

A liquid-feed solid polymer electrolyte direct methanol fuel cell operating at near-ambient conditions

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Abstract

Results on the performance of a 25 cm² liquid-feed solid polymer electrolyte direct methanol fuel cell (SPE-DMFC), operating under near-ambient conditions, are reported. The fuel cell can sustain a load current density of 100 mA cm⁻² with an output voltage of c. 450 mV at 90°C with 2 M aqueous methanol and air-fed cathode at near-ambient pressures with a catalyst loading of 5 mg cm⁻² of Pt. Preliminary data on the performance of a liquid-feed SPE-DMFC stack comprising two 25 cm² cells are also reported. These data are sufficient to suggest that further developmental work on liquid-feed SPE-DMFCs operating under near-ambient conditions (0 barg O₂ at 90°C) is well worthwhile. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Direct methanol fuel cells; Liquid-feed; Ambient pressure

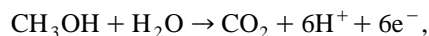
1. Introduction

Methanol is an attractive fuel: it is liquid at room temperature; it has limited toxicity, high energy–density, is inexpensive and is particularly suited as an energy source for traction power. In principle, it can be used directly in modern internal combustion engines, but its primary importance is likely to be as a fuel for a new generation of clean-energy sources based on fuel-cell technology.

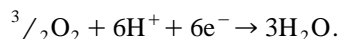
Methanol can be utilised in such fuel cells both directly and indirectly. In the latter case, the methanol may be reformed to yield hydrogen and CO₂, with the hydrogen then fed to a conventional H₂/air cell. Such reformer-based systems are now at an advanced stage of development, and the main difficulty likely to be encountered in engineering terms arises from the necessity to obtain heat from the fuel-cell stack to drive the reformer, given that the most efficient reformer reactions are endothermic. Unfortunately, during variable load conditions, the heat required is out of phase with its production. Other designs of reformers have been proposed which do not need an external heat supply but suffer from a lower overall fuel to hydrogen conversion efficiency, resulting in a lower fuel economy

[1]; in addition, control and ancillary systems will add substantially to the cost of reformer-based fuel cells, making them unattractive commercially.

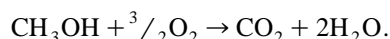
The direct use of methanol in fuel cells clearly offers considerable attractions from the point of view of simplicity of design [2] and hence, potentially, of cost. In essence, a Direct Methanol Fuel Cell (DMFC) consists of an anode at which methanol is electrochemically oxidised to CO₂ according to:



and a cathode at which oxygen is reduced to water as:



The overall cell reaction is:



The main drawback of such cells is the very sluggish anode reaction, which, coupled with the inefficient cathode reaction gives rise to very low overall cell performance, particularly at low temperatures. These drawbacks were recognised in early cell designs, utilising a dilute sulphuric acid electrolyte at 60°C, [1,3] and in which the high internal resistance of the system lead to poor performance. It was realised in the eighties that a considerable increase in efficiency might be obtained by using the ‘zero-gap’

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cell-design principle, [4] in which the liquid electrolyte is replaced by a thin proton-conducting polymer sheet. Such geometries have already proved their worth for conventional H_2/O_2 fuel cells, but design of the membrane-electrode assembly (MEA) proved rather difficult, until it was suggested that a sol form of the polymer could also be used as part binder for the electrode, see for instance, Ref. [5].

