

An investigation of scale-up on the response of the direct methanol fuel cell under variable load conditions

P. ARGYROPOULOS, K. SCOTT and W.M. TAAMA

Chemical and Process Engineering Department, University of Newcastle upon Tyne, Merz Court, Newcastle upon Tyne, NEI 7RU, Great Britain

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Abstract

The electrical response of the direct methanol fuel cell, based on solid polymer electrolyte, to variable load is reported. The dynamic power response of the direct methanol fuel cell is of importance particularly when the cell is used for transportation applications. The study reports the dynamic characteristics of a small-scale cell (active area 9 cm^2), a large-scale cell (active area 272 cm^2), and a three-cell stack. The effect of operating conditions (i.e., flow rate, cathode pressure and solution concentration) on the voltage response is described and the effect of a change of scale is discussed.

1. Introduction

The dynamic performance of fuel cells is of importance in several applications and especially under start-up, shut down and variable load applications. In particular knowledge of the dynamic behaviour of fuel cells and stacks and systems is critical to their engineering and design. A model of the transient thermal behaviour of fuel cells using a three-dimensional simulation of stack operation was developed [1]. Time constants of the transient response following load changes were determined and were in good agreement with experimental data obtained from a 100 W fuel cell stack. A model predicting transient responses of proton exchange membrane (PEM) fuel cells has been developed for a Ballard Mark V 35-cell 5 kW PEM fuel cell stack, based on mass and energy balances on the stack [2]. The thermal characterisation of the stack included changes in the sensible heat of the anode, cathode, and water streams, the energy released due to the reaction, the electrical energy produced by the fuel cell, and the heat lost from the surface of the stack. A detailed one-dimensional dynamic model of a gas diffusion electrode as part of a complete PEM fuel cell model has been produced [3]. The electrochemical performance of a large-scale PEM fuel cell stack (MEA 350 cm², 125 cell) has also been modelled and combined with a dynamic fuel cell stack model [4]. Temperature, pressure, humidity, and oxygen partial pressure distributions for the central MEA of the stack and corresponding current produced by that MEA were described. Models for heat and water transport in a polymer membrane fuel cell have been developed for evaluation of structure and material [5, 6]. The dynamic

simulation allowed the study of the transient state after changes in electrical load or gas flow rate and humidification.

A model concerned with the mass flow distribution in fuel cell stacks has been developed [7]. In particular, the flow through the manifold system connected to the parallel arrangement of the cell channels was modelled and numerically treated. The simulation was confirmed on a stack model which consisted of 100 cells. Pressure and velocity distributions were measured as a function of Reynolds numbers and geometrical shape of the manifolds. The dynamics of other fuel cells such as molten carbonate and phosphoric acid have been investigated significantly [8–13].

Overall unsteady-state behaviour of fuel cells is becoming more of an issue, especially for transportation applications, where operating conditions will normally change with time. System start-up and shutdown, and large changes in the power level, may be accompanied by changes in the stack temperature profile and in the reactant concentrations at the electrode surface. Therefore, mass and heat transfer dynamics, as well as electrochemical characteristics, are involved in determining the overall transient power response of cells.

The research of direct methanol fuel cells (DMFC) based on solid polymer electrolyte (SPE) has mainly been for steady state and small-scale operation within laboratory environments. As the research and development work continues the engineering of the system has not been studied significantly since the commercialisation of the relative technology is still some time away. Published research mainly refers to steady state systems either in the form of galvanostatic polarisation curves or in the form of durability tests [14–24]. A brief account of dynamic behaviour of a small DMFC stack was reported using current pulse operation [22]. Observations on dynamics are made in a number of the aforementioned publications but these were mainly concerned with the duration of experiments and not the response to load changes.

There are several factors which could potentially adversely affect the dynamic response of the liquid feed DMFC. In the anode side a mixture of aqueous methanol solution and carbon dioxide (the anode reaction product) flows. Carbon dioxide compressibility can potentially lower the system response under variable load conditions due to changes in system pressure and to fluid inertia. Overall the dynamic response of the DMFC will depend on the following details:

- (i) The electrochemical response of the anode and cathode reactions [25].
- (ii) The charging characteristics at the interfaces between the electrode, electrolyte and solid polymer membrane.
- (iii) The mass transfer characteristics of methanol to the catalyst sites through the diffusion layer and catalyst region.
- (iv) The mass transfer of methanol through the membrane, which influences the performance of the cathode due to a mixed potential.
- (v) The mass transfer characteristics of oxygen to the cathode.
- (vi) The production and transport of water at the cathode electrocatalyst layers.
- (vii) The production of carbon dioxide and its release from the anode catalyst layer.

