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Investigation of fractal flow-fields in portable proton exchange membrane and direct methanol fuel cells

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Abstract

The flow-field design can have great influence on the operating performance of both proton exchange membrane fuel cells (PEMFCs) and direct methanol fuel cells (DMFCs). Inhomogeneous transport of reactants to and products from the active area of these low-temperature fuel cells result in loss of power. Newly designed fractal structures are tested as flow-fields in PEMFCs and DMFCs for portable applications. To achieve a uniform fluid distribution and simultaneously minimize energy demand for mass transport (pressure loss), a computer algorithm is developed to provide a given area with a multiple ramified fluid network. By virtue of the self-similarity, the structures of such a network are called fractals. These are investigated and compared with common serpentine and parallel flow-fields. For both PEMFCs and DMFCs fractal flow-fields show similar performance to parallel designs. The most stable and highest power output is reached with the serpentine flow-field.

Keywords: Proton exchange membrane; Direct methanol; Fuel cells; Flow-field design; Portable application; Fractals

1. Introduction

Due to high electrical efficiency, flexibility with respect to power and capacity, long lifetime and good ecological balance, fuel cells have the potential to complement or to substitute batteries in portable applications such as laptops and camcorders [1,2]. In a proton exchange membrane fuel cell (PEMFC), hydrogen and oxygen react electrochemically to water and, thereby, produce electricity and heat. The reactions taking place at the anode and the cathode are as follows:

$$\text{Anode}: \quad H_2 \rightarrow 2H^+ + 2e^- \tag{1}$$

$$\text{Cathode}: \quad 2H^+ + 2e^- + 0.5O_2 \rightarrow H_2O \tag{2}$$

A direct methanol fuel cell (DMFC) operates in a quite similar manner. Here, methanol is oxidized at the anode and oxygen is reduced at the cathode. Carbon dioxide (CO_2) and water are produced according to the following electrochemical half-reactions:

$$\text{Anode}: \quad CH_3OH + H_2O \rightarrow CO_2 + 6H^+ + 6e^- \tag{3}$$

$$\text{Cathode}: \quad 6H^+ + 6e^- + 1.5O_2 \rightarrow 3H_2O \tag{4}$$

To ensure free access for reactants to the electrodes, products have to be removed from the active area and out of the cell. This removal is achieved via diffusion layers and flow channels manufactured into plates. The main tasks of these flow-field plates are to act as current-collectors and to guarantee distribution of fuel or air over the reaction surface area as well as removal of products from the cell. Currently, serpentine- and parallel-channel structures are mainly used to facilitate mass transport to and from the active area. Due to long channels, serpentine flow-fields feature high pressure drops between the inlet and the outlet. These result in large parasitic energy demands. Especially in the case of small, portable fuel-cell systems, the energy required to transport the fluids should be as small as possible. Flow-fields with parallel channels exhibit lower pressure differences, but inhomogeneous reactant gas-distribution can easily occur. Products of the electrochemical reactions like water and carbon dioxide can clog single channels as visualized in [3,4] and parts of the active area are bypassed. The aim of the new fractal approach is to obtain an uniform and continuous flow distribution and simultaneously reduce the pressure drop by using a multiple-branched structure with 'smooth' flow paths similar to biological fluid channels. The investigated flow-field designs are presented in Fig. 1.

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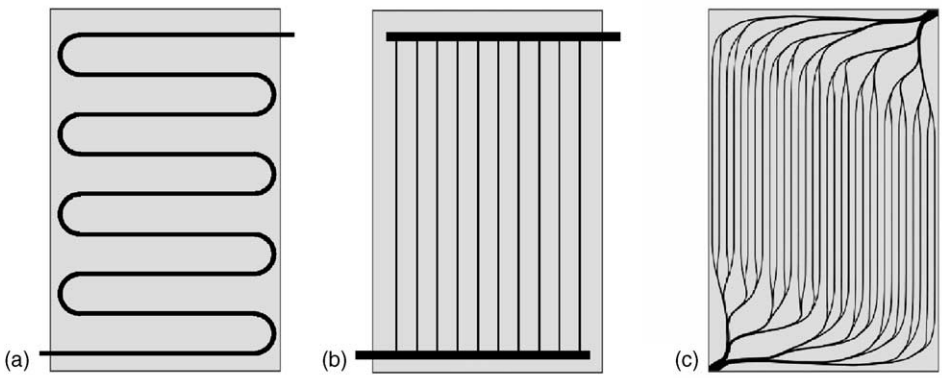

Fig. 1. Comparison of different flow-field designs: (a) serpentine, (b) parallel and (c) fractal.