In principle, the methanol might be delivered to such a 'zero-gap' cell as either liquid or vapour. Vapour delivery cells do have the advantage that MEA design can use many of the principles already worked out for H_2/O_2 cells, and can be operated conveniently at higher temperatures, giving much enhanced performance [6,7]. However, there are considerable advantages to a liquid-feed design as well: complex water and thermal management systems, including the energy-intensive vapouriser, can be eliminated, the liquid-feed can be used as a coolant (cooling being a serious problem with vapour-feed systems) and significantly lower stack size and cost. Recent results from the Jet Propulsion Laboratory [8] have illustrated the feasibility of such systems in which 0.47 V at 150 mA cm^{-2} was obtained using 0 barg air at 60°C . However, this high performance was achieved using an anode catalyst loading of 12 mg cm^{-2} of a Pt–Ru black. By increasing the pressure at which the cell operates, it is possible to move to higher temperatures, thereby improving the performance particularly of the anode; the Los Alamos group [9] were able to show that power densities of nearly 0.4 W cm^{-2} for oxygen and 0.25 W cm^{-2} for air were attainable at 130°C and 110°C and quoted pressures of 5 atm and 3 atm, respectively. The use of higher temperatures leads to increased performance from the cell but also increases methanol cross over and decreases membrane stability [13]. In addition, at higher temperatures (above 100°C), Nafion™ itself is only stable under pressure, and parasitic efficiency losses here need to be balanced against enhanced fuel cell output. The Newcastle group, using vapour-feed cells, were able to obtain similar results by differential pressurisation of the oxygen or air comburent in the cathode compartment, thereby reducing one of the most problematic aspects of the DMFC, the crossover of methanol from anode to cathode; their results [7] at 95°C and 5 atm air showed a power density of over 0.2 W cm^{-2} .¹

To date, one essential condition for achieving relatively high power densities has been the pressurisation of the oxygen (or air) feed to the cathode; clearly, however, for most conceivable applications, operation at near-ambient pressures would be essential, [10] both to reduce parasitic energy loss and to simplify the design protocol.

As part of our ongoing research programme in this area, [6,7,11] this paper reports the performance of a liquid-feed

SPE-DMFC at 65 and 90°C , using 2 M aqueous methanol as the anode feed, and oxygen (or air)-fed cathodes operating at near-ambient pressures. Under these conditions, the performance of the liquid-feed SPE-DMFC at 100 mA cm^{-2} , a current density generally accepted as being typical of those to be drawn under real operating conditions, [12] is akin to those reported in the literature with pressurised cathodes [8,9,11,13]. The results presented here suggest that an acceptable performance, namely an output of c. 500 mV under a load current density of 100 mA cm^{-2} , with a liquid-feed SPE-DMFC can be attained at 90°C using an air-fed cathode at near-ambient pressures. The two-cell stack was found to develop a power of c. 2 W under an operational current density of 100 mA cm^{-2} at 90°C with air at ambient pressure. The performances at 65°C are also very promising. These data are seminal toward practical realisation of liquid-feed SPE-DMFCs operating under near-ambient conditions.

2. Experimental

The experiments detailed below were carried out using membrane electrode assemblies (MEAs) having an active geometrical area of 25 cm^2 . The MEAs were prepared as described elsewhere [13]. In brief, the catalysts for the cathode and anode, Pt and Pt–Ru, respectively, supported on Ketjen Black (EC) 600-TD carbon (Akzo Chemie), were prepared from their sulphito complexes, as described in Ref. [13]. Both the anode and cathode structures comprised a backing layer, a gas-diffusion layer and a reaction layer of the carbon-supported catalyst. A 20 wt.% teflonised carbon paper (Kureha) of 0.3 mm thickness and c. 90% porosity was employed as the backing layer. To prepare the gas-diffusion layer, Ketjen Black carbon was suspended in Millipore Milli-Q water ($18 \text{ M}\Omega \text{ cm}$) and agitated in an ultrasonic bath. A 10 wt.% Teflon suspension (Fluon GP-2, ICI) was added to this solution with continuous stirring, followed by addition of cyclohexane (50 cm^3 per 100 mg of carbon); and the resultant ink was spread on to the teflonised carbon paper up to a loading of c. 0.5 mg cm^{-2} , and the paper was dried in air at 80°C for 2 h. To prepare the reaction layer, the required amounts of Pt/C or Pt–Ru/C were mixed with 10 wt.% teflonised carbon prepared by heating an intimate mixture of Teflon and carbon in air at 350°C for 30 min. The catalysed carbon and teflonised carbon admix was suspended in water, agitated in an ultrasonic bath, and Nafion™ solution (Aldrich) added to 15 wt.%. The paste so obtained was then applied to the gas-diffusion layer and compacted at 75 kg cm^{-2} for 5 min. The Pt content in the reaction layers of both anode and cathode was 5 mg cm^{-2} . A thin layer of Nafion™ solution was spread over the surface of each electrode, and the MEA was finally obtained by pressing the anode and cathode on either side of a pre-treated

¹ Calculated from active area and not geometrical area.