- (viii) The two-phase flow of methanol solution and carbon dioxide gas through the anode diffusion layers.
- (ix) The hydrodynamics of the two-phase flow of methanol solution and carbon dioxide gas in the flow bed.
- (x) The variations in heat release and temperature response of the cell components. These will affect local reaction rates, vaporisation (or condensation) of methanol (and water) between the liquid and gas phases, local humidification conditions and local operating parameters.
- (xi) The size and scale up of DMFC stacks.

In this paper we report the effect of applying varying loads on the voltage response of a large-scale single cell (272 cm^2 active area) and a three-cell stack and compare this to the performance of a small-scale cell (9 cm² active area) [26]. This work was part of an overall investigation, concerning the effects of operating and geometric parameters on single cell and stack dynamic response.

2. Experimental details

Two sizes of cell were used for the research, a small-scale cell of 9 cm² active cross sectional area and a large-scale cell of 272 cm^2 . A two-cell DMFC stack with its components is shown schematically in Figure 1. The small-scale cell consisted of a membrane electrode assembly (MEA) sandwiched between two graphite blocks with flow paths cut out for methanol or oxygen/ air flow. The flow bed consisted of a series of 10 parallel channels, 2 mm deep by 2 mm wide every 1.0 mm



Fig. 1. Schematic representation of a two-cell DMFC stack.

(Figure 2(a)). The cell was held together between two aluminium backing plates using a set of retaining bolts positioned around the periphery of the cell. Electrical heaters, supplied by Watson Marlow, were placed behind each of the graphite blocks in order to heat the cell to the desired operating temperature. The blocks were also provided with electrical contacts and small holes to accommodate thermocouples. The cell was used in a simple flow rig (see Figure 3(a)), which consisted of Watson Marlow peristaltic pumps to supply aqueous methanol solution, from a reservoir, and a Eurotherm temperature controller to heat the methanol solution. Air was supplied from cylinders at ambient temperature and the pressure was regulated at inlet by pressure regulating valves. All connections between the cells and equipment were with PTFE tubing, fittings and valves.



Fig. 2. Flow beds of the small and large-scale DMFC cell.

The large scale DMFC used a flow bed design, developed by the authors (Figure 2(b)), based on a plate and frame heat exchanger concept. Previous flow

visualization studies showed excellent performance in terms of gas removal characteristics [27]. The flow bed consisted of a main flow region, of 57 parallel channels,



Fig. 3. Experimental flow circuits: (a) small scale cell circuit, and (b) prototype stack experimental loops.

and two triangular inlet/outlet sections of a spot flow bed design (40 mm long which had a series of 2 mm² spots, designed for electrical contact to, and physical support of, the MEA in normal operating DMFC). Liquid and gas feeds and the product liquid and gas mixtures were supplied/removed using an internal reverse type circular cross section manifold. The diameters of the inlet manifolds and outlet manifolds were 15 mm and 25 mm, respectively. Individual cells were connected electrically in series using graphite bipolar plates which also acted as flow beds for anode side and cathode side flows.

The cell was operated in a flow circuit, shown schematically in Figure 3(b), which provided a controlled rate of fuel and oxidant flow. This circuit consisted of two centrifugal pumps (Totton Pumps with PVDF parts) connected in parallel. A bypass loop, with a control valve, was used to control the flow rate of the centrifugal pumps and a Platon Fmet series flow meter measured the flow rate. The maximum flow rate attainable from the two pumps was $7.5 \text{ dm}^3 \text{ min}^{-1}$. The necessary heat load for stack start-up and for replenishing heat losses was provided by a Watlow 1.25 kW stainless steel heater, controlled by an embedded thermocouple and an external PID temperature controller, which heated the methanol solution. The anode side exhaust fluid mixture (carbon dioxide gas and excess methanol solution) passed through a gas liquid separator. From this separator the liquid flowed to the main reservoir while the gas was vented from the top of the separator through a glass condenser, to recover methanol.

