PERGAMON

Chemical Engineering Science 56 (2001) 6773–6779

Chemical Engineering Science

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Dynamic modelling of the voltage response of direct methanol fuel cells and stacks Part II: Feasibility study of model-based scale-up and scale-down

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Received 6 April 2000; received in revised form 5 March 2001; accepted 17 April 2001

Abstract

The feasibility of using empirical state space models such as canonical variates analysis (CVA) models for the scale-up and scale-down of direct methanol fuel cells (DMFC) is explored. The development of such models to predict voltage responses of DMFCs has been previously investigated with a small-scale single cell and a three-cell stack assembly. Each system was subjected to a range of varying dynamic loads and operating conditions. A model was developed for each of the two systems for varying cell operating conditions, and these models were then validated against the other "unseen" data sets collected from the two cells. The models developed were found to give acceptable inferential estimates and one-step-ahead predictions. One outcome of that study was the possibility of using such models to aid cell scale-up and scale-down. This paper addresses the feasibility of using a dynamic state space canonical variates analysis (CVA) model of the small-scale single cell to predict the voltage responses of the scaled up three-cell stack system. In addition the feasibility of using the three-cell system model to predict the dynamic behaviour of the small system is also studied (scale-down). The results achieved are encouraging and indicate the potential of using a CVA state space representations as an aid to cell scale-up and scale-down.

Keywords: Electrochemistry; Modelling; Dynamic simulation; Fuel cell; Scale-up; Scale-down

1. Introduction

Fuel cell technology is not a well-established technology with research work ongoing into the development and testing of prototype systems. Through the development of a methodology that enables models built on data obtained from a small-scale laboratory system, to be scaled-up and used during testing and commissioning of larger scale and more complicated systems, considerable savings in time and cost could be achieved. Such a scenario may be realisable in fuel cell technology due to the modularity of the resulting stack systems. In practice the voltage, and hence the stack power output, can be adjusted to satisfy any specification by either adding or removing cells from the stack system.

In Part I of this communication (Simoglou et al., 2001), two systems formed the basis of the analysis, a small-scale single-cell system and a three-cell stack system. For the former of the two systems, four different experiments were carried out to vary the cell operating conditions covering a range of dynamic loads. For the three-cell stack, two different operating conditions were studied. The models built were based on two measurements, the applied load in terms of current density and the cell/stack voltage. A canonical variate analysis (CVA) state space model was built for each of the two systems using the data generated from one particular set of operating conditions. The models were then validated, on new "unseen" data, in terms of their ability to make inferential estimations and one-step-ahead predictions of the new data sets. The new data sets were collected for the same cell system being modelled but with the cell operated under quite diverse loading and operating conditions. Based on a CVA state space model,

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0009-2509/01/$ - see front matter
PII: S0009-2509(01)00145-2

which included five past values of the voltage and the current density for the single cell, and five values of the voltage and seven past values of the current density for the three-cell stack, acceptable inferential and one-step-ahead predictions were obtained.

In this study, the models built in Part I (Simoglou et al., 2001) are extended to address the issue of scale-up and scale-down. The aim was to investigate the hypothesis that a dynamic state space CVA model, built on data collected from a small single cell, might *scale-up* to provide good predictions for the voltage response of the three-cell stack. In addition the issue of *scale-down* was investigated by using the model built on the three-cell stack to predict the dynamic voltage responses of the single cell system. The scale-up study used the CVA model developed using the small single-cell data set (C) to predict the voltage responses of the three-cell stack captured in data sets (E) and (F) (Simoglou et al., 2001). The issue of scale-down was studied through the use of the CVA model developed for the three-cell stack using data set (F) to predict the voltage responses of the small single-cell data sets (A), (B), (C) and (D) (Simoglou et al., 2001). Both cases are extremely challenging from a model-based scale-up / scale-down perspective. For example, each single cell of the large three-cell stack has an active area 30 times larger than that of the small cell; the total stack active area is 90 times that of the single cell. In addition the fuel and oxidant stoichiometries and flows, applied current densities, methanol solution concentration and cell/stack operating temperatures cover a wide range of likely operating conditions for the DMFC.

