MASS TRANSPORT AND METHANOL CROSSOVER ASPECTS OF MATERIALS FOR DIRECT METHANOL FUEL CELLS.

K. Scott[1], P. Argyropoulos[1], C Jackson[1], W. M. Taama[1], J Horsfall[3], K Lovell[3] & K. Sundmacher[2]
[1]Department of Chemical and Process Engineering, University of Newcastle upon Tyne. Newcastle upon Tyne, NE1 7RU, UK.
[2]Max-Planck-Institut fur Dynamik komplexer technischer Systeme, Magdeburg, Germany.
[3]Department of Material and Medical Sciences, Cranfield University, UK.

A study of a small scale Liquid Feed Direct Methanol Fuel Cell (LFDMFC), based on solid polymer electrolyte membrane, is reported. The performance of a variety of flow cell designs based on a parallel flow channel, a spot design of flow bed and a series of stainless steel mesh are compared. The study was supported from a flow visualisation study analysing the effect of flow bed design on cell gas management and performance. The performance of the direct methanol fuel cell (DMFC) using membrane electrode assemblies (MEA) based on radiation grafted proton exchange membranes is also reported. The performance of the DMFC, with these low cost membranes, is as good as or superior to that of cells based on Nafion® under identical operating conditions. The use of stainless steel as material for flow beds is shown to be a viable alternative to the use of graphite and alternative structures using mesh can enhance performance. An improvement in the performance of the direct methanol fuel cell has also been achieved by performing a dynamic feeding strategy of the methanol feed to the cell.

The membrane electrode assemblies used in the work were based on Nafion® bonded carbon supported catalyst; platinum/ruthenium (2 mg cm^{-2}) for the anode and platinum (1 mg cm^{-2}) for the cathode. All experiments were performed in cells with a cross section area of 9 cm^2. The cells were either made with either graphite, stainless steel or stainless steel mesh flow beds. The membranes used in the MEA were either Nafion® 117 or radiation grafted ETFE-styrene copolymer.

Alternative flow bed designs and materials: Gas management properties and power performance

Direct methanol fuel cell flow beds have been fabricated with different stainless steel mesh (Fig 1). With the aid of acrylic transparent DMFC we examined the effect of the flow bed geometry and morphology on carbon dioxide evolution, accumulation and removal from the anode side flow bed to the exhaust manifold. As a comparative basis we use a simple flow bed, made from graphite, based on a series of parallel channels. An alternative, high voidage, structure with an embedded stainless steel mesh was evaluated as an alternative flow bed design. A variety of mesh geometry (contours, thickness and voidage) were investigated (Table 1) to try to understand the changes in the gas removal mechanism due to the mesh.

Table 1: Expamet mesh properties

	Openings size mm (LW)	Openings size mm (SW)	% of open area	Strand Width/ mm	Strand Thick/ mm	Weight per area/ kg m^{-2}	Measured Thickness /μm
941MM	1.0	0.67	-	0.2	0.15	0.8	204
957MM	1.5	0.92	46	0.22	0.15	0.62	220
927S	3.175	1.81	60	0.254	0.152	0.34	220
926S	3.18	1.95	12	0.79	0.46	2.91	1041
707S	4.75	2.38	43	0.56	0.46	1.69	853

Of the five mesh evaluated the materials coded 926S and 707S showed excellent gas removal characteristics (Fig 1 a-g) and improved electrical performance, in comparison to the graphite

flow bed design, over a wide range of operating conditions (Fig 2). Improvements of some 5-15% in terms of peak power density were measured for the two promising mesh materials. The present study identified that a thick mesh with low voidage and "rough" surface is a promising candidate material. Fine minimesh and open structure mesh showed an inferior performance. Further study is required to both characterise the electrochemical performance of these cells and to investigate a larger number of mesh to identify, and optimise, the most promising commercially available product. In terms of fabrication and cost there are distinct advantages in the use of the mesh flow beds.

Stainless steel flow beds have been tested successfully over prolonged time periods and gave comparable performance with that of graphite cells with higher pressure giving superior performance. Up till now the stainless steel DMFC cell has been operated for six months with no performance loss. Monthly visual inspections have shown no discoloration or other evidence of corrosion or passivating film formation.

