



## Regulating methanol feed concentration in direct methanol fuel cells using feedback from voltage measurements

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### ABSTRACT

Regulating methanol feed concentration in direct methanol fuel cells (DMFCs) is important for improving electrical performance and fuel utilization. Low methanol concentration reduces the reaction rate at the anode due to Nernstian effects resulting in a lower operating voltage. However, simply increasing the methanol concentration does not always lead to improved performance due to increased methanol crossover from the anode to the cathode resulting in mixed-potential losses and the associated fuel loss. Hence, there exists an optimal intermediate value of methanol concentration for each current density that will yield the highest electrical performance (V). In this paper, we describe the development of an in situ methodology which uses the measured cell voltage as the feedback to regulate the methanol feed concentration for maximum power density. This methodology is demonstrated at the current densities of 50, 100, and 250 mA cm<sup>-2</sup> and the results for optimal concentration are presented. Fuel loss as a function of methanol concentration is evaluated by oxidizing the crossover methanol at the cathode exhaust and measuring the CO<sub>2</sub> mass flux.

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### 1. Introduction

It is widely accepted that direct methanol fuel cells (DMFCs) have the potential to attain commercial success as power supplies for portable applications. Recent developments of DMFCs have focused on advances made at the system level [1–3]. However, methanol crossover from the anode to the cathode is still considered to be one of the main technical hurdles, resulting in low performance and efficiency. The methanol arriving at the anode catalyst layer through the GDL will either undergo reaction at the anode catalyst sites or will crossover from the anode to the cathode across the polymer electrolyte membrane. Methanol crossover occurs due to diffusion driven by the concentration gradient across the membrane, and due to flux associated with the electro-osmosis of H<sup>+</sup> ions. Diffusion is considered to be the dominant process because the mass flux driven by the concentration gradient is higher than the electro-osmotic flux at the low current densities prevalent in DMFCs [4].

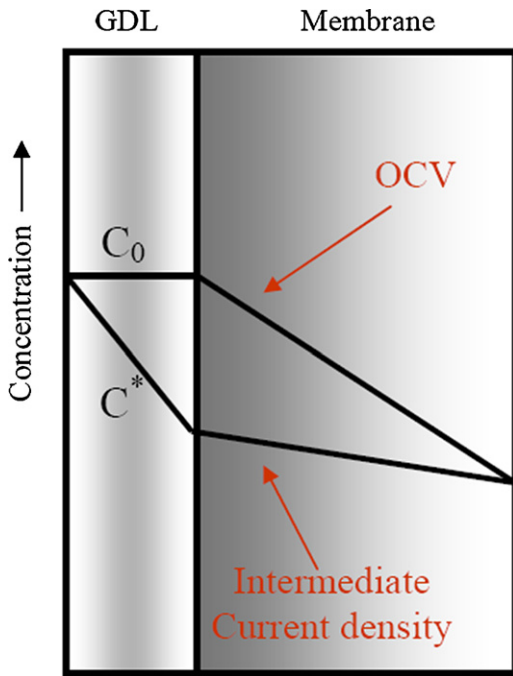
Methanol crossover is detrimental to DMFC performance for two reasons. First, the crossed over methanol reacts on the cathode side creating a mixed-oxidation potential which reduces the overall voltage of the fuel cell. Second, methanol crossover reduces the overall fuel utilization of the system. The current practice to limit methanol diffusion across the membrane in DMFCs is to employ

low concentrations of the anode methanol feed. In addition, the use of dilute methanol ensures that sufficient water is available for the anode reaction despite the removal of water by diffusion and electro-osmosis through the membrane [5]. However, a low methanol feed concentration has the corresponding adverse effect of reducing the reaction rate due to Nernstian effects and reduced catalyst site occupancy, consequently reducing cell performance. Therefore, regulating the methanol feed concentration as a function of current density in DMFCs is important for maximizing performance.

Typically, the concentration of methanol in DMFCs is monitored with concentration sensors which operate on the principle of sensing either the physical or electrochemical properties of the methanol solution [6]. However, concentration sensors for fuel cells must meet a wide range of requirements such as resolution, accuracy, and rapid response time. Concentration sensors that are based on sensing physical properties must be tolerant to carbon dioxide bubbles that are formed in-line during the operation of the fuel cell. Although electrochemical sensors are comparatively better, they lead to the degradation of the membrane electrode assembly. Additionally, these sensors must also be tolerant to various metallic impurities such as Fe and Cu ions which may be present in the methanol solution. Despite their utility, such sensors increase the weight, size, complexity and overall cost of the DMFC system.

