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Dynamic behaviour of 5-W direct methanol fuel cell stack

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Abstract

A 5-W direct methanol fuel cell (DMFC) stack has been developed to investigate the dynamic behaviour of the performance. The stack generates the 5-W peak power with 10 cells of 3 cm × 3 cm active area. Upon changing the load conditions, the transient behaviour of the stack voltage is monitored to evaluate the speed at which the stack adapts to the changes. The transient characteristics of the stack current are also studied with continuously changing fuel flow rates of 2 M methanol solution and air. The optimum operating conditions for the stable operation of the 5-W DMFC stacks are reported.

Keywords: Direct methanol fuel cell; Stack; Membrane–electrode assembly; Peak power; Fuel flow rate; Dynamic behaviour

1. Introduction

The dynamic behaviour of fuel cells is of importance to insure stable performance under various operating conditions. In particular, knowledge of the dynamic behaviour is critical to the engineering and design of the cells, stacks and systems. Among the different types of fuel cell, the direct methanol fuel cell (DMFC) offers particular advantages for portable applications [1–3]. For such service, two types of DMFC system have been investigated, namely, the stack system [1] and the flat micro system [2,3]. While a flat micro system utilizes air breathing for the cathode reaction, the stack system normally uses mechanical pumps for fuels and is therefore suitable for rather higher power portable applications than the flat-pack counterpart. For small DMFC systems to be used for portable electronic applications, the transient responses upon abrupt load changes should be well understood for ensuring stable operation. Since the time constants of the transient responses can vary with the load demand, special care should be taken when the DMFC system is operated under conditions with high time constants.

The transient response of the DMFC is inherently slower than that of the hydrogen fuel cell, and hence delivers inferior performance. This is because the electrochemical oxidation kinetics of methanol are slower due to the formation of intermediates during methanol oxidation [4]. In addition, unlike the hydrogen fuel cell, the DMFC utilizes a liquid fuel. Since the methanol solution has to penetrate a diffusion layer before reaching the anode catalyst layer for oxidation, it is inevitable for the DMFC to experience the high mass-transport resistance. The carbon dioxide produced as the result of the oxidation reaction of methanol could also partly block the narrow flow path so that it is more difficult for the methanol to diffuse the catalyst. All these resistances and limitations can alter the cell characteristics and the power output when the cell is operated under variable load conditions. The fluid dynamics inside the fuel cell stack is more complicated and thus the transient stack performance could be more dependent of the variable load conditions [4–7].

This study reports the effect of varying loads on a small-size DMFC stack (10 cells, each with 9 cm^2 active area). The transient responses of the stack voltage have been investigated to obtain information on the dynamic characteristics of the stack. Also, the transient responses of the stack current upon changing fuel flow rates have been monitored to obtain the optimum operating conditions for the stack.

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2. Experimental

The DMFC was a 10-cell stack with 3 cm × 3 cm active area (i.e., a total active area for the stack of 90 cm^2). The eight middle membrane–electrode assemblies (MEAs) were sandwiched by two graphite bipolar plates and two outside MEAs were sandwiched by a graphite bipolar plate and an end plate. The cells were held together with two plastic insulation sheets and two aluminium backing plates using a set of retaining bolts positioned around the periphery of the stack. In the stack, the fuels of methanol solution and air were introduced through a port for even distribution to 10 separate flow channels. After the fuels flow through the channels of the MEAs, the fuel streams are collected into a single path to leave the stack. In this study, a single serpentine flow-field was used in the active area of 9 cm^2. The flow channel has the dimension of 1 mm width, 1 mm depth, and 1 mm rib-width.

