PERFORMANCE & MODELLING OF DIRECT METHANOL FUEL CELL STACKS

K. Scott, P. Argyropoulos, A. Simoglou, W.M. Taama
Chemical & Process Engineering Department, University of Newcastle upon Tyne
Merz Court, Newcastle upon Tyne, NE1 7RU United Kingdom
Tel. 0044-191-2228771 Fax: 0044-191-2225292
E-Mail: K.Scott@ncl.ac.uk

ABSTRACT

A large-scale prototype DMFC stack has been built at Newcastle University (25 cells of 270 cm^2 active area per cell, nominal power output 500W) based on a flow bed design developed by the authors with the aid of a flow visualisation study and fluid flow modelling. In addition a series of engineering models were developed for predicting, stack voltage, the fluid distribution from the stack manifolds, the overall system pressure, the chemical equilibrium in both anode and cathode flow beds and the thermal management of the stack. Results of this work are presented in terms of an overall engineering model that incorporates all the aforementioned models.

Steady state and dynamic electrical performance of the prototype stack is being presented. Our experience from scaling up the system, and the problems that had to be solved prior achieving the designed power output, are also briefly discussed. A systematic methodology is described which will use modelling techniques and the experimental data collected from the prototype stack, in order to design a new DMFC stack with higher power output.

INTRODUCTION

The main research of direct methanol fuel cells (DMFC) based on solid polymer electrolyte (SPE) has been in steady state and small-scale operation within laboratory environments. As the development work continues the engineering of the system have been mainly neglected since the commercialisation of the relative technology is still far away (expected at 2008). Little published information exists on transient operation-including start up and shut down, and efficient transition between operating conditions-and hence the dynamic response of the cells is mainly unknown. A large number of issues arising from scaling up single small scale DMFCs like flow distribution from the stack manifolds, effective thermal management, increased pumping requirements due to higher friction losses within the system, large quantities of exhaust gases and liquid feed that have to be circulated, heated up, and disengaged. The exact nature and magnitude of these processes, and their effect on a large multi cell stacks have only recently been addressed in a systematic way with the aid of mathematical modelling and experimental studies [1-8].

Another major area obstructing DMFC commercialisation is the high cost of the materials being used for membrane electrode assemblies and cell fabrication. Furthermore these were mainly developed for the hydrogen SPE fuel cells and hence they are not optimised for the special needs of DMFC, lowering thus the ratio between the achieved electrical performance and the associated cost. Examples of such components are the bipolar plate material and the solid polymer electrolyte. Stainless steel based cell plates, or a combination of graphite with stainless steel or polymer materials are an attracting alternative for the cell plates, and alternative low cost and methanol permeation membrane materials are the subject of ongoing research world wide.

In the following paragraphs we briefly, report the progress made in Newcastle in these key areas for system development.

DMFC STACKS DYNAMIC ELECTRICAL PERFORMANCE AND MODELLING

The transient response of the direct methanol fuel cell (DMFC) is of paramount importance when it is used for transportation applications. With the aid of computer controlled load unit we have applied a variety of loading cycles on a small scale single DMFC, a large scale single cell and a 3-cell stack with total active area of 680cm^2, in order to evaluate the effect of the loading pattern and operating conditions on the cell's/stack's response time and performance. The cell responds rapidly, and reversibly, to changes in magnitude and rate of change of load. Under dynamic operation the cell voltage response can be significantly better than that achieved under steady state operation (see Figure 1a and 1b). Open circuit potentials are also increased, by up to 100mV, by imposing a dynamic loading strategy. This improvement, accredited, in part, to a reduction in the effect of methanol crossover, is potentially attractive in vehicle applications where higher power density and fuel efficiency can be realised.