Sensor-less monitoring of the methanol feed concentration can increase the overall efficiency of the DMFC system. Few studies have reported on the development of sensor-less control of DMFCs. However, Chiu and Lien [7] proposed a methodology to estimate

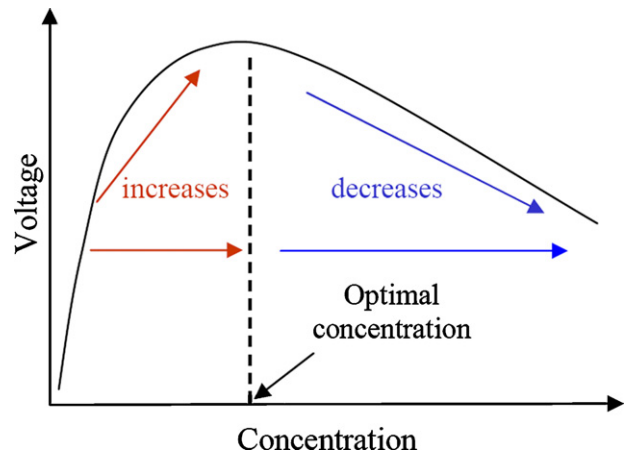
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**Fig. 1.** Schematic diagram of methanol concentration profiles in the GDL and membrane.

fuel concentration in direct liquid fuel systems based on operational variables such as temperature, voltage, and current. Although recent patents (such as US 6,589,679 and US 6,991,865) address this issue, there is little published information providing detailed insight and analysis of these methodologies. Recently Chang et al. [8,9] developed a sensor-less control algorithm – Impulse Response based on Discrete Time Fuel Injection (IR-DTFI) – which uses the fuel cell operating characteristics to regulate the fuel supply under dynamic conditions. In the current paper, we illustrate the need for optimal methanol feed concentration under different load conditions, and describe the development of a methodology to regulate the fuel supply for maximum performance and fuel utilization.

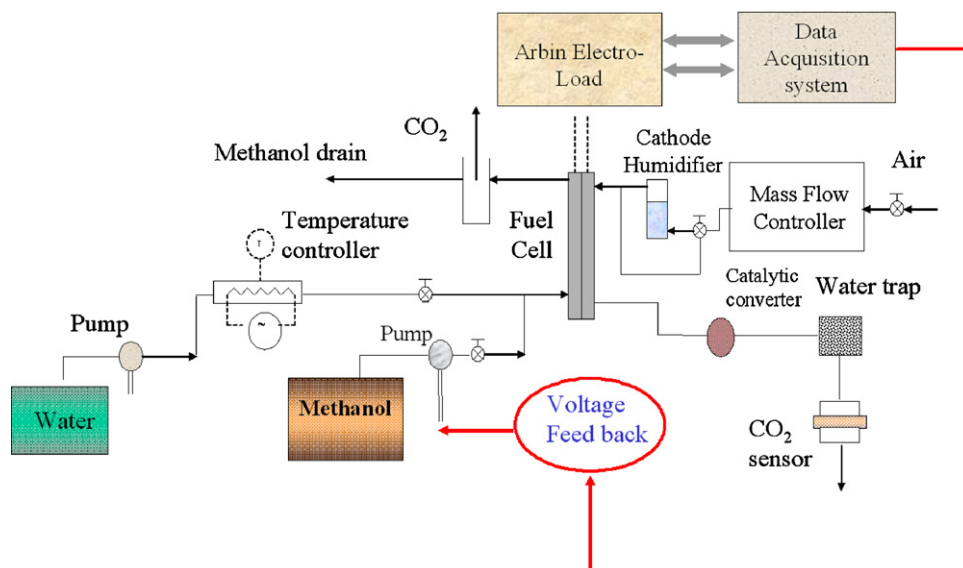
Fig. 1 shows schematic profiles for the expected methanol concentration within the GDL and in the adjacent membrane at OCV, and at an intermediate current density. At OCV, the concentration



**Fig. 2.** Schematic diagram of the expected variation of voltage with concentration at a fixed current density.

at the left edge of the membrane is equal to the bulk methanol concentration leading to higher crossover. As current is drawn from the DMFC, some methanol reacts in the catalyst layer resulting in lower concentration at the membrane leading to reduced crossover. Increasing the inlet concentration ( $C_0$ ) increases the methanol crossover, but reducing the methanol concentration to limit crossover compromises performance by reducing the reaction rate at the catalyst layer [10–12]. Hence it is apparent that an optimal intermediate value of methanol concentration should exist for a given current density. This is demonstrated schematically in Fig. 2. At a specific current density the cell voltage increases with  $C_0$  as predicted by the Nernst equation up to a certain point. Further increase of concentration increases the fuel crossover to such an extent that the cell voltage is reduced due to mixed-potential losses. At a fixed current density, voltage is a direct measure of electrical performance (power density).