A compressor supplied air at the desired pressure for the cathode. Two Platon Fmet series flow meters, with two precision valves, were used to control the flow rate of air. The cathode side exhaust gas was passed through a collection tank which acted as a reservoir for water separated from the air using a second condenser situated on the top of the tank. A precision valve, positioned at the top of the condenser, controlled the cathode side pressure. The necessary heat for start-up was provided by a pair of heating plates, with embedded resistances, with power supplied from a Farnel AR60-50 regulated power supply source, controlled by a computer. The plates were adjacent to the two graphite end blocks in the stack. The methanol concentration in the system was controlled manually by measuring the reservoir concentration at frequent intervals with an Abbe refractometer and a GLC. In practice the large methanol solution volume meant that the concentration remained practically unchanged during most runs.

For the electrical testing of the cells the loads were applied with in-house made units, which were fully controlled, by a PC. In addition to providing the required load, in a programmable way, the units also logged data of cell voltage, current load and anode and cathode temperatures. The tests were run several times to ensure reproducibility and, in addition, each loading condition was repeated several times inside a load cycle to assess the effect of the loading history on the cell response at specific conditions.

MEAs studied in this work were prepared as a sandwich of a pretreated Nafion[®] membrane between an anode and a cathode. This assembly was hot-pressed at 100 kg cm⁻² for 3 min at 135 °C.

The anode consisted of a 0.3 mm thick Teflonised (20%) carbon cloth support (E-Tek, type 'A'), upon which was spread a thin (diffusion) layer of 10 wt % teflonized carbon (ketjenblack 600) and then a catalyst layer. The catalyst layer was a 50 wt % Pt–Ru (2 mg cm⁻² metal loading) dispersed on carbon (ketjenblack 600) and bound with 10 wt % Nafion[®], from a solution of 5 wt % Nafion[®] (Aldrich). A thin coating of Nafion[®] solution was spread onto the surface of the catalyst layer. The catalyst was 35% Pt, 15% Ru (Johnson Matthey Technology Centre development material).

The cathode was made in the same way as the anode, using 1 mg cm⁻² Pt black with 10 wt % Nafion[®] in the catalyst layer in place of the Pt, Ru catalyst.

The pretreatment of the membrane involved boiling it for 1.0 h in 5 vol % H_2O_2 and 1.0 h in 1 mol dm⁻³ H_2SO_4 before washing in boiling de-ionized water for 2 h with regular changes of water. The membrane was wet when used to prepare the MEA. It was found that using a wet Nafion membrane in the assembly improved the uniformity of heat transfer during the hot press procedure.

3. Results and discussion

3.1. Small scale cell dynamic response

Investigations of the dynamic response of the small cell to changes in magnitude of current load and rate of change of load showed that it responded rapidly and reversibly [26, 28]. Under dynamic operation the cell voltage response was significantly better than that achieved under steady state operation. This improvement is potentially attractive in vehicle applications where higher power density and fuel efficiency can be realized. In addition the dynamic response of the DMFC cell voltage was significantly affected by the methanol solution flow rate, methanol concentration and applied cathode air pressure. Variations in voltage response can generally be associated with many phenomena, but methanol crossover from anode to cathode is believed to be a significant factor. Dynamic operation perturbs the methanol crossover rate, from steady state conditions, which affects the electrode reactions and associated mass transport processes and also the thermal behaviour. In addition, in practical DMFC operation, the input of methanol solution at a temperature below that of the cell will cause dynamic interactions between the operating temperature of the electrocatalyst and methanol flow rate.

Figure 4 shows the effect on the cell voltage of a load cycle consisting of constant, incremental increases in



Fig. 4. Cell voltage response under continuously increasing load with duration of 30 s of 10 mA cm⁻² followed by sudden cell unloading and instantaneous reloading to the new step load, up to a value of 200 mA cm⁻². (Methanol concentration 2.0 M; methanol flow rate 10 cm³ min⁻¹; cell temperature 85 °C; air fed system at 2 bar cathode pressure.)

current density load (10 mA cm^{-2}) with time (30 s) on load for the cell to approach a steady state performance. The cell current load, after every current step, was instantaneously removed for one second and then immediately reapplied to the next incremental value of load, up to a maximum of 200 mA cm⁻². After the maximum current density was reached the loading procedure was reversed with the loads reduced by successive 10 mA cm⁻² intervals. This test showed a feature that was common to the DMFC: after a loading cycle the open circuit voltage recovered to a higher value (\sim 20–30 mV), which was a metastable condition referred to as cell-activation. As can be seen, in Figure 4, the instantaneous value of the open circuit voltage varied from approximately 670 mV to a maximum value of approximately 770 mV. Generally, in the duration of the experiments, by not allowing the voltage to reach a stable value (i.e., application of the same, or greater, load) the cell voltage is higher than when the open circuit voltage is allowed to reach a steady state condition.

