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The effect of operating conditions on the dynamic response of the direct methanol fuel cell

P. Argyropoulos, K. Scott *, W.M. Taama

Chemical and Process Engineering Department, University of Newcastle upon Tyne, Merz Court, Newcastle upon Tyne, NE1 7RU, UK

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Abstract

A study of the effect of operating conditions; methanol solution concentration, methanol solution flow rate and air pressure on the voltage response of a small-scale direct methanol fuel cell (DMFC), under a range of variable current loads is reported. An object of this work is to investigate the transient response of the DMFC used for transportation applications. The dynamic performance of the DMFC is affected by complex interactions of electrode kinetics and mass transport processes. The cell responds rapidly, and reversibly, to changes in magnitude of load and rate of change of load. Variations in response are due to many phenomena, with methanol crossover from anode to cathode a significant factor. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Direct methanol fuel cell; Dynamic response; Transient behaviour; Operating conditions

1. Introduction

Investigations of the DMFC have mainly been at the steady state within laboratory environments. As the development work continues the engineering of the system becomes more important and issues such as long term stability, under static and dynamic loads, and response to dynamic operation become more important. Published literature generally refer to steady state systems in the form of polarisation curves or in the form of limited time-scale durability tests e.g. [1–27]. The dynamics aspects of the DMFC are usually considered indirectly by virtue of mechanistic and transport studies of electrode reactions using electroanalytical methods such as cyclic voltammetry, potential step and chronopotentiometry. Such procedures are well documented and the current or voltage response is well

known for many model reactions [28].

Published information on the transient response of the DMFC-including start up and shut down, and efficient transition between operating conditions is sparse [21]. Hence the dynamic response of cells remains mainly unknown. The lack of a systematic study on the dynamics of the DMFC has caused concern over the possible slow cell response, especially of the liquid feed cell, in comparison to its main competitor, the hydrogen based SPE fuel cell. This is largely due to the fact that hydrogen oxidation at the anode is very fast and mass transport processes are predominantly in the gaseous/vapour phase in the diffusion layers covering the catalyst layers. For methanol, six electrons must be exchanged for complete oxidation and consequently the oxidation kinetics, with current catalysts, are somewhat slower than that of hydrogen, as a result of intermediates formed during methanol oxidation. Oxidation of the intermediates to carbon dioxide requires the adsorption of an oxygen containing species (e.g. OH, H₂O) which does not occur substantially until potentials well above open circuit values.

* Corresponding author. Tel.: +44-191-222-8771; fax: +44-191-222-5292.

E-mail address: k.scott@ncl.ac.uk (K. Scott)

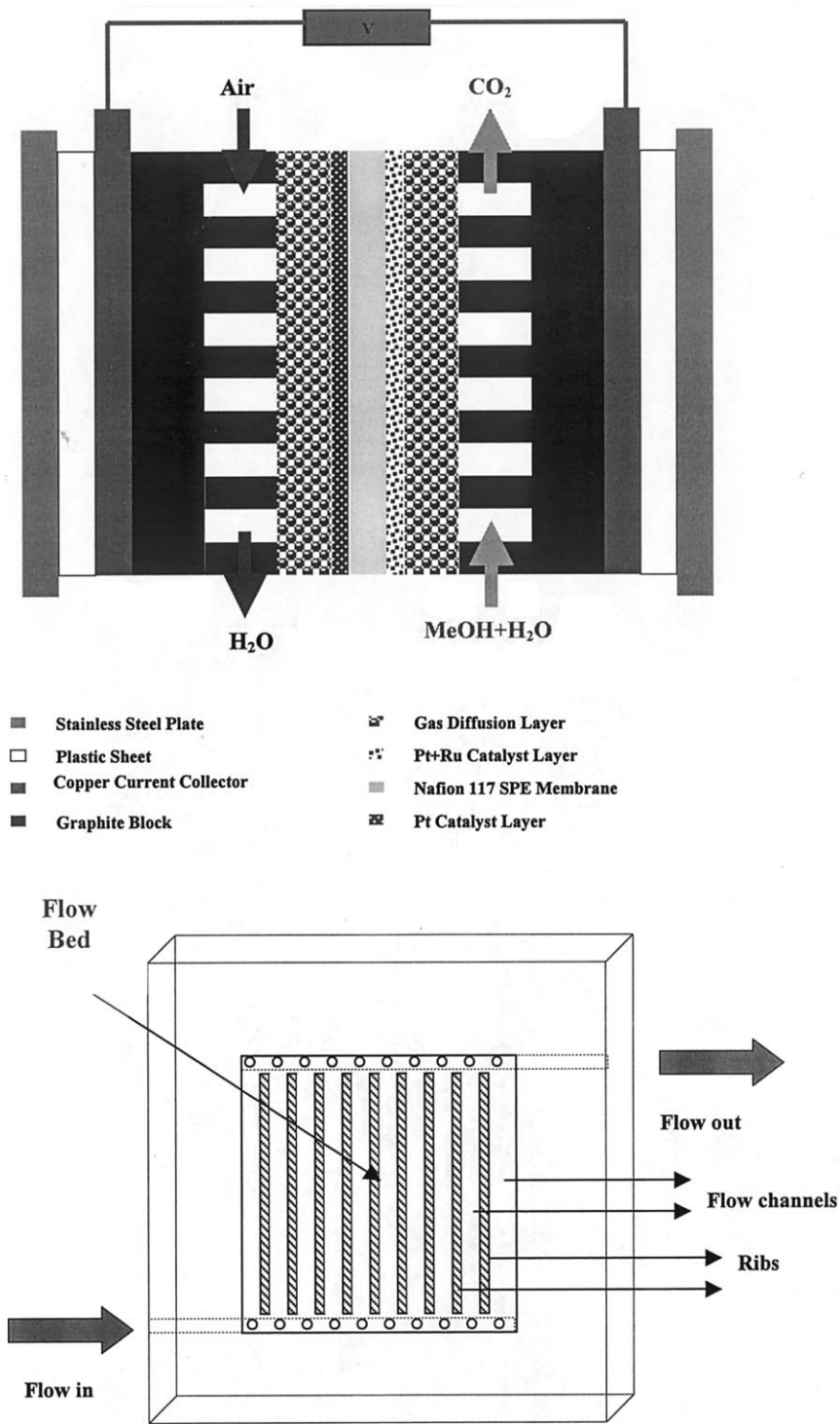


Fig. 1. Schematic representation of the DMFC used in this study.

In addition to the relatively slow anode kinetics there are other potential limitations, imposed from the system itself, which could potentially adversely effect the dynamic response of the liquid feed DMFC. In the anode side a mixture of aqueous methanol solution and carbon dioxide (the anodic reaction product) is flowing. Carbon dioxide compressibility effects, due to changes of system's pressure and fluid inertia, can potentially lower the system response under variable load conditions. Overall the dynamic response of the DMFC will depend on several factors, which are interactive:

- The electrochemical response of the anode and cathode reactions.
- The charging characteristics at the interfaces between the electrode, electrolyte and solid polymer membrane.
- The mass transfer characteristics of methanol to the catalyst sites through the diffusion layer and catalyst region.
- The mass transfer of methanol through the membrane, which influences the performance of the cathode due to a mixed potential.