In this experimental investigation, we describe the development and testing of an in situ sensor-less methodology which employs the cell voltage as the feedback to optimize the methanol concentration at the anode for maximum power density while still maintaining a high level of fuel utilization. The main advantages of the feedback algorithm are that it is able to regulate the methanol feed under any operating condition, and it functions independently



**Fig. 3.** Schematic of the experimental setup to optimize methanol feed concentration for maximum performance.

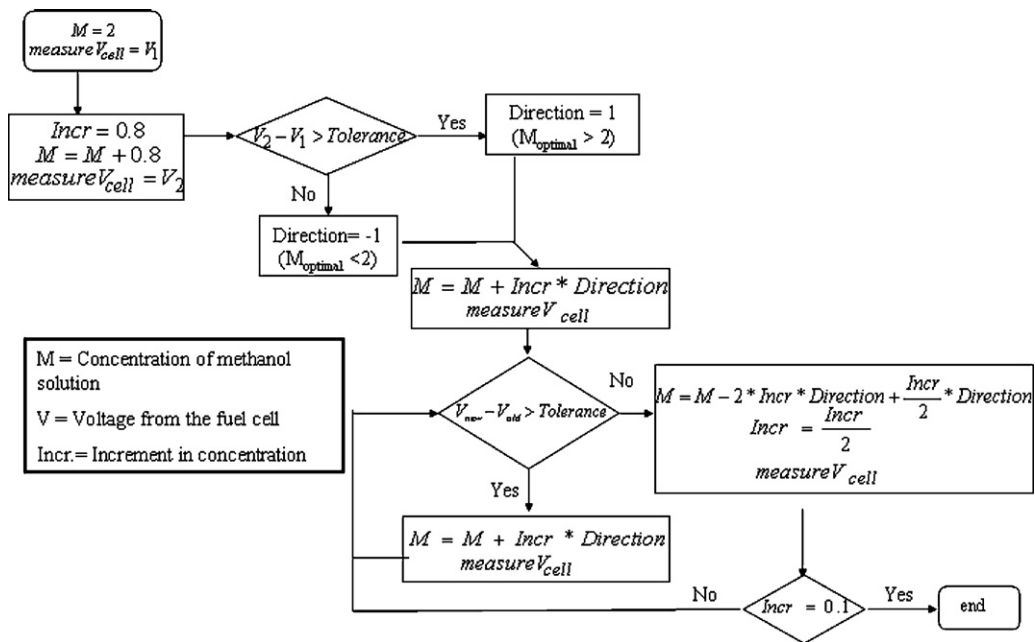


Fig. 4. Algorithm to optimize methanol feed concentration during fuel cell operation using voltage as the feedback.

of the type of fuel cell components such as membrane, GDL and catalyst layers. An efficient algorithm has been designed by characterizing voltage vs. concentration curves over a range of current densities and validated experimentally.

## 2. Experimental setup

An experimental setup was assembled as shown in Fig. 3. The methanol feed system consisted of a dual-syringe pump unit for pure methanol and a peristaltic pump for water. The methanol was injected into the water line where it underwent pre-mixing before entering the fuel cell. While the water flow rate was fixed for each experiment, the methanol concentration was controlled by adjusting the methanol flow rate continuously over values ranging from  $1 \text{ ml min}^{-1}$  (corresponding to  $10 \text{ M}$ ) to  $1 \mu\text{l min}^{-1}$ . The overall flow rate of the methanol feed solution could be increased as desired by increasing the water flow rate.

Load conditions on the fuel cell were maintained by an Arbin FCTS DAQ system, and the voltage was recorded by a National Instruments DAQmx™ board. Methanol crossover was quantified by flowing the cathode exhaust gases through a catalytic burner to oxidize the diffused methanol to carbon dioxide whose mass flux was measured with a  $\text{CO}_2$  sensor. The output of the  $\text{CO}_2$  sensor was correlated to the amount of methanol crossover through the membrane [13].

