



Carbon dioxide evolution patterns in direct methanol fuel cells

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Abstract

Carbon dioxide gas management is an important issue in the development of the liquid feed direct methanol fuel cell. Data from a flow visualisation study, designed to study carbon dioxide gas evolution and flow behaviour are reported. Two different cell designs were used, one based on a simple parallel flow channel concept and the second based on a heat exchanger design concept. With the aid of a high-speed video camera, appropriate computer software and transparent acrylic cells, gas evolution was recorded in a fuel cell working environment. The influence of current density and liquid flow rate are considered. Gas evolution mechanisms and gas management techniques are discussed. The effect of scale-up on the power performance of the parallel flow channel cell is reported. © 1999 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Recently a great deal of research has focused on the polymer electrolyte direct methanol fuel cell (DMFC), shown schematically in Fig. 1. The cell consists of a solid polymer electrolyte membrane (proton conducting) onto either side of which are attached catalyst layers; typically platinum (for cathode) or platinum/ruthenium (for anode) supported onto high surface area carbon and bonded with Nafion[®] and/or Teflon. The catalyst layers are then covered by gas diffusion layers (typically graphite cloth or paper), to form the membrane electrode assembly (MEA). This assembly is then sandwiched between graphite blocks which have

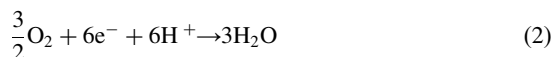
flow beds machined into the surface for the supply of fuel or oxidant and which enable electrical connection to the cell.

The reactions that occur in the direct methanol fuel cell are:

Anode:



Cathode:



The overall reaction produces water and carbon dioxide, which has limited solubility in the aqueous methanol solution and therefore is evolved as a gas in the cell. Carbon dioxide is a reaction product that should be removed from the electrode structure and

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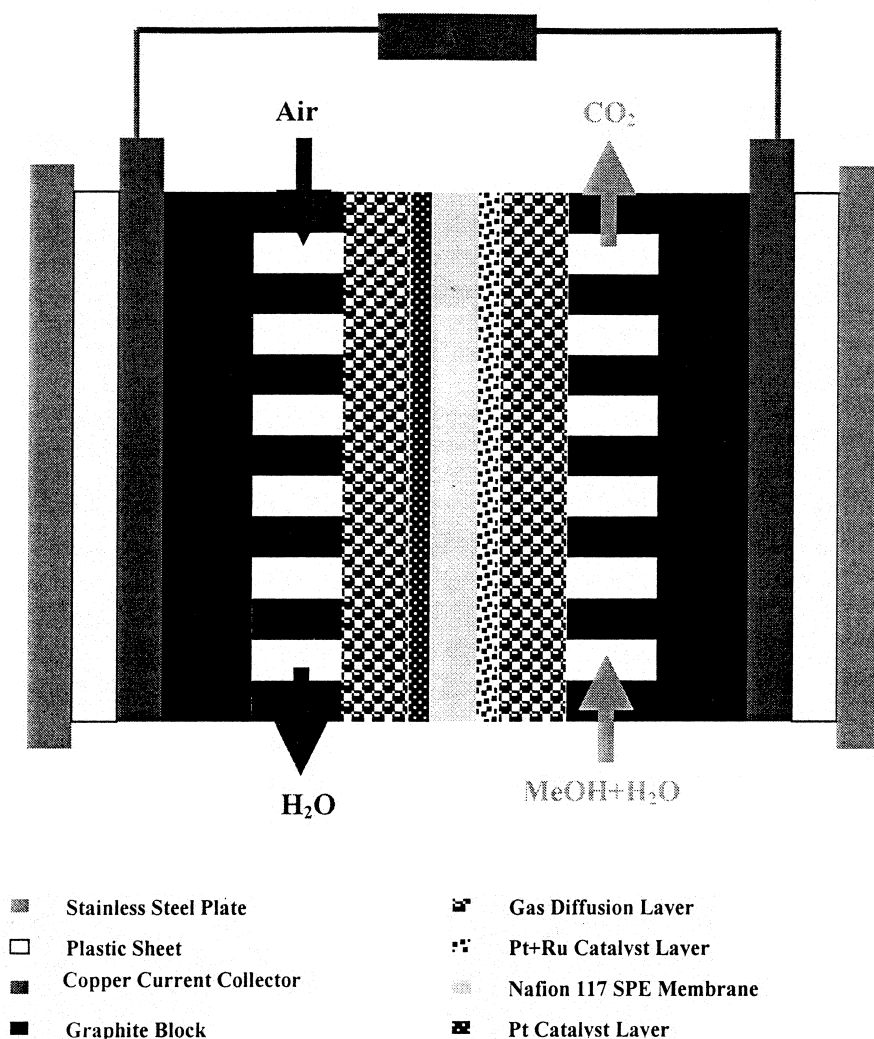


Fig. 1. Schematic representation of a DMFC cell.

cell as efficiently as possible to maintain effective reaction.

After successful operation of small scale DMFCs (e.g.[1–3]), there is a need to scale up and built stacks able to deliver sufficient power output for applications such as electric vehicles. This scale up procedure is quite complex since certain phenomena occurring inside an operating cell have not been investigated. One of these is the combination of carbon dioxide gas evolution and gas release from the interior of the membrane electrode assembly to the flow bed channels and gas removal from the cell to the exhaust manifold.

