum power of approximately 40% is achieved. The maximum power output of the design with
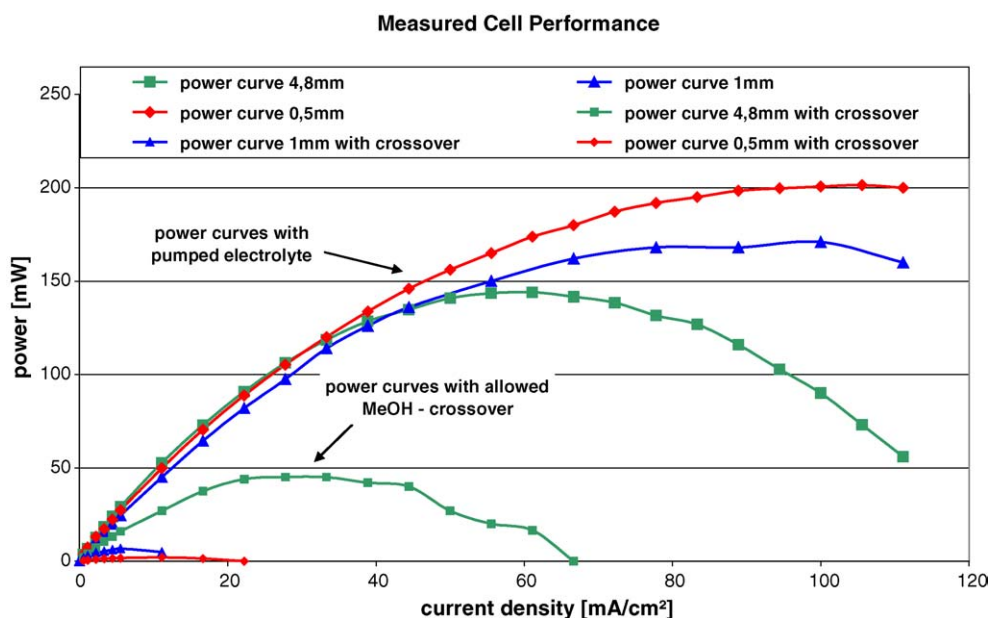

Fig. 9. Comparison of measured total power output curves of different spacer layer diameters.

a 4.8 mm thick spacer layer is approximately 16 mW cm^{-2} (144 mW cell power), increasing up to 19 mW cm^{-2} (171 mW cell power) for a 1.0 mm thick spacer layer. Finally, at a 0.5 mm thick spacer layer the maximum power output is about 23 mW cm^{-2} (201 mW cell power).

Fig. 9 clearly documents the loss in cell power associated with methanol crossover in the fuel cell and also the dependence of cell power decrease with respect to the spacer layer thickness. With a 4.8 mm thick spacer layer, the achieved maximum cell power output amounts to 45 mW and decreases down to 7 mW cell power in a cell design with a 1.0 mm thick spacer layer. The maximum power output with methanol

crossover at the same concentration levels of methanol in the electrolyte is only 2 mW cell power with a 0.5 mm thick spacer layer due to the short distance for the methanol diffusing to the cathode.