### 2.1. DMFC specifications and test conditions

The MEAs (with Nafion 117 membrane and carbon cloth GDL) employed in all the experiments were assembled with  $4 \text{ mg cm}^{-2}$  Pt/Ru catalyst on the anode and  $2 \text{ mg cm}^{-2}$  Pt catalyst on the cathode. The temperature was maintained at  $50^\circ \text{C}$  for all the experiments in this study. Water in the anode feed was supplied at a constant flow rate of  $4 \text{ ml min}^{-1}$ . The injection rate of pure

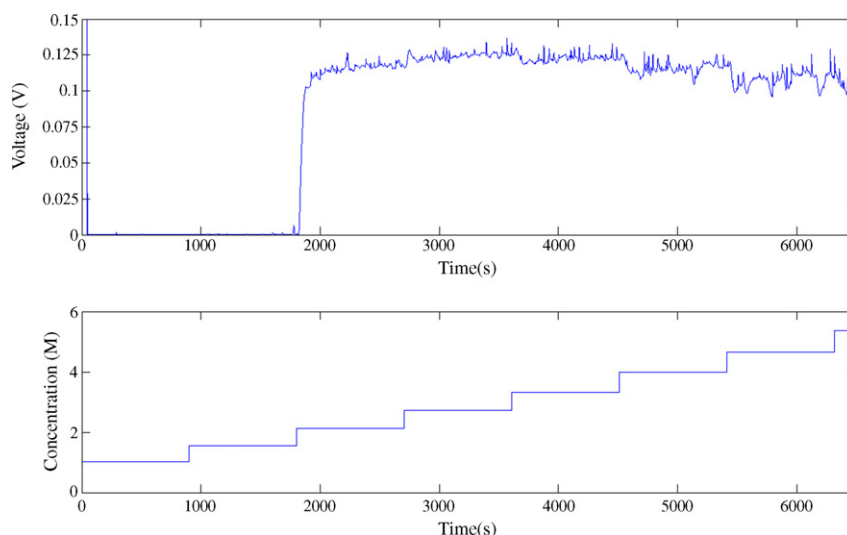


Fig. 5. Variation of voltage with concentration at  $250 \text{ mA cm}^{-2}$  with concentration increments of  $0.55 \text{ M}$ .

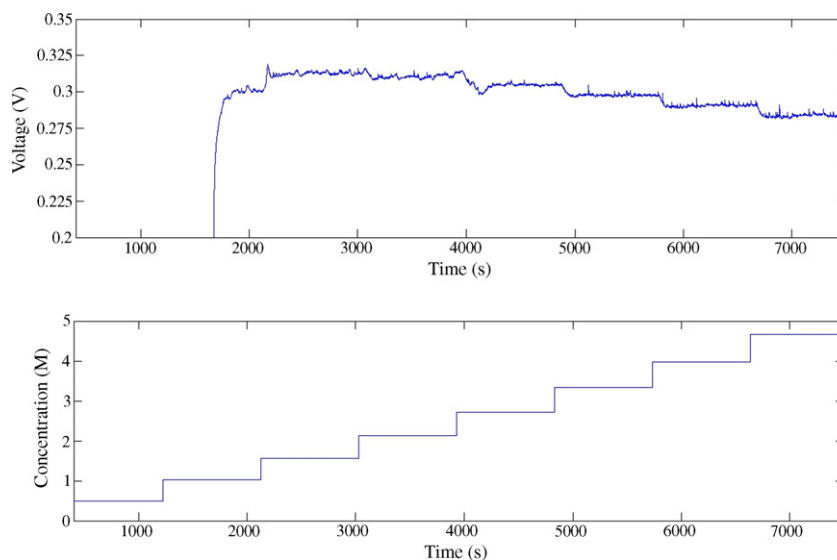


Fig. 6. Variation of voltage with concentration at  $100 \text{ mA cm}^{-2}$  with concentration increments of  $0.55 \text{ M}$ .

methanol into the water line was varied in real time to titrate the concentration of methanol solution entering the cell by an algorithm that uses the instantaneous cell voltage value as feedback. The flow rate of methanol injected in the inlet tube was varied from  $10$  to  $600 \mu\text{l min}^{-1}$ , which is small compared to that of the water, which was maintained at a constant value of  $4 \text{ ml min}^{-1}$ . Hence the overall flow rate of the methanol–water solution was considered to be constant at about  $4 \text{ ml min}^{-1}$ . The cathode was supplied with air at a relative humidity of  $70\%$  at a flow rate of  $500 \text{ sccm}$ .