As previously reported in several publications [5–9] flow-field design has a high influence on the performance stability of PEMFCs and DMFCs. A poor transport leads to an oscillating and decreasing power output caused by build-up and subsequent removal of the mentioned products from the reaction surface. The purpose of this work is to investigate the influence of fractal design on the transport properties of flow-fields, and thus on the stability of the fuel cell operation.

2. Generation of fractal structures

Theoretical descriptions of fractal structures based on their characteristic self-similarity are well known. These algorithms are not suitable, however, to fit in an arbitrarily given area. Therefore, a new algorithm (patent pending) has been developed which is capable of generating a network on a given area with fluid entry and exit. This so-called 'FracTherm' algorithm has originally been generated to design structures for heat-exchangers (e.g. absorber in a solar thermal collector). Research work on this topic is currently carried out at Fraunhofer ISE [10]. The geometric procedure of the algorithm is based on the following two rules.

1. The fluid channel is to be positioned 'in the middle' of the (partial) area, so that the distances to the right and left border or to the next fluid channel are approximately even.
2. As soon as a given maximum width (distance to next fluid channel or border, respectively) is exceeded, the fluid channel is to branch out. The bifurcation ends if the width falls below a given value.

The approach to generate a fractal flow-field on an arbitrarily given area is shown schematically in Fig. 2.

The resulting structure is strongly influenced by a couple of net parameters needed by the 'FracTherm' algorithm. In order to obtain an optimized geometry, the parameters must be varied and the resulting structures have to be assessed using appropriate theoretical models to describe the behaviour of the fuel cell. This optimization is not part of the work described in this paper. Therefore, the investigated fractal flow-fields are merely samples of many possibilities.

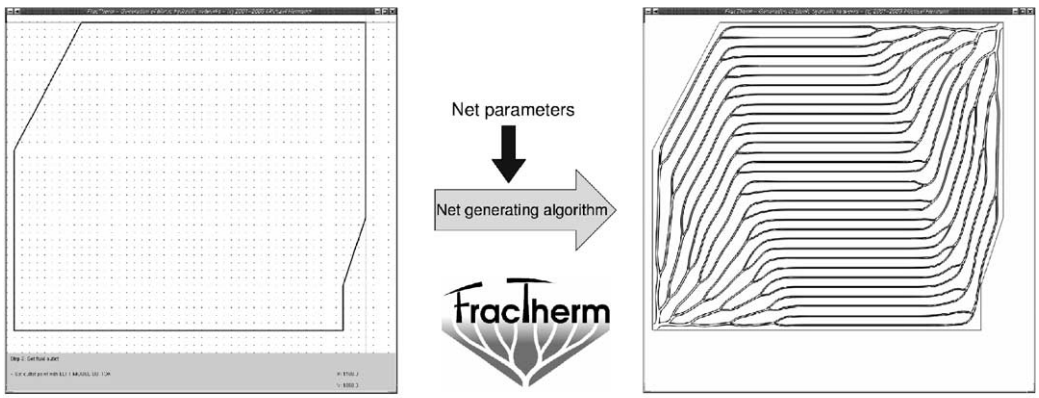

Fig. 2. Generation of a flow-field on a given area.

