MASS TRANSFER IN AND MODELING OF DIRECT METHANOL FUEL CELLS

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A study of the mass transfer behaviour, carbon dioxide gas evolution and flow and modelling in Liquid Feed Direct Methanol Fuel Cell (LFDMFC), is reported. The structure of the DMFC is a composite of two porous electrocatalytic electrodes; Pt-Ru-carbon catalyst anode and Pt black cathode, on either side of a solid polymer electrolyte (SPE) membrane (Nafion). The anode catalyst were either: Electrochem. Inc (USA);Pt, 20 wt%, Ru 10wt% on Vulcan XC-72R carbon. Johnson Matthey Technology Centre developmental material, (UK); 35 wt% Pt, 15 wt% Ru. In house catalyst; 40 wt% Pt, 20wt% Ru on ketjen black carbon. Figure 1 shows cell voltage data for three types of anode catalysts using air fed cathodes. Data for the Newcastle catalyst and Electrochem catalyst were comparable under the conditions used.

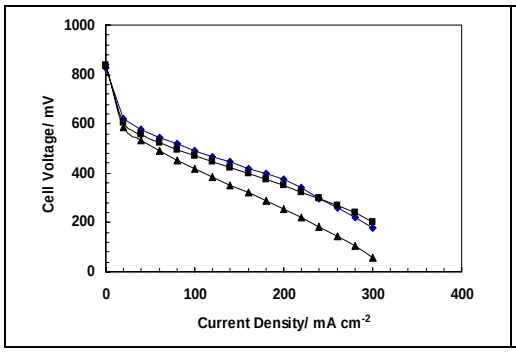



**Figure 1:** The effect of anode catalyst on the cell voltage characteristics of the DMFC. (◆: Electrochem, ■: Newcastle, ▲: JMTC. Methanol concentration: 2 moldm$^{-3}$. Methanol solution flow rate: 0.84 cm$^3$ min$^{-1}$. Cell temperature: 90°C. Teflon loading: 13 %).

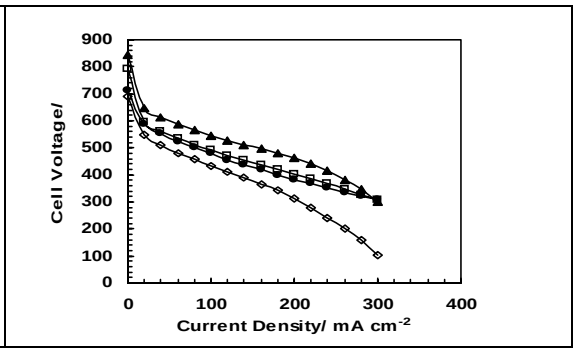


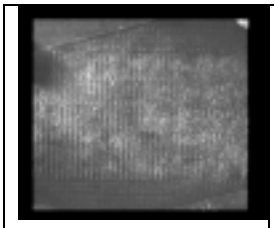

**Figure 2:** The effect of temperature on the cell voltage characteristics of the DMFC. (▲: 90°C, oxygen. ❑: 90°C, air. ●: 65°C, oxygen ✧: 65°C, air. Methanol solution flow rate: 0.84 cm$^3$ min$^{-1}$. Teflon loading 13 %).

Figure 2 presents data for the effect of cell temperatures (60°C and 90°C) on performance with an air fed cathode for the Electrochem. catalyst. The best performance was achieved at the highest temperature of 90°C. In the range 60-90°C there was an approximate 40 mV drop in cell potential per 10°C fall in temperature.

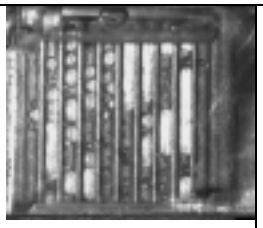
**Flow Visualisation in the DMFC**

Flow visualisation studies of the carbon dioxide gas release and two-phase flow in the anode side of the DMFC were conducted with cells manufactured with acrylic flow beds on the anode. The flow of methanol and carbon dioxide in the anode flow bed was recorded using a high-speed video camera. A number of parameters were investigated in this flow visualisation study: two different flow bed designs, two different cell sizes (25cm$^2$ & 102cm$^2$ cross sectional area), two different gas diffusion layer support materials (ETEK carbon cloth Type A & ETEK Toray carbon paper), liquid inlet flow rate and current density.