The efficient removal of carbon dioxide from the anode layer is a major factor in the successful design and operation of the DMFC. The presence of relatively large amounts of carbon dioxide reduces the free

area for the flow and penetration of reactants to the catalyst layer. This is influenced by high gas residence time inside the cell, which can result in entrapment of the gas inside the gas diffusion layer and blocking of the micro-channels in that structure. This blocking can impede the flow of methanol to the anode catalyst, induced by the anode reaction and the electro-osmotic transport of water and methanol and cause concentration polarisation at the anode, which reduces the cell voltage.

The operation of the DMFC requires that the carbon dioxide gas and aqueous methanol solution move counter currently in the catalyst layer, in the ‘gas diffusion’ layer and in the carbon cloth backing layer. Ideally the flow of carbon dioxide and methanol solution should be isolated such that discrete paths for

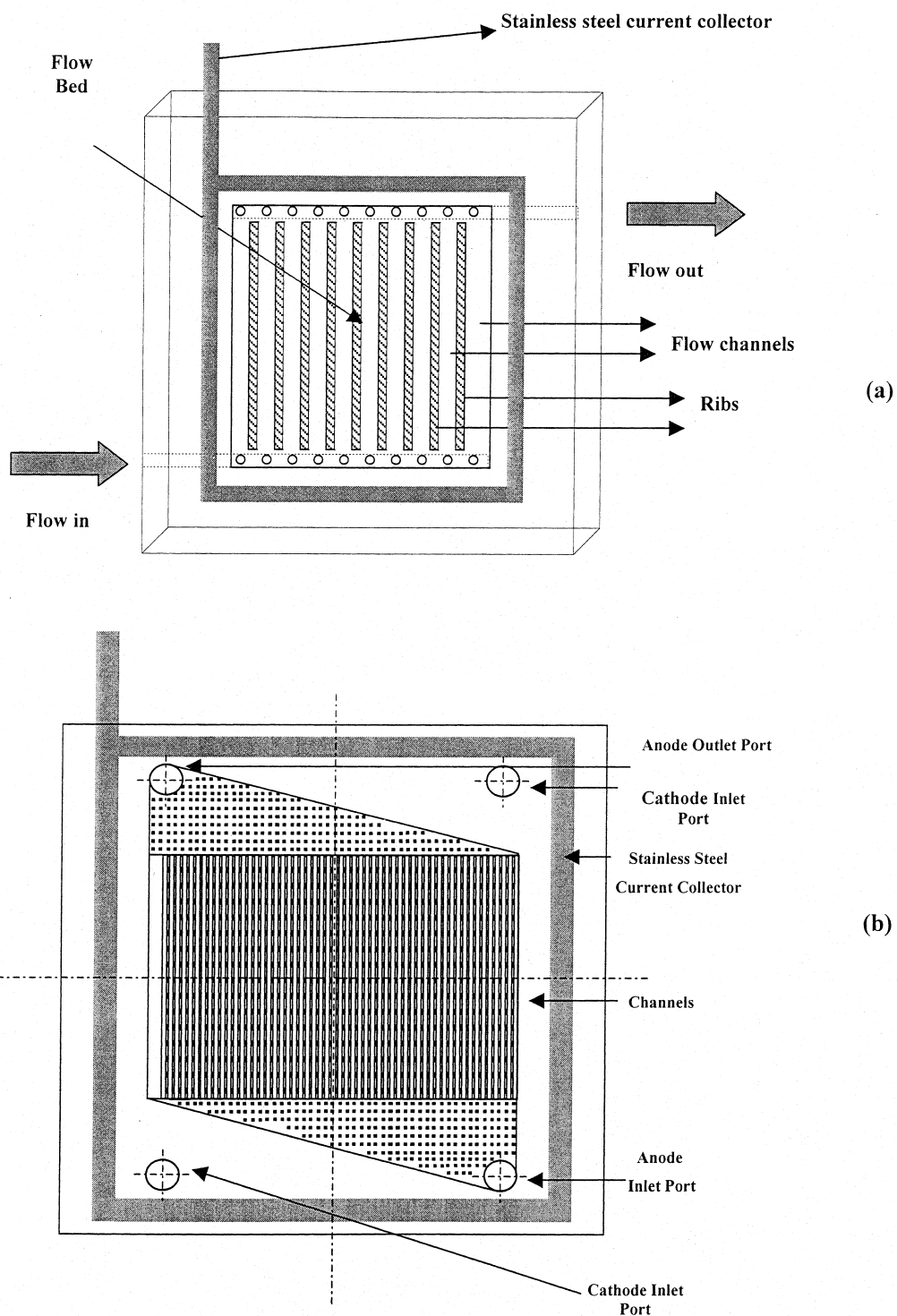


Fig. 2. Cell designs used in flow visualisation: (a) parallel channel cell design (I) and (b) cross flow channel cell design (II).

gas flow and for liquid flow exist, rather than a two phase flow with gas bubbles moving against a liquid flow. A simple way to approach the ideal flow behaviour is to make the carbon surface hydrophobic thereby creating regions for free gas movement. The approach is therefore typically to add Teflon to the carbon cloth, or gas diffusion layers, as routinely adopted in gas fed electrodes. To investigate the complex gas evolution behaviour in liquid feed DMFCs, we have built transparent acrylic cells and installed membrane electrode assemblies to create a real operating DMFC cell for visual observation of gas generation and flow.

