NOVEL STRUCTURE FOR PASSIVE CO_2 DEGASSING IN µDMFC

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Abstract

A new layout concept enabling passive CO_2-gas bubble removal from the anode side of a micro direct methanol fuel cell (µDMFC) is presented. The concept is based on a sophisticated network of microfluidic channels (flowfield), having an upside-down T-shaped cross-section and a defined opening angle along the channels. The opening angle creates an intrinsic transport mechanism removing growing gas bubbles from the electrode by capillary forces only. Applicable opening angles α and β have been determined by Computational Fluid Dynamics (CFD) simulations to be 5° and 1.5° respectively. The experimental verification was accomplished based on a transparent flow field. Additionally, a fully operational µDMFC delivering a power density output of 8 mW/cm^2 without the need of external pumps was realized. Although the fuel supply can be operated both, passively and pumped, the passive operation shows higher efficiency compared to the pump assisted fuel supply.

Keywords: µDMFC, bubble removal, capillary forces, flowfield, fuel cell

1 INTRODUCTION

Throughout the recent years lots of research has been done to assist or replace secondary batteries in the field of portable electronics by fuel cells [1,2]. The most promising type of fuel cell for these applications is the micro direct methanol fuel cell (µDMFC) since methanol allows fast refueling and furthermore a safe storage compared to hydrogen. To achieve real competitive fuel cell systems compared to the battery market several problems still have to be solved.

Among these problems are the carbon dioxide (CO_2) production resulting in a two-phase flow on the anode side of the fuel cell as well as the power consuming refueling of the system by micropumps. The exhaust gas CO_2 is produced during the reaction of liquid methanol at the membrane electrode assembly (MEA). In microfluidic systems gas bubbles are typically immobile by sticking to the channel walls or even block the complete channel [3,4]. As the methanol fuel supply is usually designed as an array of parallel channels or a serpentine structure - which is referred to as flowfield - the CO_2 also tends to block the channels during the operation of the fuel cell. The gas bubbles do not only block the channels, they also reduce the efficiency of the fuel cell, as the gas also reduces the free reaction area of the MEA. Thus the bubbles have to be removed from the flowfield continuously. Usually micropumps are used to supply the system with methanol and to remove the gas bubbles by flushing them out. However the usage of a micropump reduces the efficiency of the whole fuel cell system as the pump consumes a part of the energy provided by the fuel cell. Since micropumps typically have a low efficiency [5] the energy consumption of the micropump cannot be neglected. Thus it is favorable to abandon a pump and design a completely passive µDMFC. In this paper a new layout of flowfield design is presented that shows promising results to achieve such a passive system.

2 CHANNEL DESIGN AND WORKING PRINCIPLE

In small dimensions surface forces cannot be neglected anymore 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 development of this design is a microchannel that allows passive removal of CO_2 gas bubbles from the anode flowfield of a µDMFC. Basically the flowfield is designed as an array of parallel channels with an upside down T-shaped cross-section. Along a centered supply channel two rows of 18 parallel channels are arranged. The draft in Figure 1 a) depicts only one side of the array.

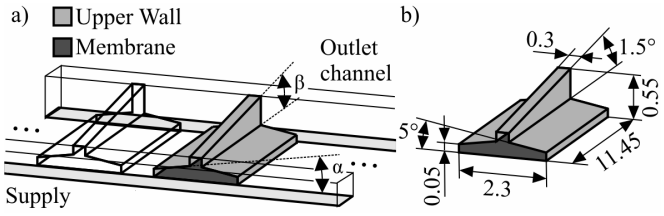

Figure 1. a) Draft of one side of the flowfield indicating the supply and outlet channel as well as the T-shaped parallel channels with their inclination angles α and β. b) Sketch of the channel dimensions of the test samples in mm (not to scale)

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) which is on top of the MEA. All other channel walls are formed by the substrate. The T-shaped channels are tapered symmetrically across their axis with the inclination angle α of 5° and widen along their axis from the supply channel towards the outlet channel with an angle β of 1.5°. Dimensions of the tapered channels are given in Figure 1 b). The distance between the parallel channels is 0.3 mm.

