

# Dynamic response of the direct methanol fuel cell under variable load conditions

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## Abstract

The transient response of the direct methanol fuel cell (DMFC) is of paramount importance when it is used for transportation applications. With the aid of a computer-controlled load unit we have applied a variety of loading cycles on a small-scale single DMFC in order to evaluate the effect of the loading pattern and operating conditions on the cell's response time and performance. The cell responds rapidly, and reversibly, to changes in magnitude and rate of change of load. Under dynamic operation the cell voltage response can be significantly better than that achieved under steady state operation. Open circuit potentials are also increased, by up to 100 mV, by imposing a dynamic loading strategy. This improvement, accredited, in part, to a reduction in the effect of methanol crossover, is potentially attractive in vehicle applications where higher power density and fuel efficiency can be realised. © 2000 Elsevier Science S.A. All rights reserved.

*Keywords:* Direct methanol fuel cell; Dynamic response; Transient behaviour

## 1. Introduction

The main research of direct methanol fuel cells (DMFCs) based on solid polymer electrolyte (SPE) has been in steady-state and small-scale operation within laboratory environments. As the development work continues the engineering of the system have been mainly neglected since the commercialisation of the relative technology is still far away (expected at 2008). Published literature mainly refers to steady-state systems either in the form of galvanostatic polarisation curves or in the form of durability tests [1–29].

Little published information exists on transient operation — including start up and shut down, and efficient transition between operating conditions — and hence the dynamic response of the cells is mainly unknown. A brief report of some dynamic behaviour of a small DMFC stack is reported with a current pulse applied [21]. Some obser-

vations on dynamics are made in a number of the aforementioned publications concerning mainly the duration of experiments carried out on working cells. The lack of a systematic study on the dynamic response of the DMFC cells has caused concern over the alleged reputation of slow cell response of the DMFC in comparison to its main competitor, namely the hydrogen-based SPE fuel cell.

A current advantage of the hydrogen cell, over the DMFC, is that hydrogen oxidation is very fast and consequently the performance of the hydrogen cell is better than that of the methanol cell. For the electrochemical oxidation of methanol, six electrons must be exchanged for complete oxidation of methanol and consequently the related kinetics are inherently slower, as a result of intermediates formed during methanol oxidation [30]. Oxidation of the intermediates to carbon dioxide requires the adsorption of an oxygen-containing species (e.g., OH, H<sub>2</sub>O). Adsorption of these species does not occur substantially until potentials well above open circuit values.

Additional limitations are imposed from the system itself, in terms of fluid dynamics, as the anode side is a mixture of aqueous methanol solution and carbon dioxide

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(the anodic reaction product). Carbon dioxide compressibility effects, due to changes of system's pressure and fluid inertia can potentially lower the system response under variable load conditions. At the current state of technology cells are mainly being operated at temperatures (typically above 80°C), which are close, or above the solution boiling point (near or above 85°C depending on local pressure and local mixture composition). Boiling initiation can affect to a large extent the cell performance since vaporised feed can easily penetrate through the gas diffusion electrode towards the anode catalyst layer and increase cell performance by reducing the mass transfer limitations at the anode side of the cell [24,31–33]. Heat transfer between the liquid feed and the cell body is also affected by boiling initiation since boiling heat transfer is more intense than convection. Both processes are strongly dependent on the amount of carbon dioxide available locally, which when the cell is operated under variable current loading conditions can alter significantly the cell physiology and its power output.

In this paper we report the effect of applying varying loads on a small-scale (9 cm<sup>2</sup> active area) DMFC cell. This work is part of a wide-ranging investigation carried out in our laboratory concerning the effect of operating, loading and geometric parameters on direct methanol single cell and stacks dynamic response. Initially the work has been carried out in a small-scale cell, which is a relatively well-characterised system [16,24,25,31,32,34–37]. In general the field of DMFC dynamic operation is of paramount importance for the system engineering and should be taken under consideration in the design of prototype systems. The present study is focused on identifying the effect of applying specific load patterns on a small cell, and assesses the effect of load pattern and previous loading history on the cell electrical output. Various load cycles were used in this study, each trying to simulate conditions of, for example, 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.