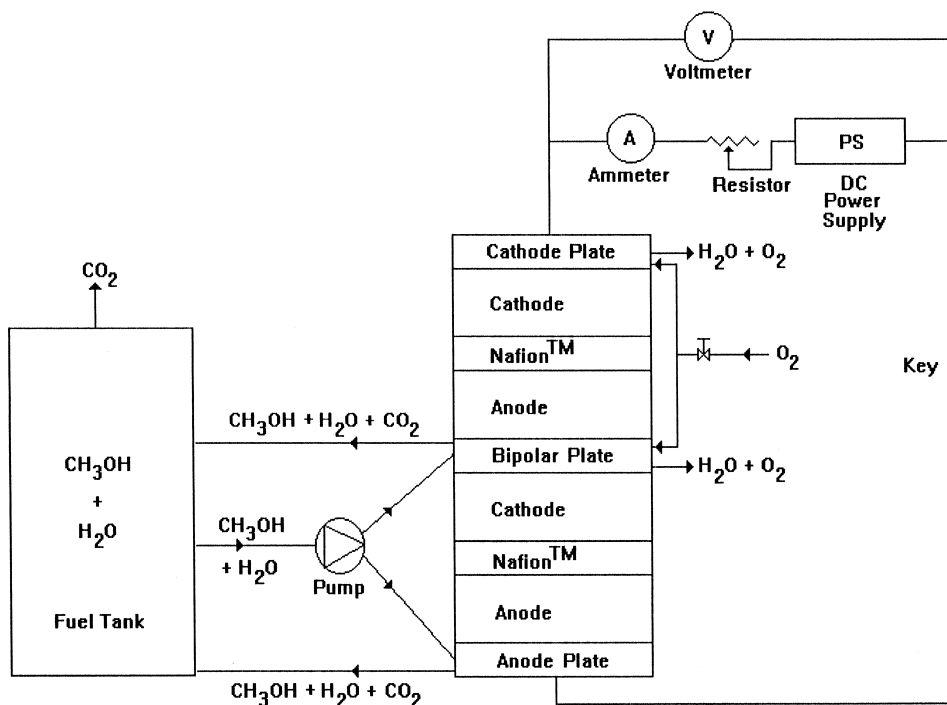


Fig. 1. Schematic diagram of the liquid-fed SPE-DMFC two-cell stack having an active cross-sectional area of 25 cm^{-2} .

Nafion-117™ membrane under a pressure of 50 kg cm^{-2} at 130°C for 3 min. The MEAs so formed were typically c. 1 mm thick.

The anode and cathode of the MEA were contacted on their rear sides with high-density graphite blocks impregnated with a phenolic resin, into which was cut the gas/liquid flow channels. The ridges between the channels provided the electrical contact to the carbon electrodes, and the total machined geometrical area of 25 cm^2 was taken as the active area of the DMFC. Electrical heaters were mounted at the rear of the graphite blocks in order to maintain the desired cell temperature which was monitored by thermocouples buried in the blocks. Metallic bolts were screwed into the blocks to allow electrical contact. The

two-cell stack was assembled from two end plates and a single bipolar plate, as shown diagrammatically in Fig. 1.

The methanol solution (2 M methanol in water) was pumped through the anode compartment of the DMFC with a Masterflex® peristaltic pump at a rate of 0.7 ml min^{-1} and the unreacted fuel returned to the storage reservoir where the CO_2 gas product was released to the atmosphere. Oxygen or air were supplied to the cathode from cylinders and provision was made to allow pressurisation, as well as venting without circulation.