It was noticeable that in the initial periods of the test, application of the load produced a drop in the voltage, to a minimum value, which then rapidly rose before slowly recovering to a near constant value. After the loading cycle was applied several times, after approximately 400 s, the initial 'minimum' in voltage response, on load, was not seen. Generally when a current step is imposed onto a single electrode reaction a rise in overpotential with time occurs. This response was not apparent, over the short time-scale of the test, in Figure 4, which is indicative of the complex interactions of slow electrode kinetics and mass transport in the DMFC.

Direct methanol fuel cell performance is significantly affected by crossover of methanol to the cathode. Methanol crossover increases cathode polarization due to a mixed potential associated with methanol oxidation at the cathode. The application of a load depletes methanol at the anode, which reduces the driving force for methanol transfer through the membrane and consequently reduces cathode polarisation, to some extent, and benefits the cell voltage. When the current is pulsed the methanol flux through the membrane is in a dynamic state. Potentially when a high current load is applied after a low, or zero, load, back diffusion of methanol could occur, from the cathode to the anode, as the membrane acts as a sink for methanol. The time scales of methanol mass transport in the membrane and diffusion layers are tens of seconds and are consistent with measured mass transfer coefficients for the DMFC. Applying a continuous instantaneous pulsed load cycle to the cell can, in principle, improve the energy output. However this would have to be balanced against the energy required to charge the 'double layer' at the electrocatalyst surface.

The range of applicable methanol concentrations in the DMFC is currently dictated by the solid polymer electrolyte (e.g., Nafion[®] 117, Du Pont de Nemours), which is methanol permeable. The majority of the methanol transferred to the cathode is oxidised at the electrocatalyst and causes a mixed potential, which lowers the cathode performance. According to Ravikumar and Shukla the upper limit of methanol concentration is 2.0 M [18] and hence we did not exceed this value in our experiments. Figure 5 shows the influence of methanol concentration (0.5-2.0 M) on the dynamic response of the small cell after a series of current pulses of 50 mA cm⁻² and then a series of current pulses at 100 mA cm⁻². The data reported in this figure is in the form of the measured cell voltage divided by the initial open circuit experimental voltage, that is, normalized cell voltage, to enable comparison with the three-cell stack data. Each current pulse was applied for 200 s followed by an off load period of 180 s. With a 2.0 M solution the cell gave a fast and stable response (i.e., rapidly reached a steady-state voltage) for both current loads, but with the penalty of a lower voltage. The lower voltage was due to increased methanol crossover at higher concentrations, which increased the cathode overpotential. Removal of the load caused a rise to an open circuit voltage, which was higher than the initial

voltage, but which then fell to a constant value. With the 0.25 M methanol the cell response was much slower then with the 2.0 M solution, and gave a low voltage at 100 mA cm⁻². Noticeably the performance, at a concentration of 0.25 M, with the continuous application of a 100 mA cm⁻² pulse, exhibited a constant improvement in cell voltage. This further illustrated the mass transfer characteristics of the cell and the time scales required for diffusion of methanol to the catalyst layers.

The data in Figure 5 shows that the 0.5 M solution gave the highest voltage output but the response time deteriorated (i.e., there was a significant voltage transient) with an increase in current density from 50 to 100 mA cm^{-2} .

3.2. Effect of scale-up of the single DMFC

The data reported in this section is in the form of the measured cell voltage divided by the initial open circuit



Fig. 5. Effect of anode side feed composition on the voltage response under constant pulsed load conditions up to a value of 100 mA cm⁻², followed by a relaxation period of 180 s. (Methanol concentration shown on chart; methanol flow rate, 5.0 cm³ min⁻¹; cell temperature 85 °C; air fed system at 2 bar cathode pressure.)

experimental voltage (i.e., normalized cell voltage) to enable more effective comparison of all data from the cells.