The MEAs used in this study were prepared by the following procedure [8,9]. The diffusion backing layers for the anode and the cathode were Teflon-treated (20 wt.%) carbon paper (Toray 090, E-Tek) of 0.29 mm thickness. For electrode polarities, a thin diffusion layer was formed on top of the backing layer by spreading Vulcan XC-72 (85 wt.%) with PTFE (15 wt.%). After the diffusion layers were sintered at a temperature of 360 °C for 15 min, the catalyst layer was then formed with Pt/Ru (4 mg cm^{-2}) and Nafion (1 mg cm^{-2}) for the anode, and with Pt (4 mg cm^{-2}) and Nafion (1 mg cm^{-2}) for the cathode. The electrodes were placed either side of a pretreated Nafion 115 membrane and the assembly was hot-pressed at 85 kg cm^{-2} for 3 min at 135 °C.

3. Results and discussion

The polarization curve of the fabricated 5-W stack at a temperature of 50 °C is shown in Fig. 1. Since the total active area of the stack is 90 cm^2, the average power density of the stack is 55.6 mW cm^{-2}, which is close to that for a unit cell at the same temperature. The flow rates of the methanol solution and air were set to be in excess (i.e., 8 ml min^{-1} of 2 M methanol solution; 5 l min^{-1} of air) to ensure maximum performance of the stack. No back-pressure was applied to either the anode or the cathode. For unit cell operation, the optimum flow rates of 2 M methanol solution and air are 0.3 and 200 ml min^{-1}, respectively, although the results are not given shown in this paper. Excessive supply of fuels has little effect on the stack performance.

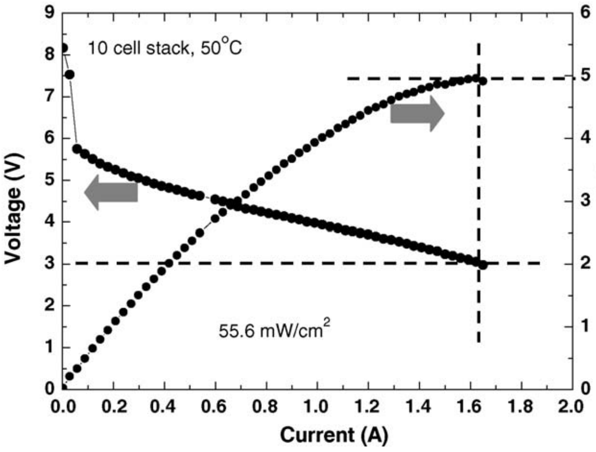

Fig. 1. Performance curves of 5-W DMFC stack, in terms of stack voltage and power. The stack is operated with 2 M methanol solution and air at 50 °C. Flow rates of methanol and air are 8 ml min^{-1} and 5 l min^{-1}, respectively.

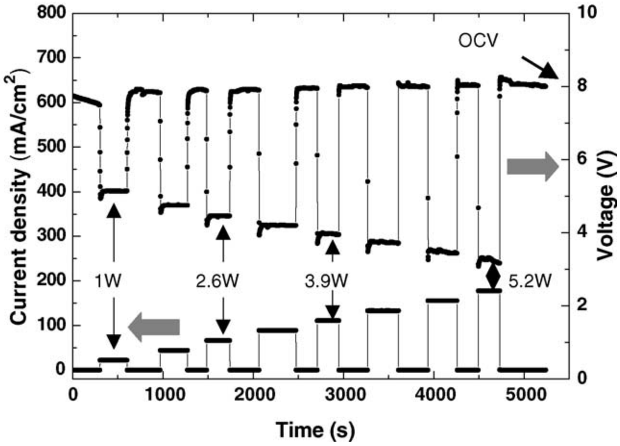

Fig. 2. Stack voltage response under increasing current load with pulses up to 178 mA cm^{-2}. The stack is operated with 2 M methanol solution and air at 50 °C. Flow rates of methanol and air are 8 ml min^{-1} and 5 l min^{-1}, respectively.