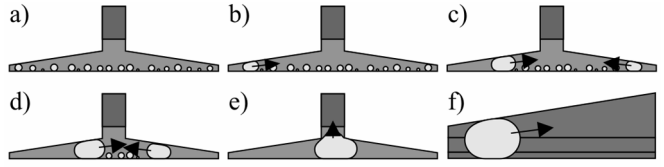

Figure 2. Schematic view of the working principle for the gas bubble movement inside a T-shaped channel.

The upside down T-shaped structure is the functional part of the flowfield. The membrane and the gas diffusion layer of the fuel cell are connected to the bottom side of the channel and thus a large part of the active area is in direct contact with the fuel. At this area the methanol is consumed and CO_2 bubbles start to grow. As the bubbles develop, the outermost bubble quickly gets into contact with the upper wall of the channel as depicted in Figure 2 a). While the bubble still grows and is in contact with the wall it has to deform from its originally spherical shape. Contemplating the channels cross-section, the bubble forms two different radii at its ends and thus has two different capillary pressures which initiate a motion of the bubble towards the channel part in the cross-sections middle. The motion towards the centre continues as long as the bubble stays in contact with the upper channel wall. The bubble might even grow by wiping of and merging with persistent bubbles on its way (Figure 2 b)-d)). If the bubble looses contact to the walls a spherical shape is attained and the motion stops. Once the central channel is reached, the bubble takes on a shape that only fills the centre channel as depicted in Figure 2 e) and f). This behavior has basically been avowed by the authors in [6] and is now enhanced by the use of a tapered channel to move the bubble to the final outlet.

3 SIMULATION

Prior to manufacture samples the basic working principle has been proofed by CFD simulations with the use of the software package CFD-ACE+ of ESI-Group (www.esi-cfd.com).

After some pretests with one defined bubble in a tapered channel and its movement, the target of the simulations switched towards designing the channels of a flowfield. By taking advantage of the channels symmetry along its length, a part of the complete channel has been modeled as depicted in Figure 3. To keep the simulation time within an acceptable timeframe only a fraction of the channel has been modeled.

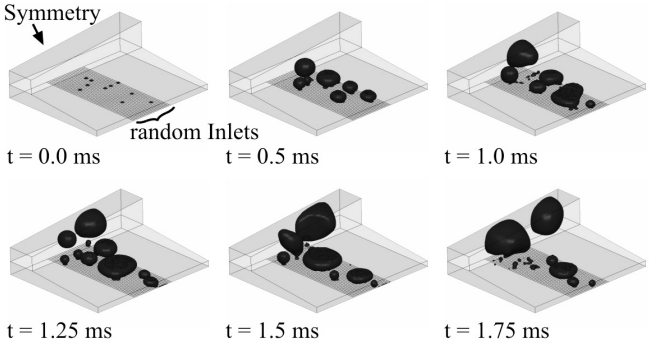

Figure 3. Simulation sequence with distributed bubble sources and bubble removal due to capillary forces. The symmetry of the channel is used to simplify the model.

As the gas bubbles develop randomly in experiments, a model mimicking this behaviour has been set up: An array of 1000 small areas, referred to as random inlets, has been built on the membrane side of the model (cf. Figure 3). The initial boundary condition of each of those areas is set to wall. A script is applied to set all boundary conditions for the simulation automatically. Within this script a routine randomly selects 10 of the 1000 areas and changes the boundary condition to a gas inlet. 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 26 ml min^{-1} cm^{-2} of CO_2. After 0.5 ms the simulation stops and the script changes the inlets back to wall and selects 10 new areas to be changed to inlet-conditions: The initial condition for the new simulation run is 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 that the tapered channels proof the assumption that the developing gas is guided out of the channel regardless of where it is created in two steps. First, the bubbles grow until they get in contact with the upper channel wall and then start to move towards the middle channel while merging with other bubbles. In a second step the bubbles in the middle channel move towards the outlet of the channel.