Before data collection was commenced, the MEAs were first hydrated by circulating 2 M methanol solution through the anode compartment at 80°C for c. 24 h. Steady-state current–voltage (polarisation) plots were obtained gal-

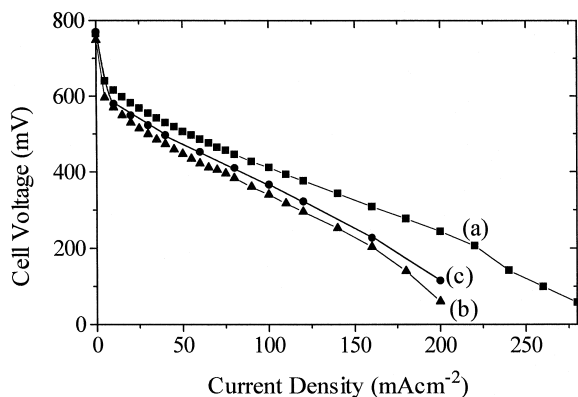


Fig. 2. Polarization data for the liquid-fed (2 M methanol) SPE-DMFC at 65°C with (a) 0 barg oxygen (20 ml min^{-1}), (b) 0 barg air (20 ml min^{-1}), and (c) 0.5 barg air (60 ml min^{-1}).

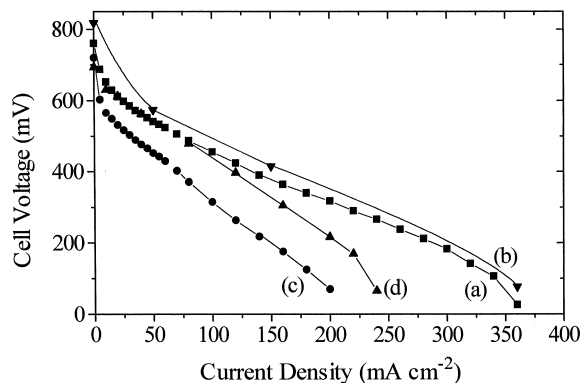


Fig. 3. Polarization data for the liquid-fed (2 M methanol) SPE-DMFC at 90°C with (a) 0 barg oxygen (20 ml min^{-1}), (b) 0.5 barg oxygen (60 ml min^{-1}), (c) 0 barg air (20 ml min^{-1}), and (d) 0.5 barg air (60 ml min^{-1}).

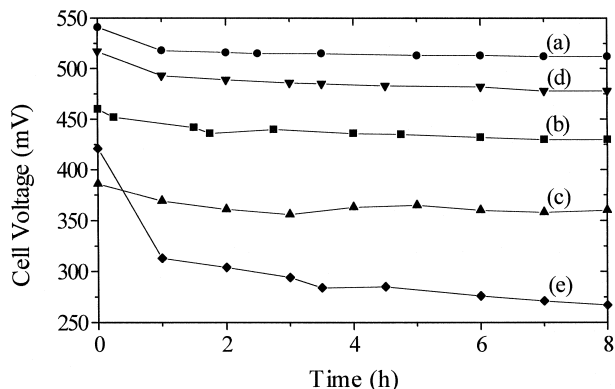


Fig. 4. Durability tests for the liquid-feed (2 M methanol) SPE-DMFC at 90°C under load current densities of (a) 50 mA cm⁻², (b) 100 mA cm⁻², (c) 150 mA cm⁻², and at 65°C under load current densities of (d) 50 mA cm⁻², and (e) 100 mA cm⁻² with 0 barg oxygen.

vanostatically, with the cell voltage being recorded only after it had reached a steady value, (usually after c. 3 min). Durability studies on the single cell and the two-cell stack were also carried out.

3. Results and discussion

Steady-state current–voltage characteristics of the liquid-feed SPE-DMFC were obtained at 65 and 90°C, and the results are shown in Figs. 2 and 3. The data in Fig. 2 show the polarisation plots obtained at 65°C using (a) 0 barg O₂, (b) 0 barg air, and (c) 0.5 barg air. The data in Fig. 3 show the same experiments, with the addition of an experiment carried out using 0.5 barg oxygen, but carried out at 90°C. As can be seen from the figures, when employing pure oxygen, the fuel cell shows a marked increase in performance as the temperature is increased. This increase may be attributed to the reduction in the ohmic resistance of the cell due to increased conductivity in the Nafion™ membrane [14], as well as an increase in