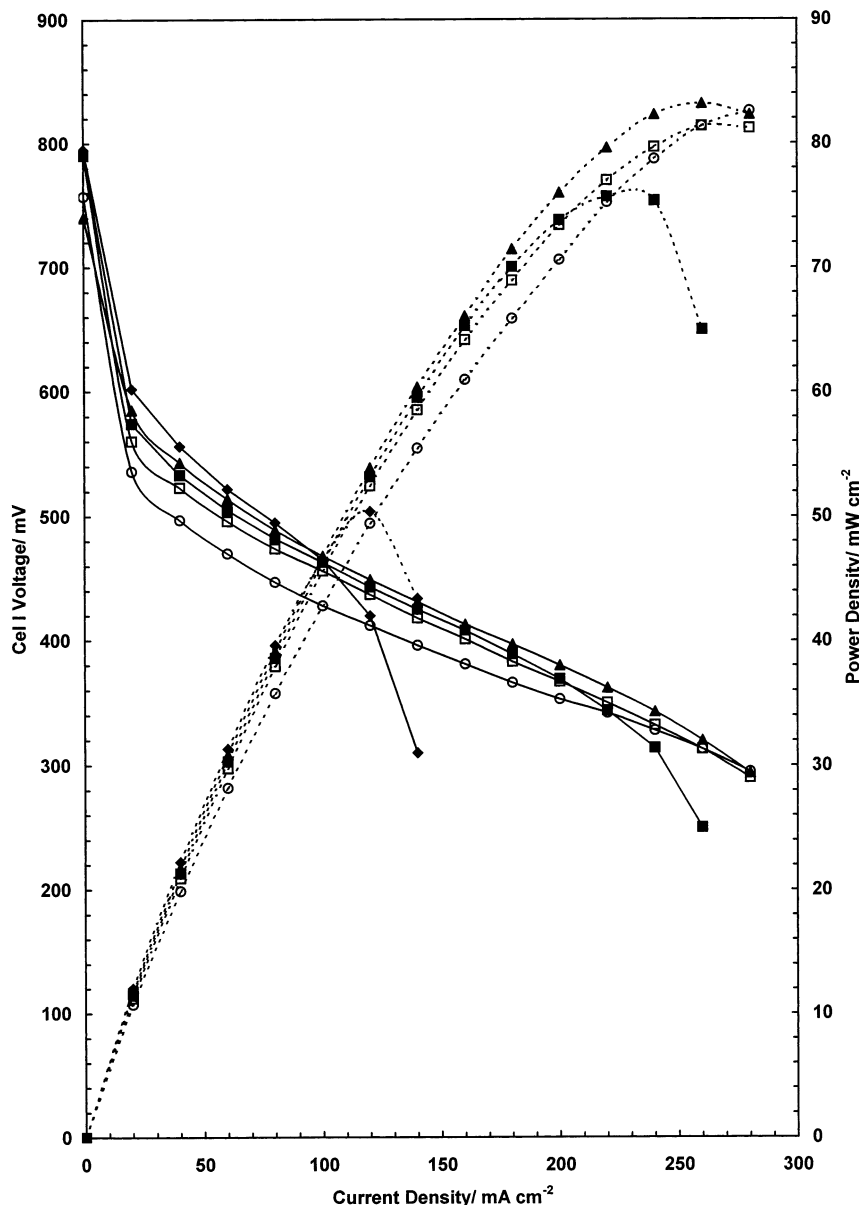


Fig. 2. The effect of methanol concentration on the DMFC cell polarisation. 85°C, 1.0 cm³ min⁻¹ methanol flow rate. ○: 2.5 M methanol. ◆: 0.5 M methanol. ■: 1.0 M methanol.

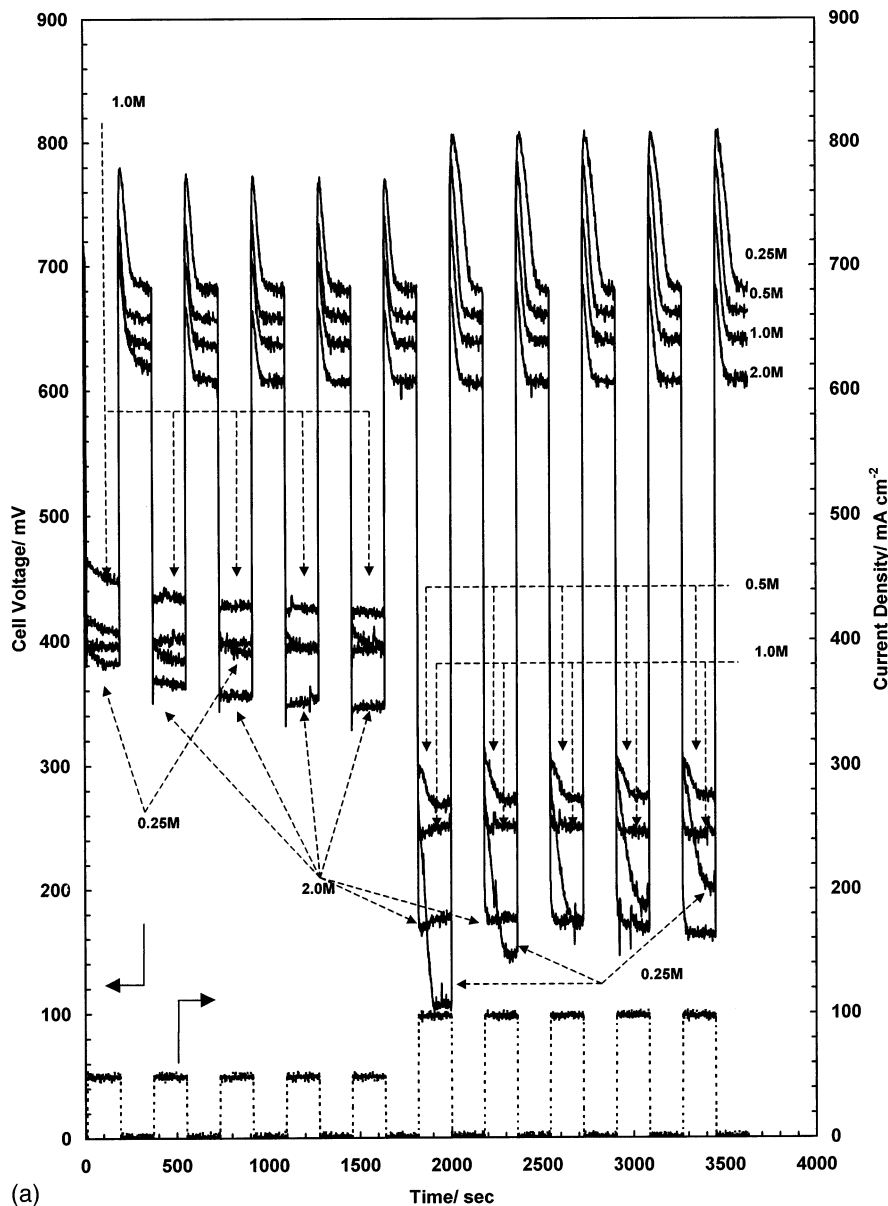


Fig. 3. The effect of anode side feed composition on the voltage response under constant pulsed load conditions up to a value of 100 mA cm^{-2} followed by a relaxation period of 180 s prior (methanol concentration shown on chart in mol dm^{-3} , $5.0 \text{ cm}^3 \text{ min}^{-1}$ methanol flow rate, 85°C cell temperature, air fed system at 2 bar cathode pressure).

- The mass transfer characteristics of oxygen to the cathode.
- The production and transport of water at the cathode electrocatalyst layers.
- The production of carbon dioxide and its release from the anode catalyst layer.
- The two-phase flow of methanol solution and carbon dioxide gas through the anode diffusion layers.
- The hydrodynamics of the two-phase flow of methanol solution and carbon dioxide gas in the

flow bed.

- The variation in heat release and temperature response of the cell, which will affect local reaction rates and also vapourisation (or condensation) of methanol between the liquid and gas phases.

