NOVEL STRUCTURE FOR PASSIVE CO_2 DEGASSING IN µDMFC

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ABSTRACT

A new flowfield design enabling fully passive CO_2-gas bubble removal from the anode of a micro direct methanol fuel cell (µDMFC) is presented. The flowfields channels have an upside down T-shaped cross-section with defined opening angles along their axis and cross-section. The angles create an intrinsic transport mechanism removing growing gas bubbles from the electrode by capillary forces only. Applicable opening angles α and β are 5° and 1.5° respectively. The experimental verification has been done based on a transparent flowfield and by a fully operational µDMFC delivering a power density output of up to 8 mW/cm^2 without the need of external pumps. Although the fuel cell supply can be operated both passively and pump assisted, the passive operation shows the highest efficiency.

1. INTRODUCTION

Assisting or even replacing secondary batteries by fuel cells has been a research goal throughout the recent years [1;2]. The µDMFC has been identified as most promising type of fuel cells due to the safer storage of methanol compared to hydrogen and also the possibility of instant refueling. Although there has been lots of progress, some problems are still not solved in a satisfying way.

One of these problems is caused by the production of carbon dioxide (CO_2) during the reaction of the methanol at the anode side of the fuel cell. This reaction results in a two-phase flow. The gas bubbles reduce the fuel cells efficiency as they block parts of the membrane electrode assembly (MEA), get immobile or even block a channel completely [3;4]. Furthermore it is common use that the refueling of the fuel-cell is realized with micropumps consuming a part of the energy produced by the fuel cell. The convective flow is also used to flush out the CO_2 bubbles that block the channels and the MEA. However, one has to keep in mind that micropumps typically have a low efficiency [5] and thus consume a non-negligible amount of energy. In this paper a new layout of a flowfield is presented that passively removes gas bubbles by means of capillary forces. Therefore it might be possible to abandon a pump in future designs and work completely passive.

2. FLOWFIELD CONCEPT

In small dimensions surface forces cannot be neglected and often cause severe problems. But the same forces can also be advantageous in certain applications. Recently it has been shown [4;6] that capillary forces can be used to increase the mobility of gas bubbles in special microchannel designs. A further improvement of this design is a microchannel, allowing passive removal of CO_2 gas bubbles from the anode flowfield of a µDMFC as described in this section.

Working principle

In general the working principle of the flowfield layout is based on the non-uniform capillary pressure ($P_{cap} = \sigma (R_x^{-1} + R_y^{-1})$) caused by a tapered channel. The considered situation is sketched in Fig. 1. The two distant ends of a gas bubble form different radii R and thus exert different capillary pressures P. The pressure difference forces the bubble to move towards the wider channel part until both capillary pressures are in equilibrium (Fig. 1c)). In this case the bubble takes on a spherical shape and the movement stops. In the fuel cell application the bubble might even increase in size during its movement along the channel. This happens, if one wall is formed by the MEA and other bubbles growing there are wiped of and merge with the passing bubble.

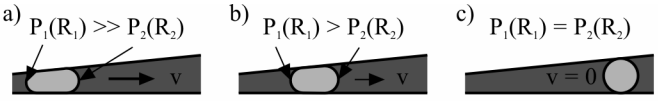

Figure 1: a) and b) 2-dimensional draft of gas bubble movement in a tapered channel, driven by different capillary pressures. c) equilibrium state with no bubble movement.

General Layout

The bubble movement can take place only if liquid can bypass the gas bubble. To enable such a bypass an upside-down T-shaped cross-section has been chosen as channel cross section (cf. Fig. 2). The complete flowfield is designed as two parallel rows of such T-shaped tapered channels with a distance of 0.3 mm between each other. A central channel and an outlet channel connect all of the 18 channels at their ends. The parallel channels are tapered symmetrically with angles $\alpha = 5°$ respectively $\beta = 1.5°$ across respectively along the channel as depicted in Fig. 2.

The bottom side of the parallel channels is formed by the MEA or a gas diffusion layer (e.g. carbon paper or a metal mesh). All other channel walls are formed by the substrate. As the MEA covers the whole bottom part of the T-shaped channels there is a large area where gas bubbles can start to

grow. At the narrowest part of the channel a growing bubble soon gets into contact with the upper wall of the channel. While the bubble size still increases, it is forced to deform from its spherical shape into a stretched oval shape as depicted in Fig. 1. Thus a pressure gradient is developed and the bubble moves towards the central channel. This motion continues towards the central channel as already described above for tapered channels. Once the central channel is reached, the bubble takes on a shape that only fills the central channel due to the T-shaped design. This behavior has basically been avowed by the authors in [6] and is now enhanced by the use of a tapered middle channel to move the bubble to the final outlet.