## 2.2. System description

The experiments were controlled by a feedback algorithm written as a MATLAB<sup>®</sup> script embedded in a LabVIEW<sup>™</sup> environment. The LabVIEW environment was also set up to collect data such as voltage,  $\text{CO}_2$  concentration in the cathode exhaust, and methanol pump flow rate information at a sampling rate of  $1 \text{ Hz}$ . The feedback algorithm was designed to employ a series of steps in order to

determine the maximum voltage and the corresponding methanol concentration. For every step change in concentration, the system was allowed to run for  $400 \text{ s}$  to reach steady state. To ensure execution of the algorithm with minimum transient error, the voltage at each value of concentration was averaged over the previous  $200$  data points. These steps ensured a more stable execution of the algorithm for determining the optimal methanol feed rate (i.e., concentration). There are various other parameters that can be controlled during the experiment such as voltage tolerance (to negate the effect of noise), the initial value of increment in concentration, and the final value of increment to define the termination point. The feedback algorithm is described in Section 2.3. Results for voltage, concentration, and crossover data collected at each step are presented in Section 3.

## 2.3. Optimization algorithm

The algorithm initializes the syringe pumps to deliver methanol at  $2 \text{ M}$  concentration. This initial concentration value is obtained

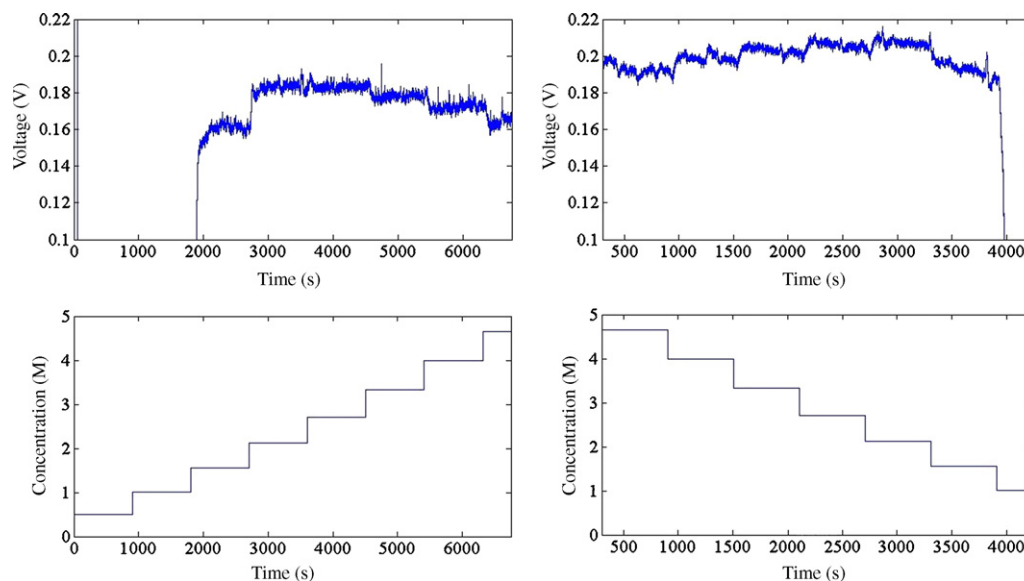


Fig. 7. Variation of voltage with concentration at  $200 \text{ mA cm}^{-2}$  with increments (left) and decrements (right) in concentration of  $0.55 \text{ M}$ .

**Table 1**

Optimal concentration, limiting concentration and corresponding maximum voltages at current densities 50, 100, 150, 200, 250 and 300 mA cm<sup>-2</sup>.

Current density (mA cm <sup>-2</sup> )	Optimal conc. (M)	Limiting conc. (M)	Maximum voltage (V)
50	0.8	0.6	0.42
100	1.6	1	0.334
150	1.8	1.229	0.265
200	2.4	1.44	0.184
250	2.8	1.898	0.113
300	3.4	1.898	0.078

from the average value of the optimal concentration at all current densities as presented in Section 3.1. Next, the algorithm increments the concentration by 0.8 M and compares the new voltage with the corresponding voltage at 2 M. If the voltage increases, then for that particular dynamic load, the optimal concentration value must exceed 2 M. Therefore, the algorithm commands the concentration to be incremented successively to search for the optimal concentration value. If, on the other hand, this initial increment of 0.8 M in concentration results in a voltage decrease, then the algorithm searches for the optimal concentration in the opposite direction by reducing the concentration. The bisection method is implemented to determine the optimal value. The initial increments or decrements are set at 0.8 M and according to the standard bisection method, at every successive change in direction the corresponding increment or decrement in concentration is halved. The algorithm terminates when the final increment or decrement reaches 0.2 M. The algorithm is depicted schematically in Fig. 4.