2. Experimental equipment

The MEAs used in this study were prepared using the following materials:

1. A Teflonised carbon support (E-Tek, type 'A' carbon cloth) density 0.33 g cm^{-3} , porosity 0.847, thickness 0.36 mm, 20 wt% Teflon content.
2. Anode catalyst layer: Pt–Ru anode catalyst was 35 wt% Pt, 15 wt% Ru (developmental material, Johnson Matthey Technology Centre, (UK)) on Vulcan carbon (2 mg cm^{-2} metal loading) and bound with 10 wt% Nafion[®] (Aldrich).
3. Cathode catalyst layer consisting of 10 wt% Pt on carbon, loading 1 mg cm^{-2} Pt black, (Johnson Matthey) bound with 10 wt% Nafion[®] (Aldrich).
4. Nafion[®] 117 membrane (DuPont).

Further details of electrode preparation can be found in Refs. [1,2].

The direct methanol fuel cells were made from transparent acrylic, for the anode side and from graphite block, for the cathode side, and were compression sealed with the aid of wet thread, Teflon tape. Current was withdrawn from the anode side of the cell using a peripheral stainless steel strip embedded into the acrylic block, which contacted the MEA. To minimise potential problems of current distribution due to the edge collection of current we limited current densities to less than 100 mA cm^{-2} and limited the cell size to 100 cm^2 . This was based on measured values of conductivity of the carbon cloth used in the MEA. Subsequent observations of gas evolution confirmed that the central region of the cell was active. Two cell designs (see Fig. 2), with different flow bed, were investigated in this study:

1. Parallel channel, cell design (I): in this cell the flow bed consisted of a series of parallel flow channels, 2 mm deep, 2 mm wide and 30 mm long. The width of the ribs which formed the flow channels was 1

mm. Flow in and out of the cell was via a series of 2 mm diameter holes, in the cell body at the end of the flow bed section, which connected into a 10 mm diameter internal manifold.

2. Cross flow, cell design (II). the cell had a flow bed different to that of the small cell, designed as a result of this research and other research on the DMFC system development [4–6]. The design is based on a compact heat exchanger concept, where flow is from corner to corner through a flow bed. The flow bed is divided in three sections:
 - A triangular enlarging inlet section, 30 mm long which had a series of 4 mm^2 spots, designed for electrical contact to, and physical support of, the MEA.
 - A central region of parallel flow channels with the same dimensions as the small cell (I).
 - A triangular outlet section, of a similar design to the inlet section.

The cells were tested in a simple flow circuit with methanol solution supplied by two Watson Marlow 505U peristaltic pumps which can give a maximum flow rate of $2.0 \text{ dm}^3 \text{ min}^{-1}$. The acrylic cell material prohibited the use of heating plates in the cell for temperature control and hence an external loop was used for supplying preheated methanol solution. This loop consisted of a Watson Marlow 505U peristaltic pump, a variable voltage supply, an in house electric heater and a Eurotherm temperature controller with a thermocouple in the methanol solution tank. Air was supplied from gas cylinders and the pressure was controlled by a needle valve at the cell cathode side outlet.

The flow characteristics of methanol solution and carbon dioxide gas were recorded using a high speed Hitachi CCTV video camera (HV-720K). A stroboscope was placed behind the camera to provide the necessary lighting. The images, recorded in the video recorder, were then converted, off-line, to a computer image with the aid of a Matrox PC card.

3. Investigation of DMFC hydrodynamic characteristics

The present study was designed to investigate carbon dioxide gas evolution from the MEA surface and its release into the liquid phase. To try to facilitate gas movement through this layer and methanol solution access to the catalyst layer, counter-current to the gas flow, the carbon cloth of the MEA was treated with a 20 wt% of Teflon. The selection of 20 wt% of Teflon was based on an investigation of the effect of anode gas management on cell performance [1] carried out by varying the Teflon content of the carbon cloth backing

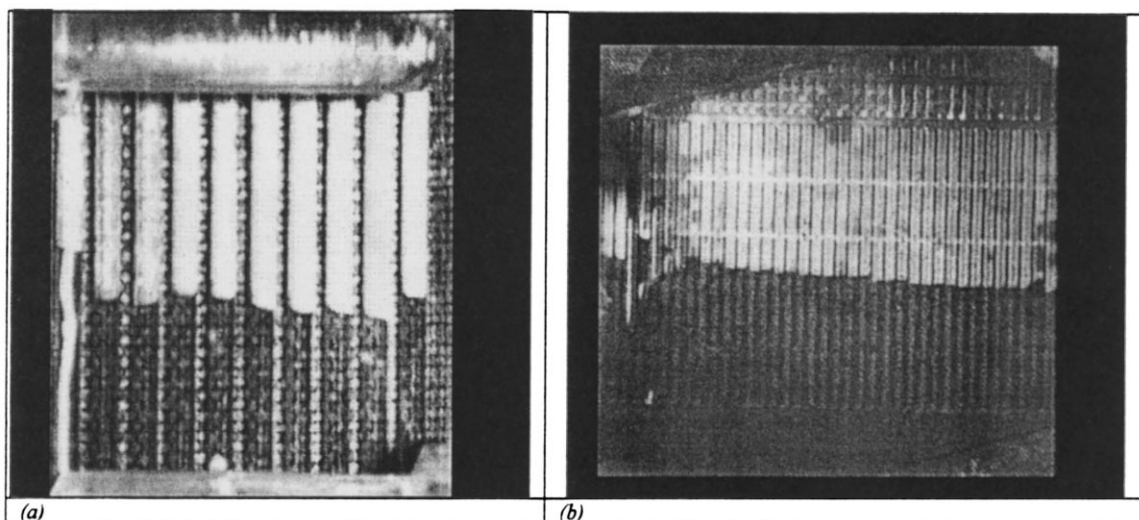


Fig. 3. Demonstration of uniform flow distribution with liquid flow only: (a) parallel channel cell design (I) and (b) cross flow channel cell design (II).