In this paper we present a study of the effect of operating conditions on the voltage response of a small-scale DMFC, under a range of variable current loads. This work is part of a wider investigation, carried out in our laboratory, concerning the effect of operating,

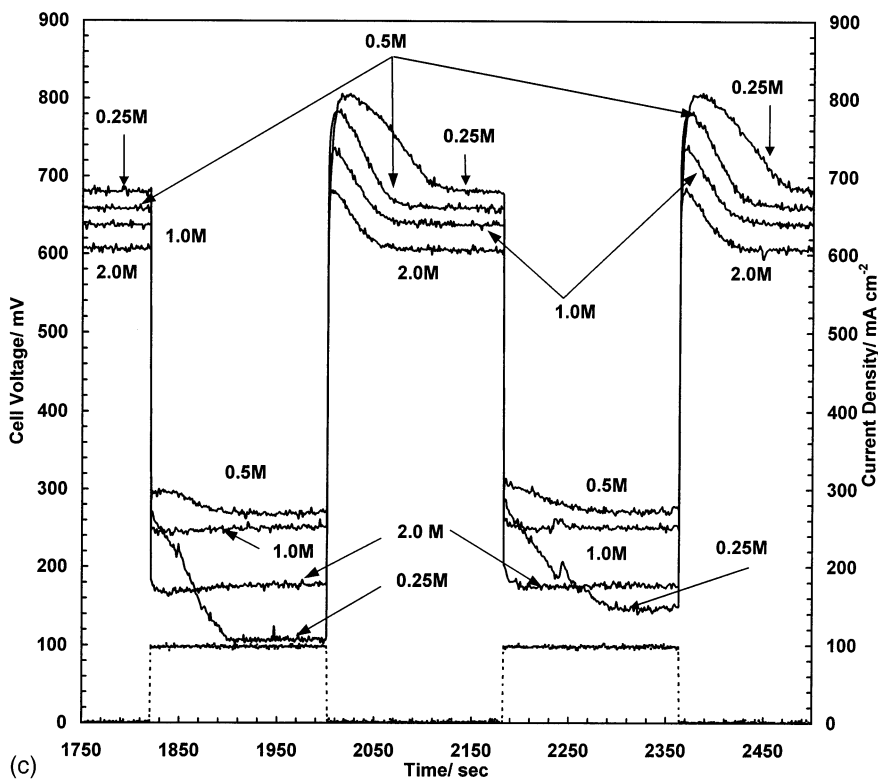
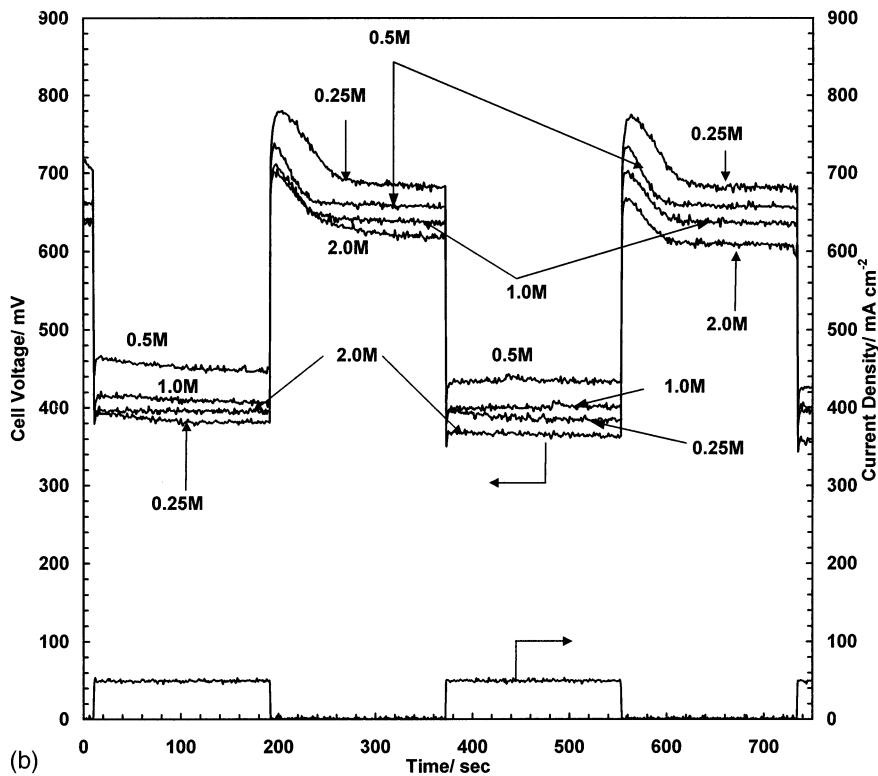


Fig. 3. (Continued)

loading and geometric parameters on DMFC single cells and stack dynamic response [29–32].

2. Experimental

Tests on the DMFC were performed in a cell, shown schematically in Fig. 1. The cell was fitted with one membrane electrode assembly (MEA), with an exposed cross-sectional area of the 9 cm^2 , sandwiched between two graphite blocks which have flow beds ($3 \times 3 \text{ cm}$), in the form of parallel channels, cut out for methanol and oxygen/air flow. Electrical heaters were placed behind each of the graphite blocks to heat the cell to the desired operating temperature. The graphite blocks were also provided with electrical contacts and small holes to accommodate thermocouples. The fuel cell was used in a simple flow rig, which consisted of a Watson Marlow peristaltic pump, to supply aqueous methanol solution, from a reservoir, via a Eurotherm temperature controller, to maintain the feed at a constant temperature. Air was supplied from cylinders, at ambient temperature, and the pressure controlled with regulating valves. All connections between the cells and equipment were with PTFE tubing, fittings and valves.

The cell used for the present study was based on a simple flow bed design (identical for both sides) which comprised ten parallel flow channels, 2 mm deep, 2 mm wide and 30 mm long (total geometrical active area of 9 cm^2) machined into a Poco[®] graphite block. The width of the ribs, which formed the flow channels, was 1 mm.

MEAs studied in this work were made in the following manner: the anode consisted of a Teflonised (20%) carbon cloth support (E-Tek, type 'A'), of 0.3 mm thickness, upon which was spread a thin (diffusion layer) layer of uncatylsed (ketjenblack 620) 10 wt% teflonised carbon, from Akzo Chemicals. The catalysed layer, consisted of 40 wt% Pt-20 wt% Ru (2 mg cm^{-2} total metal loading) dispersed on Vulcan XC72 supplied by E-TEK and bound with 10 wt% Nafion[®] from a solution of 5 wt.% Nafion[®] dissolved in a mixture of water and lower aliphatic alcohols (Aldrich). A thin layer of Nafion[®] was spread onto the surface of each electrode, by dipping in the Nafion solution. Electrode preparation are described in detail elsewhere [23]. The cathode was constructed using a similar method as for the anode, using a thin diffusion layer bound with 10 wt% PTFE, and 1 mg cm^{-2} Pt black on Vulcan XC-72, supplied by Johnson Matthey Technology Centre, with 10 wt% Nafion[®] in the catalyst layer. The electrodes were placed either side of a pre-treated Nafion[®] 117 membrane and the assembly was hot-pressed at 100 kg cm for 3 min at 135°C . The membrane pre-treatment involved boiling the membrane for 1 h in 5 vol% H_2O_2 and 1 h in 1 M H_2SO_4 before washing in boiling Millipore water ($> 18 \text{ m}^?$) for 2 h with regular changes of water.

