

Short Communication

# A vapour-feed direct-methanol fuel cell with proton-exchange membrane electrolyte

A.K. Shukla<sup>1</sup>, P.A. Christensen\*, A. Hamnett, M.P. Hogarth

*Department of Chemistry, Bedson Building, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK*

Received 12 October 1994; accepted 15 October 1994

## Abstract

Results are presented on a vapour-feed direct-methanol fuel cell employing a proton-exchange membrane electrolyte. The fuel cell could be operated with 1% methanol, giving a typical performance of 550 mV at 75 mA cm<sup>-2</sup>, and a fuel utilisation coefficient of 0.56. At 2 M methanol concentration, the cell voltage load found to be 610–550 mV at a load current density of 100 mA cm<sup>-2</sup>. The observed open-circuit potentials of this cell assembly have been found to be in the range 850–980 mV.

*Keywords:* Fuel cells; Direct-methanol fuel cells; Proton-exchange membrane electrolytes

## 1. Introduction

For vehicular applications, the most suitable long-term power systems are likely to be based on liquid fuels, of which the simplest is methanol. In principle, methanol can be burned directly in internal combustion engines, but a far more efficient and environmentally more benign solution is to use the methanol in a fuel cell, in which its chemical energy is converted directly into electrical energy. However, the most common forms of fuel cell require hydrogen as the input fuel, this hydrogen normally being derived from reformation of a primary fuel such as methane or gasoline. Whilst methanol can be reformed, it also exhibits considerable electroactivity in its own right, and can be directly oxidised to CO<sub>2</sub> and water at catalytically active anodes in a direct methanol fuel cell. The primary limitation in the practical utilisation of such cells has been the existence of electrochemical losses at both anode and cathode, leading to poor overall conversion efficiencies; a substantial effort has therefore gone into the improvement of the kinetics at the anode, with the aim of devising cells of comparable efficiency to those already fabricated for hydrogen oxidation [1–9].

The direct oxidation of methanol to CO<sub>2</sub> at platinum-based catalytic electrodes requires six electrons, and the probability of these electrons all being simultaneously transferred is negligible. Moreover, it is not possible to devise a mechanistic route for methanol oxidation solely involving low-energy solution intermediates, and low-energy routes through to CO<sub>2</sub> require surface-bound intermediates. Considerable effort has been expended in clarifying the details of this mechanism, and in understanding the rôle of such promoters as ruthenium, and this has led, in turn, to further rapid advances in catalyst's performance. The combination of improved catalysts with advances in fuel-cell design based on conducting polymer electrolyte has now led to worldwide activity in the re-engineering of the direct-methanol fuel cell, with the immediate goal being power densities in excess of 0.2 W cm<sup>-2</sup> [10].

The rapidity of progress within the last few months has been astonishing [10,11], and this communication describes the progress in our own group at Newcastle into the construction and testing of a vapour-feed direct-methanol fuel cell comprising a proton-exchange membrane electrolyte, and carbon-supported platinum–ruthenium and platinum anode and cathode, respectively. This cell has been tested under galvanostatic polarisation conditions, and its performance under endurance testing has also been monitored. The cell was found capable of delivering up to 1 A cm<sup>-2</sup>, and, during

\* Corresponding author.

<sup>1</sup> On leave from the Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore-560012, India.

endurance tests, it was found to sustain a steady current of  $200 \text{ mA cm}^{-2}$  at about  $0.5 \text{ V}$  with a  $2.5 \text{ M}$  methanol concentration. It is note worthy that the fuel cell in the present configuration could be operated with just  $1\%$  methanol in water at a load-current density of  $75 \text{ mA cm}^{-2}$  at about  $0.55 \text{ V}$  with a fuel utilisation coefficient of  $0.56$ . At the time of sending this communication, the cell had been operated continually for about a week under the latter conditions with no apparent deterioration in the cell voltage of  $0.55 \text{ V}$ . Such tests are central to the development of stacks and are highly encouraging as a prelude to practical applications. To our knowledge, such data are not readily available in the literature.