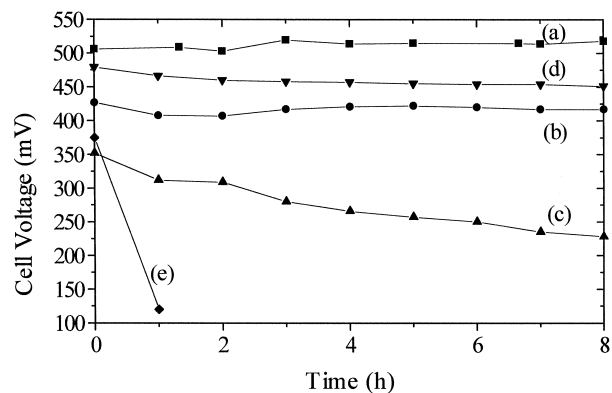


Fig. 5. Durability tests for the liquid-feed (2 M methanol) SPE-DMFC at 90°C under load current densities of (a) 50 mA cm⁻², (b) 100 mA cm⁻², (c) 150 mA cm⁻², and at 65°C under load current densities of (d) 50 mA cm⁻², and (e) 100 mA cm⁻² with 0.5 barg air.

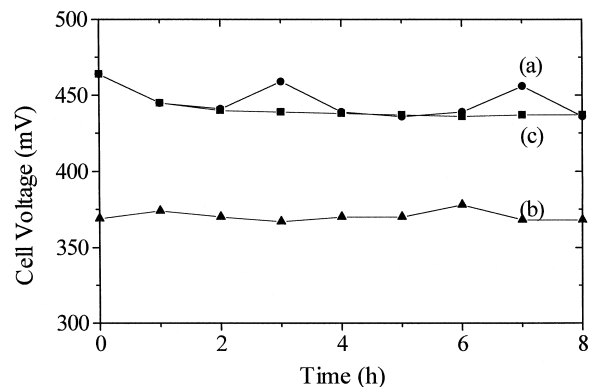


Fig. 6. Durability tests for the liquid-feed (2 M methanol) SPE-DMFC at 90°C under load current densities of (a) 50 mA cm⁻², (b) 100 mA cm⁻², and at 65°C under load current densities of (c) 50 mA cm⁻² with 0 barg air.

the rate of methanol oxidation at the anode. The absence of such an improvement on increasing the temperature while using air as the cathode feed is surprising, and may reflect the fact that increasing the temperature also increases the rate of methanol crossover and this, coupled with the decreasing concentration of O₂ at higher temperatures, may be severely inhibiting the platinum catalyst for oxygen reduction.

The durability test data for the single-cell SPE-DMFC at 65°C and 90°C are shown in Figs. 4–6. Fig. 4 shows the data obtained using a pure oxygen feed at 0 barg. Fig. 5 shows the data obtained using 0.5 barg air, and Fig. 6 the data obtained with 0 barg air. From the data in Figs. 4 and 5, it appears that the performances of the fuel cell at 50 mA cm⁻² and 100 mA cm⁻² are very similar when using 0 barg or 0.5 barg air. Indeed, Ren et al. [9] also found only a nominal increase in cell performance on employing oxygen at 3 barg and 130°C, compared to air at 1.8 barg and 110°C, up to 200 mA cm⁻². Such data may be rationalised by a relatively straight forward mass–balance calculation; thus, a liquid-feed SPE-DMFC operating with a fuel utilisation of 60% [8] at 1 A would require O₂ at a

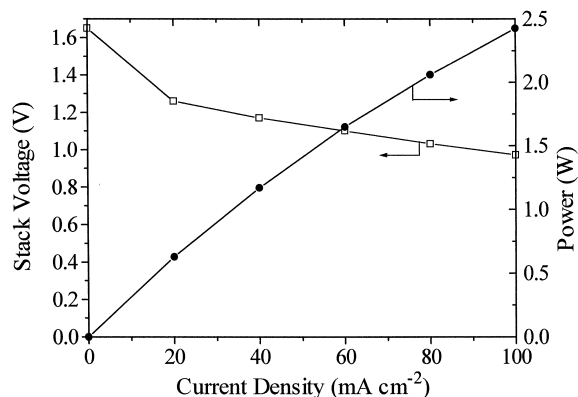


Fig. 7. Polarisation and power data on the two-cell liquid-feed SPE-DMFC stack operating at 90°C, with 2 M aqueous methanol, and 0 barg oxygen.