## 2. Experimental

Tests on the DMFC were performed with a cell with a cross-sectional area of 9 cm<sup>2</sup> (see Fig. 1). The cell was fitted with one membrane electrode assembly (MEA) sandwiched between two graphite blocks which had a flow bed, in the form of parallel channels, cut out for methanol and oxygen/air flow. The cell was held together with two plastic insulation sheets and two stainless steel or aluminium backing plates using a set of retaining bolts positioned around the periphery of the cell. Electrical heaters,

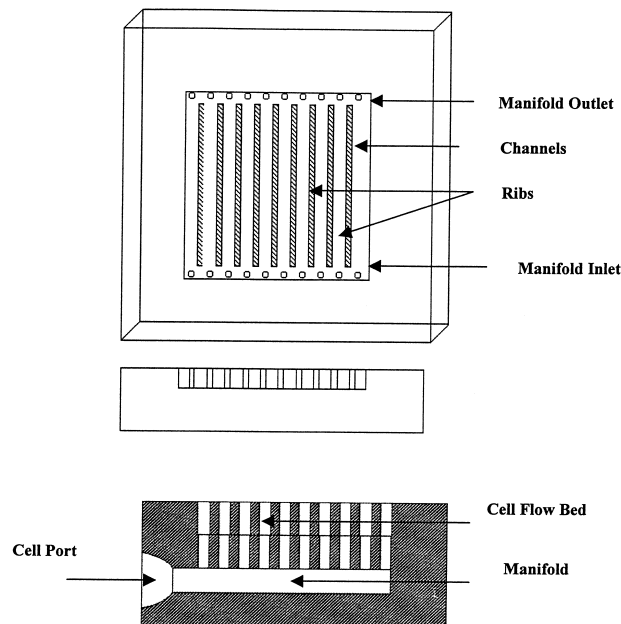


Fig. 1. Schematic representation of the small-scale DMFC used in this study.

supplied by Watson Marlow, were placed behind each of the graphite blocks in order 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 cells were used in a simple flow rig, which consisted of a Watson Marlow peristaltic pump to supply aqueous methanol solution, from a reservoir, to a Eurotherm temperature controller to maintain the cell at a constant temperature. Air was supplied from cylinders, at ambient temperature, and the pressure regulated by pressure-regulating valves. All connections between the cell 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 were comprised of 10 parallel flow channels, 2 mm deep, 2 mm wide and 30 mm long (total geometrical active area of 9 cm<sup>2</sup>) which were machined into a Poco<sup>®</sup> graphite block. The width of the ribs, which formed the flow channels, was 1 mm. The cross-section drawings in Fig. 1 show the manifold tube machined in the block body. As can be seen, a bore of 8 mm diameter was drilled in the side of the block and then small holes of 2.0 mm diameter were drilled to connect the tube with the flow bed, in line with the inlet of every parallel channel (i.e., the centre distance of two successive holes was 3 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. The catalysed layer, consisted of 40 wt.% Pt–20 wt.% Ru

(2 mg cm<sup>-2</sup> total metal loading) dispersed on Vulcan XC72 supplied by E-TEK and bound with 10 wt.% Nafion<sup>®</sup> from a solution of 5 wt.% Nafion<sup>®</sup> dissolved in a mixture of water and lower aliphatic alcohols (Aldrich). A thin layer of Nafion<sup>®</sup> solution was spread onto the surface of each electrode. Electrode preparation are described in detail elsewhere [25]. 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<sup>-2</sup> Pt black on Vulcan XC-72, supplied by Johnson Matthey Technology Centre, with 10 wt.% Nafion<sup>®</sup> in the catalyst layer. The electrodes were placed either side of a pretreated Nafion<sup>®</sup> 117 membrane and the assembly was hot-pressed at 100 kg cm<sup>-2</sup> for 3 min at 135°C. This pretreatment involved boiling the membrane for 1 h in 5 vol.% H<sub>2</sub>O<sub>2</sub> and 1 h in 1 M H<sub>2</sub>SO<sub>4</sub> before washing in boiling Millipore water (> 18 mΩ) for 2 h with regular changes of water.

The current load was provided with the aid of an in-house-developed electronic load unit, which was fully computer controlled. Apart from providing the required load in a programmable way this unit was also a data logger, logging cell response, applied load, and anode/cathode temperatures.