## 2. Electrode manufacture

A membrane and electrode (M&E) assembly, which is the principal component of the cell, was obtained by pressing the carbon-supported catalysed electrodes on to both sides of purified proton-exchange membrane (Nafion-117) under a compaction pressure of  $50 \text{ kg cm}^{-2}$  for  $3 \text{ min}$  at  $125 \text{ }^\circ\text{C}$ . The anode comprises a carbon-supported platinum–ruthenium catalyst while the cathode is constituted from carbon-supported platinum catalyst with the catalyst loading in both electrodes maintained at  $5 \text{ mg cm}^{-2}$ . Catalysed carbon samples were prepared by the following method [12–15]. Activated carbon (Ketjen Black-600, AKZO Chemie) was dispersed in a beaker containing Millipore conductivity water at  $60 \text{ }^\circ\text{C}$ . The suspension was placed in an ultrasonic bath for  $15 \text{ min}$  followed by vigorous mechanical stirring for  $15 \text{ min}$ . The appropriate quantities of  $\text{Na}_6\text{Pt}(\text{SO}_3)_4$  and  $\text{Na}_4\text{Ru}(\text{SO}_3)_3$  salts were mixed with Millipore conductivity water and the pH lowered to  $3$  with  $1 \text{ M H}_2\text{SO}_4$  whilst the salts dissolved to form a deep-blue solution. The suspended carbon was then added to this solution and the suspension mixed by mechanical stirring for  $30 \text{ min}$ . Following the addition of an excess of  $\text{H}_2\text{O}_2$  ( $30\%$ , Aldrich) causing the evolution of oxygen and sulfur dioxide gases, the suspension was mechanically stirred for  $1 \text{ h}$  and boiled for  $5 \text{ min}$ . Following filtering the platinum–ruthenium catalysed carbon was washed with copious quantities of hot distilled water. The platinum–ruthenium catalysed carbon was dried in air at  $110 \text{ }^\circ\text{C}$  for  $10 \text{ h}$ . The carbon-supported platinum-catalysed cathode was prepared in a similar manner, starting from the required quantities of the activated carbon and  $\text{Na}_6\text{Pt}(\text{SO}_3)_4$  salt.

## 3. Fuel cell assembly

The fuel-cell assembly was fabricated from the methanol feed line, oxygen supply and steel frame. The former consists of a reservoir of methanol in water which is pumped with a peristaltic pump into a quartz

vaporiser maintained at  $200 \text{ }^\circ\text{C}$ . The emerging vapour is supplied to the rear of the anode and pressurised oxygen ( $25 \text{ psi}$ ) is introduced to the rear of the cathode. Heaters are located on the outside surface of the cell to enable its operation at any desired temperature in the range  $25\text{--}125 \text{ }^\circ\text{C}$ . The cell is also provided with a small close-end hole on either of the cell compartments to accommodate a thermocouple to measure the cell temperature during its operation. The active cell area, represented by the rib-channel pattern, was  $2 \text{ cm}^2$ . The fuel-cell assembly is shown schematically in Fig. 1.

## 4. Cell operation and performance

After allowing  $24 \text{ h}$  to condition a new M&E assembly in the test fuel cell at  $60 \text{ }^\circ\text{C}$ , under atmospheric air pressure and continuous supply of  $0.5 \text{ M}$  methanol in water, the performance characteristics of the cell were measured at about  $100 \text{ }^\circ\text{C}$ . The current–voltage behaviour obtained on polarising the cell galvanostatically are shown in Fig. 2 for a  $2 \text{ M}$  methanol concentration. Each point on the current–voltage plot represents an essentially steady-state performance achieved after about  $10\text{--}15 \text{ min}$  of continuous operation at the indicated current density. Endurance tests were also conducted on the cell intermittently over a cycle of  $8$  working hours, and the data are shown in Fig. 3. The experiments have been repeated with several M&E assemblies, and the observed potentials at any given current density have been found to lie within  $50 \text{ mV}$ .

The data show that the fuel cell can sustain current densities of up to  $1000 \text{ mA cm}^{-2}$ , and the power density at  $800 \text{ mA cm}^{-2}$  is  $0.16 \text{ W cm}^{-2}$ . The  $8 \text{ h}$  test shows that steady performance at  $0.1 \text{ W cm}^{-2}$  is now possible without any discernible degradation after the first hour. The open-circuit potentials of some of the fuel cell assemblies were found to be as high as  $980 \text{ mV}$ , suggesting that the performance of the electrodes is no longer the only limiting factor in the overall behaviour of the cell, and this is borne out by the fact that much of the loss above  $400 \text{ mA cm}^{-2}$  is associated with ohmic rather than electrochemical inefficiency.