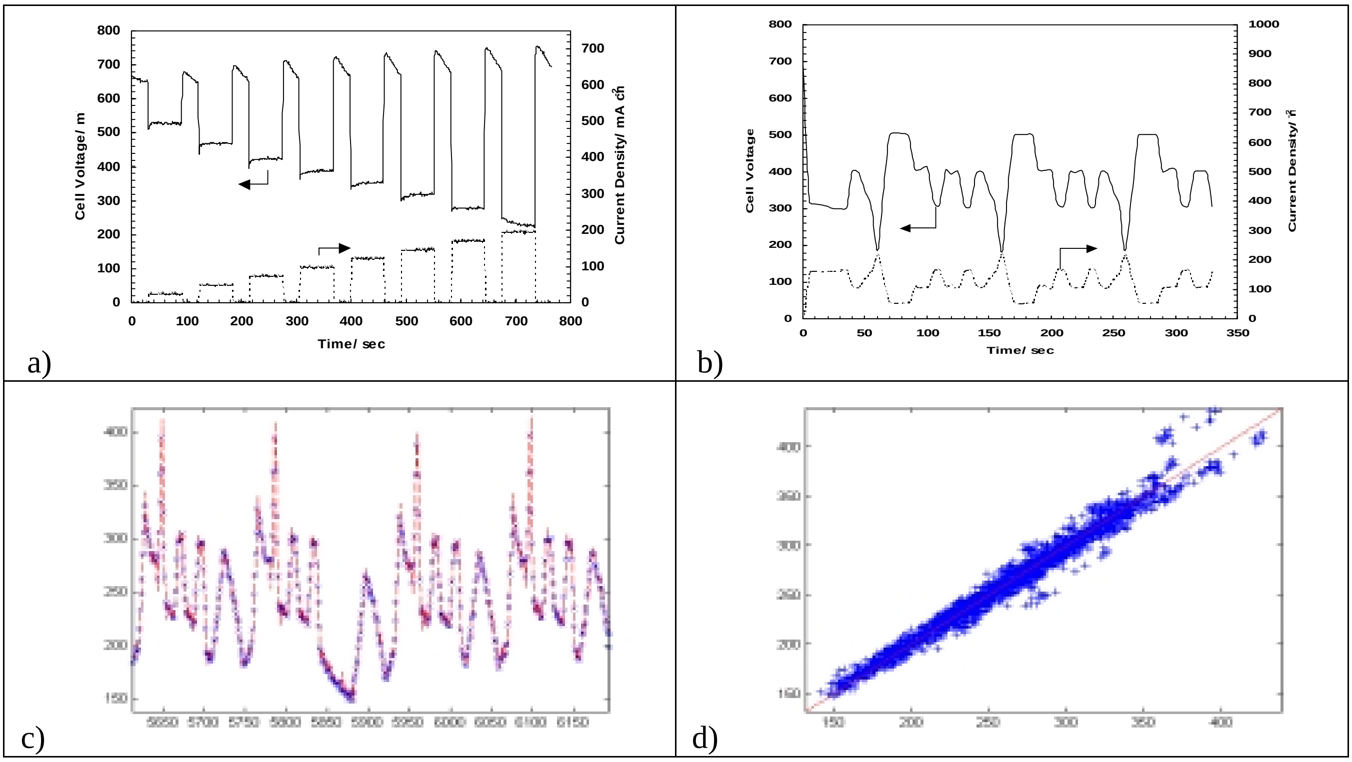


Figure 1: Dynamic response of small single DMFC cells under variable load conditions (a-b), comparison of the measured and the predicted 3-cell stack voltage with the aid of the CVA model (c-d)

A state space model of the following form was developed to provide one-step ahead predictions of the cell voltage:

$$\mathbf{x}_{t+1} = \mathbf{F}\mathbf{x}_t + \mathbf{B}\mathbf{e}_t \qquad \mathbf{y}_t = \mathbf{H}\mathbf{x}_t + \mathbf{e}_t$$

where x and y are the system states and the output (voltage) respectively. The term w represents measurement noise. The true system states were approximated using the multivariate statistical technique of Canonical Variate Analysis (CVA). The model was built with the aid of experimental data acquired from a small single cell and then used to predict the performance of all three systems already described above operating in a wide range of versatile operating conditions. Further details of the CVA state space modelling technique can be found in Simoglou et al. [9]. However it is worth mentioning that the model requires only two and one past value of the voltage and the current applied respectively to predict the cell voltage one step ahead. The CVA state space model was evaluated using various cell configurations and operating conditions and was found to provide predictions within 5% of the measured values. Figures 1c show typical results from a three cell stack when in Figure 1d it is shown that the predicted versus the actual measured values of the cell voltage are well-lying on a straight line of slope one, indicating prediction of high quality.