Various load cycles were used in this study. Each cycle was selected to try to simulate conditions of a vehicle being driven in an urban areas: gradual acceleration, deceleration, instantaneous loading with high power demands from zero load conditions, acceleration with different slope, continuous progressive loading and unloading, and arbitrary load cycles. The tests were run several times to ensure repeatability, and in addition each loading condition was repeated several times inside a load cycle in order to assess the effect that the loading history has on the cell response at a specific condition.

The dynamic response of the DMFC will depend on several factors:

- 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
- The mass transfer characteristics of oxygen to the cathode
- The production of carbon dioxide and its release from the anode catalyst layer
- The hydrodynamics of the two-phase flow of methanol solution and carbon dioxide gas
- 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

### 3. Results and discussion

Many of the factors listed above will be 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 known, e.g., through the field of cyclic voltammetry, the dynamic behaviour of complete electrochemical 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 thus report the dynamic response of the cell here and attempt to interpret behaviour qualitatively.

Fig. 2 shows a typical cycle used for all fuel-cell testing, i.e., a gradual step load application (10 mA cm<sup>-2</sup>), allowing some time for the cell to reach a steady-state performance (in this case 60 s) between steps load up to a maximum of 200 mA cm<sup>-2</sup>. At the end of the loading period the cell is gradually unloaded under the same, but reverse, pattern. This test was initially designed to run as a background reference data set, but showed a feature that is common to the DMFC: after a loading cycle the cell performance recovers to a higher open cell voltage (approximately 20–30 mV), which is a meta-stable condition and is often termed cell-activation. As can be seen, in the enlarged section of Fig. 2, the open cell voltage response is

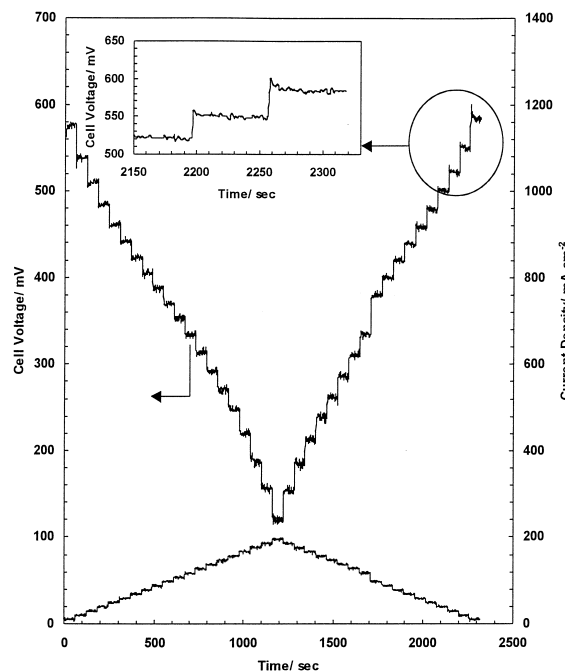


Fig. 2. Cell voltage response under continuously increasing load with steps of 10 mA cm<sup>-2</sup> and duration of 180 s up to a value of 200 mA cm<sup>-2</sup> followed by a gradual cell unloading with the same pattern (methanol concentration 2.0 mol dm<sup>-3</sup>, methanol flow rate 10 cm<sup>3</sup> min<sup>-1</sup>, 85°C cell temperature, air-fed system at 2 bar cathodic pressure). Inset of figure shows the instantaneous increase in voltage when the load is reduced.

slightly elevated during the unloading part of the cycle in comparison with the same load-step (under the same operating conditions applied) in the loading section. From our experience we knew that this phenomenon is quite intense after the cell is unloaded and its intensity increases with the magnitude of the applied load.

Fig. 3 depicts a similar load cycle as used in Fig. 2 but with an important difference; the cell after every current step is instantaneously unloaded for 1 s and then immediately reloaded to the next step load value. As can be seen in Fig. 3 the instantaneous value of the open cell voltage varies from 672 mV up to a maximum value of 766 mV. A few comments are necessary in order to understand the paramount importance of the open cell voltage. Every time a fuel cell is loaded there is an almost constant reduction of the cell voltage for every unit of load applied (when the cell is operated in the region described by Tafel type kinetics). Hence on application of a current load, the higher the initial value of the open cell voltage then a higher voltage response results. It is noticeable, from comparing Figs. 2 and 3, that at maximum current load, of  $200 \text{ mA cm}^{-2}$ , the cell voltage is much greater for the test regime of Fig. 3, than that for the test conditions of Fig. 2, by over 200 mV.