As was discussed in Simoglou et al. (2001), there are major differences in the geometric configuration of the small single cell and the three-cell stack. For example, the flow beds and manifolds of the two cell systems are of different designs. This results in very different heat and gas management characteristics that eventually affect the voltage response under variable load conditions (Argyropoulos, Scott & Taama, 1999a). A 1.0 M aqueous methanol solution was used in the three-stack cell when collecting modelling data set (F) whilst for the small single cell different solutions were used, ranging from 0.25 to 2 M, for data sets (A), (B), (C) and (D). In addition the cathode side pressure is lower for the cell stack. The combination of these factors results in significantly slower system responses for the stack. In addition, flow, current and pressure distribution, gas and thermal management, are less significant in the small single cell than in the three-cell stack. Stack dynamics, especially in terms of heat and mass transfer, are at least an order of magnitude slower than the electrochemical processes inside the limited space of the single cell membrane electrode assembly. It is also of note that the current status of DMFC technology is to operate the cells between 70°C to 100°C and rarely at temperatures below 60°C. Nevertheless, for automotive applications, a model for voltage response should be able to predict voltages during cold start-up when the equipment temperatures are well below the required operating point. In the reference data set (C) collected from the small single cell, measurements were taken over a narrow range of cell temperatures and anode side liquid feed inlet temperature. However, for the three-cell stack and in particular for data set (F), the stack was operated over a wide temperature range (30°C) and with only methanol feed being heated compared with the cell being heated for data set (C). It was observed that the operation of the small single-cell system approached steady state, (data set (C)), whilst for the three-cell stack (data sets (E) and (F)), steady state was never achieved. One issue addressed, and to be continued further, was that of including more sensors in the model building data sets. The key question was whether through the addition of additional measurements of pressures, temperatures, flows, individual cell voltages, etc., the accuracy of the voltage prediction could be improved. Of equal importance, however, is the need to achieve a balance between the costs of additional sensors and any overall improvement in model accuracy. The overall objective is to build a model that is fit-for-purpose.

2. Model assessment for cell scale-up

The issue of scale-up was investigated through the implementation of the CVA state space model developed for the small single-cell system using data set (C). This was used to predict the voltage responses of the three-cell stack for changes in operating conditions and cell loads represented by data sets (E) and (F). The continuously changing load applied to the three-cell stack, for prolonged periods of time, results in the potential for gas accumulation, temporary deactivation of the catalyst, and cathode side water-management problems. In addition, the ambient temperature was relatively low (5°C) and it was therefore anticipated that the stack membrane electrode assembly did not reach a temperature that would benefit the anodic endothermic reaction kinetics. The implication of having high liquid flow rates and low operating temperatures is that an entirely liquid fed cell can result, i.e. with no water or methanol vapour being formed. This would further slow down the response of the cell stack, in comparison to the single cell, and make the prediction of scale-up more demanding.

Table 1 summarises the results of the small singe-cell model built on data set (C) in terms of inferential estimates and one-step-ahead predictions. In Table 2, the results are given for the case where the model built from data set (F) was used to infer data generated from the three-cell system, i.e. data set (E) and (F). It can be clearly seen that the two sets of results are comparable. As expected, the one-step-ahead predictions are

Table 1
Scale-up accuracy of inferential estimates and one-step-ahead predictions

	Data set (E)	Data set (F)
Inferential estimates (%)	97.64	95.85
One-step-ahead predictions (%)	96.15	93.13

Table 2
Accuracy of inferential estimates and one-step-ahead predictions

	Data set (E)	Data set (F)
Inferential estimates (%)	99.39	99.15
One-step-ahead predictions (%)	98.99	98.64