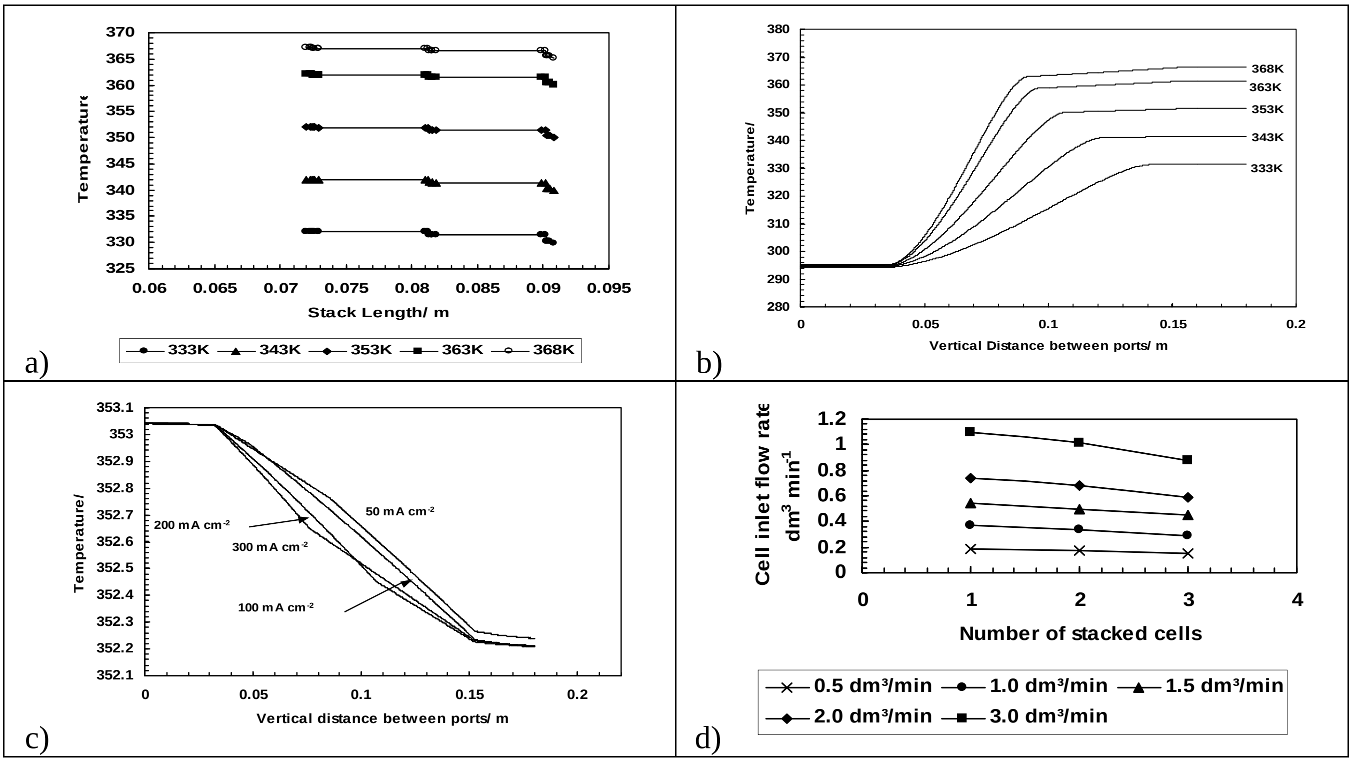
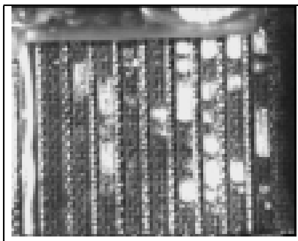


Figure 2: Model based predictions for a 3-cell stack longitudinal profile for increasing anode side feed inlet temperature, cathode side flow bed temperature profile, anode side as a function of current density and anode side flow distribution.

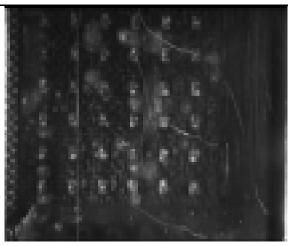
Research was continued on the area of DMFC engineering modelling where a series of simple steady state models concerning cell and stack thermal management, hydraulic behaviour, and two phase flow conditions were merged in a global model that describes DMFC stack operation in the steady state. Figure 2 is showing representative results of this work.

ALTERNATIVE FLOW BED DESIGNS & CELL FABRICATION MATERIALS

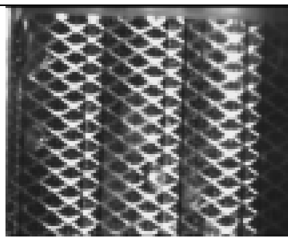
Two alternative membrane materials (fabricated at Cranfield University, UK) were evaluated for DMFC operation. Figure 3j compares the performance of the MEA with the 3747P membrane and Nafion 117. Noticeable there is a slight improvement in the open circuit voltage, approximately 35 mV, and at higher 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). On removing the MEA from the cell there was severe signs of de-lamination between the catalyst and membrane layers. Further research is required to pursue the aspects of lamination and an alternative soluble ionomer to Nafion with suitable adhesion characteristics. Alternative flow beds designs based on a combination of a stainless steel and a Poco graphite block (Fig 3h), or entirely stainless steel based ones were tested. 926S and 707S coded meshes showed excellent gas removal characteristics (Fig 3 a-g) and enhanced electrical performance over a wide range of operating conditions (Fig 3i). Stainless steel flow beds were also used with encouraging results (Fig 3k).