The same trend is noticeable in most of the data reported in this paper: the open cell voltage improves significantly with a continuously increasing applied load, with

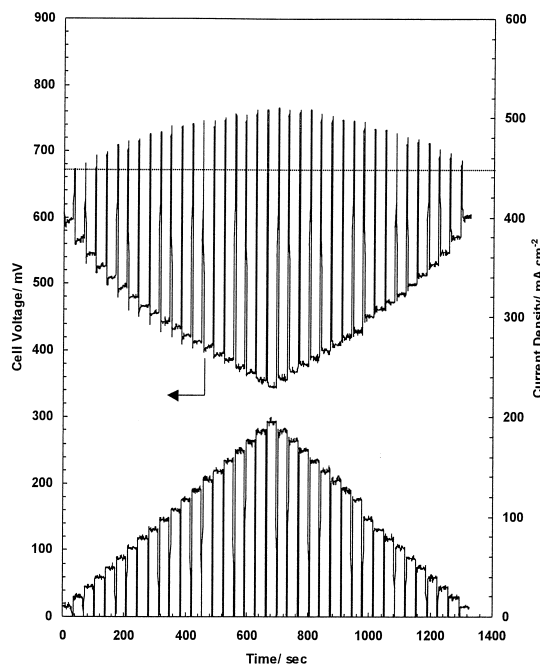


Fig. 3. Cell voltage response under continuously increasing load with steps of  $10 \text{ mA cm}^{-2}$  and duration of 30 s followed by a sudden cell unloading and instantaneous reloading to the new step value, up to a value of  $200 \text{ mA cm}^{-2}$  (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure). Dotted line shows the initial steady-state open circuit voltage.

short duration intermediate cell unloading, and, to a lesser extent, after repeated application of the same load cycle. It should be noted that this is not a stable condition, that voltage decays with time and reaches, after a few seconds, a stable lower value. Nevertheless, in the duration of our experiments, we have noticed that by not allowing the voltage to reach a stable value, i.e., loading the cell again with the same, or greater, load, there is a stable cell response with a higher voltage than in the case when the open cell voltage is allowed to reach a steady-state condition. There are several contributing factors to this behaviour of which the following is considered significant.

The response of single electrode reactions to a current step normally exhibits a rise in overpotential with time. Over the short time-scales of Fig. 3 this response is not apparent which is indicative of the complex interactions of slow electrode kinetics and mass transport in the DMFC. Production of reaction intermediates at the anode electrocatalyst surface and the mechanism of their reaction with other adsorbed species is a complex process under dynamic conditions. A factor that influences the DMFC performance is crossover of methanol to the cathode. This crossover, which is caused mainly by diffusion at low current densities, increases the cathode polarisation due to a mixed potential associated with methanol oxidation at the cathode. The application of a load depletes the methanol at the anode side of the membrane, which reduces the driving force for methanol transfer to the cathode. Consequently there is a reduction in the cathode polarisation. By pulsing the current the flux of methanol through the membrane is always in a dynamic state and potentially, at high current load (i.e., high anode side methanol utilisation at the cathode), methanol could undergo back diffusion from the cathode to the anode. In addition the membrane in the MEA may also act as a small reservoir for methanol supply to the anode. This feature of reduced cathode polarisation immediately after a load is removed is a contribution to the observed improvement in cell voltage under dynamic conditions. In principle, in DMFC operation, there is scope in applying a continuous instantaneous pulsed load cycle to the cell in order to improve the electrical performance and power output. Similar techniques are also applied in other electrochemical devices and processes, e.g., electroplating, to improve performance (reduce power input) or improve product quality. However, the possible improvement in cell power must be balanced against the fact that during the pulse duration no power can be obtained from the cell.