When a square pulse with a fixed current density is loaded to the stack, the open-circuit voltage (OCVs) is expected to drop rapidly to a value that corresponds to the current load. The voltage should then recover to the OCVs when the pulse ends. For current loads of 0–1.6 A applied to the stack as consecutive pulses, the voltage response as a function of time is shown in Fig. 2. As the current load increases, the voltage drop increases correspondingly. For a load step change from zero to a fixed current, the voltage falls instantaneously to below the steady-state value for a fixed current, and then returns relatively slowly to the steady-state value. This behaviour is observed for current densities from low to high values. When a load step change occurs from a fixed current to zero current, however, the voltage response gradually approaches the steady-state value at relatively low current densities, but tends to show a sharp rise at higher current densities that results in an overshoot and slow relaxation back to the steady-state value.

The typical transient responses of the stack voltage are shown in Fig. 3 for two different current load changes. When a current load changes from 0 to 44 mA cm^{-2} abruptly, the stack voltage drops for about 5 s from the OCVs and reaches a value below the steady-state voltage (Fig. 3(a)). Then, the voltage slowly increases back to the steady-state value that corresponds to the current density of 44 mA cm^{-2}. When the current load is decreased from 44 to 0 mA cm^{-2}, the measured voltage increases monotonically to the OCVs (Fig. 3(b)). Meanwhile, for a current load change from 0 to 178 mA cm^{-2}, (Fig. 3(c)), the stack voltage response is much faster and has similar behaviour to that shown in Fig. 3(a). For a current load decrease from 178 to 0 mA cm^{-2}, (Fig. 3(d)), the response is also very fast but it exhibits an overshoot and slow relaxation, unlike the case