4 SAMPLE PREPARATION

After the successful simulations a master tool with the channel dimensions given in Figure 1 has been milled in a brass plate. Together with the master tool a frame has been manufactured where the tool fits in. The tool has been used for hot embossing into two different polymers: A transparent sheet of PMMA and a conductive graphite filled polymer (SGL BMA5). After the hot embossing step the 6 holes for the mounting. the connection for the fuel supply and the connections for the fuel outlet have been drilled. Figure 4 shows one of the transparent samples after the drilling.

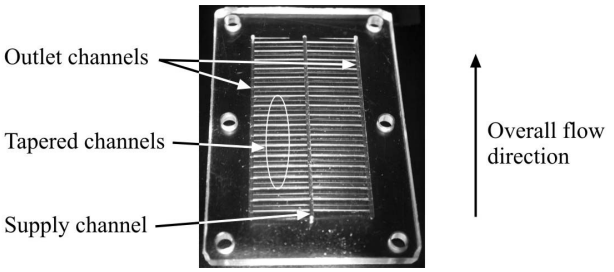

Figure 4. Photograph of one of the transparent test samples

5 EXPERIMENTAL VERIFICATION

For the experimental verification of the new flowfield design two different setups were built. The transparent test samples were used to observe the gas bubble development visually. Furthermore a functional µDMFC has been assembled and tested with the graphite filled polymer.

5.1 Translucent test cell

The translucent test cell has been assembled as a stack of a mounting frame, the PMMA-sample with the flowfield, a metal mesh, a membrane, a second metal mesh and a lower mounting frame. In between the different layers silicone has been used to seal the system. The whole stack has been screwed together. After connecting the fluidic ports the system has been primed with a 2 M methanol solution. Then the metal meshes have been connected electrically to force the creation of gas bubbles by a voltage of about 0.2 V and a current of 500 mA.

During the experiment a passive methanol flow into the flowfield is allowed as the supply channel is connected to a fuel cartridge. Methanol flows into the supply channel from the lower left corner (see Figure 5) and CO_2 can move out through the outlet channel at the upper right corner. As shown in Figure 5 the gas bubbles move towards the middle channel and grow there until they reach a certain size. Then they begin to move towards the outlet channel as anticipated due to the simulation results.

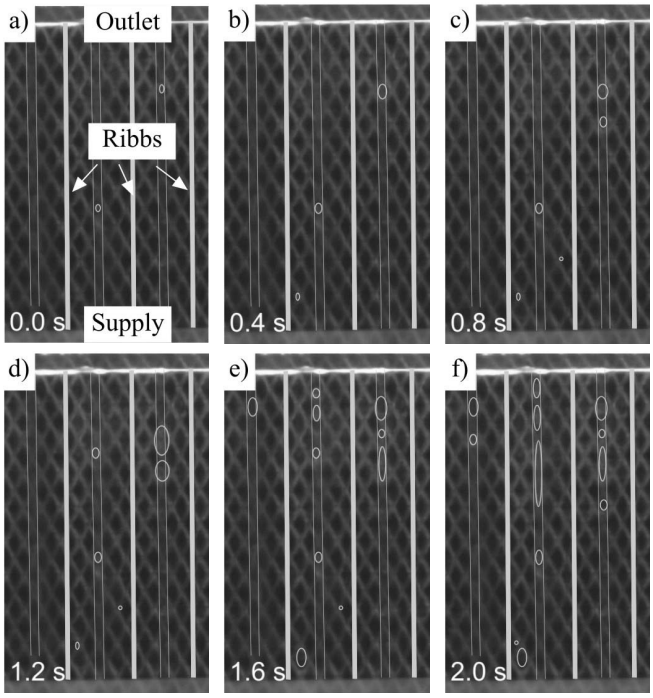

Figure 5. Picture sequence of gas bubbles developing with a 2 M methanol solution inside one test sample.