Following the above initial observations we designed load cycles not only to verify the validity of the aforementioned conclusions but also to simulate other operating conditions that may occur during the driving of a vehicle in an urban environment. One of the objectives was to investigate relatively harsh conditions and especially the sudden application of significant power output (i.e., up to 80–90% of the cell's maximum power output) to an

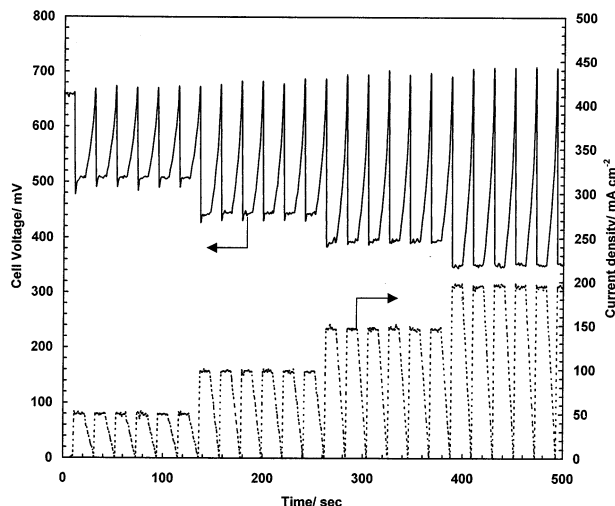


Fig. 4. Cell voltage response for instantaneous application of a specific load up to a value of  $200 \text{ mA cm}^{-2}$  followed by a constant loading period of 30 s and gradual cell unloading to zero load (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

unloaded cell. This condition will indicate the cell's ability to supply the necessary power for vehicle start up. Repeated application of the same power demand, and of increased power demands, are carried out to evaluate successive power demands of the same loads, i.e., when a vehicle stops in successive short distances (a common situation inside European city centres) and the increased loads represent different demands in terms of road surface and slope. This is the case for the data reported in Fig. 4.

Every load step is representative of instantaneous power demand (i.e., power demand to overcome inertia forces in initial motion), constant power demand to maintain movement and gradual reduction in power demand due to vehicle deceleration. As can be seen in Fig. 4, the cell responds rapidly to any change in the power demand but in a different way depending on the magnitude of the load. In the first pulse we have a rather slower cell response; at low applied loads the cell gives a voltage response, which continuously improves with time up to a maximum value. As the load increases further, and especially as it goes to relatively high values, the cell shows a stable response, which does not change with time, but progresses with repeated application of the same load. One potential explanation is in the mass transfer characteristics of the specific cell as discussed above and in the vaporisation of methanol through the formation of carbon dioxide gas (see Refs. [31,37,38]). The electrodes currently used for DMFC were originally designed for vapour-fed systems. Hence they are relatively inefficient for a liquid-fed system as used in this study. Several phenomena compete or interact in the cell, which can explain the observed behaviour:

(i) The higher applied loads lead to higher gas production which on one hand enhances turbulence and hence

mass transfer to the catalyst layers, but on the other hand blocks the flow bed channels and the void volume of the electrode reducing the ability of the reactants to reach the catalyst layer (see Refs. [34,35]).

(ii) In addition, as we have recently reported (see Refs. [24,33]), an increase in the applied current density leads to an increase in the vaporisation of the aqueous phase that, theoretically, penetrates more easily through the gas diffusion electrode resulting in an improvement in electrical performance.

Fig. 5 shows the response of the cell to a relatively intensive cycle; the load varies continuously with a linear increasing and then decreasing pattern, without the cell reaching a steady state. The cell voltage responds smoothly without any apparent anomalies in the response pattern, which is almost identical to the applied loading cycle. This is due to the fast dynamic nature of the phenomenon, which is continuously varied and does not allow sufficient time for the aforementioned phenomena to take place. Clearly the electrochemical related processes are faster than the physical processes (i.e., diffusion, accumulation etc.). We can conclude at that point that the DMFC shows a highly promising behaviour in what can be characterised as demanding power demand use.

Fig. 6 shows the cell response to a current load with a "sawtooth" pattern, that is a dynamic regime representing a demand for gradually increasing power output, up to a maximum value, followed by a sudden unload and subsequent loading. Again the cell voltage responds rapidly to the applied load and follows an almost identical response to the applied load. The beneficial effect of instantaneous cell unloading, in increasing cell voltage at open circuit