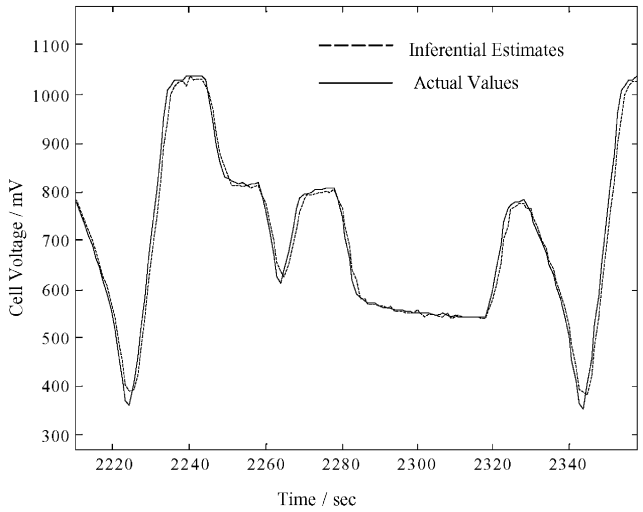

Fig. 1. Inferential estimates of data set (E).

correspondingly poorer than those obtained for the inferential estimates. However, the prediction accuracy is acceptable, especially when the major structural and operational differences between the two cell systems are considered.

The time-series plots for both the inferential estimates and the one-step-ahead predictions for the scale-up study are given in Figs. 1 and 2 for data set (E) and Figs. 3 and 4 for data set (F) for the scale-up study. The corresponding scatter plots of the actual values versus inferential estimates for data set (E) and the one-step-ahead predications for data set (F) are given in Figs. 5 and 6, respectively. In all cases, an off-set in the voltage response can be observed which was not evident in any of the cases discussed in Part 1 (Simoglou et al., 2001) where the model was built and validated on new data collected from the same cell system. This off-set is believed to be associated with a missing measurement. Studies are being progressed to investigate this issue further. Comparing the accuracy achieved when using the CVA model to predict new data collected from the same cell, with that achieved in the scale-up to the three-cell stack, it can be seen that the prediction accuracy is reduced, at most,

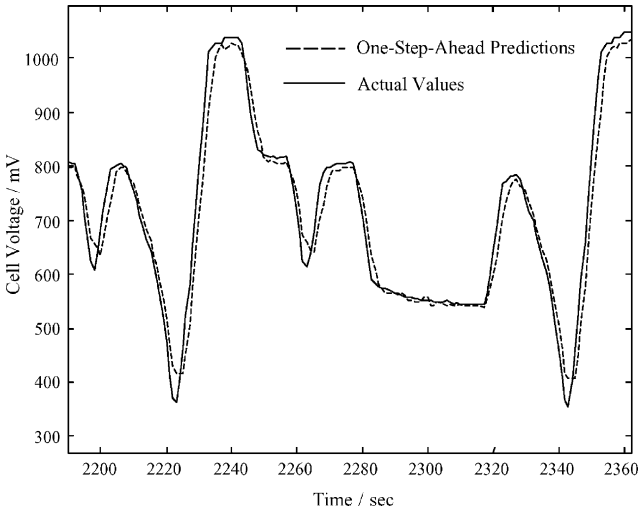

Fig. 2. One-step-ahead predictions of data set (E).

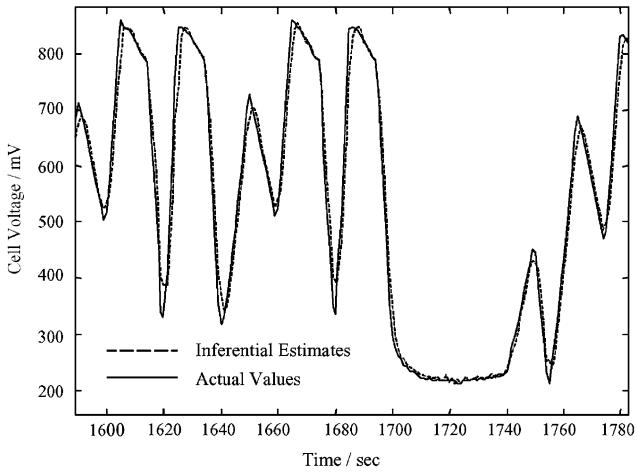

Fig. 3. Inferential estimates of data set (F).