The fuel cell was operated continuously at a defined load current with  $2 \text{ cm}^3$  methanol in  $200 \text{ cm}^3$  water (i.e.,  $1\%$  methanol), and the fuel utilisation coefficient, (measured output Ah/theoretical output Ah), was obtained, and found to be  $0.56$ . The cell voltage and fuel-utilisation profile obtained during such an experiment is shown in Fig. 4. The cell could be reactivated on replenishing the reservoir. It is noteworthy that the direct-methanol fuel cell employing a liquid-feed configuration showed a sharp fall in cell voltage under similar operational conditions at  $0.2 \text{ M}$  methanol concentration [10].

We have no reason to believe that the either electrode is fully optimised as yet, and further improvements in

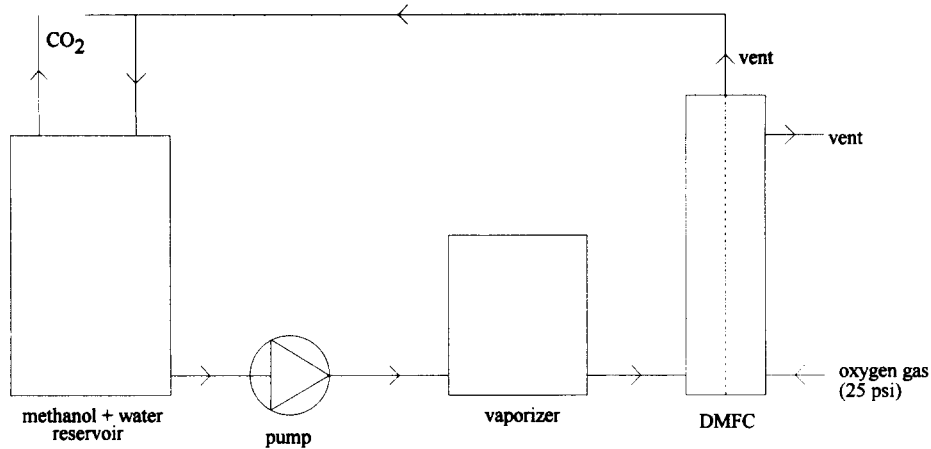


Fig. 1. Schematic description of the vapour-feed direct-methanol fuel cell developed at Newcastle. DMFC=direct-methanol fuel cells.

