Performance and Modeling of a Direct Methanol Fuel Cell

S. O. Bade Shrestha, and Sujith Mohan

Abstract—**Direct methanol fuel cells (DMFC) are getting more popular as a power source in the field of power electronics because of their high energy density. The benefits of using a fuel cell towards the environment will be enhanced if the fuel used for its application comes from renewable sources. A method of modeling of the performance of DMFC was developed and validated with the experimental data obtained from a DMFC operated under five different methanol concentrations. Impedance spectroscopy was employed to measure the ohmic, activation and mass transport losses for all concentrations. Improved performance of the cell was observed when the concentrations of methanol solutions were closer to stoichiometric values. The model predicted results were compared to the corresponding experimental values and found satisfactory.**

Index Terms—**Methanol, Fuel Cell, Alternative Energy, Modeling**

I. INTRODUCTION

FUEL cells are a device that converts the chemical energy stored in a fuel directly into electrical energy and heat through electrochemical reaction [1]. The demand for the various fuel cells have been increasing dramatically in recent years, because of stringent emission control, global warning and climate change concern and imported energy dependency issues both in motive and stationary applications. It has been augmented particularly due to new generations of fuel cells which are more efficient, reliable and durable in comparison to the old models. And the price of fuel cell has been steadily coming down in recent years.

However, most of the fuel cells still (e.g. alkaline fuel cells or proton exchange membrane fuel cells) use hydrogen directly as a fuel. The major problem associated with using hydrogen is still a lack of hydrogen infrastructure in the nation. The development of hydrogen infrastructure has been challenging due to the high cost of hydrogen storage, handling and transportation [2]. Therefore, fuel cells which use high molar energy density liquid fuel have been more attractive at least in midterm basis until hydrogen infrastructure is in place.

The direct methanol fuel cell (DMFC) uses methanol directly as fuel not requiring any use of reformers and humidifiers. Therefore it has attracted extensive interest from the research community and industry [3]. Other advantages of using methanol are readily availability, and low cost liquid fuel. Methanol also possesses higher molar energy density than hydrogen and it can be transported easily through the existing infrastructure [4].

In this contribution a passive DMFC was used to investigate the performance characteristics and to develop a semi-imperial model of the fuel cell. A passive DMFC is a fuel cell without any pumps and blowers used to circulate methanol and oxidant suppliers to feed air into the system. The absence of these accessories makes the passive DMFC a promising choice of power source in toys & electronic devices such as mobile phones and MEMS. However, DMFC suffers with one of the major problems associated with open circuit voltage (OCV) which is lower than the corresponding theoretical value. This may be attributed to the phenomenon of methanol cross over through the membrane from the anode to the cathode side which reduces the cathode potential and thereby the overall voltage of the cell [5].

The reaction mechanism for a DMFC at anode, cathode and overall are as:

Anode reaction:

$$CH_3OH + H_2O \rightarrow 6H^+ + 6e^- + CO_2 \qquad (1)$$

Cathode reaction:

$$1.5\ O_2 + 6H^+ + 6e^- \rightarrow 3H_2O \qquad (2)$$

Overall reaction:

$$CH_3OH + 1.5\ O_2 \rightarrow 2H_2O + CO_2 \qquad (3)$$

Hence, six electrons pass through the outer circuit producing current for every mole of methanol consumed. The reversible OCV for a DMFC is 1.21V at standard conditions [4].

2. EXPERIMENT ARRANGEMENT

The tests were conducted on a single cell passive DMFC manufactured by Heliocentris. The cell specifications are shown in Table 1 below.

TABLE 1
SPECIFICATION OF THE DMFC

No of cells	1
Active cell area	4 cm^2
Manufacturer	Heliocentris

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A built-in reservoir of methanol was incorporated in the test DMFC providing access to methanol to reaction areas purely through methanol diffusion. The measurement of the voltage and current were made using an Amrel test load station. Impedance spectroscopy measurements were done using the built in Frequency Response Analyzer (FRA) unit of the load. K-type thermocouples were used to monitor the temperatures of the test cell throughout the experiment. The detailed experimental method and procedure information can be found in the Ref. [6]. The cell was tested under five different methanol concentrations. All the experiments were conducted at atmospheric temperature and pressure if otherwise mentioned explicitly.

3. RESULTS AND DISCUSSION

The polarization curves of five different methanol concentrations are presented in Figure 1. It can be seen that the output voltage was increased significantly as the concentration of the methanol was increased in the mixture. The highest potential was observed at two molar (2M) concentration and further increase in molar concentration was found had a negative effect.

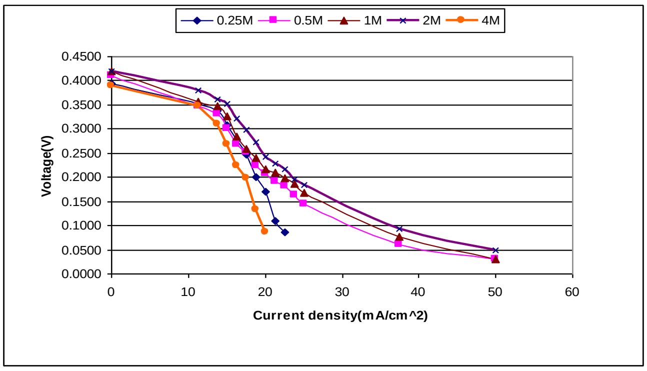


Fig 1: Polarization curve showing the effect of methanol concentration [6].