The dynamic loads were provided with the aid of an in-house built computer controlled load unit. The load unit also acted as a data logger for cell voltage, applied load, and anode/cathode temperature responses. Various load cycles were used in this study, each trying to

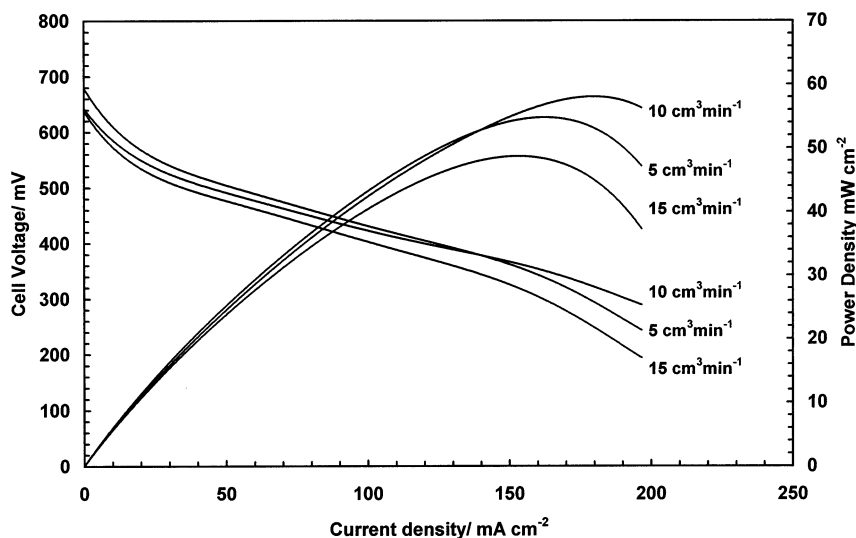


Fig. 4. The effect of methanol solution flow rate on cell voltage and power response methanol concentration 2.0 mol dm^{-3} , methanol flow rate shown in chart in $\text{cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at 2 bar cathode pressure).

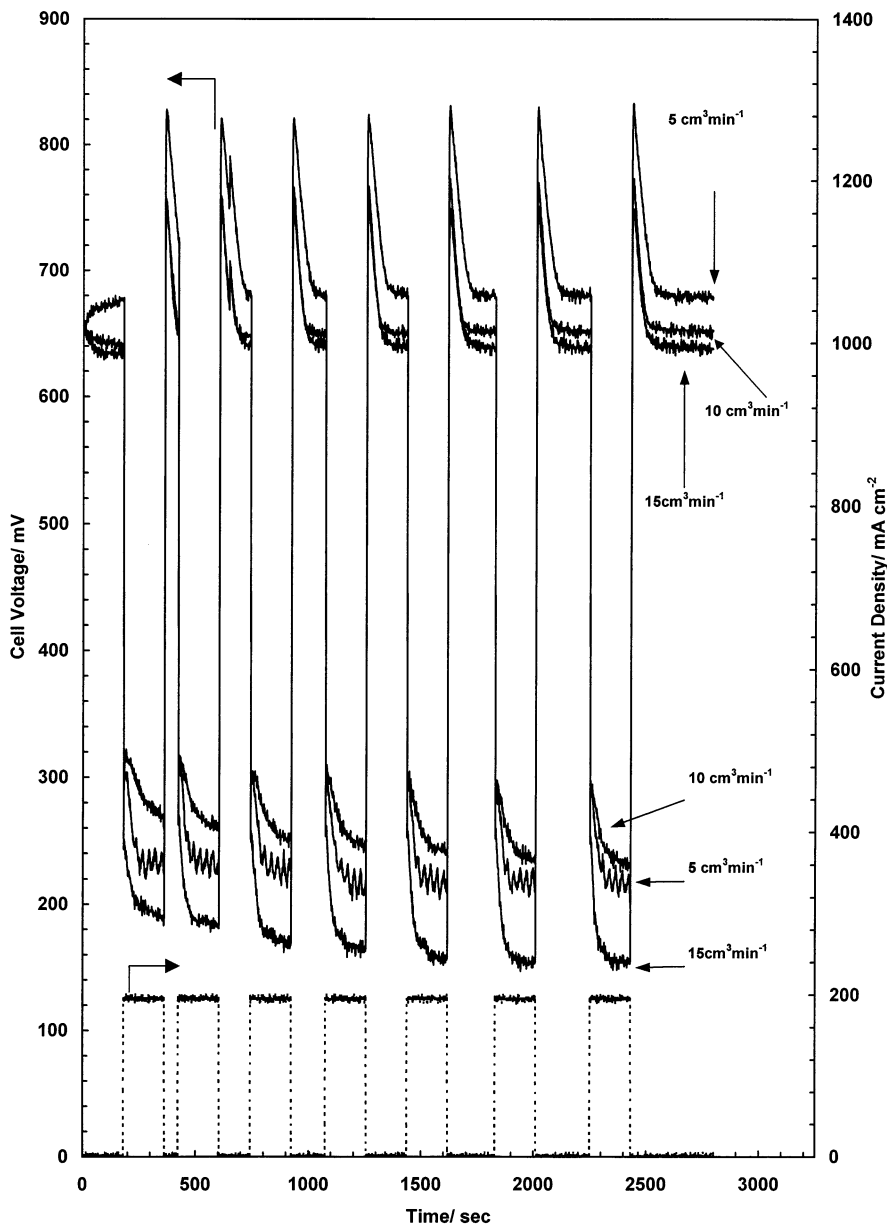


Fig. 5. The effect of anode side feed flow rate on the voltage response under constantly pulsed load conditions at 200 mA cm^{-2} followed by a 180 s relaxation period (Methanol concentration 2.0 mol dm^{-3} , Methanol flow rate shown in chart in $\text{cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at 2 bar cathode pressure).

simulate conditions of a vehicle driven in urban areas: gradual acceleration, deceleration, instantaneous loading with high power demands from zero load conditions, continuous progressive loading and unloading, and arbitrary load cycles. The tests were run several times, to ensure reproducibility, and, in addition, each loading condition was repeated several times inside a load cycle to assess the effect of loading history on cell response.

3. Results and discussion

Many of the factors which will affect overall cell dynamics are interactive and will depend on the degree of load change applied to the cell, the speed of load change and also the previous history of the load variation in the overall cycle imposed. Although the dynamic behaviour of single electrode reactions is well researched, complete cells involving three phases at both

electrodes and the transport of species in the respective phases present a much greater challenge to theoretical prediction.

We have conducted a preliminary study on the effect of varying loading patterns on the voltage response of a single small scale DMFC [33] under fixed operating cell regime. This investigation identified two critical parameters that affect the dynamic response of the cell: mass transfer rates of methanol in the MEA and gas management. These issues have already been raised in previous publications (see: [22,29–31]). A flow visualisation study [29] showed that the specific cell design suffers from gas management problems. Inefficient removal of the anodic reaction product (i.e. carbon dioxide) leads to deterioration of the cell's electrical performance due to inefficient reactants supply and blocking of the flow bed channels with gas slugs. This problem can be alleviated to a great extent with the adoption of higher flow rates and increased cathode side pressure. In addition, other studies conducted in our laboratory, concerning the mass transfer behaviour of the DMFC cell, showed that the aqueous methanol solution concentration is a critical factor that determines the cell's voltage output (see [30,31]). Hence these three parameters, methanol solution concentration, flow rate, and air pressure were selected to investigate the cell's dynamic response.

3.1. The effect of methanol solution concentration

The range of applicable methanol concentrations in the DMFC is currently dictated by the methanol permeability of the solid polymer electrolyte being used, e.g. Nafion® 117 (Du Pont de Nemours). The methanol transferred to the cathode (known as methanol crossover) is oxidised at the platinum electrocatalyst and causes a mixed potential, which lowers the cathode performance and thus the overall cell voltage output. According to Ravikumar and Shukla the upper limit of methanol concentration is 2.5 M, at which concentration a rapid deterioration in cell performance is seen [1,11]. At the lower methanol concentrations the limit to performance is associated with mass transport limitations of methanol at the anode. Although there is some variation in this behaviour in different research groups, Fig. 2 illustrates the typical variation of performance in the range of methanol concentration 0.5–2.5 M obtained with the MEAs used in this present study. The data shown in Fig. 2 is for a low flow rate of $1.0 \text{ cm}^3 \text{ min}^{-1}$ which, as we see later, leads to a better performance than at higher flow rates, because of the reduced level of cooling at the catalyst surface by the methanol solution, which is at a temperature lower than that of the cell.