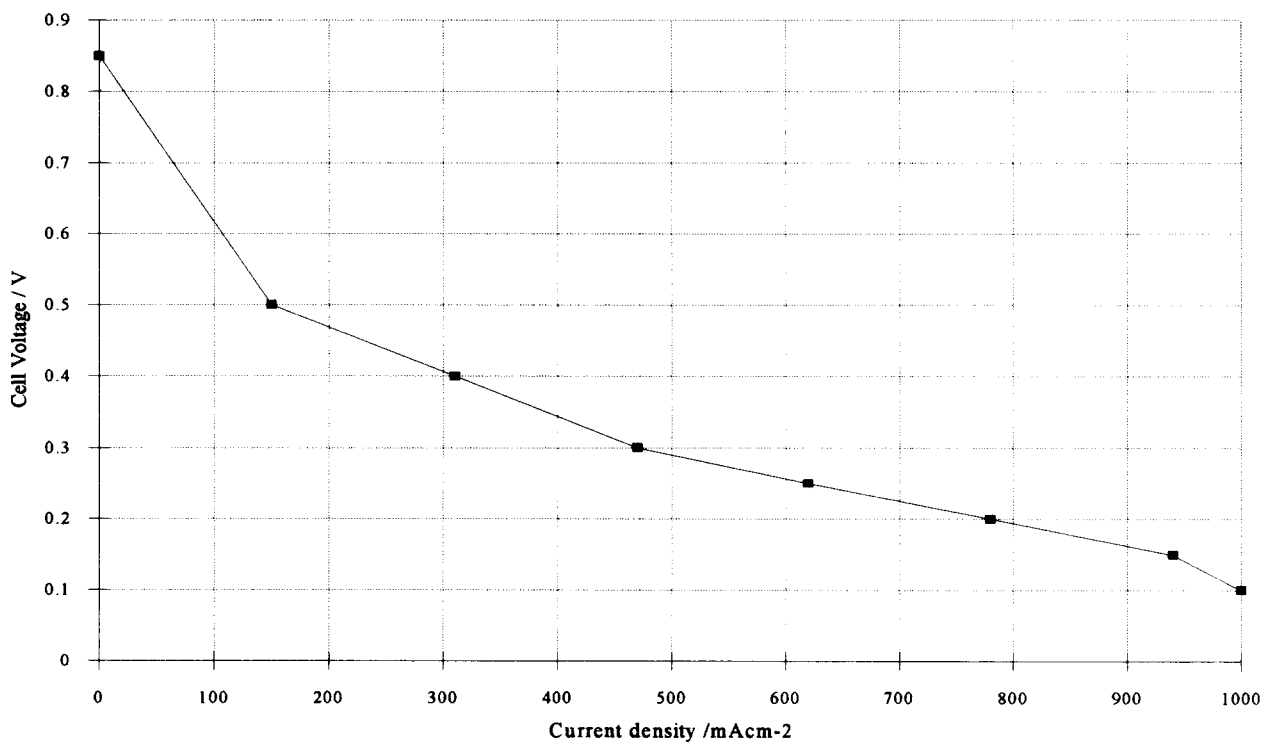


Fig. 2. Fuel-cell current density–voltage behaviour for the M&E assembly of Fig. 1 containing Nafion-117 proton-exchange membrane electrolyte and a 2 M methanol concentration. The anode was loaded with 60wt.%Pt–Ru catalyst, (5 mg platinum geometric cm<sup>-2</sup>); the cathode was loaded with 5 mg platinum geometric cm<sup>-2</sup>.

cell performance are highly likely. Such improvements will clearly lead to power densities of more than 0.2 W cm<sup>-2</sup>, sufficient to suggest that stack construction is well worthwhile.

## 5. Conclusions

It has been shown that a vapour-feed solid polymer electrolyte direct-methanol fuel cell can be operated

without any observable deterioration in performance at a fuel concentration of 1% methanol. The performance of the fuel cell under these conditions represents a significant improvement over the reported performance of the liquid-feed direct-methanol fuel cell [10]. The open-circuit potentials observed with the fuel-cell configuration employed in this study are significantly closer to the thermodynamic value, suggesting that the performance of the cell could be further optimised, and this is currently being pursued.

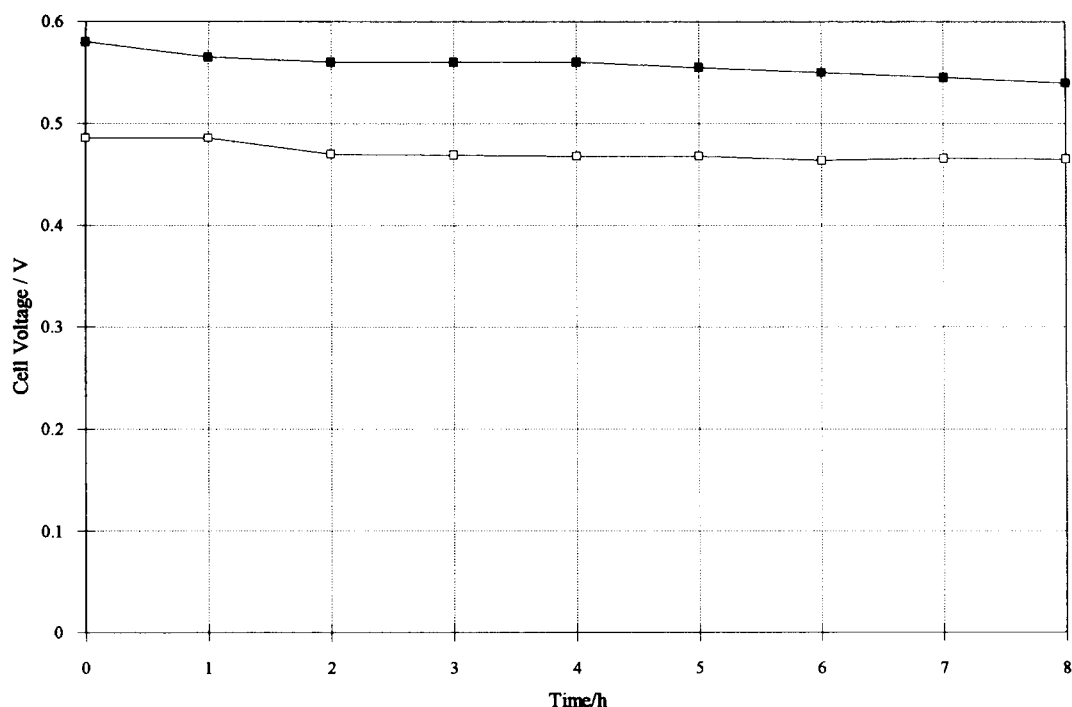


Fig. 3. Fuel-cell voltage vs. time of the M&E assembly of Fig. 1 containing Nafion-117 proton-exchange membrane electrolyte at load current densities of 100 and 200 mA cm<sup>-2</sup>, and 2 M methanol; (■) 100 mA cm<sup>-2</sup>, and (□) 200 mA cm<sup>-2</sup>.