layer between 0 to 40%. The cloth without Teflon produced the poorest performance of all the electrodes. Increasing the Teflon content up to a value of 20%

improved cell performance up to current densities of 160 mA cm^{-2} . At higher Teflon content, of 30 and 40%, the performance of the cell fell. This was due, in

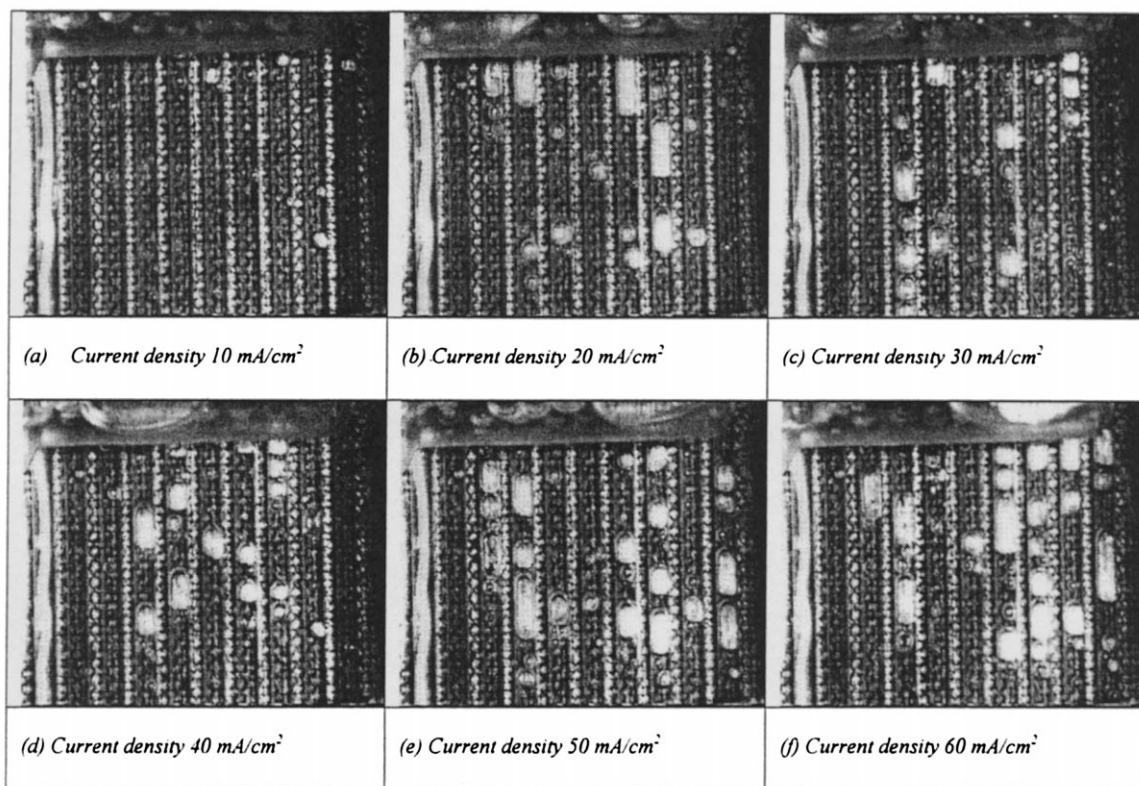


Fig. 4. Effect of current density on the gas removal characteristics for cell design (I). Current density $10\text{--}60 \text{ mA cm}^{-2}$, Anode inlet flow rate $6 \text{ cm}^3 \text{ min}^{-1}$, cell temperature 75°C , 2 M methanol solution.

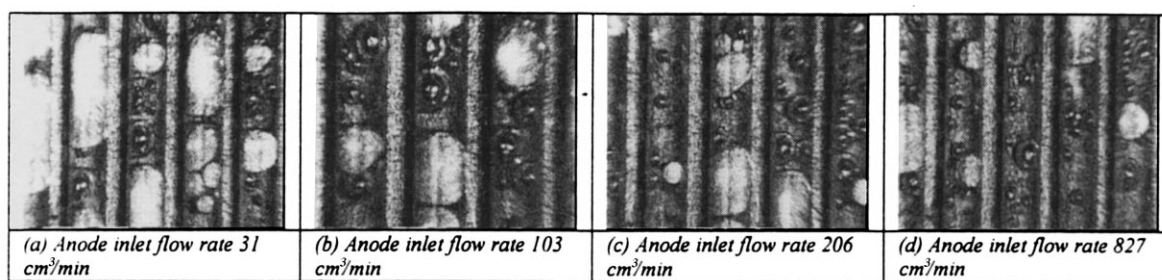


Fig. 5. Channel blocking by bubbles in cell design (I). Current density 50 mA cm^{-2} , Anode inlet flow rate $31\text{--}827 \text{ cm}^3 \text{ min}^{-1}$, cell temperature 75°C , 2 M methanol solution.

part, to the increased electrical resistance of the Teflonised carbon cloth. The Teflon loading which gave the overall better cell performance was between 13 to 20 %.