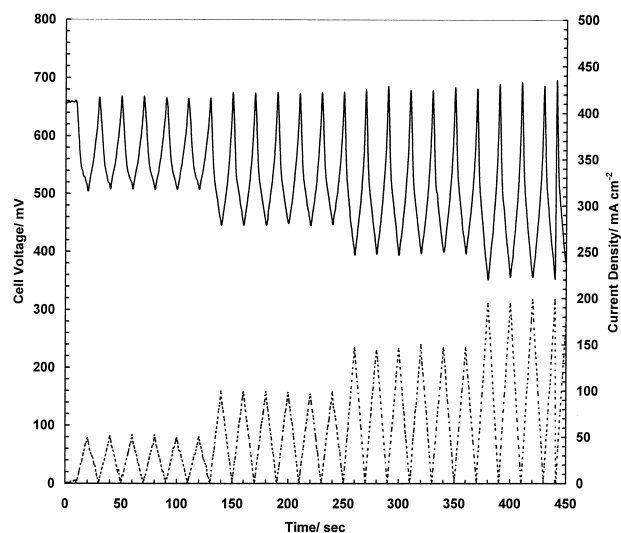


Fig. 5. Cell voltage response under continuously varying loading up to a value of  $200 \text{ mA cm}^{-2}$  followed by a gradual cell unloading with the same pattern (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

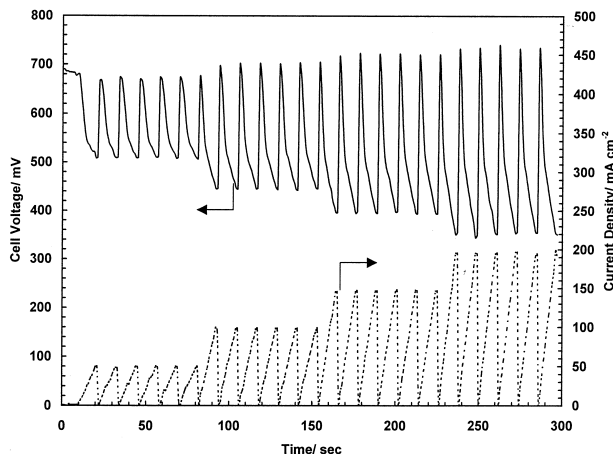


Fig. 6. Cell voltage response under continuously varying load up to a value of  $200 \text{ mA cm}^{-2}$  followed by a sudden cell unloading to zero load conditions (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic overpressure).

and at the peak power demand, compared to slow cell loading (Fig. 2) is again clear and the cell response shows good reproducibility.

Fig. 7 investigates the ability of the cell to respond to varying rates of steady increase in load. Different load rates are used, up to a maximum value of  $100 \text{ mA cm}^{-2}$ , followed by a sudden unload and a short relaxation period of 10 s. As expected, variation in the rate of change of the applied load affects the cell response; a greater rate of increase causes a more rapid decline in voltage. Over a relatively long period of increasing load (slow increase in load) the cell voltage decline decreases after an initial, near, linear decrease. Again, as previously observed, the cell responds rapidly to all the loads, irrespective of the previously applied loads.

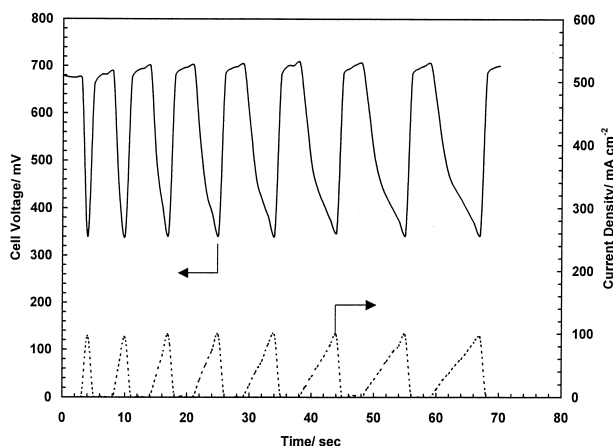


Fig. 7. Cell voltage response under increasing loading slope up to a value of  $100 \text{ mA cm}^{-2}$  followed by a sudden cell unloading and a relaxation period of 30 s prior reloading (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

Fig. 8 shows the effect of a constantly pulsed load to the cell. As can be seen, due to the relatively large duration of the pulses and the relaxation periods (180 s), the cell shows a very limited but gradual deterioration in its electrical performance. After the applied load is removed, the open circuit potential falls, initially, quite rapidly and appears to approach a steady value. However the relaxation time of 180 s is insufficient for the steady value to be achieved before application of the repeated load. Similar behaviour is also seen in Fig. 9 where a pulse of  $200 \text{ mA cm}^{-2}$  is applied to the cell for the same duration, but with an increased relaxation period between