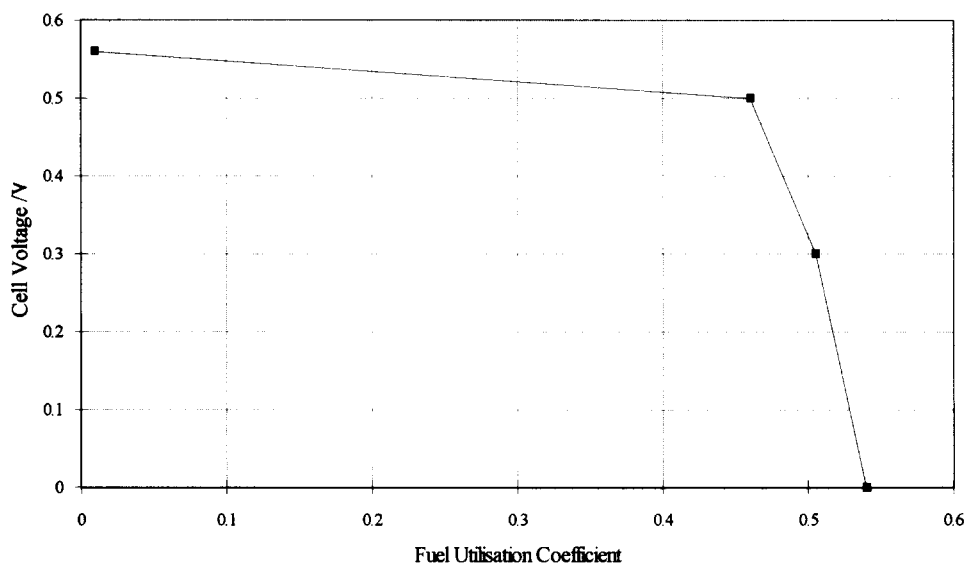


Fig. 4. Cell voltage vs. fuel utilisation of M&E assembly of Fig. 1 obtained on operating the fuel cell constantly at 100 °C with load current of 75 mA cm<sup>-2</sup> using 1% methanol and oxygen supplied at 25 psi.

### Acknowledgements

We gratefully acknowledge support from EPSRC for a fellowship (AKS) and a studentship (MPH), and the EU under the Joule Programme. We also acknowledge the enormous help given to us by Mr Roland Graham and Mr Alan Knox of the Chemistry workshops. Finally, we thank Professor K. Scott for helpful discussions.

### References

- [1] R. Parsons and T. VanderNoot, *J. Electroanal. Chem.*, 257 (1988) 9.
- [2] P.A. Christensen, A. Hamnett, J. Munk and G.L. Troughton, *J. Electroanal. Chem.*, 370 (1994) 251.
- [3] P.A. Christensen, A. Hamnett and G.L. Troughton, *J. Electroanal. Chem.*, 362 (1993) 207.
- [4] T. Iwasita-Vielstich, *Adv. Electrochem. Electrochem. Eng. (New Ser.)*, 1 (1992) 127.
- [5] L.-W.H. Leung and M.J. Weaver, *Langmuir*, 6 (1990) 323.

- [6] J.D. Roth and M.J. Weaver, *J. Electroanal. Chem.*, 307 (1991) 119.
- [7] J. Lu and A. Bewick, *J. Electroanal. Chem.*, 270 (1989) 225.
- [8] P.J. Slezak and A. Wieckowski, *J. Electroanal. Chem.*, 339 (1992) 401.
- [9] A. Hamnett, S.A. Weeks, B.J. Kennedy, G.L. Troughton and P.A. Christensen, *Ber. Bunsenges. Phys. Chem.*, 94 (1990) 1014.
- [10] S. Surampudi, S.R. Narayanan, E. Vamos, H. Frank, G. Halpert, A. Laconti, J. Kosek, G.K. Surya Prakash and G.A. Olah, *J. Power Sources*, 47 (1994) 377.
- [11] Siemens GmbH, Erlangen, Germany, unpublished data.
- [12] P. Stonehart, *Ber. Bunsenges. Phys. Chem.*, 94 (1990) 913.
- [13] H.G. Petrow and R.J. Allen, *US Patent No. 3 992 331*.
- [14] H.G. Petrow and R.J. Allen, *US Patent No. 3 992 512*.
- [15] H.G. Petrow and R.J. Allen, *US Patent No. 4 044 193*.