### 3. Results and discussions

#### 3.1. Characterization experiments

An initial set of experiments was performed to characterize the variation of voltage and methanol crossover with increasing concentration at different current densities. Figs. 5 and 6 show the variation of voltage with concentration increments of 0.55 M at current densities 250 and 100 mA cm<sup>-2</sup>, respectively. These experimental results confirm the behavior depicted schematically in Fig. 2. For a current density of 250 mA cm<sup>-2</sup>, increasing the concentration from 2 to 2.55 M causes the voltage to increase. Similarly at 100 mA cm<sup>-2</sup>, the voltage increases when concentration is increased from 1 to 1.55 M.

With further increase in methanol concentration, the voltage decreases as shown schematically in Fig. 2. The response time of the cell voltage corresponding to a step change in concentration is on the order of 100 s. It is also seen that the cell experiences a sudden increase in voltage as the methanol concentration is increased from zero to around 1 M for 100 mA cm<sup>-2</sup> (Fig. 6), and to around 2 M for 250 mA cm<sup>-2</sup> (Fig. 5). This particular concentration is termed as the limiting concentration for a given current density. To confirm this behavior we performed similar experiments at 200 mA cm<sup>-2</sup> while monotonically decreasing the concentration from 4 to 1 M. Results are shown in Fig. 7. The sudden change in voltage at the limiting concentration for a given current density is a consequence of mixed mass transport and reaction limitations on the anode side of the DMFC [14].

In order to identify the optimal concentration more accurately, the experiments with varying concentration were repeated with a smaller concentration increment of 0.23 M and the results are shown in Fig. 8. At low current densities, the drop in voltage is noticeable as the concentration is increased beyond the optimal value. Table 1 lists the optimal concentrations, limiting concentrations, and their corresponding voltages at current densities of

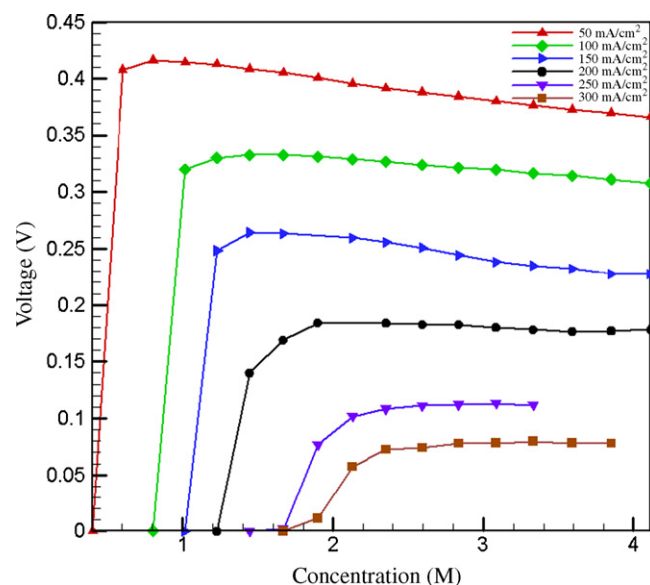


Fig. 8. Variation of voltage with concentration at current densities of 50, 100, 150, 200, 250 and 300 mA cm<sup>-2</sup> with concentration increments of 0.23 M.

50, 100, 150, 200, 250 and 300 mA cm<sup>-2</sup>. From the table we can see that the optimal value of concentration ranges from 0.8 to 3 M. This demonstrates that the optimal concentration depends strongly on the current density maintained during the fuel cell operation.

Fuel loss due to crossover is determined from CO<sub>2</sub> mass flux measurements in the cathode exhaust. Fig. 9 shows the variation of CO<sub>2</sub> with concentration at current densities of 50 and 200 mA cm<sup>-2</sup>. The CO<sub>2</sub> concentration on the y-axis is directly correlated to the amount of methanol crossing through the membrane. The behavior depicted schematically in Fig. 1 is now confirmed. As seen in Fig. 9, increasing the current density from 50 to 200 mA cm<sup>-2</sup> at a fixed concentration reduces the concentration gradient across the membrane resulting in reduced crossover. Likewise, it is observed that at most current densities the methanol crossover increases significantly with concentration. Therefore, operating at concentrations higher than the optimal concentration would reduce fuel utilization considerably. For example, at 50 mA cm<sup>-2</sup> when the cell is operated at 0.8 M (optimal concentration) the fuel loss is only