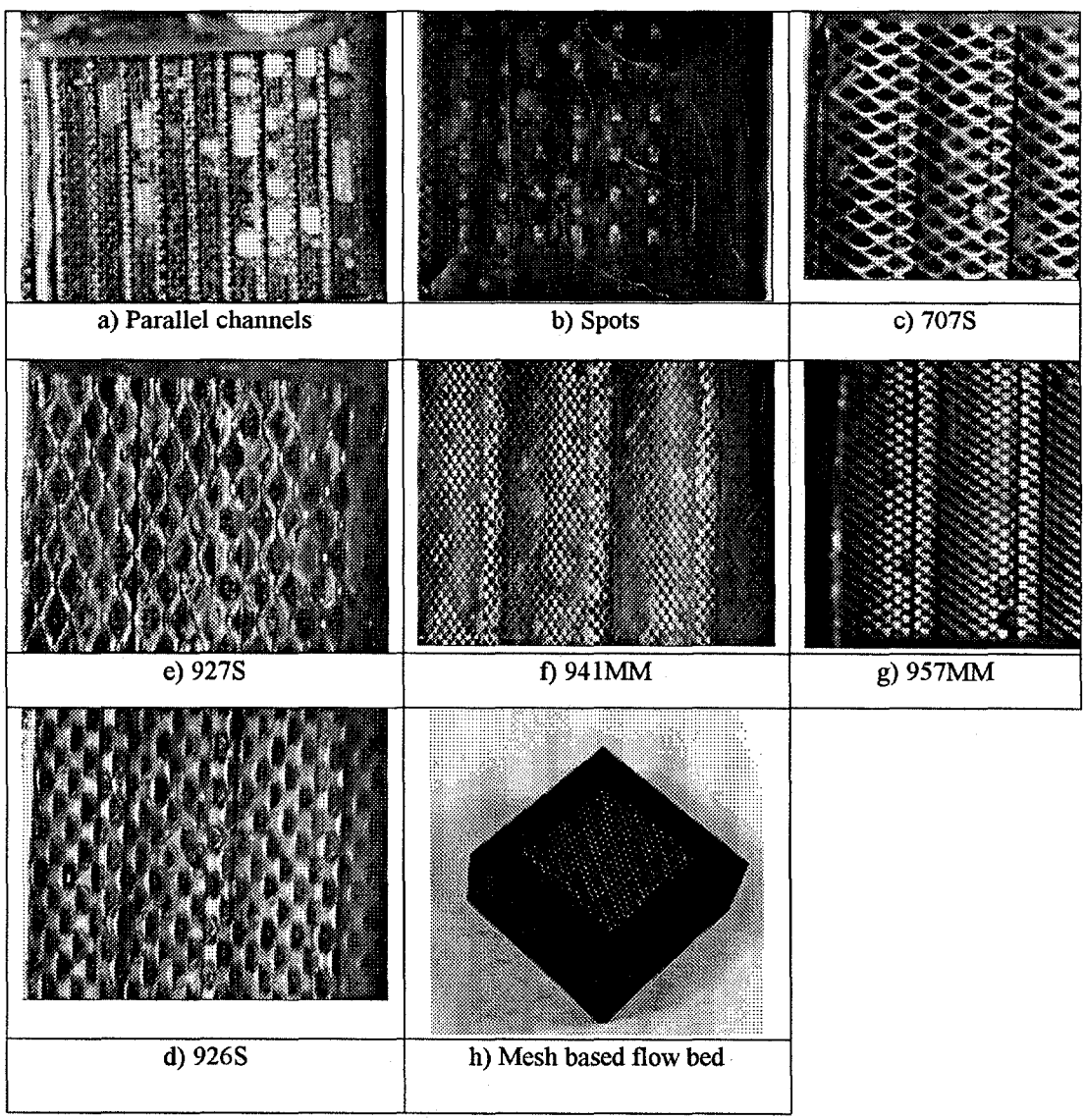

Figure 1: *Gas evolution characteristics of the various flow bed designs*

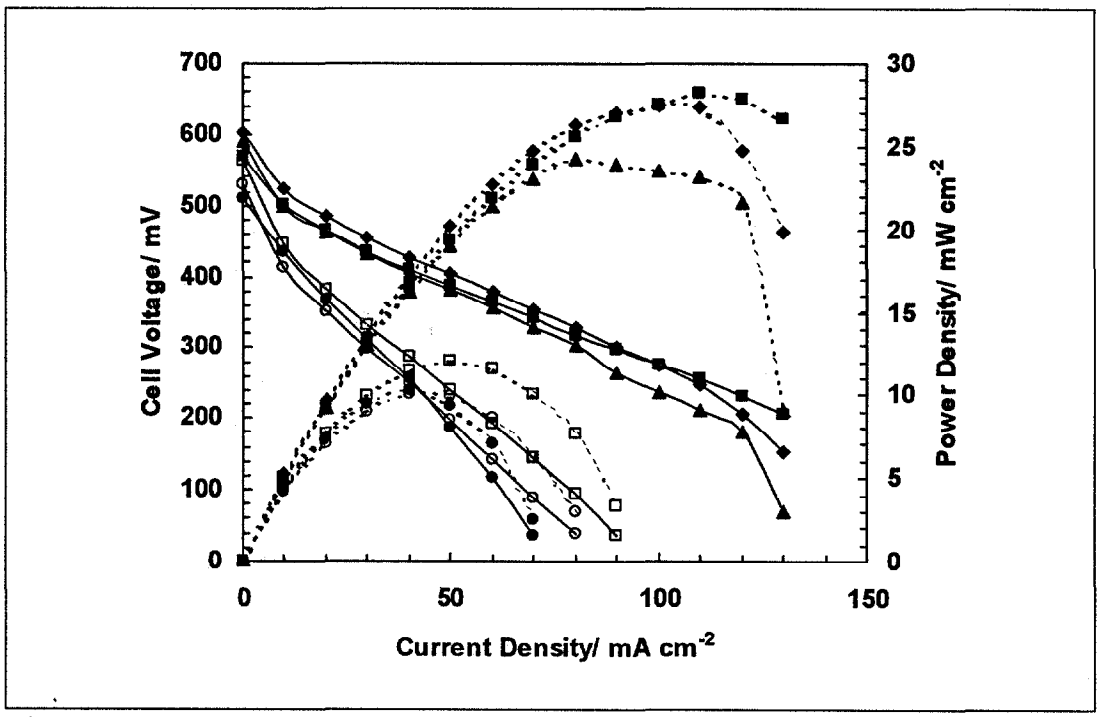

Figure 2: *polarisation data for the dmfc cells . (90℃ liquid temperature, 1.0 M