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Development of a planar micro fuel cell with thin film and micro patterning technologies

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Abstract

Technologies for wafer level fabrication of planar PEM fuel cells between 1 mm^2 and approximately 1 cm^2 were developed. These MEMS-based micro fuel cells may be potential power sources for future applications such as wireless sensor networks, chip cards or autonomous microsystems. The investigations focused on pattering technologies for the fabrication of micro flow fields, design studies for integrated flow fields, material compatibility for fuel cells, patterning of membrane electrodes, serial interconnection of single cells in a planar arrangement, laminating and assembling processes. Although wafer technologies were applied, foil materials were used which allow low-cost fabrication in future production.

Prototypes of self-breathing PEM fuel cells with a size of 1 cm × 1 cm and 200 μm thickness were fabricated. *V*/*I* curves were measured at a variety of ambient conditions. Stable operation was achieved at 80 mW/cm^2 at varying ambient conditions with dry hydrogen fuel.

Keywords: Micro fuel cell; Membrane electrode assembly patterning; Foil technology; Microstructures

1. Introduction

Recently, a number of papers have been published dealing with the development of MEMS-based fuel cells. They can be subdivided into PEM [1–7] and DMFC [8–11] systems. There are two reasons for this development:

1. Using new technologies and designs it should be possible to significantly improve fuel cell performance when micro-scale phenomena are exploited. However, such benefits can only be realized if the fuel cell devices can be fabricated using available manufacturing techniques. They are in most cases adapted from semiconductor and microsystems technology. Fuel cells built to exploit micro-scale phenomena would be smaller, make better use of volume and could obtain improved heat and mass transfer. Technologies which may have the potential to solve problems which are critical in the conventional stack technology are for example
   1.1. the fabrication of micro-porous membranes optimized for two phase transport,
   1.2. the plasma polymerization of ion conducting polymers,
   1.3. the altering of hydrophilic, hydrophobic properties by plasma treatment, and
   1.4. the fabrication of transport optimized micro flow-fields with varying dimensions.
2. The majority of research on micro-scale fuel cells is also aimed at micro-power applications. There are many new miniaturized applications which can only be realized if a higher energy density power source is available compared to button cells and other small batteries. Miniaturization of the conventional fuel cell stack technology is not possible down to these dimensions [14,17].

Most of the approaches for MEMS fuel cells comprise basic research and material development. These approaches have in common that a great effort is needed to establish the process and to optimize the electro-kinetic performance of the catalyst layer. Adapting these coating processes to a new cell geometry might lead to high set-up cost as new coating tools have to be developed.

Therefore, we used another approach. A commercially available MEA was taken from mass production and further processed in our laboratory. Micro patterning technologies were employed for current collectors and flow fields and the assembling technology was adapted from microelectronics

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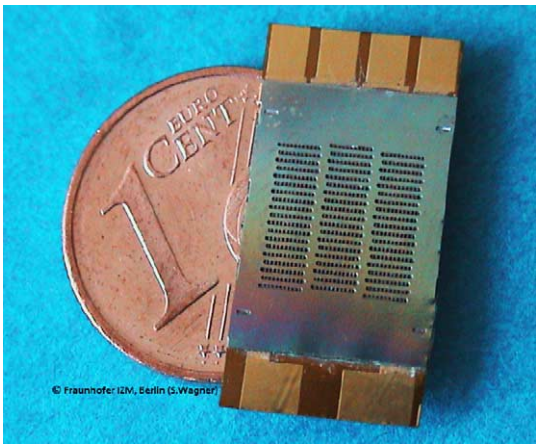

Fig. 1. Micro fuel cell with integrated serial connection of three cells.

Fig. 2. Micro fuel cell powering a LED, bended configuration.

packaging. Although wafer technologies were applied, foil materials were used which allow low-cost fabrication in future production [15,16]. Figs. 1 and 2 show prototypes of micro fuel cells described in this paper.

2. Design concept of the micro fuel cell

A planar design allows a passive, full self-breathing operation of the fuel cell. Additional fans or air movers are not needed. In order to achieve higher voltages, a plurality of cells have to be serial connected whereas the cathode is connected with the anode of the following cell.

In our design the interconnection between cells is performed outside the membrane area which reduces sealing problems.