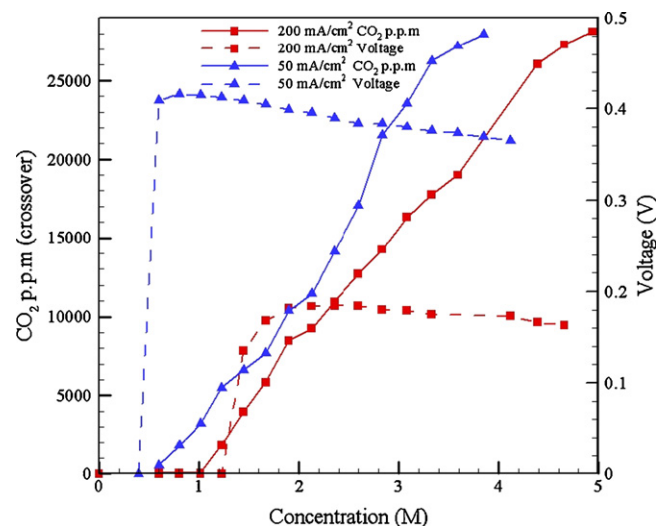


Fig. 9. Variation of methanol crossover and voltage with concentration at current densities of 50 and 200 mA cm<sup>-2</sup>.



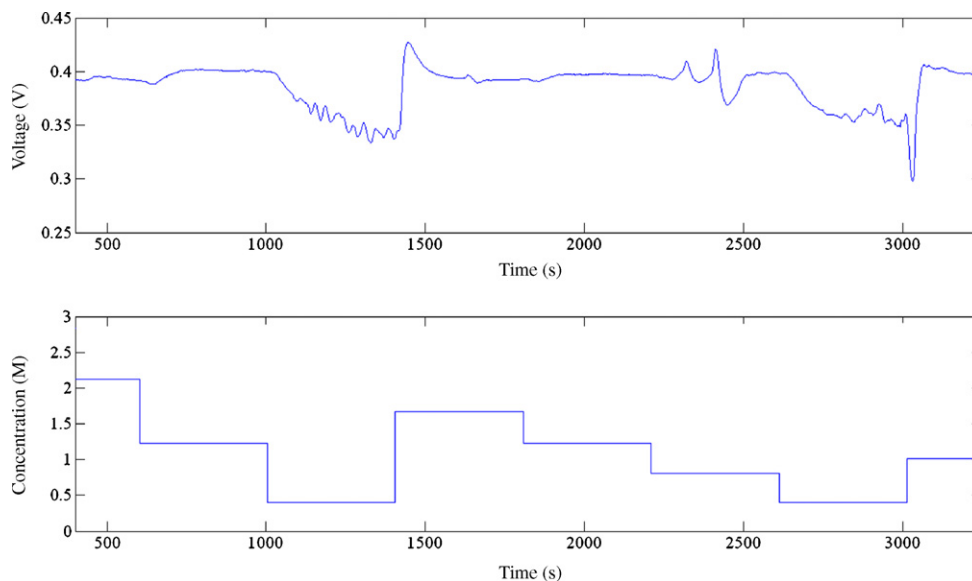


Fig. 10. Voltage response with algorithm implementation at a current density of  $50 \text{ mA cm}^{-2}$ .

1.2 times the fuel reacted on the anode; however, when the cell is operated at 2 M the fuel loss is 7.6 times the fuel reacted. Although operating the DMFC around the limiting concentration results in the greatest fuel utilization, these conditions can lead to MEA degradation in the long run. The voltage vs. concentration curves at different current densities reveal that the optimal concentrations are very close to the limiting concentrations. Therefore, it can be concluded that while the feedback algorithm seeks to only optimize the output voltage, the proximity of the optimal concentration to the limiting concentration also assures a maximization of fuel utilization.

### 3.2. Optimal feed concentration

The successful execution of the algorithm described in Section 2.3 is demonstrated at current densities of 50, 100, and  $250 \text{ mA cm}^{-2}$ . The step changes in concentration employed by the algorithm to reach the final optimal value and the corresponding voltages are shown in Fig. 10. At a current density of  $50 \text{ mA cm}^{-2}$ , the initial concentration of 2 M is higher than the optimal concentration and hence it is reduced to produce a correspond-

ing increase in voltage. Thereafter, the bisection method guides the system to reach the optimal value. Figs. 11 and 12 show the successive changes in concentrations to arrive at the optimal concentration and their corresponding voltages at current densities of 100 and  $250 \text{ mA cm}^{-2}$ , respectively. The optimal concentration at  $100 \text{ mA cm}^{-2}$  is approximately 1.6 M and it can be seen that it was achieved in four steps. At a current density of  $250 \text{ mA cm}^{-2}$ , an initial feed concentration of 2 M produced a voltage less than 0.1 V, showing that mass transport limitations are dominant in the DMFC for these conditions. Therefore, the algorithm calculates that an increment in concentration is required. The optimal concentration at  $250 \text{ mA cm}^{-2}$  was found to be 3 M. The algorithm reached the optimal concentration ( $\pm 0.2 \text{ M}$ ) in five steps.