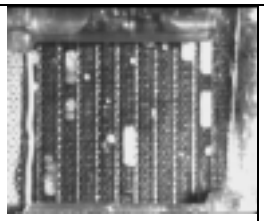
Figure 3 presents pictures of operating MEAs in both the large cell and small cell with carbon paper or cloth under the same conditions (current density 50mA/cm$^2$, channel flow rate 2.5 ml/min). Overall, in the study, we observed that carbon dioxide is not uniformly produced over the surface of the gas diffusion layers, especially in the case of the small cells. A number of point sources of gas release exist, with a continuous high rate bubble generation, and areas with no such activity. This is attributed to the structure of the electrode and the use of Teflon. Tortuous paths that connect the surface with the catalyst area are probably "flooded" with the liquid phase. Hence there are a limited number of "hydrophilic" open channels for carbon dioxide flow. Thus gas could accumulate in the diffusion layer and the reaction layer, and form large bubbles or slugs (compared with the layer structure) which move partly in a vertical plane until they will find an open, horizontal, channel for flow from the reaction site.



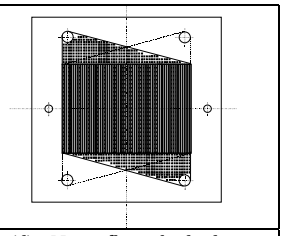
*(a) Gas evolution for carbon cloth in the large cell (Current density 50 mA/cm$^2$, Liquid flow rate 10 ml/min/channel,, Cell Temperature 75°C, Active area 102 cm$^2$)*



*(b) Gas evolution for carbon paper in the small cell (Current density 50 mA/cm$^2$, Liquid flow rate 10 ml/min/channel, Cell Temperature 75°C, Active area 9cm$^2$)*



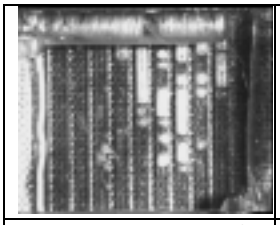
*(c) Gas evolution for carbon cloth in the small cell (Current density 50 mA/cm$^2$, Liquid flow rate 10 ml/min/channel, Cell Temperature 75°C, Active area 9cm$^2$)*



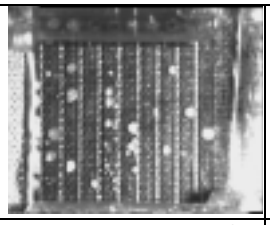
(d) New flow bed design based (Active area of 272cm$^2$)

**Figure 3:** Gas evolution properties for two cell sizes, two backing layer materials, and the new flow bed design.

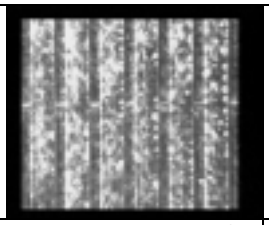
With carbon paper MEA large gas slugs are formed (0.8-1.8 mm) which attach to the surface of the paper and block the channel. With the carbon cloth MEA the flow regime is bubbly with relatively small gas bubbles (0.6-0.8 mm), which have a tendency to coalesce and form bubble swarms. In the case of the large cell the bubble flow pattern is even better, with a more uniform flow of bubbles. This is attributed to the better flow manifold design in the larger cell.



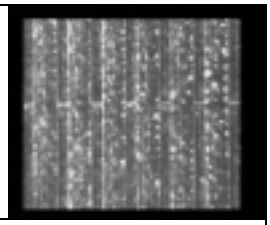
*(a) Gas evolution for carbon cloth in the small cell (Current density 30 mA/cm$^2$, Anode inlet flow rate 6 ml/min, Cell Temperature 75°C, Active area 9cm$^2$)*



*(b) Gas evolution for carbon cloth in the small cell (Current density 30 mA/cm$^2$, Anode inlet flow rate 1137 ml/min, Cell Temperature 75°C, Active area 9cm$^2$)*



*(c) Gas evolution for carbon cloth in the large cell (Current density 50 mA/cm$^2$, Anode inlet flow rate 26 ml/min, Cell Temperature 75°C, Active area 102 cm$^2$)*