Four different methanol solution concentrations were

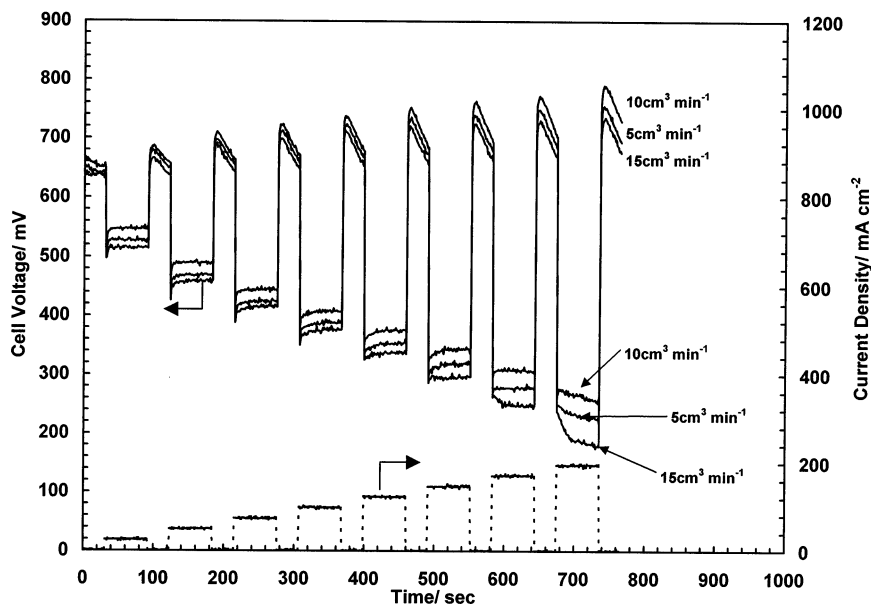


Fig. 6. The effect of anode side feed flow rate on the voltage response under constantly pulsed load conditions up to a value of 200 mA cm^{-2} followed by a relaxation period of 30 s prior the application of the next pulse. Methanol concentration 2.0 mol dm^{-3} , Methanol flow rate shown in chart in $\text{cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at 2 bar cathode pressure.

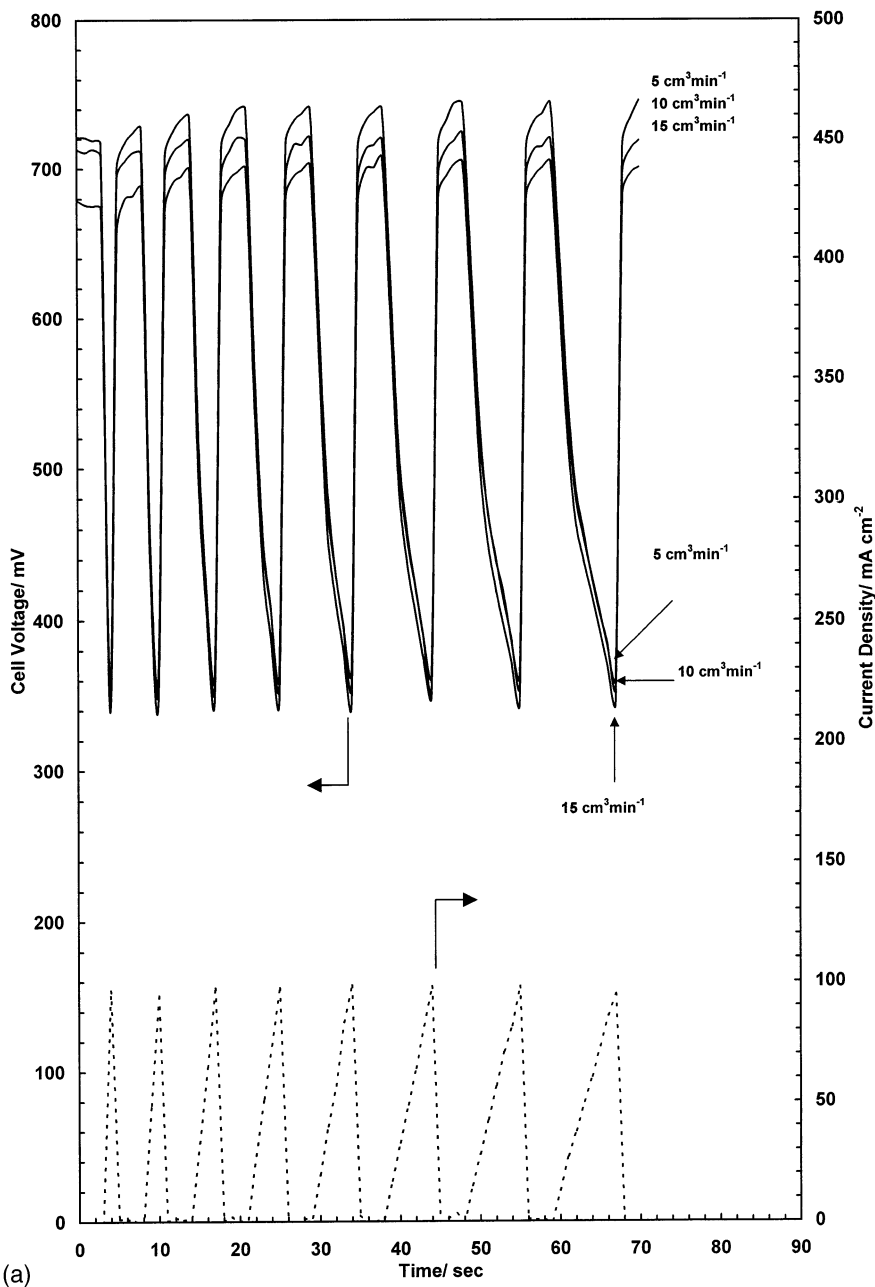


Fig. 7. The effect of methanol solution flow rate under a range of variable load conditions. (a) The effect of anode side feed flow rate on the cell voltage response under increasing loading up to a value of 100 mA cm^{-2} followed by a sudden cell unloading and a relaxation period of 30 s prior reloading (methanol concentration 2.0 mol dm^{-3} , methanol flow rate shown in chart in $\text{cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at 2 bar cathode pressure). (b) The effect of anode side feed flow rate on the cell voltage for instantaneous application of a specific load up to a value of 200 mA cm^{-2} followed by a constant loading period of 30 s and gradual cell unloading to zero load.

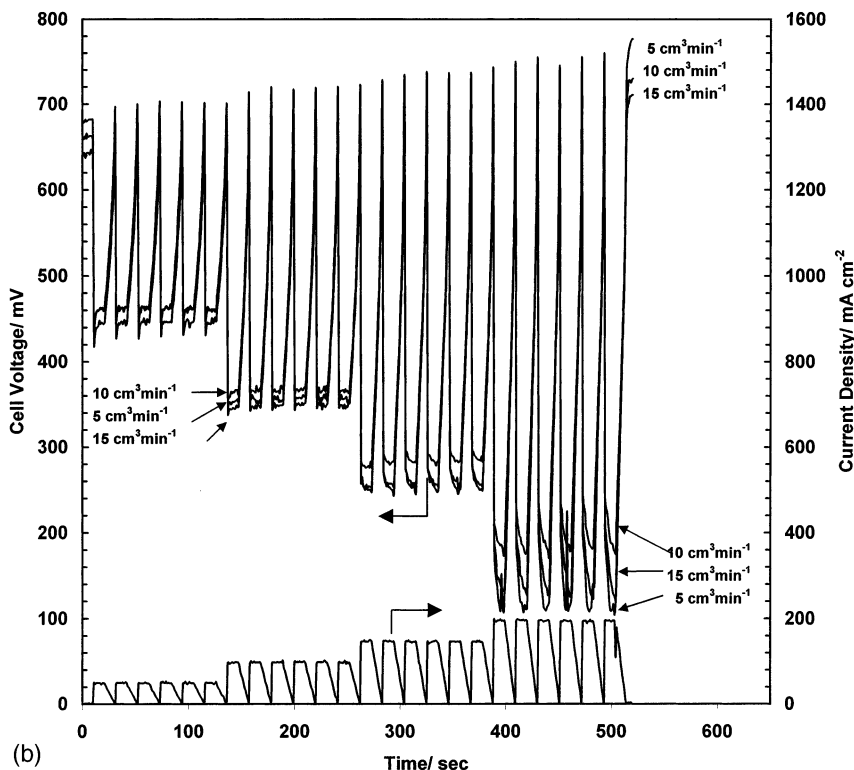


Fig. 7. (Continued)