For this concept it is necessary that the fuel cells are constructed without additional gas diffusion layers (GDL) because by using a continuous piece of GDL a short-circuit will occur between adjacent cells. In order to avoid this a separate GDL for each single cell must be assembled, which

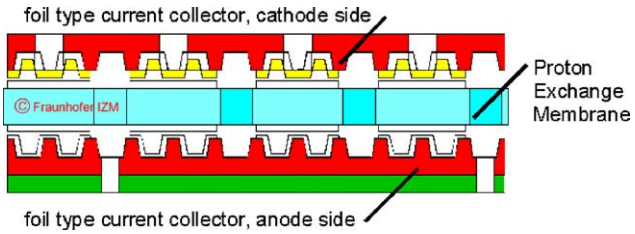

Fig. 3. Cross-sectional view of micro fuel cell.

is contrary to the idea of processing thousands of fuel cells at the same time using wafer and foil processing. Therefore, in this design concept diffusion layers are not used.

The function of a conventional diffusion layer assumes a microstructure which is merged of the anode and cathode side. The microstructures fabricated at the inner sides of the current collectors are in the dimension of the carbon fibers in conventional diffusion layers. Moreover, the microstructures serve as flowfield and are designed to assure a homogenous gas supply all over the MEA.

This way the complete fuel cell consists of only three foils: the current collector foils with integrated flow fields on top and bottom and the patterned MEA foil in-between. Fig. 3 shows a cross-sectional view of the micro fuel cell. A multitude of fuel cells of varying sizes and number of cells can be fabricated at the same time.

A demonstrator with three serial interconnected cells with an active area of 0.18 cm^2 according to Fig. 4 was fabricated. The total area of the micro fuel cell is 1 cm × 1 cm. Each individual cell can be accessed from outside with help of electrical test pads. A sealing track is designed at the periphery of the active area for all three cells at the same time. Nevertheless, each cell has its own hydrogen inlet and outlet and is sealed against the other cells, but at a lower tightness compared to the outer sealing.

For comparison purposes and study of the MEA processing another design was fabricated with one single cell of 0.54 cm^2 active area.

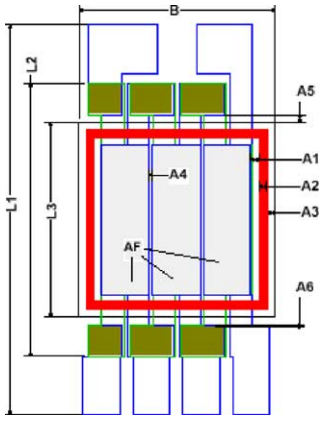

Fig. 4. Demonstrator layout.

3. Technology

The foil-type planar micro fuel cell technology is based on the following key technologies:

- sandwich laminate of polymer–stainless steel foils,
- lithography and patterning of free standing grid microstructures,
- micro patterning of flow fields,
- subtractive patterning of MEA-electrodes,
- adhesive sealing and electrical interconnection.

3.1. Fabrication of current collectors and flowfield

The current collector foils with integrated flow field of the anode and cathode side consist of metalized and microstructured sandwiched metal–polymer foils.

The flowfield, sealing joint and gas inlets at the anode side and the openings for the air inlet at the cathode side were fabricated by micro patterning. The metal foils act as the housing of the fuel cell. The foils are fixed on a silicon-wafer during fabrication. This wafer is only used as carrier substrate and allows the use of thin film processing and wafer level packaging equipment.

A stainless steel foil of 10–30 μm thickness is provided with openings for the gas and air inlets by means of wet etching, laser cutting or punching.

Afterwards the metal foil is laminated onto a polyimide foil using the technology of flexible printed circuit board manufacturing. For polymer foils DuPont Pyralux® coverlay is used which is made of DuPont Kapton® polyimide film, coated on one side with a proprietary B-staged modified acrylic adhesive. For flex circuits usually copper foils are used, so the process and surface treatment had to be modified for stainless steel foils. The metal–polymer sandwich foil assures the mechanical stability and stiffness of the micro fuel cell during processing as well as during later use. The multilayer foil is very thin (below 100 μm) for low volume consumption and mechanically flexible for easy integration into the surface of any housing of electronic equipment.

Next the micro flowfield is patterned in the polymer by reactive ion etching (RIE). Lateral dimensions down to 5 μm and a structure depth down to 50 μm were realized. In future mass production other processes like hot embossing may be more appropriate.

Finally electroplated 5–20 μm thick Au is deposited and patterned on top of the micro flowfield as current collector layer. To reduce the thickness of the Au metallization long term tests and corrosion experiments were carried out with copper, nickel gold and chromium multilayers as well. Reliable long term performance of PEM and DMFC operation was achieved with pure Au layers only [18].

The openings at the cathode side current collector which are essential for the self-breathing function are structured by RIE as well. The perforated stainless steel foil is used as dry etch mask and acts as outer surface of the fuel cell afterwards.

