

A novel, simplified micro-PEFC concept employing glassy carbon micro-structures

Bernhard C. Seyfang^{*}, Markus Kuhnke¹, Thomas Lippert, Guenther G. Scherer, Alexander Wokaun

Paul Scherrer Institut, Electrochemistry Laboratory, CH-5232 Villigen PSI, Switzerland

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Abstract

A novel, simplified concept for polymer electrolyte micro-fuel cells is introduced that combines several functions in fewer parts. It consists only of three elements; two glassy carbon sheets with micro-structured flow fields and a catalyst-coated membrane. The micro-structures are prepared in a sequence of three processing steps, i.e. sputtering, laser ablation, and reactive ion etching. Fuel cell tests were carried out with different flow fields, and a maximum power density of $\sim 415 \text{ mW/cm}^2$ at a cell voltage of 425 mV was obtained up to now.

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1. Introduction

Micro-fuel cells are expected to be a possible energy source for handheld devices, such as laptops or cell phones. The increasing number of functions combined in one electronic device causes an increasing energy demand. A theoretical energy density of $\sim 4800 \text{ Wh/l}$ for MeOH/air fuel cells and $\sim 3200 \text{ Wh/l}$ for H_2 /air fuel cells makes them more attractive as energy source than Li-ion batteries ($\sim 1300 \text{ Wh/l}$) [1]. Several concepts for micro-scale fuel cells, including micro-fabricated flow-fields prepared from silicon, stainless steel or metal-coated polymers, have been investigated [2,3].

Each of the flow field materials used in these concepts has at least one disadvantage (silicon: brittle; stainless steel: high weight; polymer: not conducting, which necessitates a conductive coating). Therefore, materials should be employed, which exhibit the following required properties:

- electrically and thermally conductive,
- mechanically and chemically stable,
- not permeable for gases fed into the fuel cell,
- low density.

Glassy carbon combines all these features, although a multi-step micro-structuring process has to be applied.

Additionally, a gas diffusion layer can be neglected in our concept, due to the narrow distances between the channels ($< 40 \mu\text{m}$). This should yield a sufficiently short distance for electron conduction from the catalyst sites to current-collecting sites. No porous elements are used in the micro-fuel cell, resulting in a simple sealing concept.

2. Experimental

The micro-structuring of glassy carbon (Type G, HTW, Thierhaupten, Germany) is a sequence of polishing, followed by sputtering of an aluminum mask onto the glassy carbon surface. The structure is written by laser ablation into this mask. Finally, the micro-channels are formed by oxidative removal of the glassy carbon material from the

^{*} Corresponding author. Tel.: +41 56 310 20 92; fax: +41 56 310 44 16.
E-mail address: bernhard.seyfang@psi.ch (B.C. Seyfang).

¹ Present address: Robert Bosch GmbH, D-72703 Reutlingen, Germany.

unmasked areas by reactive ion etching under oxygen atmosphere. The flexibility of the two-dimensional laser ablation allows us to produce different flow fields. Parameters like the number and the distance of the channels, the shape of the curves as well as the macrostructure of the flow field (e.g. meander, spiral meander, branched meander, and mesh) can be varied easily. The channels are $\sim 120\ \mu\text{m}$ deep; the width yields $60\ \mu\text{m}$ at the bottom and $100\ \mu\text{m}$ from edge to edge. Cha et al. [4] have examined different channel sizes in micro-fuel cells by modelling. They regard a cross section area of $100 \times 100\ \mu\text{m}$ and a distance between the channels of $100\ \mu\text{m}$ as optimum to achieve high power densities when air is used as oxidant. A homogeneous oxygen distribution can be obtained then, although the pressure drop can appear as a limiting factor with channels in this order of magnitude. In our case the whole micro-structured area is $1 \times 1\ \text{cm}^2$. Detailed information about the micro-structuring process has been previously described by Kuhnke et al. [5–7].

The test fuel cell consists of two stainless steel end plates, in which the functions of electrical contact, gas supply to the micro-structures, temperature control and mechanical compaction are combined. In-between these steel plates, two micro-structured glassy carbon plates, which are separated by the catalyst-coated membrane, are fixed. The micro-structured glassy carbon plates used in the fuel cell tests have seven (A) and eleven (B) parallel channels in meander shape. Another flow field utilizes eleven channels at the gas inlet, which are then reduced to six and finally to three channels by merging (C) (see Fig. 1). In the latter case, two laterally reversed micro-structures were employed due to operation of the fuel cell in co-flow of the two gases. The micro-structures were polished with a suspension of $3\ \mu\text{m}\ \text{Al}_2\text{O}_3$ particles (Buehler) in demineralized water (Ser-

alpur, conductivity $< 0.1\ \mu\text{S}/\text{cm}$) for 2 min prior to assembling of the fuel cell. The catalyst-coated membranes (CCM) were purchased from Paxitech (Grenoble, France) (thickness: $50.4\ \mu\text{m}$, platinum loadings: anode: $0.18\ \text{mg}/\text{cm}^2$; cathode: $0.25\ \text{mg}/\text{cm}^2$; Pt/C 40%; active area: $1\ \text{cm}^2$) and were applied without any further treatment.