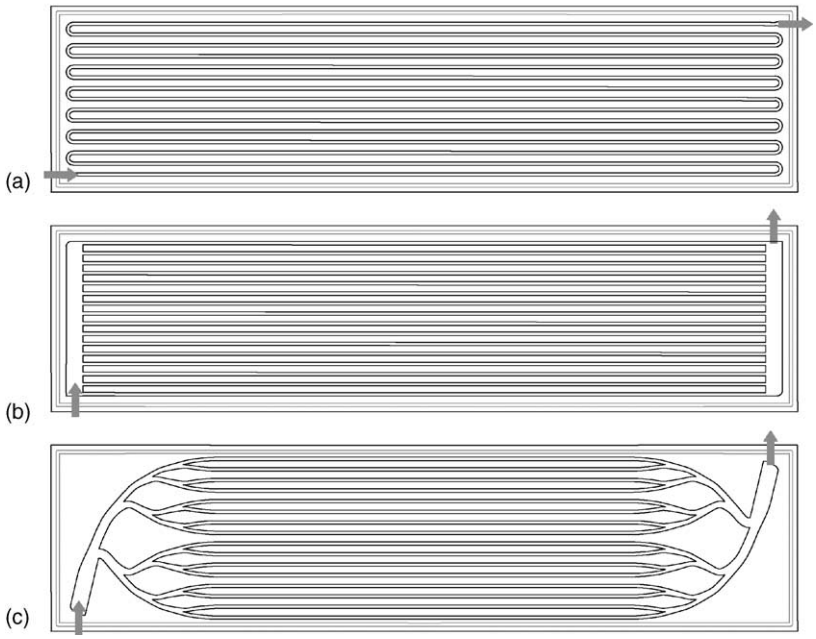

Fig. 3. Investigated air flow-fields for PEMFC: (a) serpentine, (b) parallel and (c) fractal.

3. Experimental

3.1. PEMFC

In case of a PEMFC, performance losses arise mainly due to inhomogeneous distribution of air because of product water blocking the active area. Therefore, the investigation of different flow structures was focused on various air flow-fields that were milled into the graphite composite material SIGRACET® BMA 5 from SGL Technologies GmbH (SGL). The chosen designs are presented in Fig. 3.

The flow-field plates were 3 mm thick, 55.4-mm wide and 222 mm long. All gas channels were 1.5-mm deep. Their width was mostly 1 mm. Only in case of the fractal design did the width increase from 1 mm at the centre of the flow-field towards the exits due to channel merging. The hydrogen flow-field had a double serpentine structure with 1 mm deep and 2-mm wide channels. The active area defined by the gasket was 109.5 cm^2. Independent of the investigated flow-field, each PEMFC used a Gore PRIMEA® membrane electrode assembly (MEA) (series 5510, ionomer thickness between electrodes: 25 μm, catalyst loading of anode and cathode: 0.4 mg Pt cm^{-2}) that was sandwiched between standard TORAY® carbon paper (TGP-H-090).

Performance of the PEMFC with different flow-field designs were compared by means of current–voltage curves and constant-current discharge measurements. The hydrogen flow during the experiments was adjusted to a stoichiometric factor of 1.3. To investigate the influence of various air flow rates, experiments with stoichiometric factors of 2 and 5 were performed. Both gases entered the dry PEMFC (<10% relative humidity) at a temperature of around 22 °C and at ambient pressure.

3.2. DMFC

Unlike in PEMFCs, the anode as well as the cathode experiences mass-transport problems in a DMFC. This is

