# AN IMPROVED-PERFORMANCE LIQUID-FEED SOLID-POLYMER-ELECTROLYTE DIRECT METHANOL FUEL CELL

P Argyropoulos, A. K. Shukla*, C. L. Jackson, K. Scott, G Murgia

Chemical and Process Engineering,
University of Newcastle, Newcastle upon Tyne,
NE1 7RU, U K

* On leave from Solid State and Structural Chemistry Unit, Indian Institute of Science, Bangalore - 560 012, India.

Solid-polymer-electrolyte direct methanol fuel cells (SPE-DMFCs) are presently under active development particularly for applications in transport and various portable electronic devices. Over the years, significant progress has been made in the performance of SPE-DMFCs [1]. But one essential condition for achieving relatively high power-densities has been the pressurisation of the air/ oxygen feed to the cathode. However, for most conceivable applications, operation of the SPE-DMFCs at near-ambient conditions would be essential both to reduce parasitic energy losses and to simplify the design protocol. As a part of our ongoing research programme in this area [2-4], this communication reports the performance of a liquid feed SPE-DMFC at near-ambient pressures.

## EXPERIMENTAL

The experiments were carried out using membrane electrode units (MEUs) having a geometrical area of 25cm$^2$. The anodes of these MEUs comprised a 1:1 at. wt.% carbon-supported Pt-Ru catalyst with a Pt loading of 1mg cm$^{-2}$ and a Ru loading of 0.46 mg cm$^{-2}$, while the cathodes comprised carbon-supported Pt with a Pt loading of 4.6 mg cm$^{-2}$. In the SPE-DMFC, the anode and the cathode of the MEU were contacted on their rear with high-density graphite blocks, into which were cut gas/liquid flow channels.
Prior to the data collection, the MEUs were fully hydrated by circulating 1M aqueous methanol through the anode compartment of the SPE-DMFC at 90$^o$C for c. 24 h. Subsequently, galvanostatic current-voltage polarisation On polarising the anode galvanostatically, hydrogen was evolved at the cathode, which also served as a reference electrode.

## RESULTS AND DISCUSSION

The galvanostatic polarisation data for the anode with 1M aqueous methanol feed at 15cm$^3$ min$^{-1}$ and temperatures of 60$^o$C and 90$^o$C are shown in Fig. 1(a) and (b), respectively. The data reflect that at 60$^o$C, the anode tends to polarise due to transport limitations at a load current density of c. 400 mA cm$^{-2}$. By contrast, the anode mass transport polarisation occurs at a load current density as high as about 1 A cm$^{-2}$ at 90$^o$C.

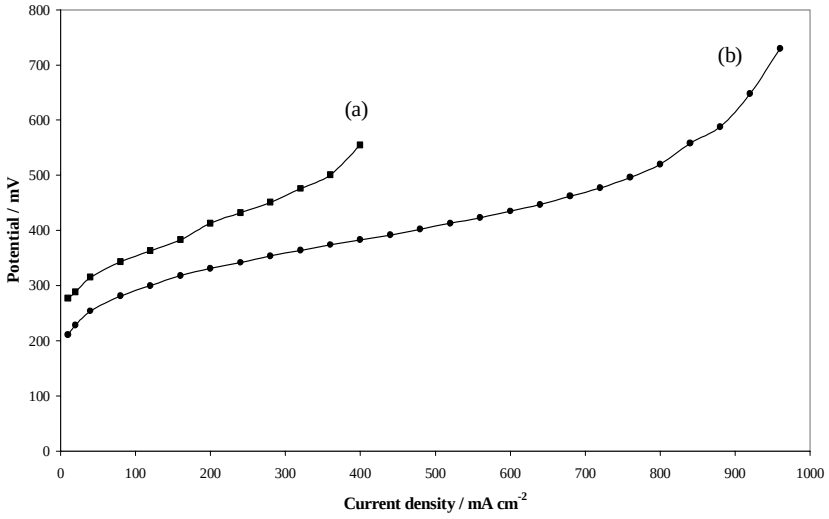


Fig. 1. Galvanostatic polarisation data for the anode with 15 cm$^3$ min$^{-1}$ 1M methanol (a) 60$^o$C and (b) 90$^o$C.

The limiting current densities lead to calculation of effective mass-transfer coefficients as 1.6 x $10^{-5}$ m $s^{-1}$ and 0.64 x $10^{-5}$ m $s^{-1}$ at 90°C and 60°C, respectively. The difference in mass-transfer coefficient values are not simply related to the changes in the solution physical properties and diffusion coefficients with temperature.