Fuel cell tests were carried out in a test rig where the cell temperature, degree of gas humidification, and gas pressures applied to the fuel cell can be adjusted. The electrochemically active area was determined by cyclic voltammetry and hydrogen under potential deposition according to Kocha [8] and Schneider et al. [9], followed by integration of the desorption peak in the resulting cyclic voltammogram. AC impedance spectroscopy was recorded in pseudo-galvanostatic mode (constant DC current with superposed AC potential of $5\ \text{mV}$ amplitude). A Zahner IM6 electrochemical workstation was used for these experiments.

3. Results and discussion

Kuhnke et al. [7] presented a flow field structure, which employs five channels each with a depth of $52\ \mu\text{m}$. A PTFE foil was sandwiched between two of those micro-structures and $10\ \text{sccm}$ of dry oxygen flow was adjusted, resulting in a pressure drop of $1.5\ \text{bar}$. This is in good agreement with pressure drop calculations carried out in parallel according to Tilton [10]. Such a pressure drop would exceed the pressure under which the test fuel cell could be operated without an additional sealing. For a structure having seven parallel channels with dimensions described above, a pressure drop of $440\ \text{mbar}$ with a flow of $10\ \text{sccm}$ dry oxygen was calculated and a pressure drop of $470\ \text{mbar}$ was measured. Experiments showed that such a pressure does not

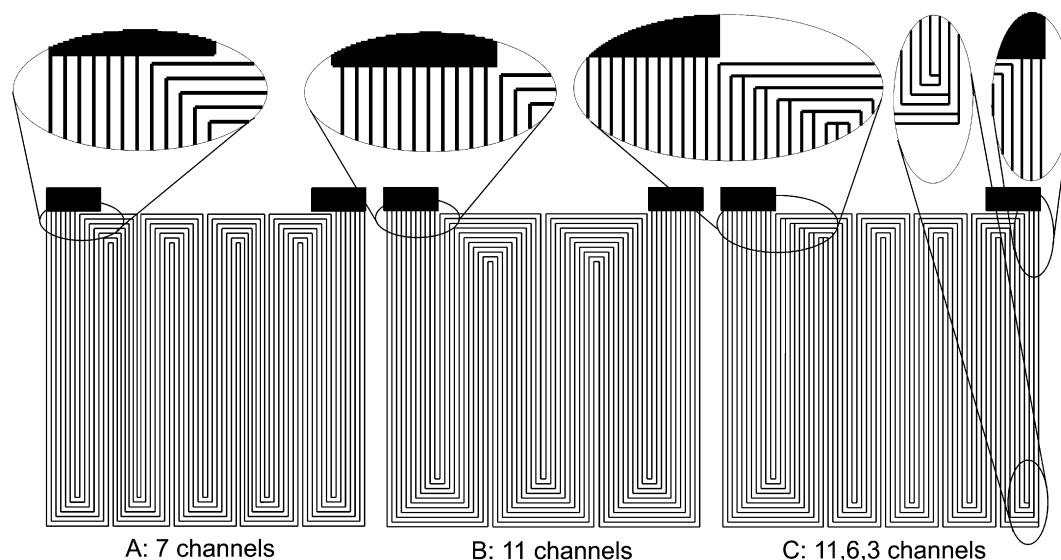


Fig. 1. Schemes of micro-fabricated flow fields employed in fuel cell tests; seven (A) and eleven (B) parallel channels as well as eleven channels at the gas inlet, merged to six and for the last meander to three channels (C). The expanded views show the gas inlets with the adjacent channels as well as the merging channels in flow field C.

cause gas leaks in the fuel cell. To further reduce the pressure drop, the number of channels was increased to eleven, resulting in a calculated pressure drop of 250 mbar, while a measured drop of 260 mbar for dry 10 sccm oxygen flow was recorded.

The polarisation curves shown in Fig. 2 were recorded under the conditions listed in Table 1. The values for the experimental parameters were obtained by a screening process, during which each single parameter was varied to yield the optimum setting. While the polarisation curves were recorded under galvanostatic conditions the system was allowed to equilibrate at each data point for 2 min.