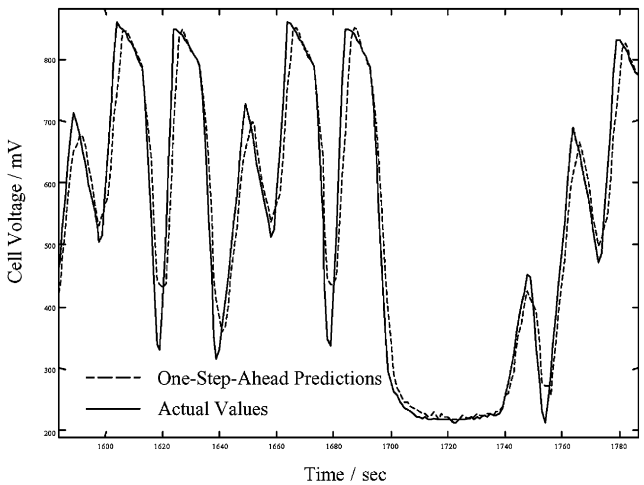

Fig. 4. One-step-ahead predictions of data set (F).

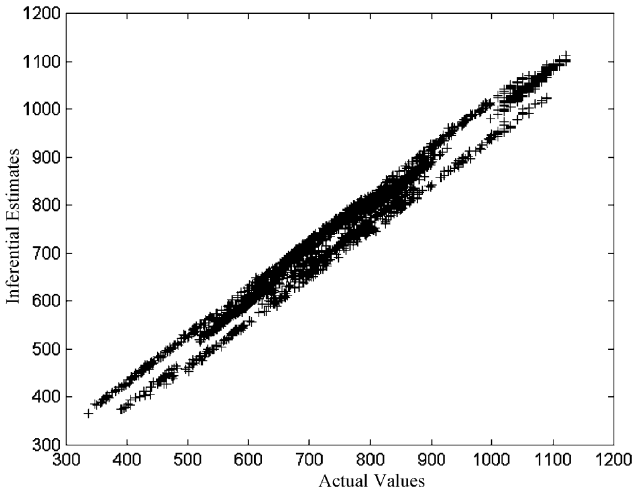

Fig. 5. Actual versus inferential estimates for data set (E).

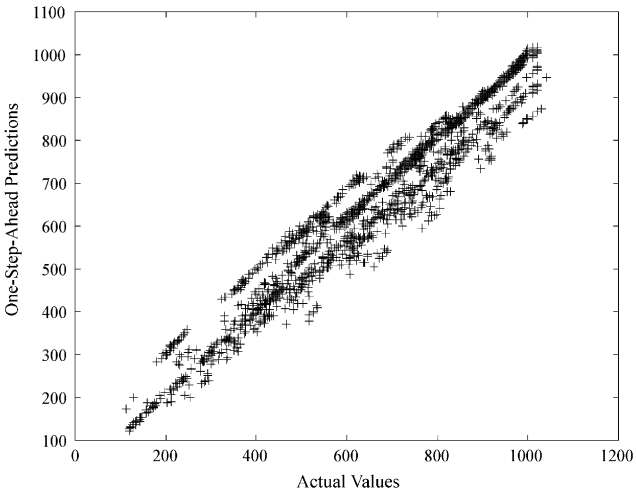

Fig. 6. Actual versus one-step-ahead predictions for data set (F).

by 5%. In all the experiments carried out, the accuracy of the model predictions are acceptable, especially when the differences between the two cell systems, is taken into account, as discussed previously, and that the CVA model was not optimised or built from statistically designed experiments. Prediction accuracy, especially for the one-step-ahead predictions, are expected to improve significantly with the use of statistical design of experiments during the cell testing phase to acquire model building data. This is also related to the persistency of excitation, an issue in all process model parameter identification experiments.

3. Model assessment for cell scale-down

In this study, a CVA model was built using data set (F) that had been collected from the three-cell stack. This model was then used to predict the voltage responses of the four data sets collected on the small single-cell system, data sets (A), (B), (C) and (D). Table 3 summarises the inferential estimates and the one-step-ahead model predictions of the four single-cell data sets. For comparison, the results of the single-cell model predictions of data sets A, B, C and D from the CVA model built from the single-cell data set (C) are presented in Table 4. Typical corresponding inferential estimates are presented in Figs. 7 and 8, respectively, with the associated scatter plots of the actual versus inferential estimates in Figs. 9 and 10. The corresponding one-step-ahead time series predictions are plotted in Figs. 11 and 12 with the associated scatter plots in Figs. 13 and 14.