The flow characteristics of the cathode side of the DMFC are quite different to those of the anode side. The cathode flow is an air stream which becomes saturated with, predominantly, water and which potentially can contain some entrained water droplets at high current densities when flooding of the porous structure occurs. Brief observations of the flow at the cathode side of the DMFC have confirmed the absence of liquid water. The problem of flooding does not limit cell performance at the typical current densities used in the DMFC.

Generally in this flow visualisation study the lighter areas of the photographs are the regions of bubble flow and the darker areas are the liquid flow regions.

3.1. Cell design (1)

An important issue in designing a DMFC is to ensure that there is a uniform distribution of liquid between all the flow channels in the cell to achieve a uniform supply of methanol fuel to the MEA. In addition this will avoid regions of 'dead-flow' (i.e. areas with stagnant liquid) which will lead eventually to carbon dioxide accumulation. This uniformity of flow over a range of flow rates was investigated by observing the rise in liquid level in all channels. A representative snapshot of the liquid flow is presented in Fig. 3 where the liquid level is indicated by a change from the dark to lighter regions. In the parallel channel cell design (I) there are higher flow rates in the first and last channels than in the remaining central channels, although generally the single phase flow is relatively uniform.

3.1.1. Bubble generation over the surface

Over the duration of the study we observed that gas was not uniformly produced at the surface of the gas diffusion layer. There were a number of point sources

of gas release, with continuous, high rate, bubble generation and areas with no such activity. This is attributed to the structure of the electrode and the influence of Teflon. Many of the tortuous paths that connect the surface with the catalyst area were probably either blocked or flooded with the liquid phase. Hence, there were only a limited number of 'hydrophilic' open channels to serve as carbon dioxide removal paths. This meant that the gas could have accumulated in the diffusion layer and the reaction layer and could have formed relatively large bubbles which moved partly in a vertical plane until they found an open channel for removal away from the reaction site. In practical operation the gas generation sites multiplied in two cases: when the current density was increased and when the cathode side pressure was increased. Both phenomena lead to an increase in the pressure at the reaction layer, which appeared to be the driving force for the gas removal. Also the formation on the carbon substrate surface of large gas slugs appeared to block the local generation of bubbles.

The types of flow observed in the flow channel of the cells (see Fig. 4) spanned the range of fine dispersed bubbles, to large bubbles, to slugs of gas and annular flow [7]. The bubbly flow regime is characterised by discrete bubbles of gas dispersed in a continuous liquid phase. In bubbly flow the mean size of the bubbles is generally small compared to the cross section of the channel. At slightly higher gas fractions, smaller bubbles can coalesce into slugs that can span almost the entire cross section of the channel. The resulting flow regime is usually referred to as slug flow. At much higher gas fractions the two-phase flow generally assumes an annular configuration, with most of the liquid flow along the wall of the channel and the gas flowing in the central core.

3.1.2. Channel blocking

Channel blocking refers to filling of the channels with large gas slugs, which restrict the supply of reactants through the diffusion layer to the catalyst layer and hence lead to deterioration in the cell electrical