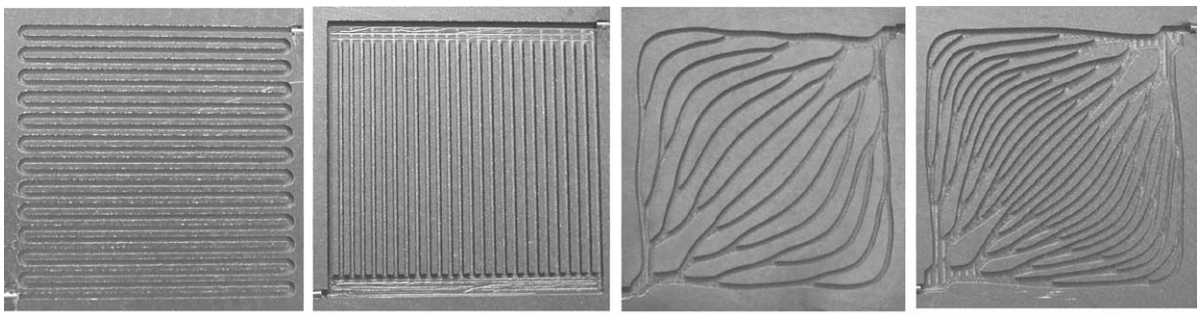

Fig. 4. Investigated methanol flow-fields for DMFC: (a) serpentine, (b) parallel, (c) fractal_1 and (d) fractal_2.

due to carbon dioxide formation and subsequent bubble growth, which blocks the catalyst area. Therefore, the anode flow-field design was varied to observe the effect on removal of such bubbles. A serpentine, parallel and two fractal structures were milled into the same material as was used in the PEMFC experiments, see Fig. 4.

All channels were 1.0 mm deep, the serpentine and parallel channels were also 1.0 mm wide. Due to the 'FracTherm' algorithm the fractal channels varied in width. On the cathode, a serpentine flow-field, as shown in Fig. 4, was used for all experiments. The active area of the cells was 25 cm^2.

A Nafion N117 membrane with 1 mg Pt cm^{-2} and 0.5 mg Ru cm^{-2} on the anode and 4 mg Pt cm^{-2} on the cathode was employed as a membrane electrode assembly. On both sides of the MEA, there were 270-μm thick graphite papers that acted as diffusion layers. The complete MEA was supplied by Johnson Matthey Fuel Cells.

The experiments were carried out at 50 °C with 300 ml min^{-1} air flow at ambient pressure and 15 ml min^{-1} 1 M methanol flow (pulse free). A high air flow was chosen to avoid flooding problems on the cathode. Current–voltage measurements and long-term operation for 3 h at constant current discharge were performed, as well as visual experiments with a liquid/gas mixture flow.

4. Results and discussion

4.1. PEMFC

It has been previously mentioned that a higher pressure difference results in a larger parasitic energy demand to supply the active area of a fuel cell with reactants. The effect of air flow on the pressure drop between the gas inlet and outlet of different flow-field designs is presented in Fig. 5. The pressure drop increases with increasing air volume flow, whereby flow conditions result in a superposition of laminar (volume flow and pressure drop are linearly dependent) and turbulent (volume flow and pressure drop are quadratic dependent) regimes. Similar measurements were presented in [9]. The pressure difference is much greater in the serpentine design than in either the parallel of fractal flow-field designs. Due to an increased cross-sectional channel area,

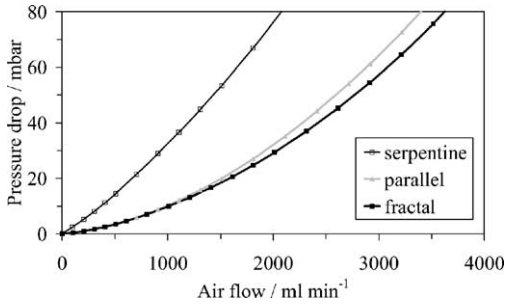

Fig. 5. Effect of flow rate on pressure drop in different air flow-fields.

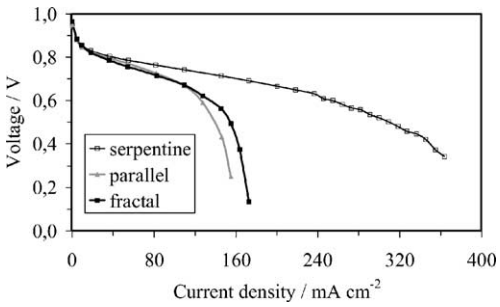

Fig. 6. Current–voltage characteristics of three PEMFCs with different flow-fields and an air stoichiometry factor of 2.

the pressure drop at an air volume, of say, 2000 ml min^{-1} in parallel and fractal, structures is only about 30 mbar compared with around 75 mbar in the case of a serpentine design. Compared with a parallel flow-field design, fractal structures feature a minimal reduction in the pressure differential. The aim to reduce parasitic energy demand while using fractal flow-fields to supply air to the cathode can be verified.