From Table 3 it can be observed that for data set (A), the accuracy of the inferential estimates are better when the voltage response data was inferred from the model generated from the three-cell stack data set (F), than when it was inferred from the model built using data set (C) from the same cell system, Table 4. This behaviour can be explained by examining in more detail the experimental conditions used for data collection in the case of data sets (A) and (F). Both systems were operated under similar operating conditions but with different methanol concentrations. The small-scale cell CVA model was developed from data set (C) that was collected during a pulse type load cycle. The excitation pattern for data sets (A) and (F) show greater similarity than data sets (C) and (A). Thus there is a clear indication that the scalability of the model is dependent upon the excitation pattern imposed on the system to generate the model building data sets. Figs. 7 and 8 illustrate the results of the inferential estimates for data sets (A) and (C), respectively, and Fig. 9 shows the scatter plot of the inferential estimates for data set (A).

The large-scale three-cell stack system data set (F) covers only one mode of operation. This relates to a high anode side liquid phase inlet flow rate supplied at temperatures well below the boiling point of the solution. However, as the small single-cell system was operated at elevated temperatures (up to 90°C) it can potentially be operated in either liquid-feed mode or in a mixed vapour–liquid feed state. The exact mode of operation depends on a large number of parameters including feed temperature, cell temperature, feed flow rate, solution concentration

Table 3
Scale-down accuracy of inferential estimates and one-step-ahead predictions

	Data set (A)	Data set (B)	Data set (C)	Data set (D)
Inferential estimates (%)	99.44	97.08	97.24	93.02
One-step-ahead predictions (%)	89.46	94.42	95.24	86.24

Table 4
Accuracy of inferential estimates and one-step-ahead predictions for the single-cell

	Data set (A)	Data set (B)	Data set (C)	Data set (D)
Inferential estimates (%)	96.60	97.53	98.25	96.53
One-step-ahead predictions (%)	95.41	96.65	98.02	94.76

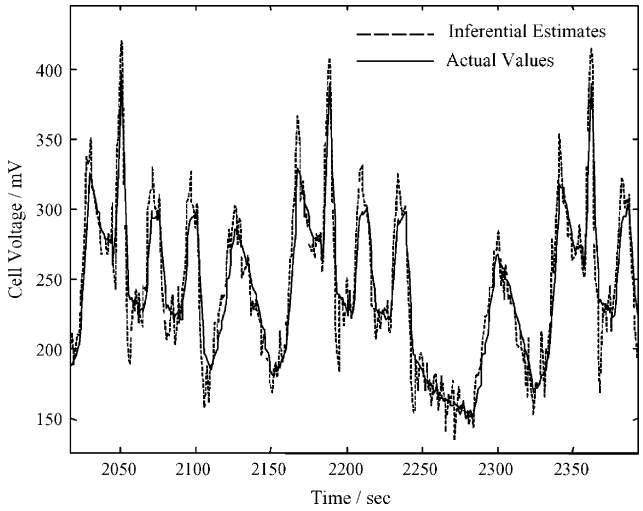

Fig. 7. Inferential estimates of data set (A).

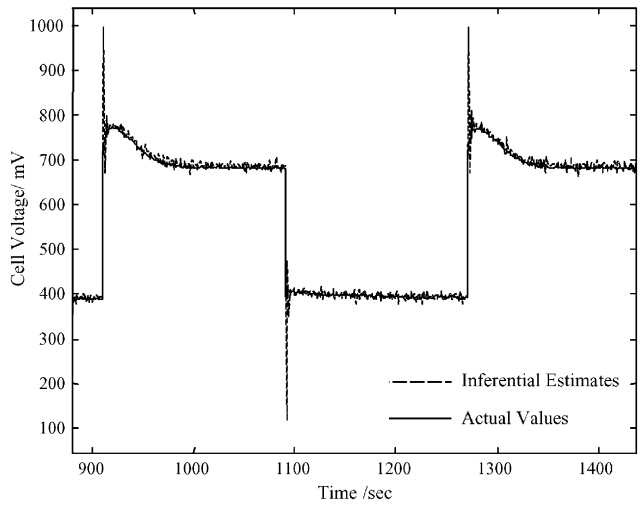

Fig. 8. Inferential estimates of data set (C).