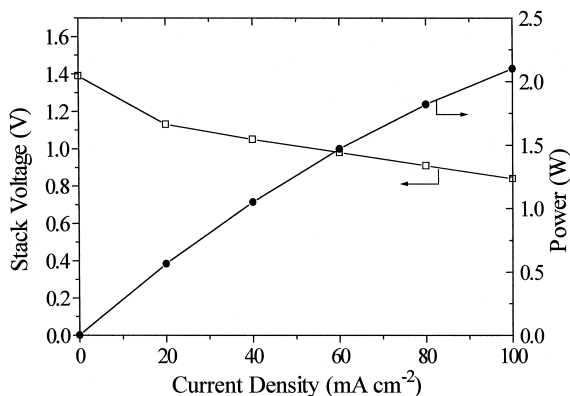


Fig. 8. Polarisation and power data on the two-cell liquid-feed SPE-DMFC stack operating at 90°C, with 2 M aqueous methanol, and 0 barg air.

rate of $9.64 \times 10^{-5} \text{ dm}^3 \text{ s}^{-1}$, and will result in a cathode exhaust comprising $3.83 \times 10^{-5} \text{ dm}^3 \text{ s}^{-1}$ of unreacted oxygen and $9.24 \times 10^{-8} \text{ dm}^3 \text{ s}^{-1}$ of liquid water. Under similar conditions with an air-fed cathode, the cell would require $4.6 \times 10^{-4} \text{ dm}^3 \text{ s}^{-1}$ of air, and will result in a cathode exhaust amounting to $4.02 \times 10^{-4} \text{ dm}^3 \text{ s}^{-1}$ of unreacted air and $9.24 \times 10^{-8} \text{ dm}^3 \text{ s}^{-1}$ of liquid water. These data suggest that volume changes in the cathode chamber of either of these cells will be insignificant. By contrast, under similar operating conditions, the anode of the cell will require $1.46 \times 10^{-6} \text{ dm}^3 \text{ s}^{-1}$ of 2 M aqueous methanol, and will result in an exhaust comprising $1.32 \times 10^{-6} \text{ dm}^3 \text{ s}^{-1}$ of water, $4.71 \times 10^{-8} \text{ dm}^3 \text{ s}^{-1}$ of unreacted methanol and $3.87 \times 10^{-5} \text{ dm}^3 \text{ s}^{-1}$ of CO_2 . This represents a c. 26-fold volume change in the anode compartment during cell operation and these simple calculations clearly indicate that CO_2 management will be of paramount importance when considering flow path design. In the present study, the anode flow path was designed so as to facilitate the efficient expulsion of CO_2 product gas bubbles from the flow channels and so prevent blocking.

The durability test data at 65 and 90°C using 0 barg air at current densities between 50 and 100 mA cm^{-2} are shown in Fig. 6. The data suggest that the performances of

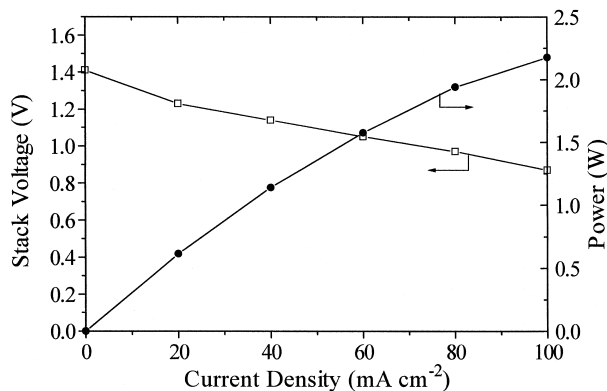


Fig. 9. Polarisation and power data on the two-cell liquid-feed SPE-DMFC stack operating at 65°C, with 2 M aqueous methanol, and 0 barg oxygen.