The following experiments were undertaken to compare the performance of PEMFCs with different flow-field designs. The current–voltage characteristics of PEMFCs with serpentine, parallel or fractal air flow-fields were measured galvanostatically with a stoichiometric factor of 2. The results are presented in Fig. 6.

Due to activation, ohmic and concentration overpotentials, the operating voltage decreases with increasing current density. It is remarkable that a serpentine flow-field facilitates a much higher performance than that use in by parallel and fractal structures. Due to mass transport limitations, the performance characteristics of PEMFCs with parallel or fractal flow-fields decrease at current densities of about 160 mA cm^{-2}. The cell temperatures increase only slightly from 23 to 25 °C. In the case of the serpentine design, a current density up to 365 mA cm^{-2} is reached and gives rise to a cell temperature of about 36 °C. The water that is produced during PEMFC operation accumulates mainly in liquid form due to the low-temperatures. By virtue of the pressure-driven mass flow in the channels, the removal of this water is eased by a serpentine structure. In the case of parallel and fractal flow-fields with low pressure differentials, the product water can inhibit the transport of reactant to the active layer. These findings are verified by the data presented in Figs. 7 and 8, which describe the constant-current (14 A corresponding to 128 mA cm^{-2}) discharge performance of three PEMFCs with different flow-fields at air stoichiometries factor of 2 and 5, respectively.

The results in Fig. 7 shows that only a PEMFC with a serpentine flow-field is able to operate at a constant output voltage, when air is supplied with a stoichiometric factor of 2. Under a constant load of 128 mA cm^{-2} over 120 min, the voltage is steady on a level of about 0.7 V. For PEMFCs with parallel or fractal flow-fields, the initially voltage of 0.7 V drops down immediately during operation.

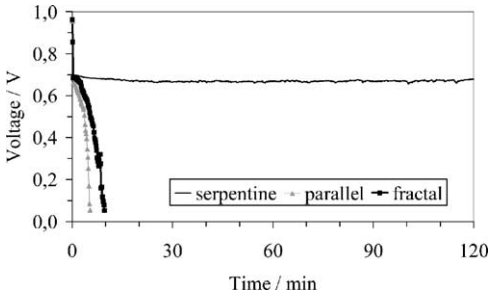

Fig. 7. Constant-current (128 mA cm^{-2}) discharge performance of three PEMFCs with different flow-fields and an air stoichiometry factor of 2.

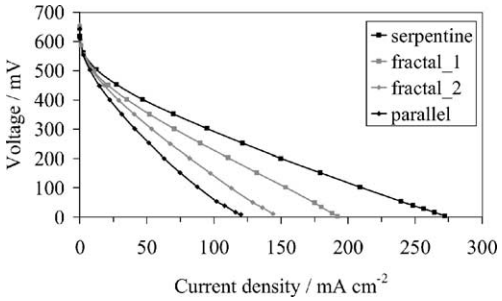

Fig. 9. Performance of the different DMFC anode flow-fields at 50 °C.

The performance of PEMFCs with parallel and fractal air flow-field designs has to be interrupted after 5.3 and 9.7 min, respectively. Similar results are obtained during discharge at constant currents of 7 and 21 A. While constant operation of a PEMFC with a serpentine flow-field is possible, experiments with both of the other designs had to be terminated.

With air flow rates at a stoichiometry factor of 5, the performance of PEMFCs with parallel and fractal, designs can be improved, see Fig. 8. While the constant-current discharge of a PEMFC with as serpentine design is unchanged, operation of PEMFC with parallel and fractal structures over 120 min is possible. Nevertheless, the output voltage in both cases decreases dramatically and shows an oscillating characteristic. Output voltages of only about 0.5 V are reached at the end of measurement.