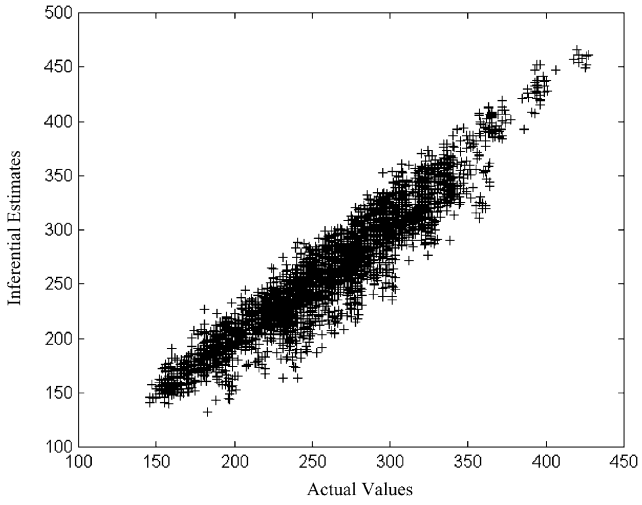

Fig. 9. Actual versus inferential estimates for data set (A).

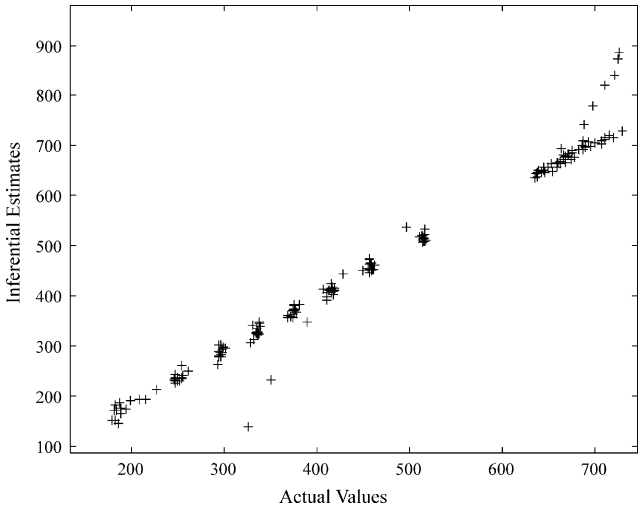

Fig. 10. Actual versus inferential estimates for data set (D).

and carbon dioxide evolution rate which is directly related to current density and anode side pressure. In addition the severe gas management problems which can occur in the small-scale single cell, compared with the improved gas management characteristics of the large-scale flow bed design (Argyropoulos, Scott, & Taama, 1999b, c) also has a major influence on cell behaviour. All these factors contribute to the rather poor one-step-ahead predictions summarised in Table 3. More specifically examining the results for the voltage response predictions for the small single-cell data sets (B), (C) and (D) using the model built from the three-cell stack data set (F), the quality of the prediction are poorer than for all the other cases examined in the study. This was not unexpected since the operation of the three-cell stack is very different to that of the small single-cell system. Figs. 8–14 present the results for scale-down.

The poorest prediction was obtained for data set (D) for the application of a pulsed load with a maximum current density of 200 mA/cm^2. This is a potential problem since the model was developed from a data set collected from a load cycle with a maximum load of 80 mA/cm^2.

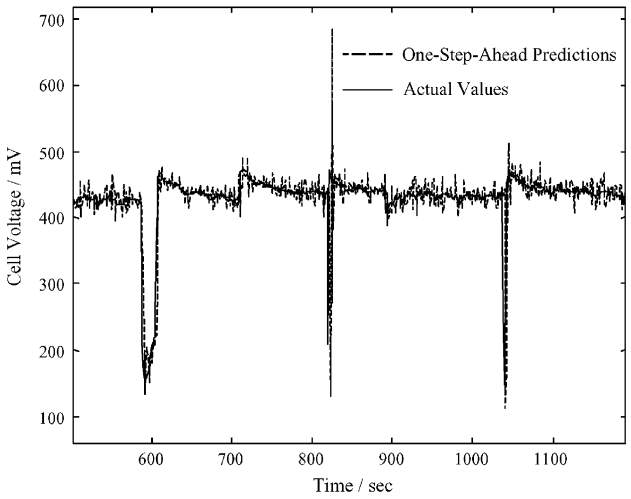

Fig. 11. One-step-ahead predictions of data set (B).