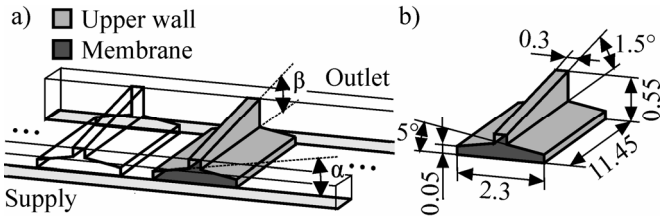

Figure 2: a) Draft of one side of the flowfield indicating the supply and outlet channel as well as the T-shaped parallel channels with their inclination angles α and β. b) Sketch of the channel dimensions of the test samples in mm (not to scale).

3. SIMULATION

Prior to experimental verification the working principle has been validated by CFD simulations. CFD-ACE+ of ESI-Group (www.esi-cfd.com) has been used to model a part of the flowfield. Making use of the channels symmetry to simplify the geometry the simulation time could be kept within an acceptable timeframe of several days. A method has been developed to mimic the randomly distributed gas development at the fuel cells membrane as follows: Out of an array of 1000 small areas at the MEA side of the channel, ten areas are randomly chosen by an automatic script. They are switched from wall boundary condition to inlet boundary with a defined mass flow rate. The mass flow rate of CO_2 through each inlet is based on the estimation that a typical current density of 100 mA cm^{-2} generates 0.26 ml min^{-1} cm^{-2} of CO_2. Every 0.5 ms the simulation stops; the script sets the

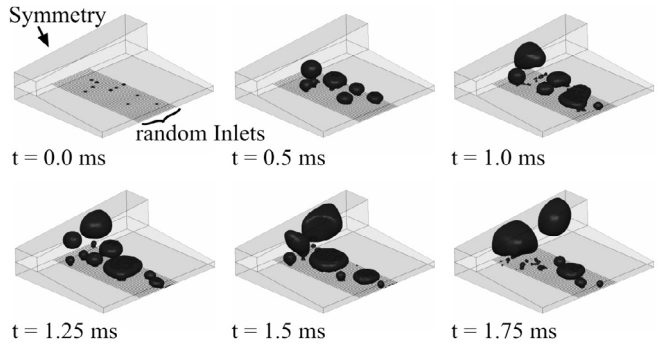

Figure 3: Simulation sequence with distributed bubble sources and bubble removal due to capillary forces.

10 inlets back to wall boundary condition and ten new areas are selected and defined as inlet. Afterwards the simulations are restarted with the initial condition set to be the last result of the previous simulation sequence. This procedure is repeated several times as can be observed by the position of the small bubbles (dark gray) in Figure 3. The results show the anticipated bubble behaviour. The bubbles randomly grow in the channel and start to move towards the centre channel once they touch the upper channel wall or when wiped away by larger bubbles. When they arrive at the middle channel they start to move to the outlet.

4. SAMPLE PREPARATION

A negative of the structure with the dimensions given in Fig. 2b) has been milled into a brass plate to form a hot embossing tool for the flowfield. To avoid the polymer to spill out sideways a frame for the master tool has been manufactured as well. Transparent PMMA (cf. Fig. 4) and a conductive graphite filled polymer (SGL BMA5) have been used as substrates for the hot embossing. After hot embossing of the substrates, mounting holes and fluidic interconnection holes were drilled.

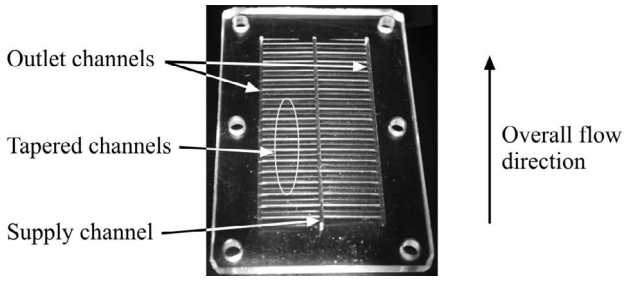

Figure 4: Photograph of one of the transparent test samples

5. EXPERIMENTAL VERIFICATION

Two different experiments were set up to study the functionality of the new flowfield design. Visual studies of the bubble behavior inside the flowfield have been performed with the transparent samples while the graphite filled samples were used to build a functional μDMFC.