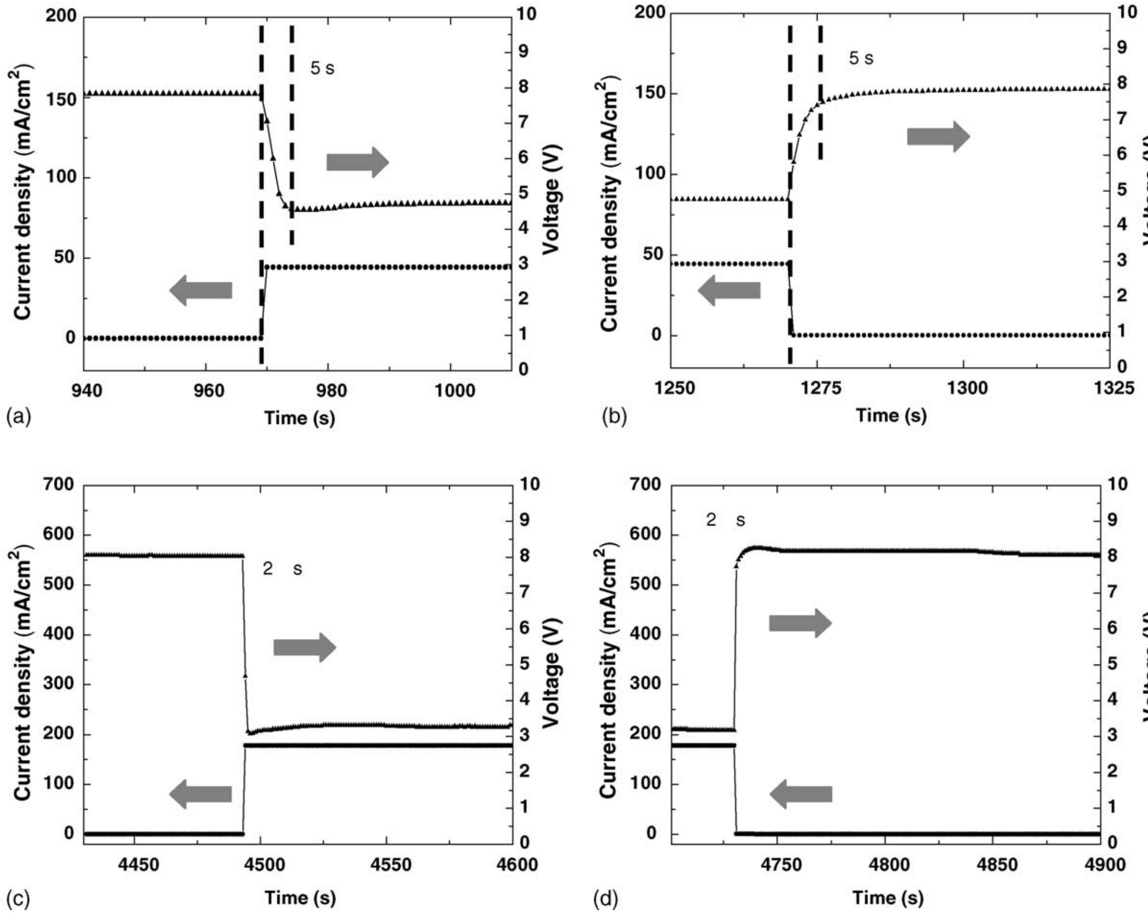

Fig. 3. Dynamic behaviour of stack voltage for current step changes; (a) from 0 to 44 mA cm^{-2}; (b) from 44 to 0 mA cm^{-2}; (c) from 0 to 178 mA cm^{-2}; (d) from 178 to 0 mA cm^{-2}.

of Fig. 3(b). Generally speaking, the voltage response changes faster at higher current loads for both increasing and decreasing loads. This can be attributed to the fact that higher current density leads to an increase in the vaporization of the aqueous phase so that the methanol penetrates more easily through the diffusion layer and causes an improvement in electrical performance. The dynamic behaviour of the DMFC voltage has been explained by Kallo et al. [4] by the introduction of catalyst cleaning and a poisoning effect. These workers observed similar transient behaviour to that shown in Fig. 3, even though their results were obtained for a gas-fed DMFC. The overshoots and slow relaxations of the voltage response in Fig. 3(a), (c) and (d) have been explained by the poisoning of catalyst surface with CH_2OH_{ads} and CO_{ads} [4].

The dynamic response of the stack voltage to step changes with increasing applied current densities is presented in Fig. 4. Like the former case of applied current pulses, the response exhibits overshooting and relaxation that are caused by the methanol oxidation kinetics on the catalyst surface. The steady-state stack voltage is found to be the same for both pulse and step loads with the same current density.

A 2 M methanol solution was fed to the stack at a flow rate of 8 ml min^{-1} and the stack was operated at a constant voltage output of 3.8 V and a temperature of 50°C. The transient response of the stack current density on varying the flow rate of air to the cathode is shown in Fig. 5. When the stack current is maintained at the air flow rates above than 2 l min^{-1}, at the air flow rates less than the flow rate the stack current density begins to decrease, as does the output power. This means that the air should be deficient for a power output of 4 W with flow rates of less than 2 l min^{-1}. The flow rate of the methanol solution

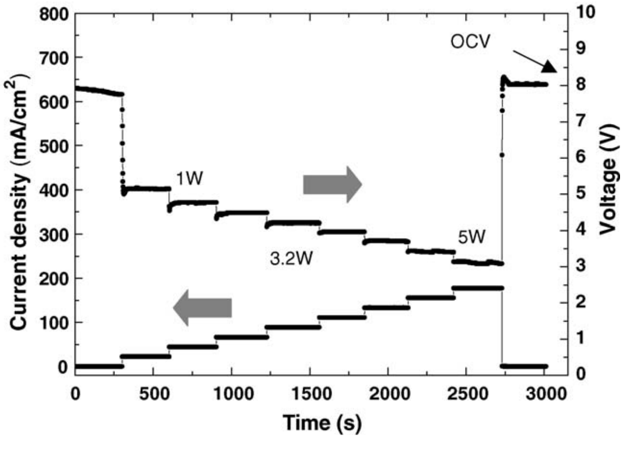

Fig. 4. Stack voltage response under continuously increasing current load with steps up to 178 mA cm^{-2}. The stack is operated with 2 M methanol solution and air at 50 °C. Flow rates of methanol and air are 8 ml min^{-1} and 5 l min^{-1}, respectively.