*(d) Gas evolution for carbon cloth in the large cell (Current density 50 mA/cm$^2$, Anode inlet flow rate 1137 ml/min, Cell Temperature 75°C, Active area 102 cm$^2$)*

**Figure 4:** Effect of anode side liquid phase inlet flow rate on gas removal characteristics for the small and large cell

Figure 4 shows the effect of flow rate, with other conditions the same (current density 30 mA/cm$^2$, 75°C), for the carbon cloth material in the small cell. It is evident that as the flow rate increases the gas slugs are removed and the bubble size becomes smaller and eventually blocking is virtually

eliminated. At the same time, with the increase in liquid flow rate, conditions in the exhaust manifold improve and, at the highest flow rates, no gas slugs are present.

The manifold design used for the small cell comprised of a straight circular cross section tube machined inside the main body of the acrylic block, with holes open on its periphery. This design was shown to produce poor gas, liquid flow distributions. From this study the improved flow bed design of the large cell (Figure 3(d)) was produced. Figure 4 shows the two phase flow in the channels of the large cell for flow rates of 26 ml/min and 1137 ml/min. The beneficial effect of an increase in flow rate is apparent from the data, i.e. reduction in bubble size and in bubble hold-up in the channels.

The issue of methanol solution flow rate and its effect on cell electrical performance is complicated by the nature of the unusual electrode structure of solid polymer electrolyte cells. The solution flow will influence the cell behaviour through several effects; access of methanol solution into the structure, removal of carbon dioxide from the active catalyst sites, heat exchange between the solution and the catalyst layer. If the solution temperature is lower than that of the catalyst layer, higher flow rates will encourage greater heat removal from the catalyst causing greater cooling of the catalyst and lower catalyst temperature with thus a reduction in the cell voltage, at a fixed current density. Thus potentially an optimum solution flow rate could exist which gives a maximum in cell voltage performance as the benefits of mass transfer become less significant in comparison to the cooling of the catalyst layer. Others have reported indeed such a maximum power performance in the literature.

**Single cell Mass Transport Characteristics & Engineering modeling for DMFC stacks**

To examine the effect of flow rate on methanol mass transfer we operated the DMFC with lower methanol solution concentrations. The latter had the effect of imposing limiting current operation on the fuel cell as is apparent in Figure 4.

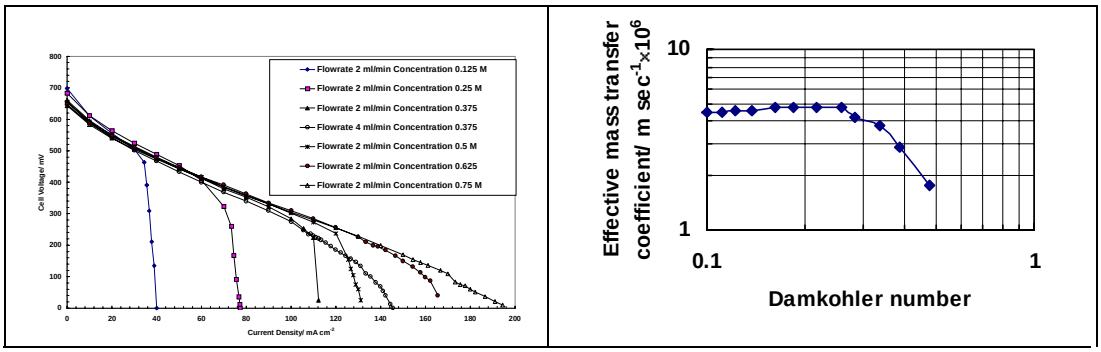



**Figure 5:** (a) Effect of methanol solution concentration on DMFC limiting current behaviour, (b) The effect of Damkohler number on the effective mass transfer coefficient in the DMFC

Measuring the limiting currents, $i_{lim}$ , for the fuel cell we were able to determine the impact of flow rate on cell mass transfer. Fig 5 shows the variation of effective mass transport coefficient with Damkohler number, Da, which is a dimensionless group defining the ratio of limiting current density to volumetric flow rate, Q, ($Da = i_{lim} A / 6 F C_{methanol} Q$). In this data as Da increases, i.e. flow rate increases, the mass transport coefficient increases, which corresponds to the anticipated beneficial effect of carbon dioxide removal from the surface of the MEA.