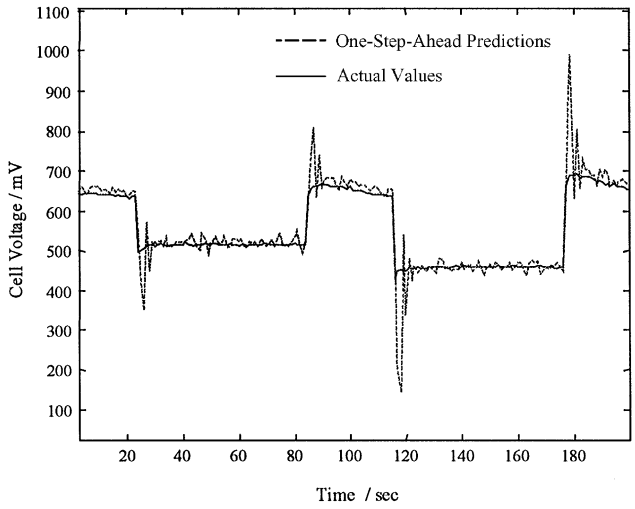

Fig. 12. One-step-ahead predictions of data set (D).

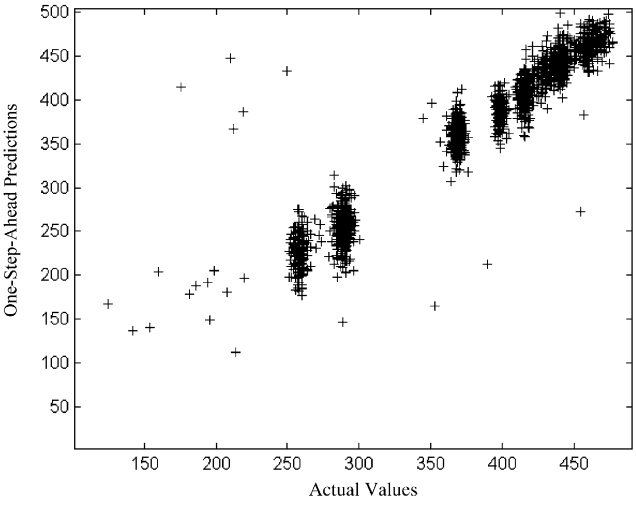

Fig. 13. Actual versus one-step-ahead predictions for data set (B).

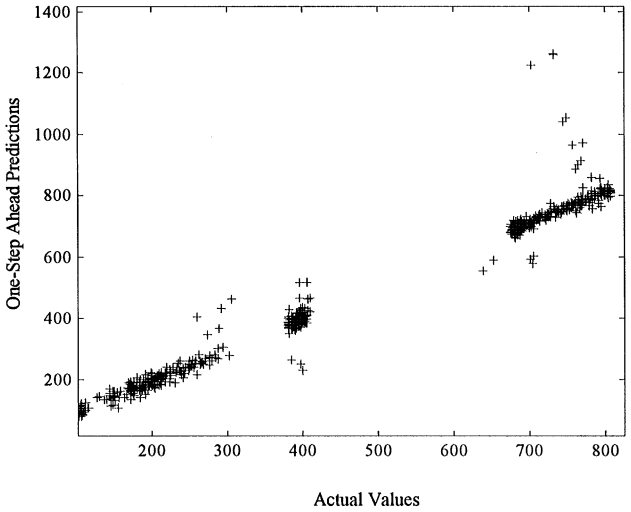

Fig. 14. Actual versus one-step-ahead predictions for data set (C).