The Au current collector of the cathode side is designed as a connected metal mesh. This way the current collector covers the area of the openings of the air slots in the sandwich foil as well. These free standing, micron sized metal lines are an important feature of the described technology. It results in homogeneous current density and low loss current collection.

3.2. Patterning of MEA electrodes

By using a continuous piece of MEA for several cells in a planar arrangement, internal bypasses due to the lateral electrical conductance of the catalyst electrodes may occur [13]. This effect must be avoided by structuring electrically insulated segments in the catalyst/electrode layer. If separate electrodes are realized during MEA fabrication, the distance between adjacent electrodes is usually several millimeters wide. This is not appropriate for micro fuel cells, were the total dimensions are in the millimeter region. Therefore, a subtractive patterning technology was developed to minimize the space between cells for best utilization of the MEA area using reactive ion etching (RIE) and LASER ablation [19]. During RIE, the MEA is covered by a shadow mask. Design of experiments have been carried out to optimize the etch rate and minimize MEA degradation due to vacuum processing. In the end laser ablation of the electrode layers proved to be the better process. Since the adsorption of laser radiation of the electrode layers is very high while the membrane is rather transparent, the electrodes of both sides of the MEA can be patterned at the same time which eliminates adjustment inaccuracies. A local overheating has to be avoided during laser patterning. Otherwise the highly electrochemical active catalyst of the MEA might catch fire. To avoid any ignition the laser ablation should be carried out in inert gas atmosphere or in a vacuum chamber. With these technologies the distances between MEA segments can be reduced to less than 200 μm.

3.3. Micro fuel cell assembly

The contact pads from the cells to be interconnected overlap in the area outside the membrane. Thus, a serial connection is realized by merging the overlapping pads as illustrated in Fig. 4. The connection is realized by electrical conducting adhesives [12]. The contact resistance and contact strength was substantially improved by micro patterning of the contact surface area. A dispensing technique or screen printing was used for deposition of the adhesive and integrated planar sealing.

During assembly the fuel cell foils are clamped to vacuum chucks and adjusted to each other. Finally the fuel cell is mounted at the housing which has the integrated hydrogen supply mainfold.

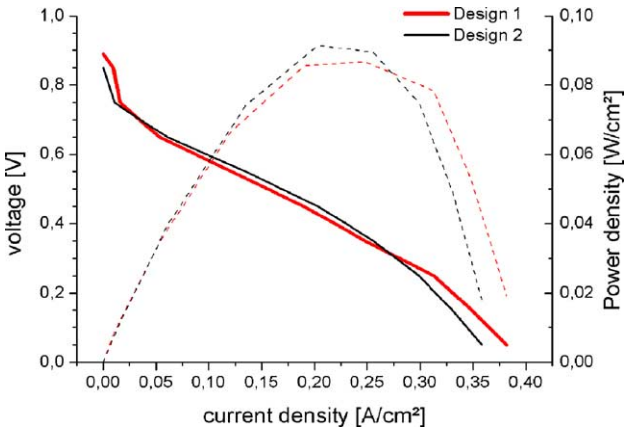

Fig. 5. Characteristic of PEM-micro fuel cells. Design 1: meander anodic flow filed, design 2: parallel rib flow field.

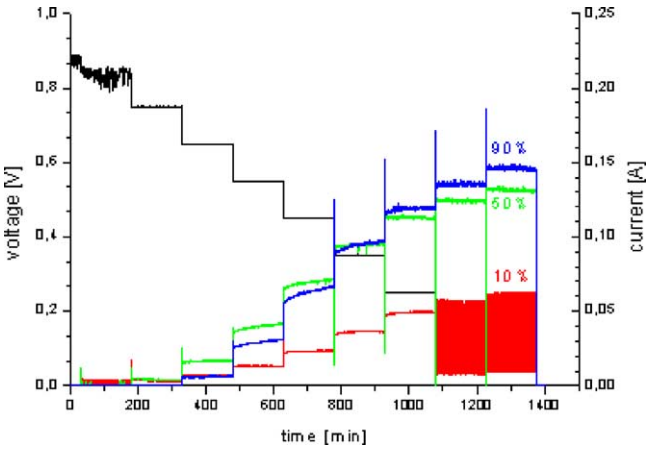

Fig. 6. Characterization of micro fuel cell at varying ambient humidity and 60 °C at potential steps.