Although air is supplied with a stoichiometry factor of 5 and the cell temperature in all three cases has increased from 23 °C at the start to about 44 °C at the end of measurement, the liquid water that arises cannot be removed effectively by parallel or fractal, flow-field designs. As reported previously [3,9], the water can accumulate in the flow-field structure result in totally clogged channels. In flow-field designs with several channels, as in the case of the investigated parallel and fractal structures, the reactant flow in clogged channels is constrained and parts of the active layer are bypassed. In low-temperature PEMFCs that have to deal with liquid water, parallel and fractal air flow-field designs can not be recommended. Here, serpentine flow-fields that can remove excess water due to their higher pressure drop are favoured.

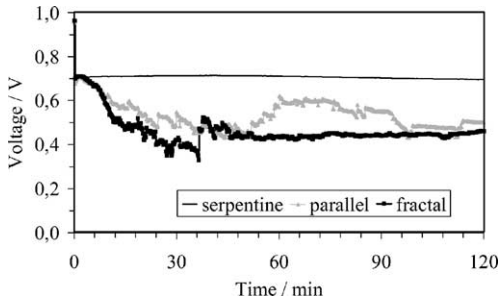

Fig. 8. Constant-current (128 mA cm^{-2}) discharge performance of three PEMFCs with different flow-fields and an air stoichiometry factor of 5.

4.2. DMFC

Removal of carbon dioxide in DMFCs is facilitated by the methanol flow. Due to the higher density of liquid compared with gas, a homogeneous flow distribution over the whole reaction surface is sufficient to push the formed gas bubbles out of the cell. Current–voltage curves obtained for DMFCs with different flow-fields at 50 °C are presented in Fig. 9. An oscillating output voltage is observed, which is a characteristic of low-temperature DMFCs. As the current increases, the oscillating effect intensifies. After each current adjustment, the corresponding voltage values are read after some minutes, depending on the stability of the voltage. Both the fractal and parallel flow-fields exhibit a lower performance than the serpentine counterpart. The distinctive property of the serpentine design is the forced flow direction from inlet to outlet. All of the methanol/water mixture has to flow through the only channel. In the fractal and parallel designs, methanol and carbon dioxide can flow in one or more of the many channels. This can lead to areas with no reactant flow, that gives rise to electrochemically inactive regions occupied by the produced CO_2 gas. Similar results have been obtained for other flow-fields with a non-forced flow direction [5]. A somewhat higher cell resistance is measured for the parallel and fractal flow-fields. This is most likely due to the difference in the contact area between the graphite and the diffusion layer.

As the cell current increases, the difference in performance also increases. More methanol and water is consumed and more carbon dioxide is produced, which has to be transported out through the flow-field channels. CO_2 bubbles are formed at the anode surface and thus block further oxidation of methanol. During galvanostatic operation the cell, the voltage decreases to compensate for the reduction in active area. As the bubbles grow, the blocked catalyst area becomes larger until the bubbles are released and transported away in the flow-field. As a consequence, the available reaction area increases, which also means that the cell voltage increases. This continuous forming and breaking of CO_2 bubbles causes the unstable voltage.

In addition to current–voltage measurement, 3 h tests at a constant-current discharge have been performed in order

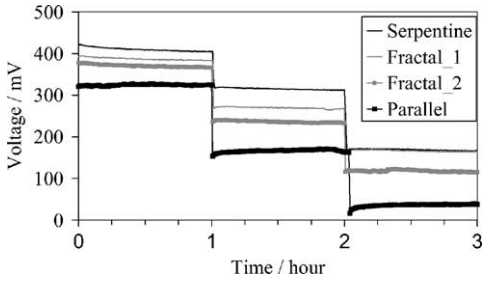

Fig. 10. Constant-current discharge performance of four DMFCs. The cells are operated at a total current density of 1, 2 and 3 A (serpentine 4 A). This corresponds to a current density of 40, 80 and 120 (160) mA cm^{-2}, respectively.

to investigate the long-term behaviour of the output voltage, see Fig. 10. At first, the cells are operated for 1 h at 1 A, corresponding to 40 mA cm^{-2}. Subsequently the cell current is increased to 2 and 3 A, or 80 and 120 mA cm^{-2}, except for the serpentine flow-field which is operated at 4 A instead of 3 A. For all levels, the serpentine flow-field operates at the highest cell voltage, and the order of performance is the same as previously seen in current–voltage plots. Differences due to flow-field design arise, at current densities as low as 40 mA cm^{-2}. The more channels the fractal flow-fields have, the more they seem to behave like a parallel flow-field, despite the lower pressure loss and optimal flow design. By comparison with the parallel and fractal designs in Fig. 1, it can be seen that as the number of channels in the fractal design increases it approaches a parallel structure. In both designs, there are possibilities for channels being blocked by bubbles of carbon dioxide.