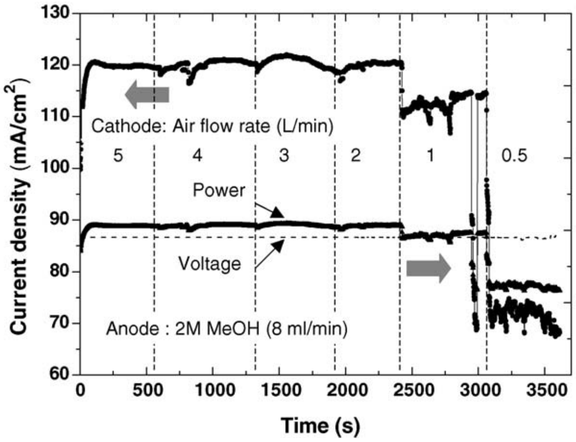

Fig. 5. Transient stack performance as air flow rate is reduced from 5 to 0.5 l min^{-1}, at 50 °C under constant output voltage of 3.8 V. Flow rate of 2 M methanol solution is fixed at 8 ml min^{-1}.

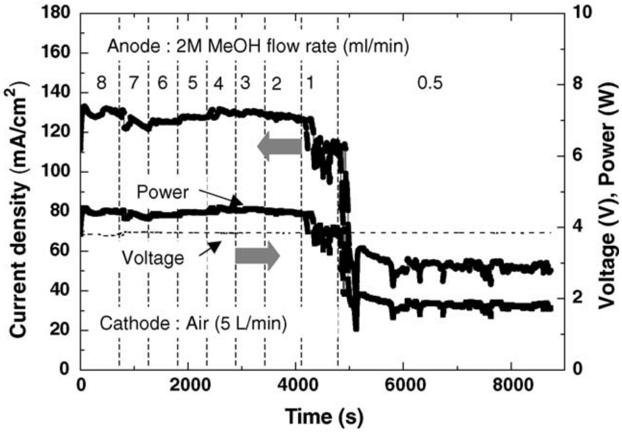

Fig. 7. Transient stack performance as methanol (2 M) flow rate is reduced from 8 to 0.5 ml min^{-1}, at 50 °C under constant output voltage of 3.8 V. Air flow rate is fixed at 5 l min^{-1}.

has been set at 8 ml min^{-1}, which should be in excess for the power output, so as to determine the lowest flow rate of air for a power output of 4 W. If the flow rate of 2 M methanol solution is reduced to 2 ml min^{-1}, the current density is then sustained further to a 1 l min^{-1} air flow rate, as shown in Fig. 6. This appears to be due to higher methanol cross-over at the higher methanol flow rate through the Nafion membrane. At a methanol flow rate of 8 ml min^{-1}, the current density is close to 120 mA cm^{-2} at an output voltage of 3.8 V. On the other hand, the current density at a flow rate of 2 ml min^{-1} is about 130 mA cm^{-2} at the same output voltage. Thus, it is concluded that the effect of methanol cross-over is more pronounced at the higher methanol flow rate and results in a lower current density.

Similar results are shown in Figs. 7 and 8 for varying methanol flow rates at two different air flow rate of 5 and 2 l min^{-1}, respectively. At a methanol flow rate of 8 ml min^{-1}, the current density initially reaches a value of about 130 mA cm^{-2} and then starts to decrease, (Fig. 7). This is probably due to methanol cross-over. As this flow rate decreases, the stack current density increases slowly until the rate reaches 3 ml min^{-1} because of reduced methanol cross-over. At an air flow rate of 5 l min^{-1}, the current density begins to decrease from a methanol flow rate of 2 ml min^{-1}. When the latter reaches 1ml min^{-1}, the current density drops quickly from 120 to 50 mA cm^{-2} due to the depletion of methanol. Meanwhile, once the flow rate of air is reduced to 2 l min^{-1}, the current density declines rapidly when the methanol flow rate is 2 ml min^{-1} (Fig. 8).