This behaviour had been anticipated following earlier experimental work on the dynamic response of the DMFC (Argyropoulos, Scott & Taama, 1999a, 2000a, b) where it was shown that the cell/stack response is strongly affected by the applied current density load. For example, high applied current densities, high liquid phase flow rates and suppression of vapour phase formation significantly reduces the system voltage and slows the response time. Thus the three-cell stack data collected during the experiments was relatively limited in terms of information about system behaviour and, although the model follows the system dynamics, it fails to give accurate voltage predictions for the small single-cell system and hence provides a lower level of prediction accuracy. Nevertheless, in all the experiments the accuracy of prediction never falls below 9% of that achieved when the model built on data from a particular cell system is used to calculate the inferential estimates and one-step-ahead predictions of new "unseen" data from the same cell system.

4. Discussion

The issue of scale-down is rather unusual as most development work starts from small-scale cells in order to minimise development time and costs, and where engineering issues are of less importance for correct operation. In this context the proposed CVA state space representation is a promising route for investigating the scale up of DMFC systems. There are, however, situations where during process development, a designer needs to develop a simulation of a large scale system and in this instance the ability to scale-down would be a major advantage. For example in the production of power supplies for miniaturised transmitters. Although for the scale-down experiments, an accuracy of only 90–95% was achieved, such accuracy is still far better than that obtained from

complex deterministic models. In addition, the time and effort to develop a CVA state space dynamic model is much less than that for mechanistic models and more important is non-system specific. This is a major benefit of this new approach. A further advantage of the present dynamic modelling approach is that it can be used for on-line real-time cell performance monitoring as well as for on-line fault detection (Simoglou, 1999).

The models developed in this work have been based on two measured values, cell/stack voltage and applied current density. Based on these two quantities, inferential estimates of at least 90% accuracy were achieved, with the accuracy of the one-step-ahead predictions being at least 85%. To enhance the model predictive performance, the provision of additional measurements was investigated. These included cell temperatures and anode/cathode side inlet/outlet temperatures. The resulting model predictions were marginally better, with improvements in accuracy of the order of 1%. Although it is premature to exclude the use of additional sensors such as temperatures, individual cell voltages, methanol concentration, mass flow and rates, pressure, the early indications are that improvements to the results may not be substantial.

The accuracy achieved utilising only two sensor measurements provides impetus for the continuation of the study into the use of CVA state space methodologies for the dynamic modelling of the DMFC. One of the main problems is the issue of the time delay between system start-up and the time required using traditional control techniques to collect sufficient appropriate data to control the system effectively. The state space CVA technique, in part, addresses this issue. Only five values were required before the model was computed and able to provide predictions resulting in minimum time delay. This is potentially a major advantage in automotive applications. It is also important to stress that the models were built from data that was collected as part of a wider study aimed at assessing the dynamic response of DMFC single cells and stacks and not specifically for scale-up and scale-down predictions. It is well known that in empirical modelling, the quality of the final process model and its fitness-for-purpose is intrinsically linked to specifically designed experiments, the persistency of the system excitation and the quality of the data collected.

Finally, the use of a dynamic state space modelling approach to represent the dynamics of other fuel cells, e.g. hydrogen PEM cells, should also be possible. In principle this is a relatively straightforward task since the two polymer electrolyte membrane systems are quite similar in terms of geometry, design and materials.

5. Conclusions

CVA state space dynamic models have been used to infer and predict in a one-step-ahead sense, with reasonable accuracy, the scale up voltage responses of a three-cell DMFC stack that was significantly different, both in terms of geometry and physiology, than the small-scale system. In contrast, using the CVA state space dynamic model, built from the three-cell stack data, to predict the voltage response of the small single-cell system, i.e. scale-down, although feasible, gave predictions that were slightly inferior to the case of scale-up.

Acknowledgements

The authors would like to acknowledge the following for support of this research: the EPSRC Innovative Manufacturing Initiative Award, SCIENTIA (GR/L28029) for supporting Dr. A. Simoglou; the European Commission for a TMR Marie Curie B20 research-training grant to Dr. P. Argyropoulos; the EPSRC for support of Dr. W.M. Taama; and Johnson Matthey Technology Centre for the supply of developmental catalyst under their catalyst loan scheme.

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