methanol, 1bar air anode side flow rate 500 cm^3min^{-1}) ♦:926S ●:927S ■: 707S □: Poco® ≤: 957MM □: 941MM*

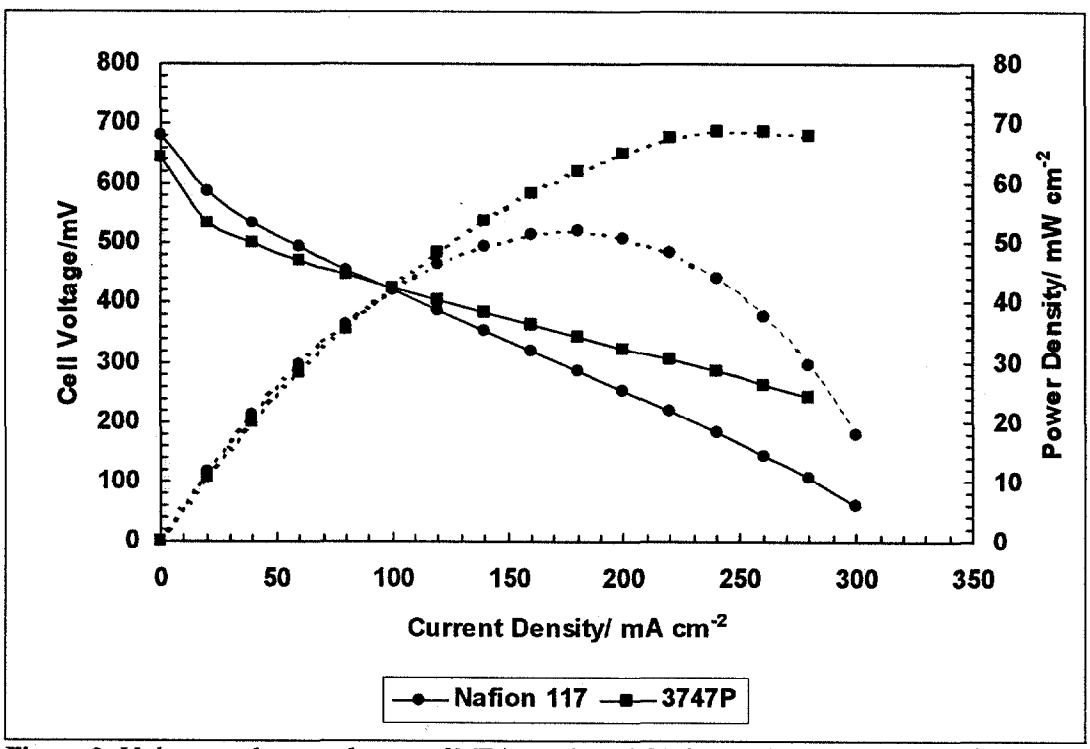

Figure 3: *Voltage and power density of MEAs made with Nafion and ETFE-3747P membranes*