4. Electrical characterization

4.1. V/I curves of single cells as function of ambient air conditions

The cell prototypes are electrically characterized by *V*/*I*-measurements. The measurements were carried out at room temperature and under natural air convection of the cathode. All measurements were made with dry hydrogen 0.5 sccm hydrogen flow and no additional humidification. Other measurements were conducted in an environmental chamber at a variety of temperatures and relative humidity. In the climate chamber the fuel cells were placed in an extra enclosure to keep off any air movement produced by the circulation system. Fig. 5 shows the *V*/*I* characteristic of a single cell with an active area of 0.54 cm^2. Both cells, which are referred to as designs 1 and 2 have the same cathode current collector with 400 μm openings. The anodic flowfield of design 1 has a meander shape with 250 μm wide channels while design 2 has a rib structure and 100 μm wide channels. The structure depth is 20 μm. As can be seen from Fig. 5 there is only a minor difference in performance between both types.

In another experiment the depth of the anode flowfield was varied between 25 and 40 μm. Here the differences of the *V*/*I* curve is within the measurement error. Cells with lower channel depth show higher power fluctuations during long term tests.

Fig. 6 gives an example of long term tests in the climate chamber. At high temperatures (60 °C) the cell performs best at high humidity while the optimum at low temperatures (10 °C) lays at lower humidity. Compared to conventional fuel cells with gas diffusion layers (GDL) the micro fuel cell responds at slightly lower temperatures to dry ambient conditions (membrane dry out) compared to cells with GDL. On the other side, at high humidity and low temperatures the micro fuel cell current density drops slightly faster. At low and medium relative humidity of the air, the performance of

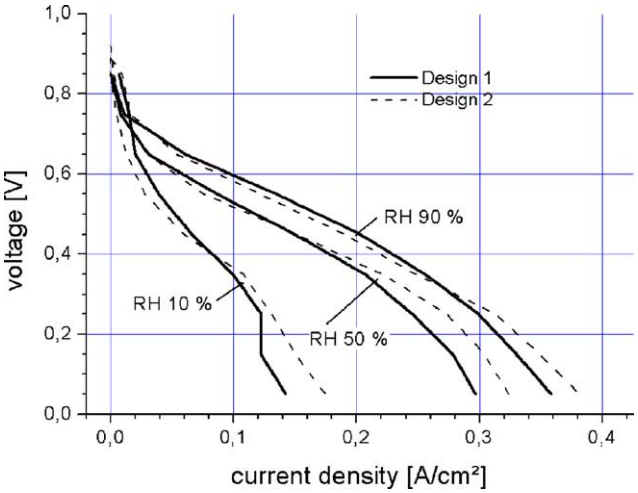

Fig. 7. Comparison of *V*/*I* curve of rib and meander design as function of relative humidity at 45 °C.

the meander design is slightly superior to the rib structure as can be seen in Fig. 7.

In summary: stable operation of the micro cells was achieved at 80 mW/cm^2 in long-term tests at varying air conditions. A power density of 120 W/cm^2 can be achieved in a narrow climatic range. The fuel cells perform best at normal ambient conditions.

4.2. MEA segmentation and serial interconnection

As outlined above, the segmentation of MEA electrodes is a key process to implement the concept of integrated fabrication of micro fuel cells which consists of merely three foils. Fig. 8 shows the electrical characterization of the serial interconnected three cell demonstrator. Approximately 40 mA can be drained at 1.5 V. To illustrate the importance of MEA patterning a fuel cell has been assembled with three serial interconnected current collector structures according to Fig. 4 but with a continuous piece of MEA. In this case

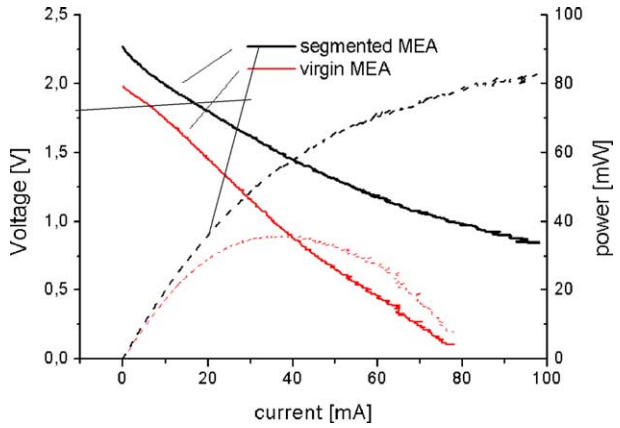

Fig. 8. *V/I* characteristic of micro fuel cell demonstrator, three cells 0.18 cm^2 serial inter-connected, 25 °C, 50% RH.