5.2 Fuel cell assembly

The planar fuel cells used in the experimental part are made of ordinary printed circuit boards (PCB) on the cathode and a hot embossed graphite plate (SGL BMA5) providing the micro structure on the anode. The PCB consists of a thin copper layer (35 µm) laminated on a substrate, which is a composite material of glass fibre and epoxide. The cathode plate consists of parallel, rectangular openings (3 mm × 21 mm) having a distance of 1 mm. The electrochemical active area of this geometry has a size of 21 mm × 43 mm. In the active area, the copper layer of the PCB acts as current collector and outside as current conductor towards external electrical contacts. On the anode a copper plate was placed below the graphite plate and used as current collector. The membrane electrode assembly (MEA) is attached by adhesives between two 100 µm thick foils to avoid short circuits between the copper layers plates and later on glued to the anode. Nafion 117 with a PtRu/Pt loading of 3.5 mg cm^{-2} and an ionomer thickness of 180 µm is used as the MEA. Diffusion layers are located between the plates and the MEA. As diffusion layers, Toray carbon paper with a thickness of 350 µm was used. This assembly is pressed together by six screws (size M3) with a torque of 0.5 Nm each. For future applications, the contact pressure between the plates will be realized by adhesives at the edges which will be pressed together while curing.

5.3 Fuel cell testing

As the fuel cell assembly has been designed to operate either totally passive or with pump assisted fuel supply a direct comparison of experimental results in active and passive mode is possible. The results of short time measurements with a 4 M methanol solution are depicted in Figure 6. The curves of the polarisation plot and the power densities show that with decreasing flowrate the fuel cells efficiency is increasing.

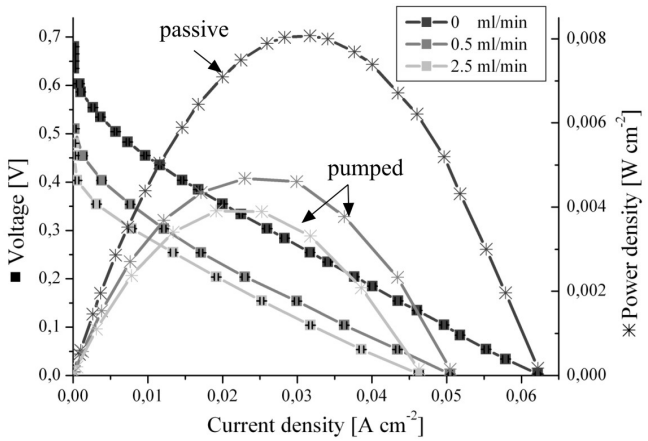

Figure 6. Short time measurements with a 4 M methanol solution at two pumped flow rates and a passive system setup.

With a decreasing flowrate the amount of methanol after the electrochemical reaction also decreases. This yields a lower crossover of methanol through the membrane from the anode to the cathode side and a better system performance.

Besides this, additional effects appear if the pump is switched off. As methanol is consumed and its concentration decreases, the crossover also decreases. In analogy to the previously mentioned case the overall performance increases. Another effect is connected to the evolution of methanol in the vapor phase. It is well known that this leads to better kinetics on the anode and a lower crossover through the membrane [7]. Thus it is advantageous to have a low flowrate or even almost no flow. However no flow would result in a power-breakdown after all methanol is converted. There are several options to overcome this problem: In one case the cell assembly runs for a certain time and then new fuel is pumped into the system until the missing volume is refilled again. Pumping only at intervals with pauses of several minutes (approximately 15 min) and a pumping time of 15 s shows an even better performance compared to continuously pumped systems. The benefit of this approach is twofold: On the one hand the cell efficiency is higher and on the other hand there is no continuous energy demand to drive the pump.

6 CONCLUSIONS AND OUTLOOK

A passive removal of gas bubbles in a µDMFC has been proofed using microchannels. First it has been simulated with a CFD-model and afterwards manufactured by conventional techniques. With the aid of transparent test-samples the working principle of the structures has been demonstrated. Furthermore a complete µDMFC has been assembled and it showed a higher efficiency when operated passively compared to the situation when methanol is pumped into the cell continuously.

Concerning simulation, a connection of a 1-dimensional membrane model to the CFD-model with the randomly selected inlet boundary conditions is planned. The 1-D-model locally determines the methanol reaction and thus also the local gas flow rate. This data should than be used for the switching of the boundary condition which leads to a more realistic simulation. On the experimental side, long term measurements have to be accomplished to prove a continuously self sustained passive operation.

7 ACKNOWLEDGEMENTS

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