A close-up of the 2 A load period is shown in Fig. 11. It should be noted that the voltages do not correspond to the experimental values shown in Fig. 10. For practical reasons, the voltage curves are off-set by 135 mV (parallel), 20 mV (fractal_1) and 65 mV (fractal_2). This way the voltage characteristics and the oscillating effect can be better visualized and compared. The behaviour is the same as that shown by current–voltage characteristics. While the serpentine voltage is high and reasonably stable, all other flow-fields give an inferior performance. A pulsed outlet flow of carbon dioxide is observed during operation with the fractal flow-field,

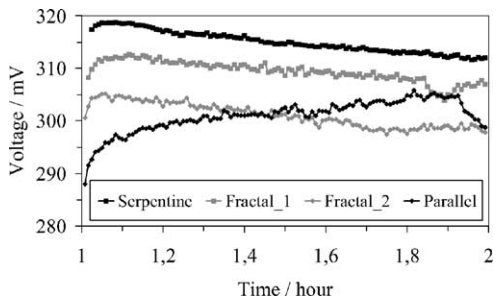

Fig. 11. Voltage characteristics of four DMFCs at medium-to-high currents. Fractal and parallel voltage curves are off-set for practical reasons.

which indicates that gas removal is not homogeneous in the absence of a forced flow direction.

A transparent dummy cell with a gas/liquid flow is used to examine how the flow pattern in the different flow-fields evolves. This provides a visual view directly into the channels. When liquid and gas are introduced to the flow-field, an in-homogeneous distribution between the channels in the parallel and fractal design can be observed. While the middle channels in the parallel flow-field experience the highest flow rate, the flow direction in the same fractal channels is sometimes reversed. A constant flow pattern is only seen with the serpentine structure, which can explain the differences between the flow-fields during operation of the fuel cell.

Of the four flow-fields, the serpentine design is the most stable. Compared with fractal and parallel designs, only small peaks are seen. It has been shown in [5] that the presence of liquid in the cathode channels has a higher influence on cell performance than gas bubbles in the anode. This observation was based on a correlation found between cathode outlet temperature and output current. During the experiments presented here, the same correlation is not observed. This indicates that there are no flooding problems at the cathodes. Given the possibility of channels being blocked by carbon dioxide, parallel and fractal structures are not suited as anode flow-fields in low-temperature portable DMFCs. A serpentine design ensures a more homogenous flow, which is even more critical during the operation of fuel-cell stacks.

5. Conclusions

The effect of flow-field design on the performance of low-temperature PEMFCs and DMFCs has been investigated. In addition to the commonly used serpentine and parallel structures, fractal geometries are tested. With a recently developed algorithm (‘FracTherm’), it is possible to generate fractal structures in an arbitrary given area. It has been shown that various structures have a large impact on the stability of fuel-cell operation due to their different ability to remove product water and CO_2, respectively. Under the present operating conditions, serpentine flow-fields give both the highest and the most stable performance. While serpentine channels force the products out of the cells due to their higher pressure drop, parallel and fractal designs can suffer from exhibit blocked channels. Thereby, inhomogeneous flow distribution occurs and parts of the catalyst surface are bypassed.

In other operating conditions, parallel flow-fields are well proven and applied fractal structures may be an advantageous alternative. The lower pressure loss in the latter structures decreases the parasitic energy demand and a more homogeneous flow distribution compared with the parallel design is achievable. When one-phase mass transport is guaranteed, fractal structures can also improve fuel-cell performance.

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