Polarisation data for the SPE-DMFC with 1 $dm^3$ $min^{-1}$ air cathode at (a) 60°C, and (b) 90 °C; (c) power-density are shown in Fig. 2. It is noteworthy that the maximum power density of 180 mW $cm^{-2}$ was achieved with SPE-DMFC, while operating at 90°C with the oxygen-fed cathode. Under similar conditions, the SPE-DMFC could provide a maximum power density of only about 90 mW $cm^{-2}$, while operating with an air-fed cathode. The marked increase in the performance of the SPE-DMFC while employing oxygen suggests that a decrease in concentration of oxygen surely inhibits the platinum catalyst for oxygen reduction. The increase in the performance of the SPE-DMFC at 90°C in relation to 60°C may be attributed to the reduction in resistance of the cell due to increased conductivity of Nafion-117 membrane electrolyte, as well as an increase in the methanol oxidation of the anode. Tafel plots from the current-voltage polarisation data both at 60°C and 90°C were obtained. Although there was little change in the Tafel solpes (c. 100 mV $dec^{-1}$) in the current density range between 10 – 100 mA $cm^{-2}$ for the methanol-oxidation reaction while increasing the temperature from 60°C to 90°C, the exchange current-density was found to increase from c. 1 x $10^{-5}$ A $cm^{-2}$ to c. 5 x $10^{-5}$ A $cm^{-2}$ which are in conformity with the values reported in the literature [5].

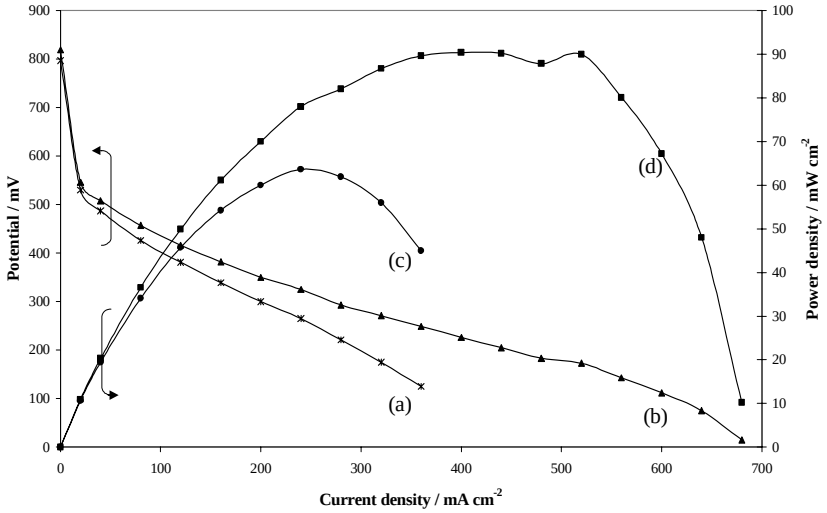


Fig. 2. DMFC polarisation data.

A comparison of the performance of the DMFC with, and without, air fed with the aqueous methanol solution to the anode was made. A superior performance of the cell is demonstrated with this strategy. The experimental performance of the mixed reactant anode system is numerically modelled using phenomenological transport equations for electrocatalyst layers, diffusion layers and the polymer electrolyte membrane.

## EMPIRICAL MODEL EQUATION.

To model the performance of the DMFC we propose the following semi-empirical equation for the cell voltage, $E_{cell}$,

$$E_{cell} = E_O^* - b_{cell} \log j - R_e j + C_1 \ln(1 - C_2 j)$$

where:

$$b_{cell} = \frac{2.303 R\,T}{F}\left(\frac{1}{\alpha_a} + \frac{1}{\alpha_c}\right), \quad C_1 = \frac{NRT}{\alpha_a F}$$

$$C_2 = \frac{1}{nFk_{eff}C_{ME}}, \quad E_O^* = E_{Ocell} - \frac{RT}{\alpha_c F}\ln\left(\frac{p_O^{ref}}{j_{Oc}\,p_O}\right) - \frac{RT}{\alpha_a F}\ln\left(\frac{C_{ME}^{ref}}{j_o C_{ME}^N}\right)$$

In the above j is the current density, $\alpha_a$ and $\alpha_c$ are transfer coefficients for the oxidation of methanol and reduction of oxygen respectively, $R_e$ is the internal cell resistance (mainly due to the polymer electrolyte membrane), N is a reaction order for methanol oxidation, $k_{eff}$ is an effective mass transport coefficient for the anode side of the cell, $C_{ME}$ is the methanol concentration and $p_o$ is the oxygen pressure. $E_o^*$ is the standard potential for the DMFC overall reaction.