Transparent test cell

A mounting frame, the transparent PMMA-sample with the flowfield, two sheets of metal mesh with a MEA in between and a lower mounting frame formed the stack for the bubble development experiments. To avoid methanol leakage, the stack was sealed with silicone and tightly screwed together. The metal meshes were connected electrically and the system was primed with a 2 M methanol solution. By applying a current of 500 mA and a voltage of approximately 0.2 V the creation of gas bubbles has been forced (cf. Fig. 5). To allow continuous passive fluid flow during the experiments a fuel cartridge was connected to the supply channel. CO_2 could be released through the outlet channel at the upper right corner. First the bubbles moved towards the central channel. Once

there, they grew until they once again started to move. This time they moved towards the outlet channel as anticipated due to the simulation results.

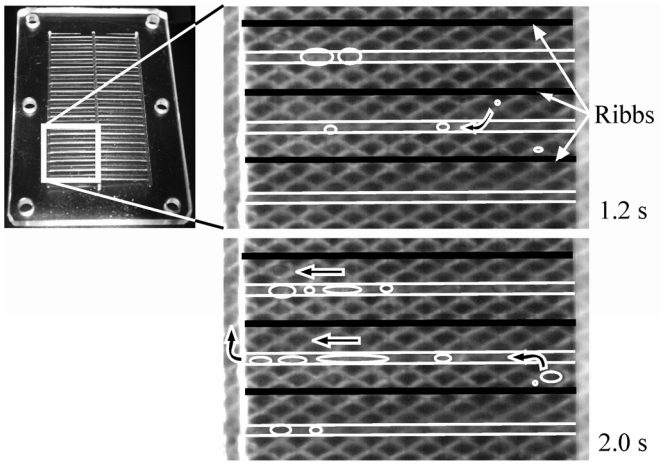

Figure 5: Picture sequence of gas bubbles developing and their movement inside one test sample with a 2 M methanol solution.

Fuel cell assembly

To test the flowfield for fuel cell operation a planar fuel cell has been assembled (cf. Fig. 6). The cathode was made of an ordinary printed circuit board (PCB). The PCB is a laminate of a substrate - a composite material of glass fibre and epoxide – sandwiched between two copper layers of 35 µm thickness. In the cathode material parallel rectangular openings of 3 mm × 21 mm with a spacing of 1 mm have been milled. This results in an electrochemical active area of 21 mm × 43 mm. As current collector and outside electrical contact the copper layer of the PCB was used. The hot embossed anode consists of a graphite plate (SGL BMA5) with the flowfield structure described above imprinted. As anode contact a copper plate was placed on top of the graphite plate. The MEA was sandwiched between two 100 µm thick foils to avoid short circuits between the electrodes. This sandwich was glued to the anode. Nafion 117 with a PtRu/Pt loading of 3.5 mg cm^{-2} and an ionomer thickness of 180 µm was used as the MEA. Toray carbon paper with a thickness of 350 µm was applied as diffusion layers between the plates and the MEA. The whole assembly was pressed together by six M3 screws with a torque of 0.5 Nm each. Adhesives at the edges which were pressed together while curing ensured sufficient contact pressure between the plates also for future operation.

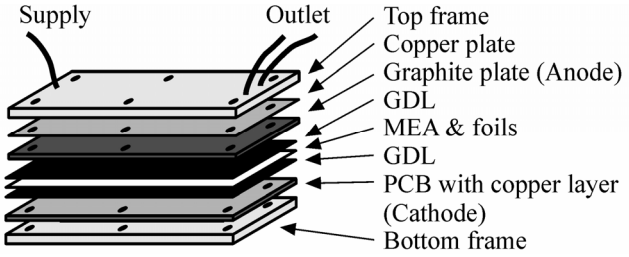

Figure 6: Draft of the fuel cell assembly (not to scale).

Short time testing

The considered flowfield was designed for totally passive as well as for pump assisted operation. Thus a direct comparison of experimental results in active and passive mode is possible. Fig. 7 shows the polarization plots and the power densities of short time measurements with a 4 M methanol solution. With decreasing flowrate the efficiency of the fuel cell increases as shown by the increasing power densities.

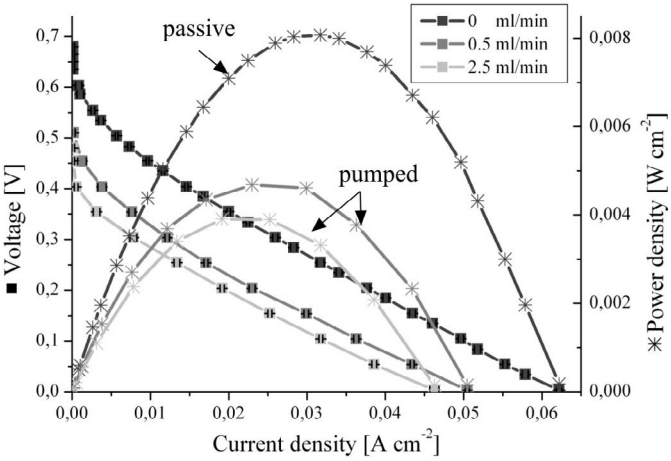

Figure 7: Short time measurements with a 4 M methanol solution at two pumped flow rates and a passive system setup.