Figure 6(a) shows the influence of low methanol concentration (0.25 and 0.5 M) on the dynamic response of the small scale DMFC with a repeated pulsed load of



Fig. 6. Comparison of the effect of methanol solution concentration on the small (a) and large (b) single cell voltage response under constantly pulsated load conditions of 50 mA cm⁻² followed by a relaxation period of 180 s prior to the application of the next pulse. (Methanol concentration shown on chart; methanol flow 10.0 cm³ min⁻¹ and 500.0 cm³ min⁻¹, respectively; cell temperature 85 °C; air fed system at 1.0 bar cathode pressure.)



Fig. 7. Effect of anode side feed flow rate on the large cell voltage response under constantly pulsed load conditions of 50 mA cm⁻² followed by a relaxation period of 30 s prior to the application of the next pulse. (Methanol concentration 0.5 M; methanol flow rate shown in chart in cm³ min⁻¹; cell temperature 85 °C; air fed system at 2 bar cathode pressure.)

 50 mA cm^{-2} . As can be seen the higher methanol concentration gave the greater voltage on load and the faster response time with a near uniform voltage. When the load was removed, the higher concentration of methanol gave the lower initial open circuit voltage, which decayed relatively rapidly (in comparison to that with the 0.25 M methanol), in approximately 40 s, to a stable voltage, equal to the steady state open circuit voltage.

Figure 6(b) shows the influence of low methanol concentration (0.2 and 0.5 M) on the dynamic response of the single large scale DMFC to a repeated pulsed load of 50 mA cm⁻². The difference in response of the large cell with different methanol concentrations was small under the conditions considered. This is in accord with observations of the steady state response of the large cell [29]. The dynamic response of the small and large cells (Figure 6(a) and (b)) were different; the large cell showed a somewhat slower response, and approached a steady state voltage after 100 s or more on load. When the load was removed the large cell showed a relatively small increase in voltage in comparison to the steady state open circuit voltage. A contributing factor to the different responses experienced was the much greater current drain from the large cell (factor of 30) compared to the small cell. In addition the thermal responses of the two cells would have been different as the small scale cell temperature was controlled by the use of heating plates on the cell and heating of the methanol solution feed, whereas the large cell was 'heated' only by the preheated methanol solution feed.

Figure 7 shows the effect of anode side inlet flow rate on the transient response of the large cell for a 0.5 M methanol solution at a cell temperature 80 °C. The higher flow rate did not benefit cell performance. An increase in the flow rate of methanol solution, which is at lower temperature than the cell body, caused an increase in localised cooling at the anode catalyst layer, which correspondingly reduced voltage performance. Over the period when the current load was applied the voltage response had not really approached a steady state at the higher flow rate.

3.3. Effect of cell stacking

Figure 8 compares the electrical response, to a pulse load, of three cell systems operating under similar condition (0.5 M methanol, 80–85 °C, 1 bar air): a small cell, a large cell with an active area of 272 cm² and a three-cell stack with a total active area of 816 cm². The flow rates used were comparable in terms of the ratio of flow to active electrode cross sectional area. The three systems responded differently: the single cell had a relatively fast response rapidly reaching a 'steady state'. The response of the single large cell showed a slow decay in voltage and required almost 60 s to reach a near steady state response which is significantly lower, by approximately 40 mV, than the response measured in the first few seconds on load. The three-cell stack, on



Fig. 8. Comparison of the voltage response, under constantly pulsed load conditions of 50 mA cm⁻², followed by a relaxation period of 180 s prior to the application of the next pulse for the three systems: (a) small scale cell (methanol concentration 0.5 mol dm⁻³; methanol flow 10 cm³ min⁻¹; cell temperature 85 °C; air fed system at 1 bar cathode pressure.), (b) large scale cell (methanol concentration 0.5 mol dm⁻³; methanol flow 500 cm³ min⁻¹; cell temperature 80 °C; air fed system at 1 bar cathode pressure.) and (c) three-cell stack (methanol concentration 0.5 M; methanol flow 1500 cm³ min⁻¹; cell temperature 80 °C; air fed system at 1 bar cathode pressure.).

load, had a voltage decay transient intermediate to those of the small cell and the large cell and approached a near steady state condition after 120 s on load. A potential influence in the response of the stack of three cells was that the cells did not respond identically. There will have been variations in flows to the cells, due to the internal manifold design, and there are variations in temperature of the cells, particular the catalyst layers, due to the flow variations and the variation in the thermal/heat transfer characteristics of the stack. As explained in the previous section the anode side flow rate affected the cell response and, according to our previous modelling work [30, 31], there will have been significant variations in flow to individual cells in the stack, which also affect the temperature profile of the stack. Overall it is believed that the combination of a variation in local flow and heat transfer characteristics in individual cells contributed towards the difference in dynamic response of the cell stack compared to the single cells.