In all cases, the experimental data show that the voltage instability increases at limiting concentrations. The oxidation of methanol on the catalyst layer at limiting concentrations is just sufficient to meet the current demand from the load, and small disturbances in the methanol supply rate cause the voltage to fluctuate. In addition, our observations indicate that extended operation of the DMFC at limiting concentration values can oxidize the catalyst and degrade

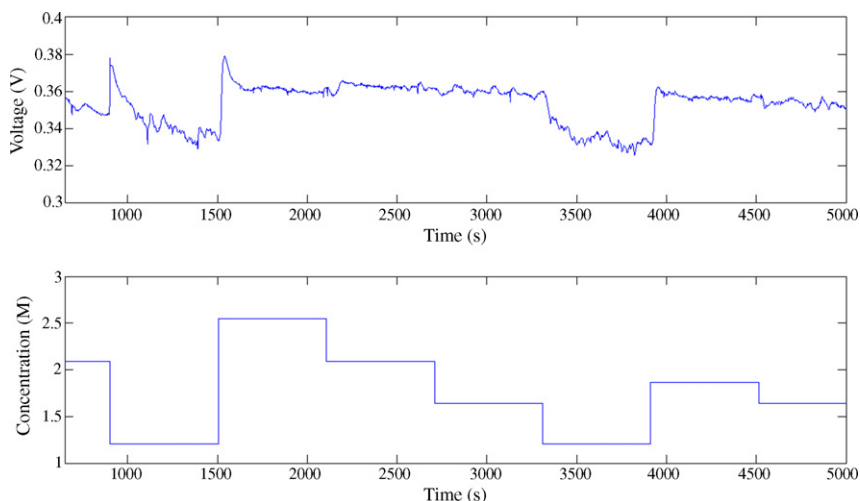


Fig. 11. Voltage response with algorithm implementation at a current density of  $100 \text{ mA cm}^{-2}$ .

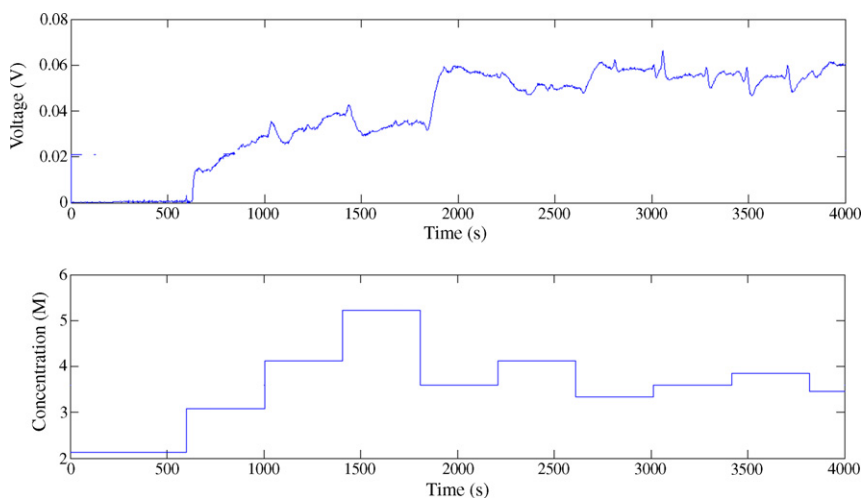


Fig. 12. Voltage response with algorithm implementation at a current density of  $250 \text{ mA cm}^{-2}$ .

MEA performance. Hence, it is not advisable to operate the DMFC very close to the limiting concentration value.

#### 4. Conclusions

We have developed and demonstrated a control strategy which uses the DMFC voltage as feedback to optimize methanol concentration as a function of current density for maximum power. Our experimental results revealed the following voltage behavior as the concentration is steadily increased for a given current density: first, the voltage increases rapidly from an initial value of zero at a particular concentration which we denote as the limiting concentration. Further increase in concentration produces a corresponding increase in the voltage until a maximum value is obtained, after which a further increase in concentration causes a reduction in voltage. Based on these results, we have developed a bisection algorithm which regulates the methanol feed concentration to the DMFC under dynamic operating conditions using the cell voltage as feedback to obtain the maximum power. The reduction of voltage due to mixed-potential losses under conditions of high crossover is also confirmed with crossover measurements. The results confirm that the optimal methanol concentration for maximum power density is a function of current density. It is also found from our

crossover measurements that operating the DMFC at optimal concentration improves fuel utilization.

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