Alternative membrane materials for Direct Methanol Fuel Cell

Two alternative membrane materials were evaluated for DMFC operation. These membranes exhibited relatively low methanol diffusion coefficients, in comparison to Nafion, and were thus felt to be potentially useful in reducing the problem of methanol crossover from anode to cathode. Fig. 2 compares the performance of the 3747P membrane and Nafion 117. Noticeable there is a slight improvement in the open circuit voltage, approximately 35 mV, and at higher current densities a significant voltage and power performance improvement is seen. The data indicates that the electrical resistance of the MEA with the 3747P membrane is lower than with Nafion® (the slope of the voltage current curve is lower).

Dynamic feeding of the DMFC

A major problem to be overcome with the direct methanol fuel cell is that of methanol crossover from anode to cathode. Most membranes facilitate the transfer of methanol due to the diffusion and electro-osmotic drag effects. The crossover of methanol depolarises the cathode and reduces the cell voltage. The effect can be reduced in principle by reducing the methanol concentration at the anode side of the MEA, but this results in voltage loss due to either mass transport limitations or kinetic limitations. We have adopted an alternative strategy in which the feed concentration of methanol to the cell is dynamically oscillated which results in a performance improvement in voltage some 10% greater than that with a steady methanol feed concentration (Fig 4). For example as shown in Fig. 4 by pulsing the feed concentration a steady improvement in voltage is achieved. The factor behind this performance improvement is a reduction in the impact of methanol crossover, i.e. when the methanol feed is stopped back diffusion of methanol, from membrane/cathode to anode, occurs reducing cathode polarisation.

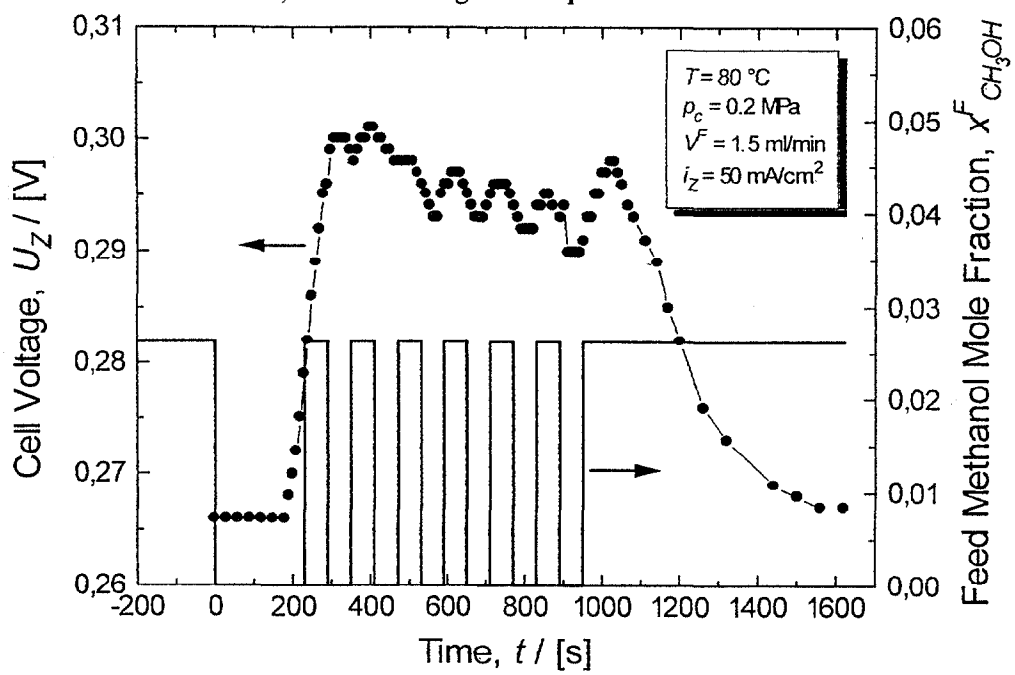

Figure 4: Voltage response with dynamic feeding of the DMFC

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