examined: (0.25, 0.5, 1.0 and 2.0 M) under a pulse type load cycle in this work (see Fig. 3a–c). A first important point is that the cell open circuit voltage is higher at lower methanol concentrations as a result of reduced methanol crossover by diffusion. Two distinct regions were investigated: pulses at 50 and 100 mA cm⁻². The problem with the lower methanol concentrations is that they cannot sustain operation with high current densities due to initiation of limiting current operation. Hence the current density of 50 mA cm⁻² was chosen as one that can be potentially sustained at all concentration used.

The data of Fig. 3 shows that, depending on the applied load and the methanol concentration, we have a different type of response. The 2.0 M solution gives a fast and stable response for both current loads, reaching a steady state at approximately ten seconds after the pulsed load is applied, but with the penalty of lower voltage. Removal of the load caused a rapid return to open circuit voltage which is higher than the initial starting condition, but which then proceeds to fall to a constant value after approximately fifty seconds. The 0.25 M solution gave a much slower response and can hardly sustain satisfactory operation above 100 mA cm⁻². The 0.5 M solution gives the best voltage output

but the response time deteriorates with the increase in the current density load from 50 to 100 mA cm⁻². Overall in terms of electrical performance and response time, to a step change in the cell load, around 1.0 M is the best compromise between electrical performance and reduced methanol crossover [11,14] at steady state conditions.

It is noticeable in the data that application of an increased load increases the open circuit voltage. Here methanol crossover is initially reduced as the anode side concentration is lower with the application of load. Hence on returning to open circuit the impact of crossover on the cathode potential is reduced, until the anode side concentration is re-established. This behaviour is better illustrated in the Fig. 3b and c, which are exploded views of the dynamic response given in Fig. 3a. The time scales of this mass transport in the membrane and diffusion layers are tens of seconds and are consistent with measured mass transfer coefficients for the DMFC.

A further comment should be made about the performance at the lower concentration used, namely 0.25 M. As can be seen with the continuous application of a 100 mA cm⁻² pulse the cell's performance constantly improves (e.g. the cell voltage is almost doubled from ap-

proximately 100–200 mV at the end of each pulse). This is a further illustration of the mass transfer characteristics of the cell discussed above. The dynamic state of operation has apparent benefits in reducing the effect of methanol crossover on DMFC performance.

3.2. The effect of anode side flow rate

The anode side liquid flow rate affects the cell response as can be seen from typical cell polarisation curves in Fig. 4 for a 2.0 M methanol solution. In the operating region with current densities of up to 150 mA cm^{-2} , the lower flow rate ($5 \text{ cm}^3 \text{ min}^{-1}$) gives the better performance. This feature may be due to several factors. The methanol feed is introduced at a lower temperature to that of the cell, as would be adopted in practical operating DMFCs in vehicular applications, and that at the lower flow rate the temperature of the fluid at the catalyst surface is higher due to localised

heat generation. As we move towards the limiting current operating region then the medium flow rate ($10 \text{ cm}^3 \text{ min}^{-1}$) gives enhanced performance. At the higher flow rate ($15 \text{ cm}^3 \text{ min}^{-1}$) the localised cooling is greater and can cause a significant fall off in performance, as observed experimentally. In addition the higher flow rate may increase methanol transport to the catalyst sites and the membrane which may result in an increase in methanol crossover.

Fig. 5 shows the effect of methanol solution flow rate on the cell response (2.0 M methanol, 85°C) after repeated application of high current pulses (200 mA cm^{-2}). In Fig. 5, we see that the intermediate flow rate gives the better response (higher voltage) under dynamic loaded operation and the higher flow rate the poorest performance. This is in agreement with the steady state performance data (Fig. 4) at the same current density. The lower flow rate results in electrically unstable response from the cell (the middle line in

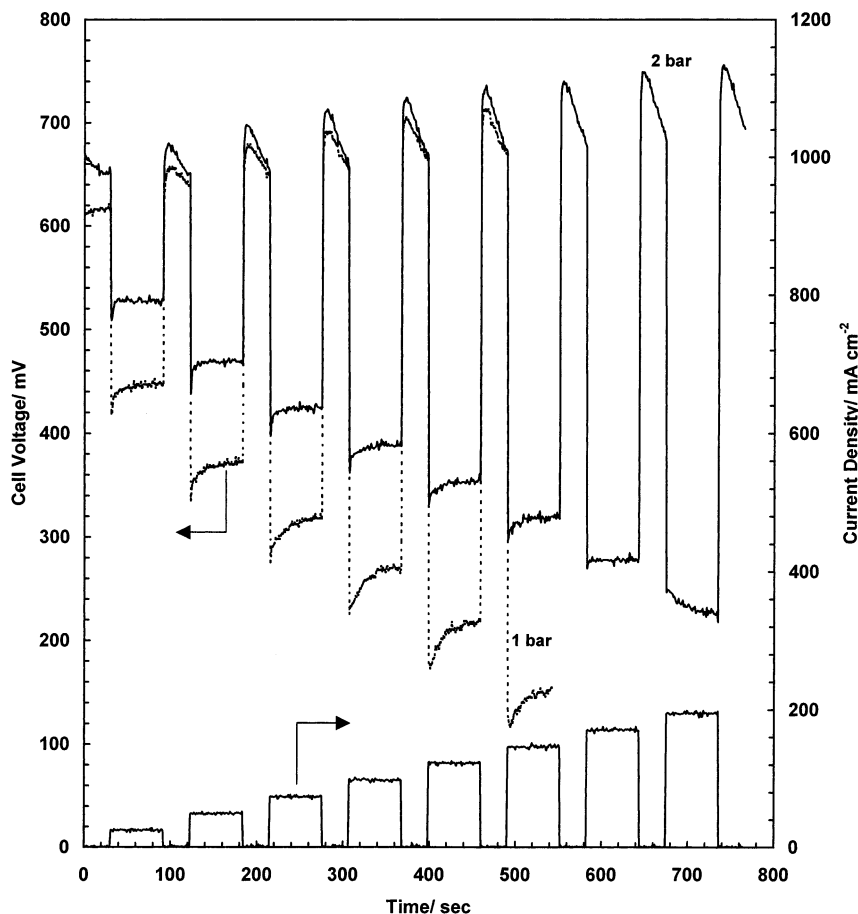


Fig. 8. The effect of cathode side pressure on cell voltage response under constantly pulsed load conditions, up to a value of 200 mA cm^{-2} , followed by a relaxation period of 30 s prior to the application of the next pulse (methanol concentration 2.0 mol dm^{-3} , methanol flow $5 \text{ cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at cathode pressure in bars shown in chart).