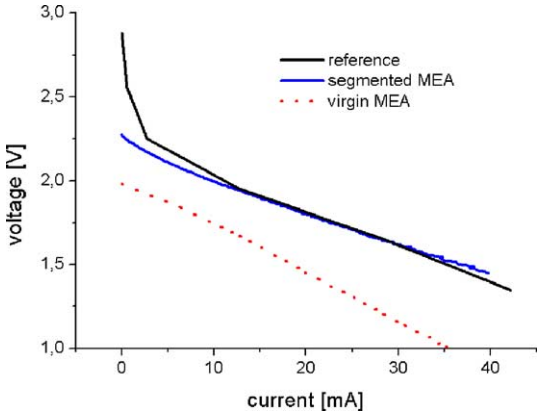

Fig. 9. *V/I* characteristic of micro fuel cell demonstrator, three cells 0.18 cm^2 serial inter-connected, 25 °C, 50% RH.

the voltage is clearly reduced resulting in less than 50% output power in comparison with the segmented MEA. An enlarged view of Fig. 8 is shown in Fig. 9. As a reference the *V/I* curve of three serial interconnected single cells with active area of each 0.18 cm^2 is added. The open circuit voltage of the reference cells is higher compared to the integrated and segmented micro fuel cell. But both curves merge already at ca. 10 mA and power density of both cells is almost identical. The lower voltage of the segmented MEA may be attributed to minor losses, probably due to internal leakage currents between adjacent cells. An equivalent circuit of the segmented fuel cell is shown in Fig. 10. R_L is the lateral surface resistance between neighboring cells which may result from insufficient removing of the electrode layers in the segmentation procedure. U_{FC}, R_{ion} and R_{si} are the open circuit voltage, the ionic membrane resistance and the resistance of the serial interconnection, respectively. To minimize internal losses

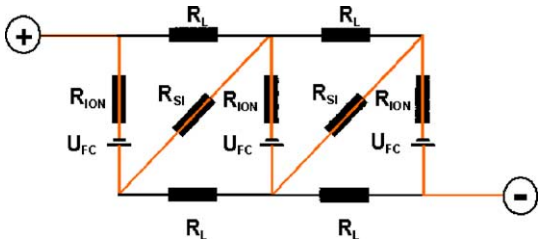

Fig. 10. Equivalent circuit of the segmented fuel cell.

$$R_L \gg R_{ion} + R_{si} \quad (1)$$

must hold.

To prove the concept of leakage currents between cells through the electrode layers, the open circuit voltage of the non-patterned fuel cell of Fig. 8 will be estimated.

At first the resistance R_L is calculated according to

$$R_L = \rho \frac{d}{wt} \quad (2)$$

with $\rho = 18.7\,\Omega$ mm, the specific resistivity of the electrode layer, $d = 200\,\mu$m, the distance between adjacent current collector/ flowfield of adjacent cells, $w = 7.6$ mm, the length of the cells, and $t = 7.5\,\mu$m, the thickness of the electrode layer, a resistance of $R_L = 66\,\Omega$ results.

As can be seen from Fig. 10, at open circuit condition the outer fuel cells are shorted with one resistance R_L while the middle cell is shorted with two resistances R_L from both sides of the MEA.

The resulting open circuit voltage of the system V_0 can thus be calculated according to

$$V_0 = 2V_{FC}(R_L) + V_{FC}\tfrac{1}{2}R_L \quad (3)$$

with $V_{FC}(R_L) = 0.72$ V, the voltage of a single cell according to Figs. 5 and 7 under the load R_L, $V_{FC}(R_L/2) = 0.67$ V, respectively. The resulting open circuit voltage is 2.11 V which is very close to the measured value of 1.98 V in Fig. 8.

By comparing the *V/I* curve of the segmented MEA with the reference curve in Fig. 9 it can be seen, that the patterning process of 200 μm isolating lines can be performed without degradation of the MEA and ionic drift currents between cells can be neglected.

5. Summary

A technology has been developed which allows the fabrication of PEM micro fuel cells based on commercially available membrane electrode assemblies. Planar micro fuel cells with size of 1 cm × 1 cm and 200 μm thickness with 40 mA output current at 1.5 V (=120 mW/cm^2, 25 °C, 50% RH) has been successfully demonstrated. Cell performance was validated under varying ambient conditions. Stable long term operation at 80 mW/cm^2 was achieved. The total performance of the micro fuel cells is in the same range of current and power density compared to the best conventional planar PEM fuel cells. At the same time this technology offers a high degree of miniaturization and the capability for mass production which is a clear success of our micro patterning approach.

Further work will be carried out to transfer this technology to the development of micro direct methanol fuel cells (DMFC).

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