The reason why a thicker spacer layer raises the power output despite of quite the same methanol concentration in the electrolyte, is due to the fact, that the methanol in the electrolyte reacts faster at the cathode than concentration equilibrium can be established. The membrane with a determined methanol diffusion coefficient of $D = 3.15 \times 10^{-6}$ cm^2 s^{-1} acts as a methanol barrier, because the determined methanol diffusion coefficient for the liquid
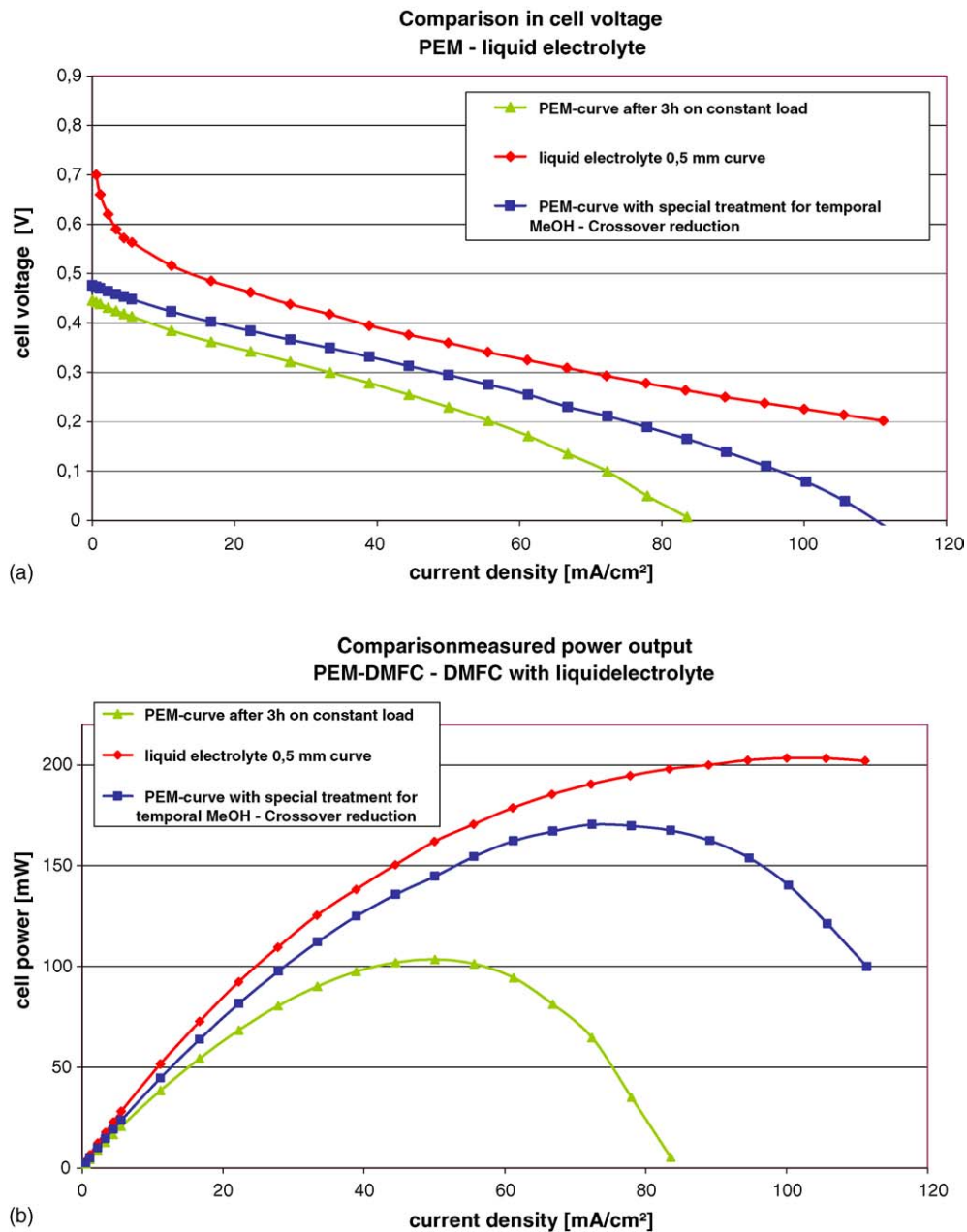

Fig. 10. (a) Measured cell voltage curves for PEM–DMFC and DMFC with liquid electrolyte, (b) measured total power output curves for PEM–DMFC and DMFC with liquid electrolyte.

electrolyte at the operating temperature of 60 °C was found to be $D = 1.47 \times 10^{-5}$ cm^2 s^{-1}. Additionally, the spacer material itself is a small methanol barrier, because it is an additional physical barrier and the uptake of methanol molecules by the spacer material must also be considered at the beginning—even if the found diffusion coefficients for the spacer material are in the range of the diffusion coefficient of the electrolyte. The established concentration near the cathode is quite lower than in the overall electrolyte. At a thinner layer thickness most of the methanol reaches the cathode because of the shorter distances and the power maximum is reduced.

7. Power increase compared to assembled PEM–DMFC

To evaluate the advantages of introducing a liquid electrolyte assembly independent from the overall performance of the fuel cell, it is necessary to design a PEM–DMFC made with the same components used in the liquid electrolyte fuel cell.

The measurements are carried out at 60 °C with the same pumping velocities applied to the 0.5 mm spacer layer design. The electrolyte pumping velocity is 7 ml min^{-1} (in case of liquid electrolyte) and the pumping velocity of the 2 M methanol feed is again set to 10 ml min^{-1} for all cells.

In Fig. 10b the upper cell power PEM–DMFC curve (middle) is obtained after the methanol feed has been taken away and the fuel cell got rinsed with deionized water until all the methanol is totally removed from the anode. After reattaching the methanol feed, the measurement is done very quickly, so that methanol crossover through the membrane is reduced. The obtained power maximum lies at a current density of about 70 mA cm^{-2} and the maximum power value is 170 mW cell power. The lower PEM curve is obtained after running the cell for 3 h on constant load (vent), and shows the power maximum at a current density of approximately 50 mA cm^{-2}. The maximum power value is 103 mW cell power. The power level obtained with the fuel cell with liquid electrolyte operated under these conditions and a spacer layer thickness of 0.5 mm is 204 mW at a current density of 106 mA cm^{-2}.

Comparing the curve derived from the measurements with the DMFC operated with a pumped liquid electrolyte to the power maximum or the cell voltage as shown in Fig. 10a of

the PEM–DMFC in the case of the pretreated spilled fuel cell, a significant improvement in power is derived.

8. Conclusions

It is demonstrated, that a direct methanol fuel cell with a pumped liquid electrolyte is able to minimize the methanol crossover considerably. Additionally the performance after an intended methanol crossover is regained after starting the pumping of the electrolyte again.

A significant increase in performance compared to an assembled PEM fuel cell, made of the same components and operated under equal conditions is proven.

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