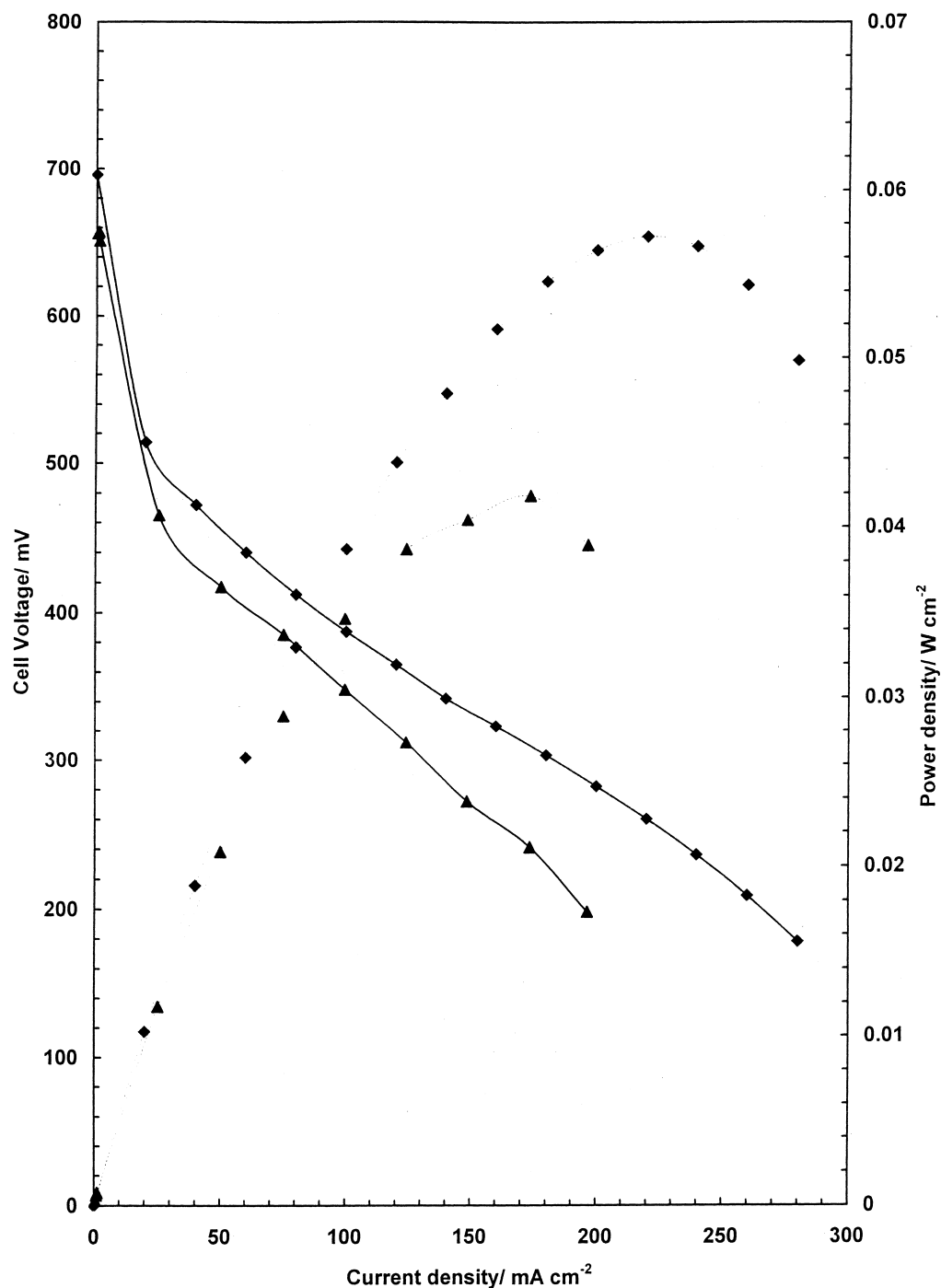


Fig. 6. Comparison of cell voltage and power density performance of a small scale and a large scale DMFC based on cell design (I). ◆, Small scale cell (9 cm²); ▲, large scale cell (226 cm²). 90°C cell temperature, air fed cathode at 2 bar pressure, 2.0 M methanol solution, Anode side inlet flow rate: small cell 1.0 ml min⁻¹, large cell 600 cm³ min⁻¹.

performance. Channel blocking is demonstrated in Fig. 5 and was characteristic of low flow rates and high current densities i.e. high gas content in the cell. It is a

crucial aspect of fuel cell operation, for efficient performance, that the channels are relatively clear of gas slugs and are fed continuously with fresh solution.

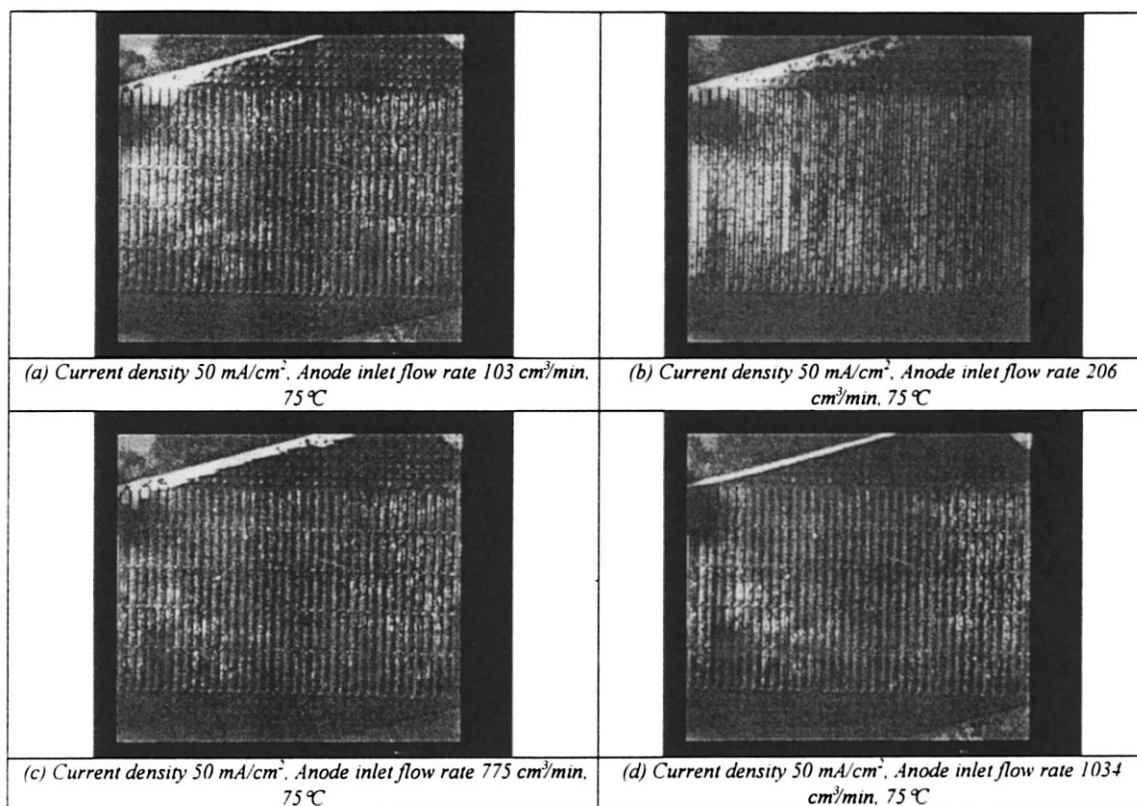


Fig. 7. Demonstration of cell design (II) gas removal characteristics. Current density 50 mA cm⁻², anode inlet flow rate 103–1034 cm³ min⁻¹, cell temperature 75°C, 2.0 M methanol solution.