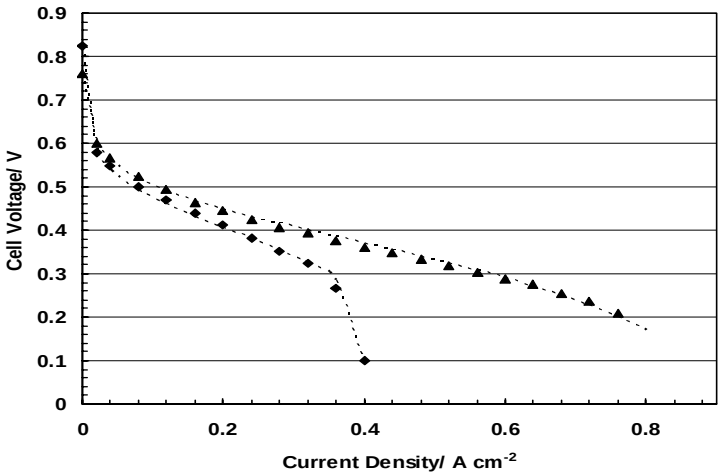


Figure 3: Demonstration of the empirical equation to an oxygen fed DMFC operated at ambient pressure with 1.0 M methanol solution. (Cell temperature, ●: 60°C ▲: 90°C).Dashed line model data.

The model equation is applied to experimental data for a small-scale fuel cell and produces electrochemical parameters (see Table 1) generally consistent with those expected for the individual components of the fuel cell MEA (Fig. 3).

**ACKNOWLEDGEMENTS**.

The authors would like to acknowledge the following: European Commission for IHP Marie Curie B30 research training grants to Drs. P. Argyropoulos and G Murgia. EPSRC and the MOD (through the joint grant scheme) supported Professor A. K. Shukla with a visiting fellowship. EPSRC supported Mr. C. Jackson through a PhD studentship.

**REFERENCES**

[1]. A. S. Aricò, S. Srinivasan and V. Antonucci, Fuel Cells 1(2001)1.
[2]. M. Neergat and A. K. Shukla, J. Power Sources 104(2002)289.
[3]. M. K. Ravikumar and A. K. Shukla, J. Electrochem. Soc. 143(1996)2601.
[4]. K. Scott, W. Tamma and J. Cruickshank, J. Power Sources 65 (1997)159.
[5]. A. S. Aricò, V. Antonucci, N. Giordano, A. K. Shukla, M. K. Ravikumar, A. R. Roy, S. R. Barman and D. D. Sarma, J. Power Sources 50 (1994) 295.
[6] A. K. Shukla, C. L. Jackson, K. Scott and G. Murgia, J.Power Sources (in press).

| ***Cell Temperature/ K*** | ***MeOH Solution Concentration/ M*** | ***Calculated values for the Argyropoulos, Scott et al. empirical equation coefficients*** | | | | |
|---|---|---|---|---|---|---|
| | | ***Eo/V*** | ***B/V*** | ***R/Ωcm$^{-2}$*** | ***$C_1$/V*** | ***$C_2$/ cm$^{-2}$A$^{-1}$*** |
| ***343.15*** | ***0.125*** | *0.39* | *0.1176* | *0.126645* | *0.085* | *52.3* |
| ***348.15*** | ***0.125*** | *0.4043* | *0.119* | *0.094513* | *0.09* | *43.34* |
| ***353.15*** | ***0.125*** | *0.42* | *0.121* | *0.0649* | *0.095* | *35.45* |
| ***358.15*** | ***0.125*** | *0.432* | *0.123* | *0.041364* | *0.108* | *29.4* |
| ***363.15*** | ***0.125*** | *0.448* | *0.125* | *0.0225* | *0.12* | *23.57* |
| ***343.15*** | ***0.25*** | *0.36* | *0.11766* | *0.126645* | *0.057* | *20.82* |
| ***348.15*** | ***0.25*** | *0.37* | *0.119* | *0.094513* | *0.061* | *16.93* |
| ***353.15*** | ***0.25*** | *0.38* | *0.121* | *0.0649* | *0.065* | *13.665* |
| ***358.15*** | ***0.25*** | *0.3912* | *0.12297* | *0.041364* | *0.069* | *11.45* |
| ***363.15*** | ***0.25*** | *0.4058* | *0.125* | *0.0225* | *0.073* | *10.6* |
| ***343.15*** | ***0.5*** | *0.347* | *0.11766* | *0.126645* | *0.07* | *8.62* |
| ***348.15*** | ***0.5*** | *0.3636* | *0.119* | *0.094513* | *0.077* | *7.69* |
| *353.15* | *0.5* | *0.368* | *0.121* | *0.0649* | *0.082* | *6.2* |
| *358.15* | *0.5* | *0.382* | *0.123* | *0.04136* | *0.088* | *5.77* |
| *363.15* | *0.5* | *0.4* | *0.125* | *0.0225* | *0.12* | *4.75* |
| *303.15* | *0.75* | *0.215* | *0.109* | *0.346* | *0.053* | *25.5* |
| *313.15* | *0.75* | *0.25* | *0.111* | *0.29451* | *0.059* | *16.5* |
| *323.15* | *0.75* | *0.28* | *0.113* | *0.248* | *0.078* | *10.43* |
| *333.15* | *0.75* | *0.32* | *0.115* | *0.192* | *0.102* | *6.6* |