Both, the seven- and eleven-channel structures delivered relatively high current densities, as shown in Fig. 2, but did not show a steady-state performance. Under high current densities, the product water was removed from the cell in large and irregular droplets. Consequences are fluctuations in the pressure drop and cell voltage, caused by intermediate accumulation of water. The cathode reaction consumes oxygen, decreasing its flow along the channels, while the amount of liquid water is increased along the channel. This effect results in insufficient convective water removal from the cathode flow field. To avoid this effect, merging flow fields were designed, where the number of channels, i.e. the cross-sectional area is reduced. It keeps the gas velocity in the same order of magnitude, resulting in a rather regular water removal and less cell voltage and pressure drop

fluctuations. The calculated and measured pressure drop for those flow fields was 390 mbar and 440 mbar, respectively, with a flow of 10 sccm of dry oxygen.

The number of channels influences not only the pressure drop but also the voltage that can be obtained at relatively high current densities (at 1 A/cm²: A – 124 mV; B – 286 mV; C – 414 mV). After start-up operation of a seven or an eleven-channel flow field fuel cell, it might be possible that some catalyst area is not active because some channels are filled with water and bypassed. Hence, O₂ is prevented from reaching those water-blocked catalyst sites. The higher the number of channels the larger is the probability for a channel to be bypassed.

Structures with merging channels (C) do not only show the best performance, concerning cell voltage and pressure drop fluctuations, but also the ability to deliver slightly higher current densities than structures having only parallel channels. The abrupt voltage decrease in the area of mass transport limitation (at ~1050 mA/cm²) is a significant observation here. A similar effect was observed by Kim et al. [3] and explained by a hydrogen mass transport limitation. A typical mass transport limitation on the cathode side can be excluded, due to application of pure oxygen as oxidant. One reason could be the limited gas supply to the active sites. The structure of flow field C was originally designed for optimum water removal, but had to be adapted to reduce the pressure drop and due to a limited number of parallel channels on a 1 cm wide flow field. Hence, it is possible that some of the channels on the cathode side are filled with water originating from the reaction. This water hinders the gases to access the active sites of the catalyst.

During all experiments, an increased back pressure on the cathode side of 1060 mbar absolute was applied while the back pressure on the anode side was kept at 1000 mbar absolute. It was observed during the experiments that this adjustment improves the fuel cell performance, i.e. the voltage in the low current region (<200 mA/cm²) is about 10% higher than with a pressure of 1000 mbar. This may be due to an improved humidification of the membrane and of the ionic phase of the catalyst layer, which would reduce the proton conduction resistance. A decrease of the electrolyte resistance (198 Ohm/cm² vs. 207.5 mOhm/cm²) under increased back pressure on the cathode side (60 mbar) could be observed at a current density of 100 mA/cm² by AC impedance spectroscopy, while at higher current densities (>250 mA/cm²) no such difference could be detected. We assume the influence of increased back pressure being superposed here by increased water production, which causes an improved humidification of the ionic phase.

Corresponding to the polarisation curves in Fig. 2, power density curves are shown in Fig. 3. The maximum power density for the fuel cell, which employs the merging micro-structures (C), reached a value of 415 mW/cm² at a potential of 425 mV (395 mW/cm² at 500 mV) at a cell temperature of 50 °C. A comparison to published data obtained with other micro-fuel cells by parameter screening

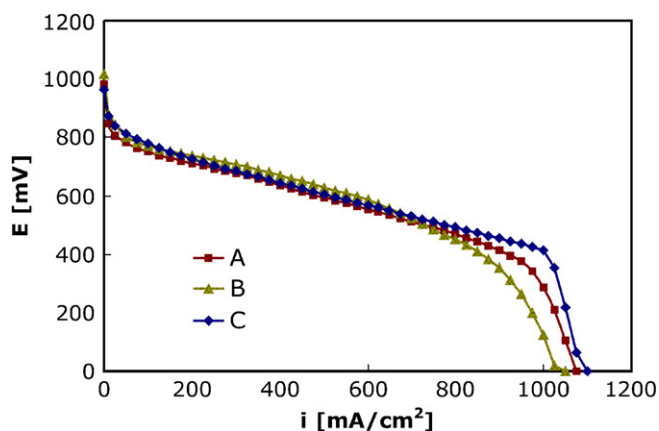


Fig. 2. Polarisation curves of 1 cm² micro-fuel cells employing different flow fields, recorded under the experimental parameters listed in Table 1.