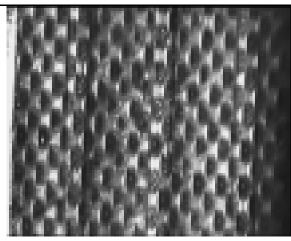
a) Parallel channels



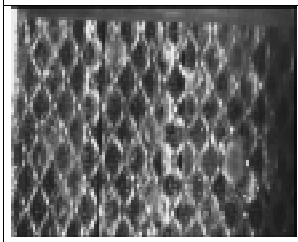
b) Spots



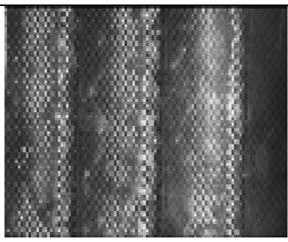
c) 707S



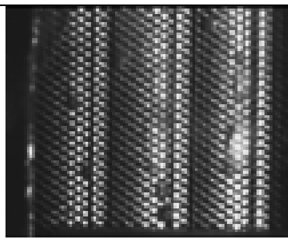
d) 926S



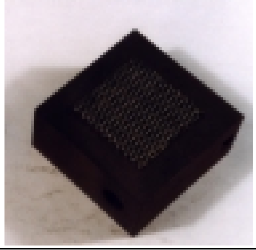
e) 927S



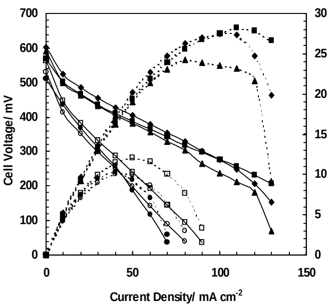
f) 941MM



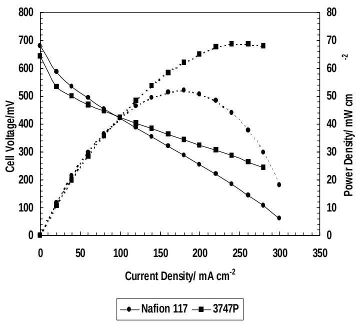
g) 957MM



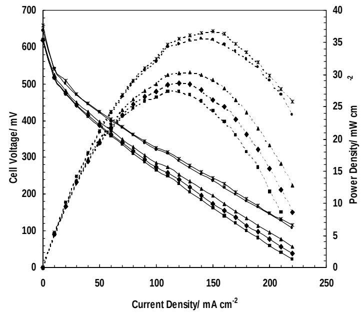
h) Mesh based flow bed



i) Mesh based vs Poco flow beds



j) Nafion 117 vs. 3747P



k) Poco vs Stainless steel cells

References

1. Argyropoulos, P., K. Scott, and W.M. Taama, *Modelling pressure distribution and anode/cathode streams chemical composition in direct methanol liquid feed fuel cells.* Journal of Applied Electrochemistry, 1999.
2. Argyropoulos, P., K. Scott, and W.M. Taama, *Pressure drop modeling for liquid feed direct methanol fuel cells (DMFCs). Part I. Model development.* Chemical Engineering Journal, 1999.
3. Argyropoulos, P., K. Scott, and W.M. Taama. *Engineering and modeling aspects on large scale liquid feed DMFC stacks.* in *5th European Symposium on Electrochemical Engineering*. 1999. Exeter, UK: IChemE.
4. Argyropoulos, P., K. Scott, and W.M. Taama, *Pressure drop modeling for liquid feed direct methanol fuel cells (DMFCs). Part II. Model based parametric analysis.* Chemical Engineering Journal, 1999.
5. Argyropoulos, P., K. Scott, and W.M. Taama, *One dimensional thermal model for DMFC stacks. Part I. Model Development.* Journal of Power Sources, 1999. **79**(No. 2): p. 169-183.
6. Argyropoulos, P., K. Scott, and W.M. Taama, *One dimensional thermal model for DMFC stacks. Part II. Model based parametric analysis and predicted temperature profiles.* Journal of Power Sources, 1999. **79**(No. 2,): p. 184-198.
7. Argyropoulos, P., K. Scott, and W.M. Taama, *Modeling reactants and products flow distribution for internally manifolded DMFC stacks.* Journal of Fluids Engineering, 1999.
8. Argyropoulos, P., K. Scott, and W.M. Taama, *Hydrodynamic modeling of direct methanol fuel cell stacks.* Journal of Applied Electrochemistry, 1999.
9. Simoglou, A., P. Argyropoulos, A.J. Morris, K. Scott, E.B. Martin, and W.M. Taama, *Application of CVA state space modeling for predicting the voltage response of a direct methanol fuel cell stack.* Chemical Engineering Science, 1999.