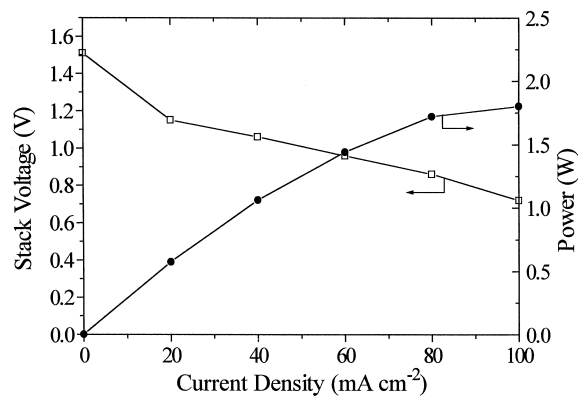


Fig. 10. Polarisation and power data on the two-cell liquid-feed SPE-DMFC stack operating at 65°C, with 2 M aqueous methanol, and 0 barg air.

the cell at these temperatures at 50 mA cm^{-2} are very similar. Interestingly, the output voltages of c. 450 mV at 50 mA cm^{-2} using 0 barg air at 65°C, see Fig. 6(a), are not too inferior to the values of c. 520 mV obtained at 90°C using 0 barg oxygen, see Fig. 4(a). The small decreases in the cell performance seen between c. 2 and 8 h running time during the durability tests have been tentatively attributed to a small temperature decrease of $\sim 5^\circ\text{C}$ observed in the cell during the experiments.

The construction of the two-cell liquid-feed SPE-DMFC stack is shown in Fig. 1 and polarisation and power data for 2 M methanol liquid-feed at 65°C and 90°C with 0 barg oxygen, and at 65°C with 0 barg air are shown in Figs. 7–10, respectively. As can be seen, the stack is capable of delivering a power of c. 2.5 and c. 2 W at 100 mA cm^{-2} with oxygen and air feeds, respectively. Durability data for the stack at 90°C under a load of 100 mA cm^{-2} with 0 barg oxygen are shown in Fig. 11(a) and (b), and the data show that the two-cell stack performance represents exactly the sum of the individual cells, indicating the reproducibility of the engineering parameters within this cell

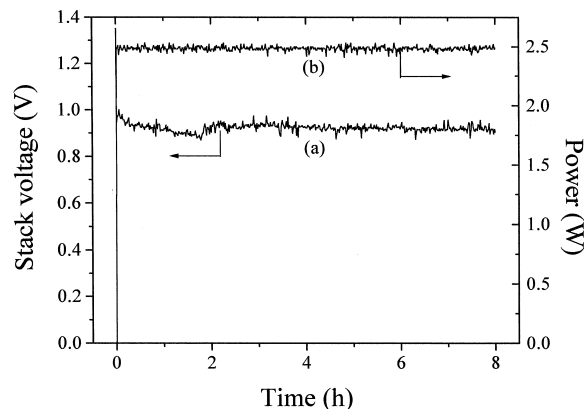


Fig. 11. (a) Voltage vs. time; (b) power vs. time for the two-cell liquid-feed SPE-DMFC stack at 90°C under a current density load of 100 mA cm^{-2} using 0 barg oxygen.

design, which is critical to scale-up. From the data, the two-cell stack can sustain a load-current density of 100 mA cm⁻² at an average output of c. 1 V, providing an output power of 2.5 W. There is no reason to believe that the stack engineering is yet fully optimised, and further improvements in performance are highly likely.

4. Conclusion

It is now generally accepted that a commercially viable DMFC must be capable of: (a) operating under ambient conditions, and (b) sustaining load-current densities of 100 mA cm⁻² at an output voltage of 0.5 V per cell. We have reported the construction of a two-cell liquid-feed SPE-DMFC stack operating at near-ambient conditions which can deliver output voltage of c. 0.9 under load current density of 100 mA cm⁻², and applications of such stacks to vehicular traction, remote-area communication, and portable power packs for a wide variety of purposes can be envisaged in the future. In addition to whether the cell is run on oxygen or air, this study has shown that management of the CO₂ produced will be of paramount importance.

Acknowledgements

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