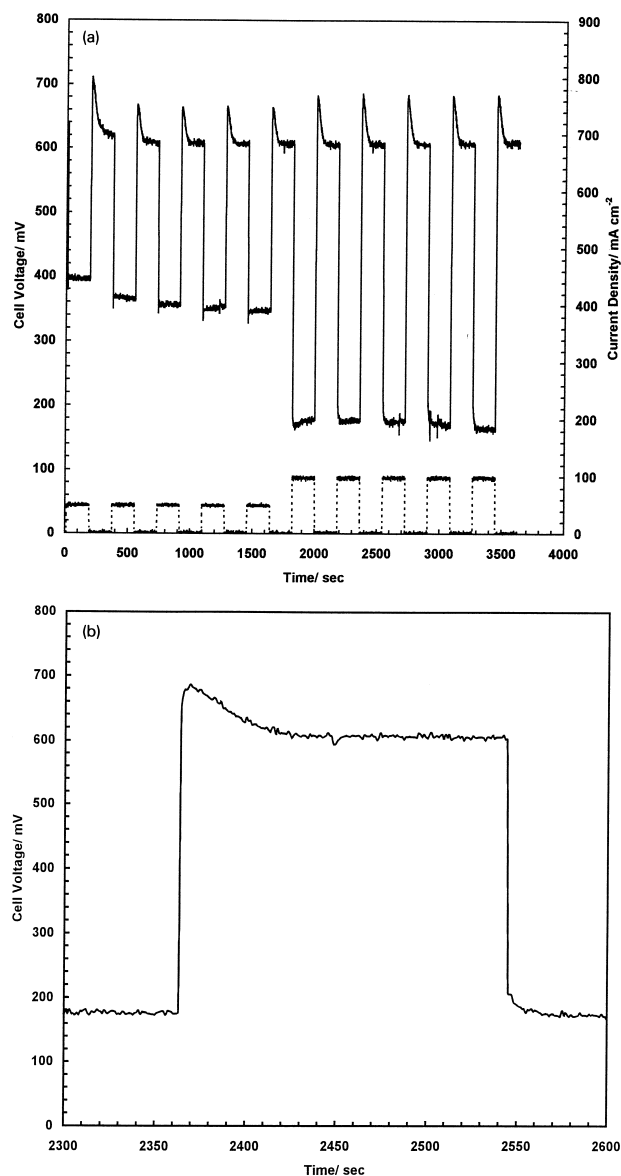


Fig. 8. Cell voltage response under constantly pulsed load conditions up to a value of  $100 \text{ mA cm}^{-2}$  followed by a relaxation period of 180 s prior the application of the next pulse (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure). The inset (b) shows the typical transient voltage response on the application of a current interrupt.

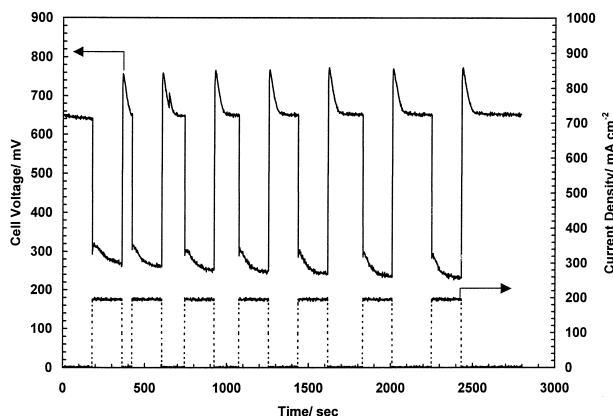


Fig. 9. Cell voltage response under constantly pulsed load conditions at  $200 \text{ mA cm}^{-2}$  (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

two successive pulses. As the relaxation period increases, the cell voltage output appears to deteriorate slightly. This behaviour is due to the complex phenomenological interaction in the cell including methanol crossover, where an increased relaxation time is sufficient to allow the “steady-state” methanol supply to the cathode to be established and the application of relatively high current density and thus high gas generation. The applied current density is significant and generates an excess amount of gas that is difficult to remove from the cell.