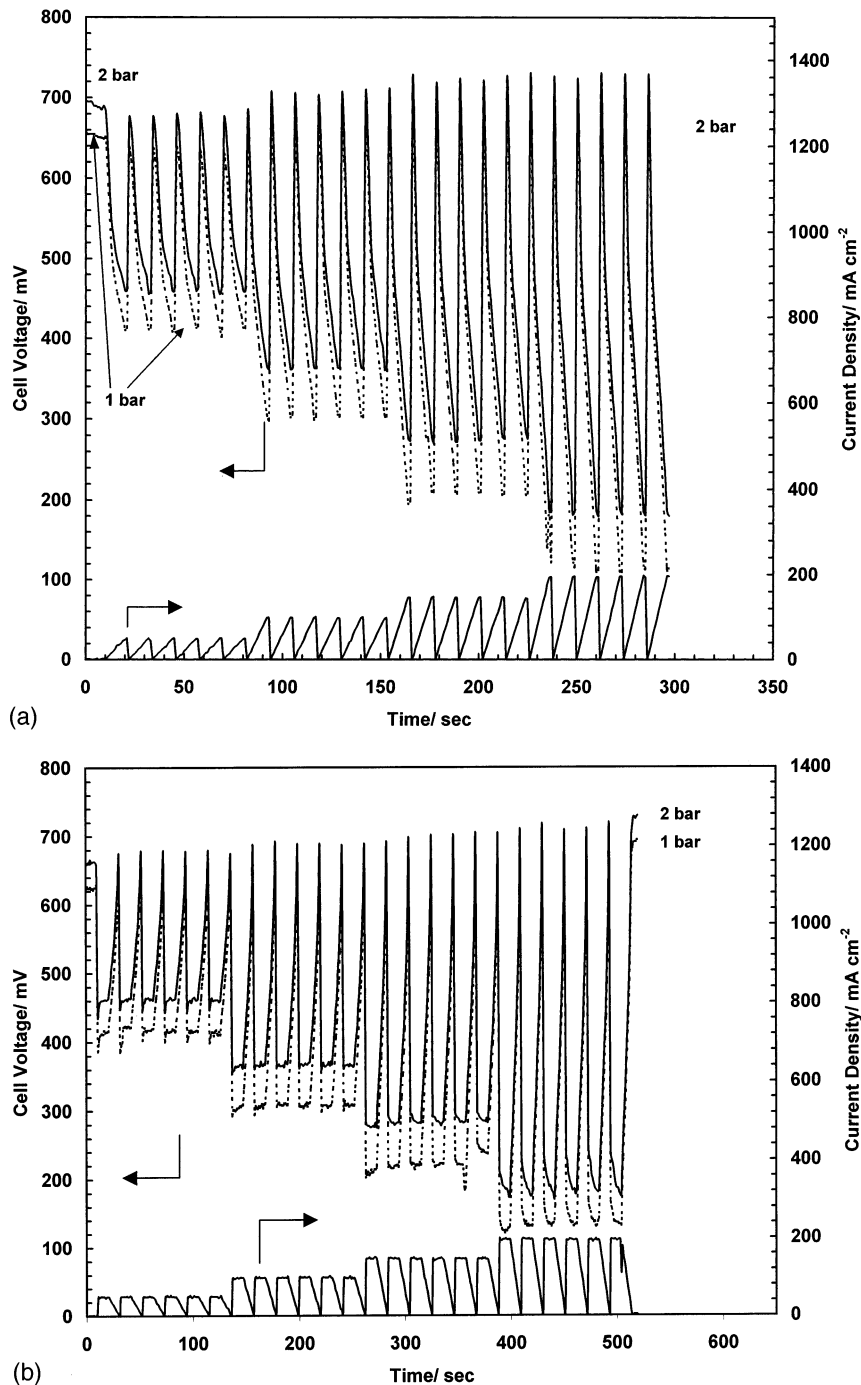


Fig. 9. The effect of cathode side pressure on the cell voltage response under a range of variable load conditions (methanol concentration 2.0 mol dm^{-3} , methanol flow $5 \text{ cm}^3 \text{ min}^{-1}$, 85°C cell temperature, air fed system at cathode pressure in bars shown in chart). (a) The effect of cathode side pressure on cell voltage response under gradually increasing load up to a value of 200 mA cm^{-2} followed by a sudden cell unloading to zero load conditions and immediate reload. (b) The effect of cathode side pressure on the cell voltage for instantaneous application of a specific load up to a value of 200 mA cm^{-2} followed by a constant loading period of 30 s and gradual cell unloading to zero load. (c) The effect of cathode side pressure on the cell voltage response under continuously varying loading up to a value of 200 mA cm^{-2} followed by a gradual cell unloading with the same pattern. (d) The effect of cathode side pressure on the cell voltage response under increasing loading up to a value of 100 mA cm^{-2} followed by a sudden cell unloading and a relaxation period of 30 s prior to reloading.

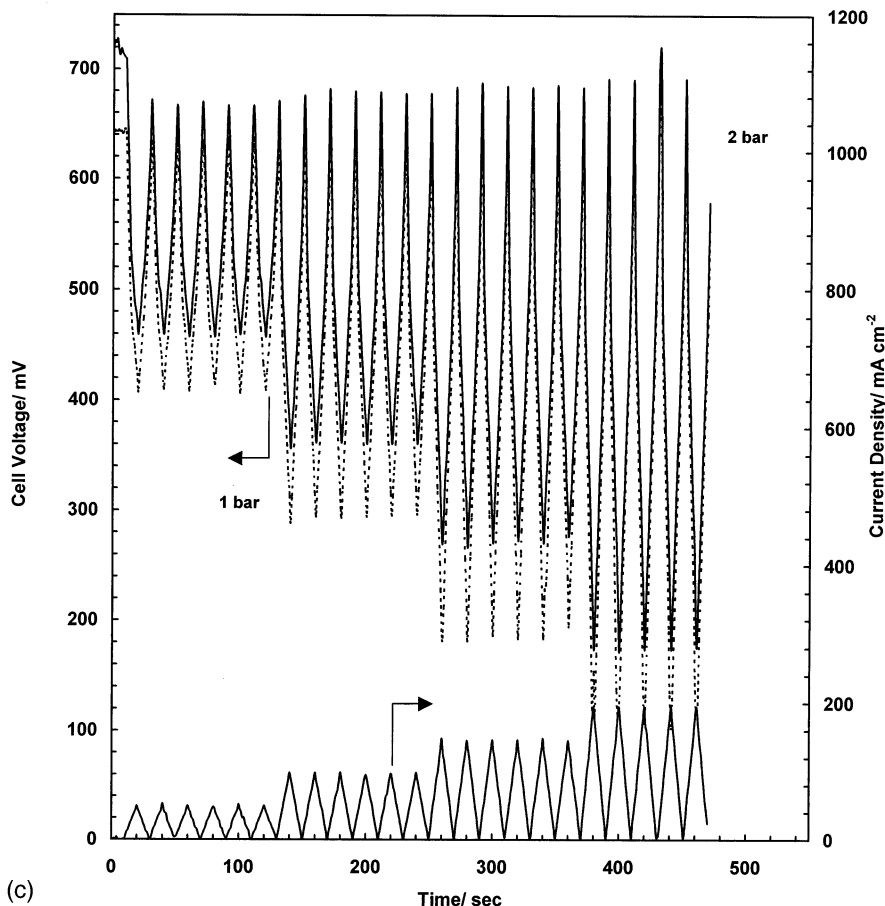


Fig. 9. (Continued)

the graph with the oscillatory behaviour). This response may be attributed to gas management problems in the anode side of the cell. Recently published flow visualisation studies, conducted in an identical cell, revealed that the application of high current densities coupled with low liquid flow rates results in a flow bed mainly occupied by trapped gas bubbles [29]. This gas apparently hinders the supply of reactants to the active electrocatalyst sites and the removal of the reaction product (namely carbon dioxide). An additional cause of the unstable cyclic nature can be attributed to the observed periodic ‘flashing’ of gas through the outlet manifold. The faster approach to steady state conditions at the higher flow rate ($15 \text{ cm}^3 \text{ min}^{-1}$) can be attributed to the enhanced gas removal. A recent modelling study revealed that the anode side flow rate also affects the amount of aqueous feed being vaporised [34]. The lower the flow rate the higher the amount of feed vaporised and the larger the volume that a two-phase methanol and water vapour mixture exists. The

electrodes currently used for DMFC were originally designed for vapour fed systems. Hence they are less efficient for a liquid fed system than a vapour fed system. If a vapour phase is formed mass transport through the gas diffusion electrode can be more efficient, resulting in an electrical performance improvement.