Together with the decreasing flowrate the amount of available methanol for the chemical reaction decreases too. Hence the methanol concentration is lower. This yields a lower methanol crossover through the membrane and thus a better system performance. Furthermore additional effects appear if the pump is switched off completely. Comparable to the case of lower flowrates, the methanol concentration decreases over time as well as the methanol crossover. Due to this the efficiency also increases. On the other hand there is another effect that is connected to the phase change of methanol which also gains influence. As the methanol is not flushed through the flowfield together with the gas bubbles more methanol enters the vapour phase. It is well known that this leads to better kinetics on the anode and a lower crossover through the membrane [7]. Due to this a low flowrate or even no flow is advantageous. But to operate the fuel cell without any flow would yield a power-breakdown after all methanol had been converted. To overcome this problem one possible solution is to pump fuel into the system at certain intervals to refill the missing volume and to increase the methanol concentration again. The benefit is twofold: The fuel cells efficiency is higher compared to a continuously pumped system and there is no continuous energy demand of the pump as it is deactivated most of the time.

Long time measurements

The assumption that the efficiency increases by pumping at intervals has been tested in long time measurements with a 4 M methanol solution. For the experiments three configurations have been chosen: Pumping continuously, pumping at intervals (approximately 23 min pause, 15 s pumping) and an open cartridge without any pump. In the case of pumping continuously a stable current density of about 14.5 mA cm^{-2} was reached (cf. Fig. 8). As expected the results of the other configurations showed a higher current density during extended operation. It can be seen that over the time the performance for this two configurations increases until the depletion of methanol leads to a decline of the current density. In the pump driven configuration the cell assembly runs for 23 min and then new fuel is pumped into the system for 15 s. During the time the pump is switched off, no flow of methanol takes place from the cartridge into the cell. In the case of the open cartridge a small flow refuels the system continuously due to a small difference in hydrostatic height (about 10 mm) of cartridge and cell. This leads to an even better performance compared to the other configurations. But also for this setup the methanol depletes after a while. Therefore the level of the cartridge was increased for a few seconds after about 25 min to flush new fuel into the flowfield by hydrostatic pressure.

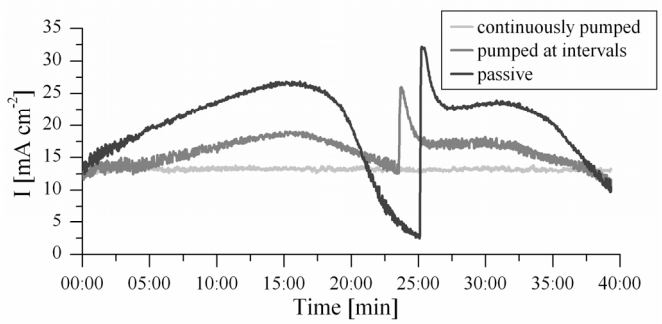

Figure 8: Long time measurements with a 4 M methanol solution at 0.25 V. Continuously pumped (0.225 ml/min), pumping at intervals (~23 min pause; 15 s pumping) and passive with refueling by hydrostatic pressure after ~25 min.

6. CONCLUSIONS AND OUTLOOK

A passive removal of gas bubbles in a µDMFC has been proofed using tapered microchannels. The feasibility was demonstrated with a CFD-simulation and a prototype flowfield was manufactured by hot embossing techniques. With the aid of transparent test-samples the working principle of the structure has been demonstrated. Furthermore a complete µDMFC has been assembled. It exhibited a higher efficiency when operated passively compared to the situation when methanol was supplied continuously or at intervals. Long term measurements lead to the conclusion that an open system that would be assisted by pumping at intervals could perform best.

Concerning simulation, a connection of a 1-dimensional membrane model to the CFD-model is planned in the future. The 1-D-model locally determines the methanol reaction and thus also the local gas flow rate. This data can than be used as boundary condition which will lead to a more realistic simulation. On the experimental side further experiments have to be accomplished as the long term goal is a fuel cell system that allows for a continuously self sustained passive operation without using a pump.

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