Table 1
Fuel cell test parameters

Parameter	Value
Volume flow H ₂	9 sccm
λ (H ₂) at 1 A/cm ²	1.3
Volume flow O ₂	6 sccm
λ (O ₂) at 1 A/cm ²	1.7
Back pressure anode	1000 mbar absolute
Back pressure cathode	1060 mbar absolute
Cell temperature	50 °C
Relative gas humidity	80%

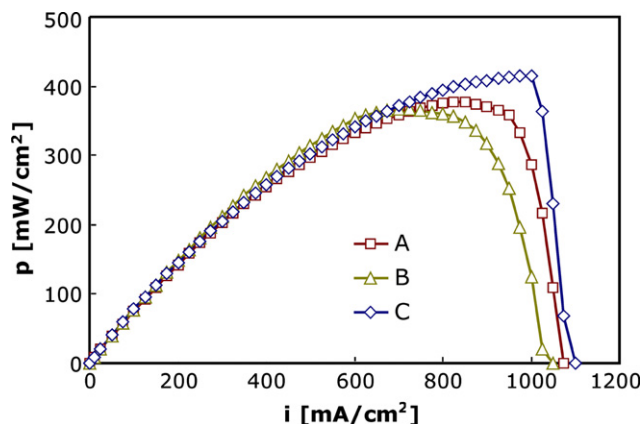


Fig. 3. Power density curves of 1 cm² micro-fuel cells employing different flow fields, calculated from the polarisation curves in Fig. 2.

Table 2
Comparison of power densities of selected micro-fuel cells

Power density (mW/cm ²)	Voltage (mV)	Flow field material	Reference
395	500	Glassy carbon	This work
315	350	PMMA	[11]
261	454	Silicon	[3]
194.5	466	Silicon	[12]

(see Table 2) shows that these values are the highest ones obtained and published so far. Nevertheless, a comparison has to be handled with care, due to different micro-fuel cell designs, micro-fabricated materials, micro-structuring processes, catalyst loadings, and stoichiometries of the feed gases.

Under operation, the pressure drop values were different from those calculated and measured with dry oxygen flow. At the anode side, the pressure drop was less, due to a lower gas flow caused by the consumption of the anode reaction. At the cathode side, the pressure drop nearly doubled in comparison to dry oxygen flow. Reasons for this might be condensation of product water, resulting in a two-phase flow, as well as swelling of the membrane into the channels and roughening of the catalyst layer, which would reduce the cross section area of the channels (Fig. 4).

The electrochemically active area was determined by cyclic voltammetry in the H_{upd} region and resulted in values of 56–58 cm²/cm²_{geo} for the anode and 77–79 cm²/cm²_{geo} for the cathode, respectively.

The fuel cell with merging flow fields (C) could be operated for 19 days with merging flow fields (C) could be operated for 19 days with a minimum power density of 325 mW/cm², corresponding to 80% of the maximum value. After disassembling of the fuel cell, a laterally reversed structure of the flow field was detected on the membrane surface. The SEM picture of the dried CCM (Fig. 4) reveals a dehiscent of the catalyst layer, which is due to membrane swelling into the channels, possibly in combination with mechanical stress caused by the gas flow.

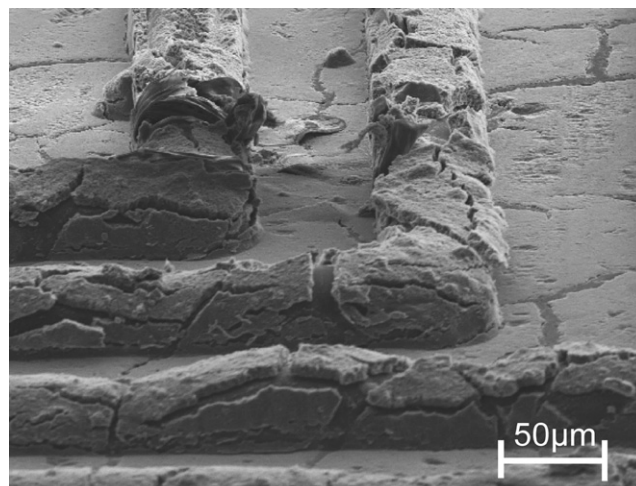


Fig. 4. Post mortem SEM micrograph of the catalyst layer, which is still attached to the membrane.

4. Conclusion

First results obtained with of a novel, simplified concept for a micro-fuel cell reveal power density values of 425 mW/cm². The performance is at least comparable to other micro-fuel cell concepts described in the literature. Nevertheless, further development work has to be carried out to optimize the micro-structuring process as well as the interplay between micro-structured flow field and catalyst-coated membrane. A set of analytical methods will be used in the future to obtain a deeper understanding of the limiting effects, such as influence of liquid water, active sites, diffusion, or degradation. Due to the rather simple principle of this micro-fuel cell, it might also be a powerful tool to examine phenomena observed in technical PEFCs.

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