Fig. 10 shows the effect of applying pulsed loads of different magnitude on the DMFC. As can be seen we have three different response patterns under applied load: a relatively fast stable voltage at low current densities, followed by a slower response to a steady voltage at intermediate values of current densities and then a slower, decreasing, response in voltage at a current density of  $200 \text{ mA cm}^{-2}$ . The unstable nature of the cell voltage recovery is

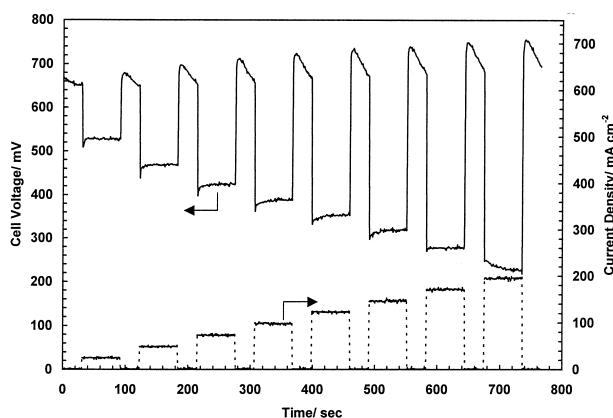


Fig. 10. Cell voltage response under constantly pulsed load conditions up to a value of  $200 \text{ mA cm}^{-2}$  followed by a relaxation period of 30 s prior the application of the next pulse (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

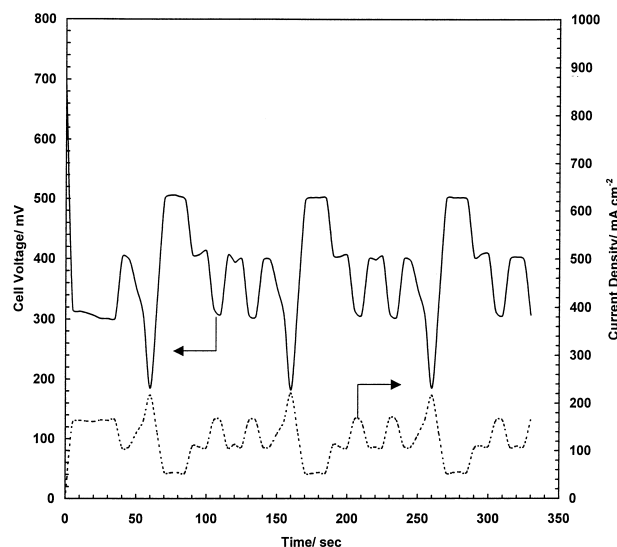


Fig. 11. Cell voltage response under arbitrarily varying load simulating an urban driving cycle (methanol concentration  $2.0 \text{ mol dm}^{-3}$ , methanol flow rate  $10 \text{ cm}^3 \text{ min}^{-1}$ ,  $85^\circ\text{C}$  cell temperature, air-fed system at 2 bar cathodic pressure).

apparent and actually affects the cell’s response time, and hence we can conclude that this effect is beneficial for the cell performance when it is not followed by a prolonged relaxation time, i.e., a steady increase in the open circuit voltage is seen under repeated application of the load.

Finally Fig. 11 shows the cell response to an arbitrary load cycle, simulating a situation that is likely to occur when driving a vehicle on a motorway. High power demands are continuously applied in a varied loading/unloading pattern, and no cell relaxation is allowed. As can be seen, the cell response is excellent in all situations and follows the exact loading pattern without apparent delays.

#### 4. Conclusions

This study has shown that 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 in load and rate of change of load. On current interruption, the initial cell voltage can rise to a value greater, of the order of 100 mV, than the steady open circuit voltage. This effect is due to the reduced impact of methanol crossover on cathode polarisation, i.e., the transfer of methanol, mainly by diffusion, is lower immediately after current interrupt. Following the current interruption the cell takes approximately 100 s to fall to a near stable voltage and under dynamic operation the cell voltage response can be significantly better than that achieved under steady-state operation. This improvement is potentially attractive in

vehicle applications where higher power density and fuel efficiency may be realised. However, this potential benefit can only be determined from a calculation of the overall power of the cell, including the power losses associated with dynamic operation, e.g., during current interruption. This is the subject of current research where dynamic models are to be applied to interpret the cell dynamic behaviour [39].

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