This will secure that the anode side catalyst layer is adequately supplied with reactants and that the carbon dioxide gas is rapidly removed from the interior of the cell. Using a high liquid inlet flow rate is beneficial and effective in meeting all the above requirements. Cell design (I) used a manifold which consisted of a straight circular cross channel machined inside the main body of the acrylic block, with holes open, to the flow bed channels, on its periphery. In this design gas slugs can accumulate in the manifold and in the flow bed. Larger gas slugs formed in the flow bed have to be forced through a hole, achieved by either compressing the gas or by breaking the slug into smaller bubbles. Both of these mechanisms are enhanced by a higher liquid phase flow rate.

Fig. 4 shows the effect of current density between 10 to 670 mA cm⁻² on the gas patterns for a flow rate of 6 cm³ min⁻¹. It is evident that the amount of gas present in the flow bed rapidly increased with current density and that for the higher current densities some channels were blocked. Nevertheless, the bubble size, the presence of gas slugs and the channel blocking phenomenon were significantly reduced when higher liquid flow rates were used.

3.1.3. Cell voltage performance

It was anticipated that on scale-up of the DMFC the flow behaviour of the methanol solution and carbon dioxide would affect the power performance of the cell. Fig. 6 compares the cell voltage and power performance of two sizes of single cells (9 and 225 cm² cross sectional area) at identical liquid flow rates per channel. It is clear that there was a deterioration in performance on scale-up, e.g. there was an approximate 40 mV lower cell potential at a current density of 100 mA cm⁻² for the large cell and that the difference in cell voltage, at a fixed current density, increased as current density rises. In addition the cell voltage response of the large was not stable at the higher current densities and fluctuated continuously during the collection of the data. As the current density increased, and thus gas evolution also increased, it was apparent that the anode outlet manifold could not manage the relatively large volumes of gas produced and restricted the liquid flow. Presumably within the cell anode channels there were severe problems with gas flow and the formation of gas slugs under the conditions of operation used. Cell performance could not be maintained above 200 mA cm⁻².

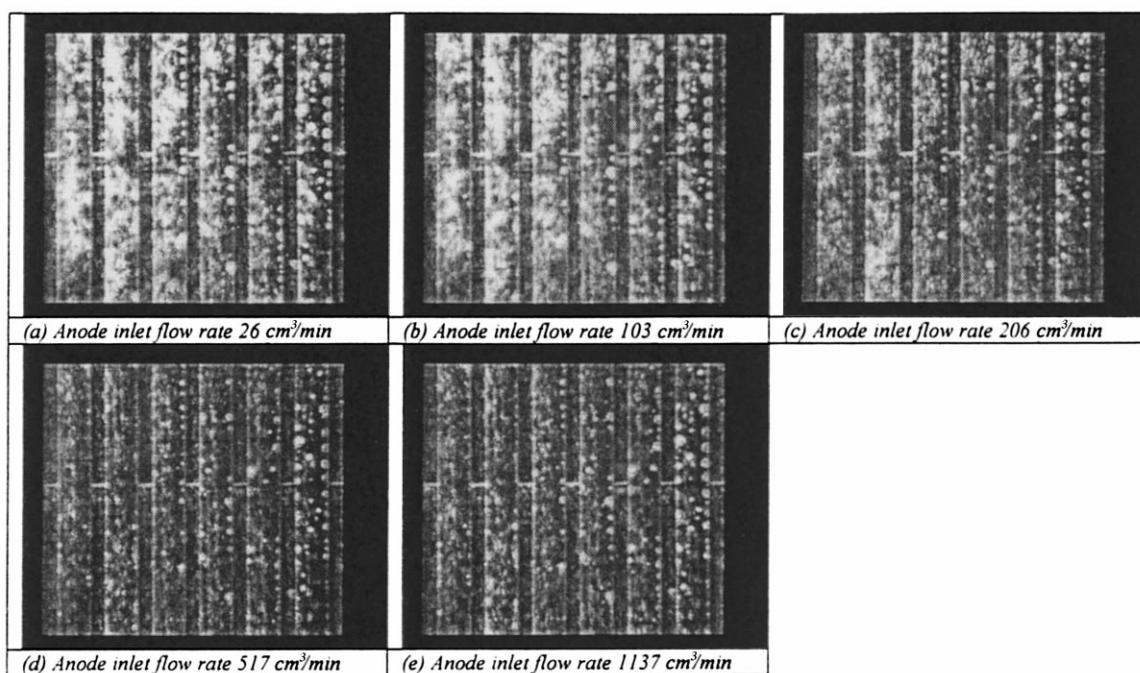


Fig. 8. Effect of inlet flow rate on the gas removal characteristics for cell design (II). Current density 50 mA cm^{-2} , Anode inlet flow rate $26 \text{ cm}^3 \text{ min}^{-1}$, cell temperature 75°C , 2.0 M methanol solution.