3.4. Effect of stack operating conditions

Figure 9(a) shows the effect of the methanol solution flow rate on the three-cell stack response with a pulsed load, for a 0.5 M methanol concentration and cell temperature of 70 °C. As can be seen the lower flow rate ($1.5 \text{ dm}^3 \text{ min}^{-1}$) gave a higher voltage, of



Fig. 9. Effect of anode side feed flow rate on the small scale cell and stack response. (a) Three-cell stack voltage response under constantly pulsed load conditions of 50 mA cm⁻² followed by a relaxation period of 180 s prior to the application of the next pulse. (Methanol concentration 0.5 M; methanol flow show on chart in dm³ min⁻¹; cell temperature 80 °C; air fed system at 1 bar cathode pressure.) (b) Small scale cell pulse (methanol concentration 2.0 M; methanol flow show on chart; cell temperature 80 °C; air fed system at 1 bar cathode pressure.)

approximately 30 mV. A further increase of the inlet flow rate, above $3.5 \text{ dm}^3 \text{ min}^{-1}$, did not result in a significant change in the electrical response of the DMFC. Similar results were also obtained for the small cell as shown in Figure 9(b) (The only available data for the small scale cell was for a variable step load, but serves to illustrate the effect of flow rate for the small cell). The response of the stack was very slow and, on load, a steady state condition had barely been achieved in the duration of the pulse. Figure 10 shows the effect of cathode pressure on the cell response, to variable load conditions, for a methanol concentration of 0.5 M and a cell temperature of 70 °C. As shown in Figure 10, the stack voltage increased at the higher pressure and showed a faster response to an approximate steady state when a load was applied. A similar response was seen for the small cell when, with a reduction of pressure, of 2 bar to 1 bar, there was a decrease in the normalized cell potential of approximately 0.09, for the small cell, which was comparable to



Fig. 10. Effect of cathode pressure on the three-cell stack voltage response under constantly pulsed load conditions of 50 mA cm⁻² followed by a relaxation period of 180 s prior to the application of the next pulse. (Methanol concentration 0.5 M; methanol flow 1500 cm³ min⁻¹; cell temperature 80 °C; air fed system at cathode pressure shown on chart in bars.)

the reduction in voltage for the stack with a pressure change of 1 to 0.5 bar. With a low pressure of 0.2 bar the stack exhibited an unstable performance on load with a long transient in which, for the duration of the load, a steady state was not achieved. In addition the stack showed a slow response to a steady open circuit potential when the load was removed. Overall the influence of pressure in the stack is complicated by variations in flow that occur to the individual cells with the internal manifold design and the variation in pressure distribution in the cells. This is in addition to the potential effect of accumulation of relatively large quantities of water in the cathode side of the MEA and elsewhere in the cell.

4. Conclusions

The dynamic performance of the DMFC is affected by complex interactions of electrode kinetics and mass transport processes, fluid dynamics and temperature effects. The response of the small scale cell, to changes in magnitude and rate of change of load was rapid, and reversible. Under a pulsed dynamic load regime the cell voltage response was significantly better than that achieved under steady state operation. This characteristic is potentially attractive in vehicle applications. The dynamic cell voltage response was significantly affected by the methanol solution flow rate, methanol concentration and cathode air pressure. Variations in response were due to many phenomena, but methanol crossover from anode to cathode was a significant factor. In addition, in practical DMFC operation, the input of methanol solution at a temperature below that of the cell caused dynamic interactions between the actual catalyst region operating temperature and methanol flow rate. On scale-up, the response of the cell was slower and influenced less by a change in concentration and in methanol solution flow rate. On the other hand, a reduction in air pressure resulted in a marked deterioration in performance when the pressure approached atmospheric.

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