Fig. 6 shows the cell response, for a methanol concentration of 2.0 M and temperature of 85°C , for continuously increasing load pulses, up to a value of 200 mA cm^{-2} . The relaxation time (i.e. the time that the cell is kept unloaded between two successive pulses) is reduced to 30 s in comparison with that in Fig. 5, which is 180 s. In this case the intermediate flow rate again gives the better cell output voltage. This is in accord with the steady state performance shown in Fig. 4. The dynamic response of the cell under load is noticeably different at the lower current densities than at higher current densities. The difference in voltage over the range of flow rates increases as the magnitude

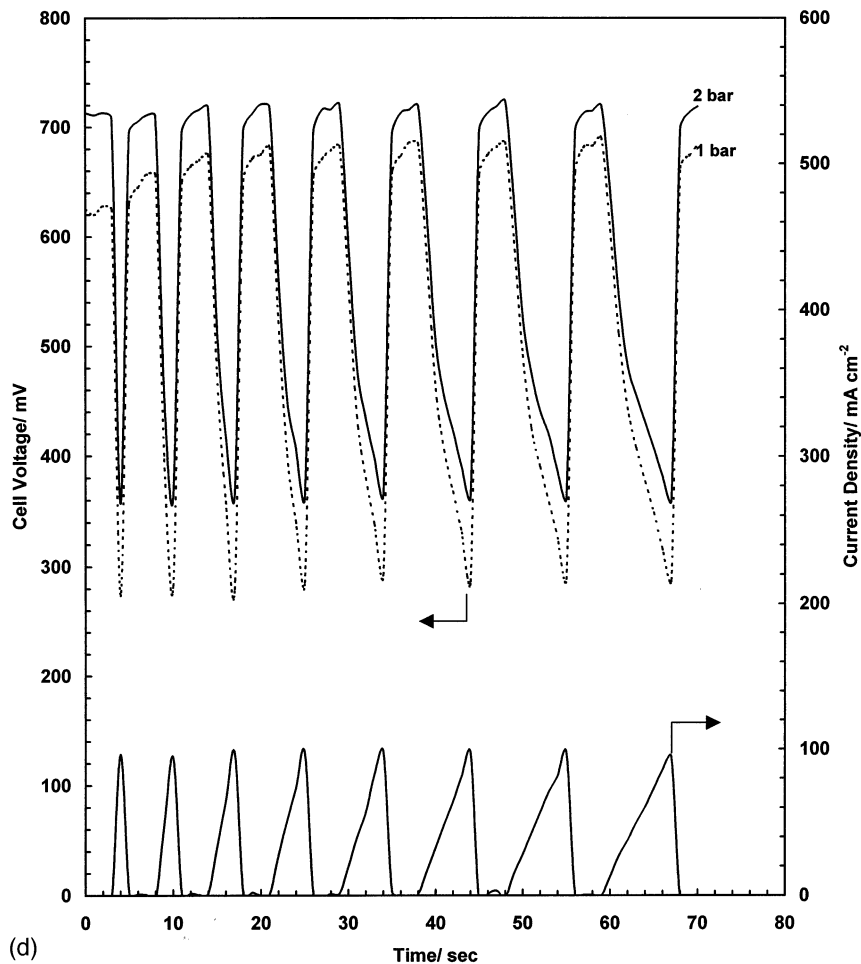


Fig. 9. (Continued)

of the current load increases. A major difference in the responses shown in 5 and 6 is that in the latter the open circuit potentials have not reached a steady state. Indeed the pulsing behaviour causes a continuous increase in the values of open circuit voltage and influences the overall dynamic behaviour of the DMFC.

We have investigated the effect of flow rate on the voltage response under a range of varying loading cycles, which are designed to simulate driving conditions: vehicle acceleration, deceleration, start of movement, repeated start of movement, sudden load changes etc. Fig. 7 shows a sample of the response of the cell to different load domains. Generally the lower flow rate gives the highest voltage response but the stability of the response and the response time is lengthened with increasing applied current densities where the higher flow rate gives a more stable and fast response.

In the case of a repeated application of a rapid

increase in load to a maximum value followed by a sudden removal of the load (Fig. 7a) the response under load is similar at the three flow rates considered. The intermediate flow rate ($10 \text{ cm}^3 \text{ min}^{-1}$) gives a slightly higher potential, by approximately 5–10 mV at the peak load, than the lowest flow rate. The difference in voltage is a real change in response of the electrode to a variation in flow rate and is not experimental error. The repeated application of a sudden load followed by a period of constant load and a gradual reduction in load (Fig. 7b) produces a similar response to that seen in Fig. 6. At peak load the lowest flow rate gives the highest cell voltage and the difference in voltage at the low and high flow rates increases as the magnitude of the peak load increases, i.e. approximately $65 \text{ mV at } 200 \text{ mA cm}^{-2}$.

Overall it can be said that the flow rate does not affect significantly the cell dynamic response in the case of low to mid current densities and when changes in cell

loading condition are gradual. On the contrary when the cell is operated at high current densities and when sudden steep changes in the cell loading condition take place the cell response time is significantly affected by the flow rate.

3.3. The effect of cathode side pressure

Fig. 8 shows the effect of cathode side pressure on the dynamic response of the cell. The cathode pressure seems to have a positive effect on the cell response to variable load conditions. As can be seen from Fig. 8, the cell shows a faster, and more stable, response when operated with high pressures. With the load cycle used here there is approximately an 80 mV lower performance under load at the lower air pressure. This is an issue that is discussed by other workers in the area, i.e. that despite the steady state electrical performance of a DMFC not being affected dramatically by operation with reduced cathode pressure, the cell response time increases significantly at the lower pressure. A contributing factor to this behaviour will be the effect of higher cathode pressure reducing the crossover of methanol to the cathode [2]. It is also noticeable that the repeated application of increasing load causes an increase in the cell voltage, by approximately 100 mV, at intermediate open circuit conditions.

Fig. 9 shows the effect of cathode pressure on the dynamic response under a range of different loading cycles as used for the data presented in Fig. 7. Under all conditions the best performance is achieved at the higher cathode air pressure. The effect of cathode pressure is less significant for low to medium current densities and for gradual changes in the loading conditions. The repeated application of an increasing load serves to increase the open circuit voltage after the cell has been unloaded (Fig. 9a–c), as already shown in the data of Fig. 8. A more gradual increase in load (Fig. 9d) enables the cell to respond better, in terms of a slower reduction in the voltage as the load is applied.

4. Conclusions

This study has shown that the dynamic response of the DMFC cell voltage is significantly affected by the methanol solution flow rate, methanol concentration and applied cathode air pressure. The cell responds rapidly, and reversibly, to changes in magnitude in load and rate of change of load. Variations in response are due to many phenomena, but methanol crossover from

anode to cathode is a significant factor. Dynamic operation perturbs the methanol crossover rate from steady state conditions which will affect the electrode reactions and associated mass transport processes and also the thermal behaviour. In addition, in practical DMFC operation, the input of methanol solution at a temperature below that of the cell will cause dynamic interactions between the operating temperature at the actual electrocatalyst region and methanol flow rate.

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