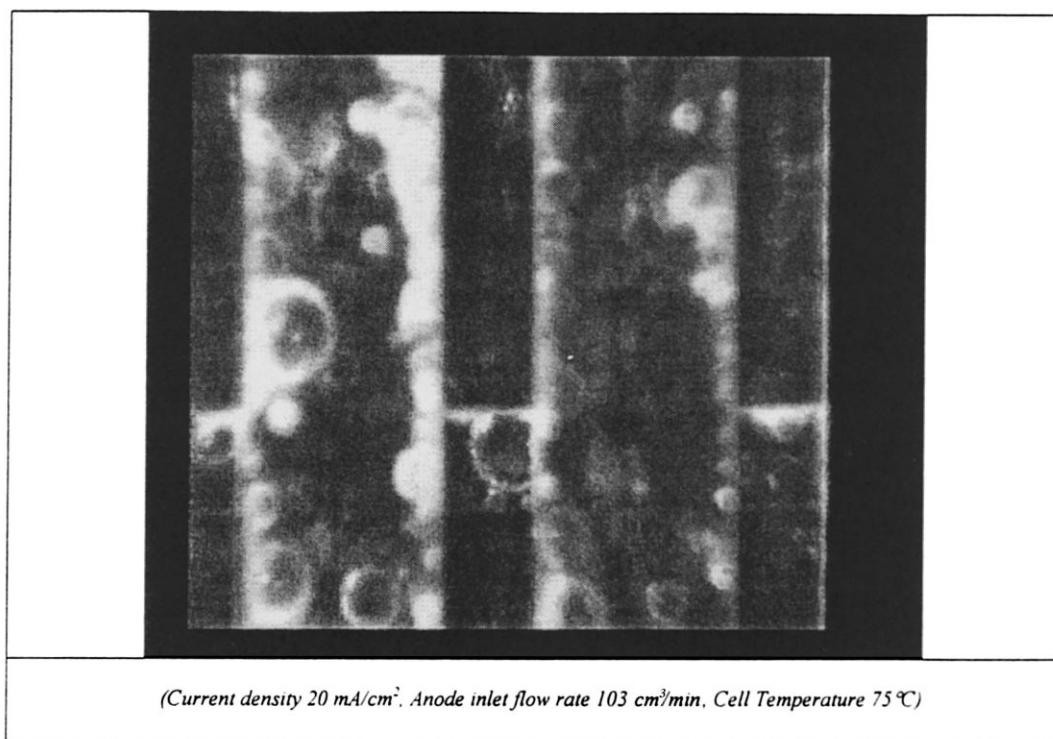


Fig. 9. Bubble formation under the cell flow bed ribs of the DMFC. Current density 20 mA cm^{-2} , anode inlet flow rate $103 \text{ cm}^3 \text{ min}^{-1}$, cell temperature 75°C , 2.0 M methanol solution.

3.2. Cell design (II)

Fig. 3 shows the typical single phase flow of liquid methanol solution in the channels of cell design (II). The flow is quite uniform, even at high flow rates (in excess of $2.0 \text{ dm}^3 \text{ min}^{-1}$). In the case of cell (II) the use of a triangular shaped outlet section resolved the gas bubble removal problem, from the flow bed to the manifold, encountered in cell design (I). As can be seen, in Fig. 7, at the top left corner of the cell gas was collected on the inclined edge of the section and formed a continuously moving gas stream. The structure of the triangular section (spots that support the MEA and leave a large void area) did not impose a significant barrier to movement of bubbles. As the flow rate increased the width of gas zone decreased and, at high flow rates, there was little gas accumulation.

The effect of the anode liquid phase inlet flow rate, in the range of 26 to $1137 \text{ cm}^3 \text{ min}^{-1}$, on bubble generation and flow was investigated (see Fig. 8), at 50 mA cm^{-2} and 75°C . The benefit of an increase in flow rate is apparent from the data, i.e. there was a reduction in bubble size and in bubble hold-up in the cell channels. Any gas slugs attached to the channel walls were also flushed out of the cell. In the case of cell (II) flow was typically in the bubble regime, if not for the whole cell at least for the lowest parts. Depending on the current density and the liquid-phase flow rate a transition from bubble flow regime to an intermediate region of mixed bubble and slug flow took place at some point in the flow bed. As a general rule the higher the liquid-phase flow rate the higher (vertical distance measured between the ports) the transition point was. Depending on the values of the two operating parameters there was always a limit above which there was no transition and the flow remains bubbly for the whole flow bed length.

A feature revealed in this study was bubble formation under the ribs which form the flow channels. Fig. 9 shows that bubbles were not only formed on the cloth surface, exposed to the flow bed channels, but also were formed under the ribs. This could explain the gas bubble accumulation along the side-walls of the channels. These bubbles emerge from the edge of the ribs into the channel main flow stream and would indicate that the anode area shielded by the ribs was active.

4. Conclusions

The present study showed that a well designed flow bed, based on a cross flow heat exchanger concept,

with a relatively large exit area is beneficial to gas management. In the ranges of parameters investigated in cell design (II) there was no evidence for the formation of gas slugs even at high current densities and at low flow rates; very small, rapid moving gas bubbles are formed. On the contrary in cell design (I), operated under similar conditions, there was always a tendency for gas slug formation or at least for bubbles to coalesce into larger ones that block the channels.

Overall the combination of improved flow bed design, uniform flow distribution and a successful selection of outlet port and exhaust manifold design led to the improvement in gas bubble flow characteristics in cell design (II). Increasing the liquid phase inlet flow rate is extremely beneficial for gas removal. Cell stack tests, with this flow bed design, are currently underway and will be reported subsequently.

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