The mass transfer behaviour associated with the two phase flow in the MEA diffusion layer has been modelled on the basis of diffusion and convection augmented by the electro-osmotic transfer of methanol and water through the structure to the catalyst surface. This model with appropriate kinetic and resistance models of the MEA structure has enabled good prediction of the cell voltage response under a mass transport controlled regime (see Figure 6).

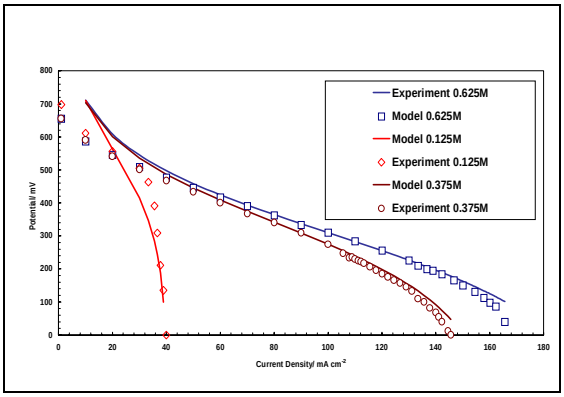



**Figure 6:** Modelling cell voltage response under a mass controlled regime

A model was developed for estimating a liquid fed DMFC stack temperature profile, heat flows, and to make decisions on thermal management strategy. Heat production and losses to the cell surroundings are calculated with the aid of a one-dimensional steady state thermal model based on the energy conservation equation. Figure 7(a) shows typical temperature profiles in the DMFC stack, where clearly significant variation in temperature can result, which will have important implications in fuel stack performance.

A model was developed to assess the pressure drop performance of the anode and cathode side of a liquid feed DMFC cell with a flow bed design based on a plate heat exchanger concept. Based on the pressure drop model for a single DMFC cell, we formulated a stack model that predicts the flow distribution and the overall stack pressure drop characteristics. Figure 7(b) shows results on anode side flow distribution, and more specifically on cell's inlet flow rate. These results were based on the assumption that each cell requires a flow of 1.0 $dm^3min^{-1}$ of methanol solution. There are severe flow maldistribution problems especially when the number of cells in stack exceeds 10 or more. This factor is quite critical because it determines the efficiency of carbon dioxide removal, the flow pattern inside the flow bed, the overall stack heat management, and most significantly the electrical performance.

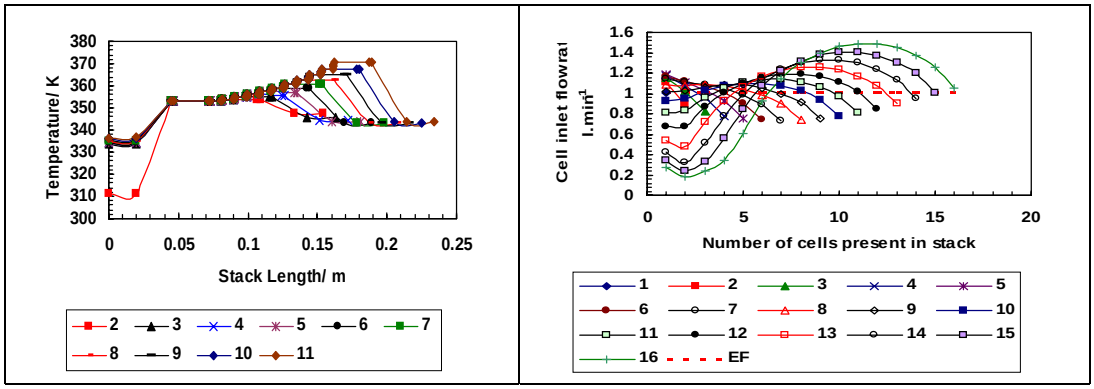



**Figure 7:** Model predicted temperature profiles and anode side flow distribution for DMFC stack operated at 80°C anode side inlet temperature, flow rate 1.0 l/min/cell.

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