It is worthwhile to note here that in Figs. 6 and 8 the current densities measured at a methanol and air flow rates of 2 ml min^{-1} and 2 l min^{-1}, respectively, show inconsistency even under the same operating conditions. This is attributed to the water produced at the cathode. The measured current density response appears to be unstable and scattered at low air flow rates in Fig. 6, but is stable even at the low methanol flow rates in Fig. 8. This instability of the measured current density in Fig. 6 could have been caused by the water formed at the cathode during operation of the stack. In fact, it has been observed that the water produced at the cathode accumulates in the cathode flow channels for a while and then bursts out intermittently to the cathode outlet. For a fixed air flow rate throughout stack operation, it is expected

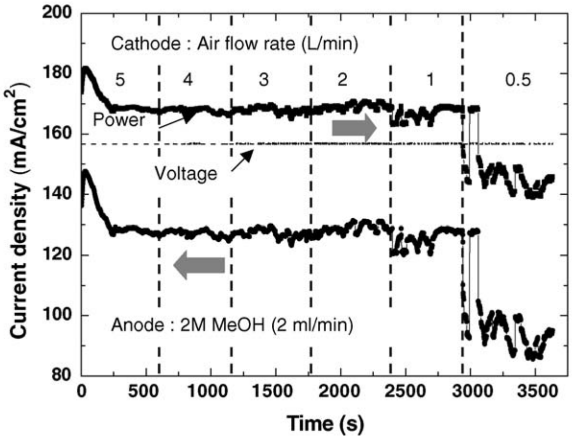

Fig. 6. Transient stack performance as air flow rate is reduced from 5 to 0.5 l min^{-1}, at 50 °C under constant output voltage of 3.8 V. Flow rate of 2 M methanol solution is fixed at 2 ml min^{-1}.

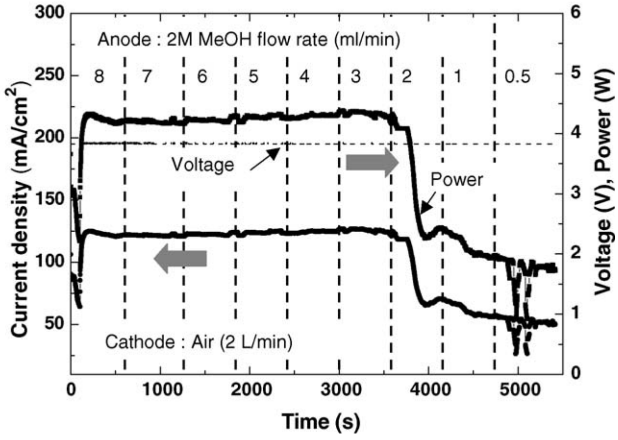

Fig. 8. Transient stack performance as methanol (2 M) flow rate is reduced from 8 to 0.5 ml min^{-1}, at 50 °C under constant output voltage of 3.8 V. Air flow rate is fixed at 2 l min^{-1}.

that the air and water flow in the cathode channels could both be at steady-state. By contrast, on changing the air flow rate during stack operation water may accumulate or dissipate to cause an unstable current response. Based on the experimental observations, for stable operation of the 5-W DMFC stack fabricated in this study, the minimal operating conditions are flow rates of $3\,\mathrm{ml\,min}^{-1}$ and $2\,\mathrm{l\,min}^{-1}$ for 2 M methanol and air, respectively.

4. Conclusions

The dynamic behaviour of a 5-W DMFC stack is examined when current loads are changed in the form of pulses and steps. The stack voltage responds quite fast when the current load changes abruptly, i.e., it reaches a steady-state voltage in 1–5 s for a change of $0\text{–}178\,\mathrm{mA\,cm}^{-2}$. In order to determine the optimum operating conditions of the stack, the dynamic behaviour of the current has been studied at a constant voltage output of 3.8 V and varying flow rates of 2 M methanol solution and air. For stable operation of the 5-W stack, the minimal fuel flow rates are $3\,\mathrm{ml\,min}^{-1}$ and $2\,\mathrm{l\,min}^{minus1}$ for 2 M methanol and air, respectively.

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