The average potential increase for 2M concentration was found to be 45% higher than the average potential for 0.25M or 4M concentration. Furthermore, the average potential for 2M concentration was only 8% higher than the average potential of 1M concentration, clearly indicating that the cell performance continued to increase only up to a certain level of methanol concentration after which the performance of the cell began to fall since the methanol crossover from the anode to cathode began to increase considerably. The cell potential began to drop substantially when the cell was run with rich methanol concentration solution of 4M than other concentrations.

In fact one mole of methanol requires one mole of water to produce 3 moles of hydrogen and 1 mole of carbon dioxide in the stochiometric condition (Equation 1). In terms of mass, 32.04 gm of methanol requires 18 gm of water, making the stoichometric ratio of methanol to water is 1.78. Therefore, whenever higher (or lower) concentration of methanol is used there is insufficient (or excess) amount of water to combine with the entire methanol to produce corresponding amount of hydrogen. Thus, the lower levels of the performance of the test cell were found as the molar concentrations were set away from the stoichiometric. This trend can be seen in the polarization curves in Figure 1.

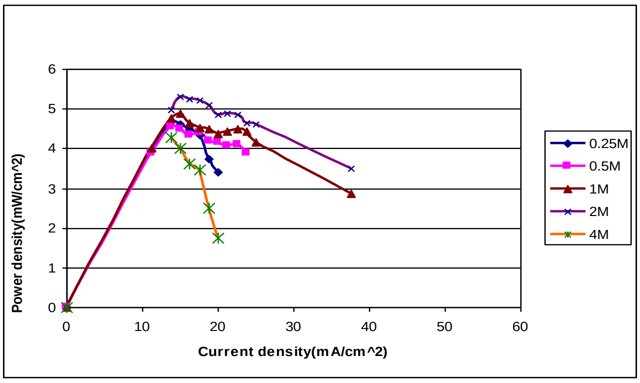


Fig: 2 Power density curves at different methanol concentrations [6].

The effects of methanol concentration on power density were presented in Figure 2 and it can be observed that at low current densities, the power outputs were similar. However, at higher current density, a little higher power density was obtained with the low methanol concentration solution. The performance of the DMFC was found better at higher current densities with a higher methanol concentration. This may be the result of relatively high temperature obtained and higher molar content that enhanced electrochemical kinetics in comparison to the too low or too high molar concentration solution. In fact at very high concentration the power density plummeted quickly as in the case of 4M concentration shown. It may be caused by increased crossover of methanol at higher concentration.

The polarization curves give a general qualification and quantification of the fuel cell performance, though for more accurate determination of different performance parameters of the cell more sophisticated experiment techniques are necessary to profound. One of the widely used techniques to determination of various major losses in the fuel cell is electrochemical impedance spectroscopy [7]. For this technique an electronic load with a built in Frequency Response Analyzer (FRA) unit was used to analyze various losses associated with the test cell in the experiment. A number of Nyquist plots were generated during the experiment to determine the losses over a frequency range of 10Hz to 15,000Hz. In Nyquist plot provides a fair estimation of the ohmic losses, cathode & anode activation losses and the mass transport losses in the fuel cell investigation.

A typical Nyquist plot is shown in Figure 3, where R_{Ω} indicates the ohmic resistance of the cell that is associated with the transportation of electron and ions through the system, R_a the anode activation losses, and R_c the cathode activation losses. Activation losses are mainly associated with the initial electrochemical reactions to overcome the activation energy of the reaction. Generally, the cathode side activation losses dominate significantly in this category [8]. And R_m represents the mass transport losses that are associated with the reactants and product species transportation within and out of the cell [7].

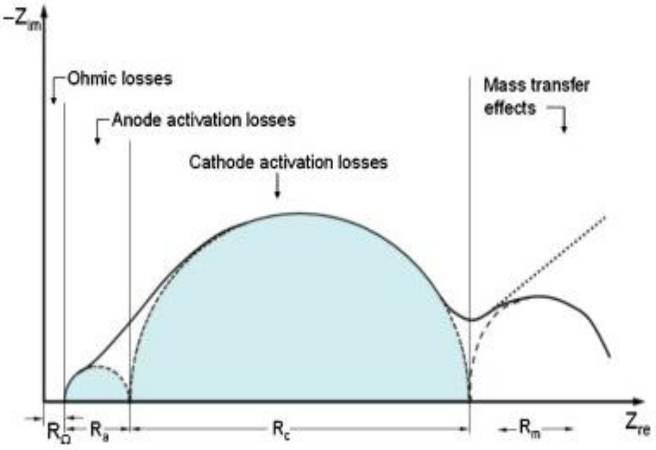
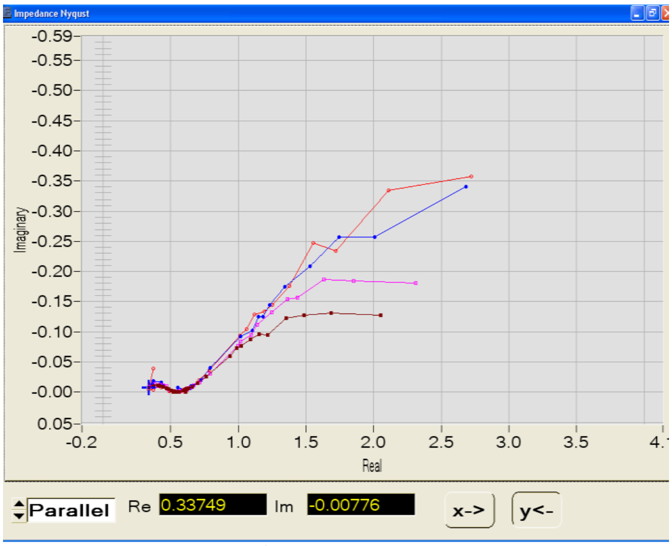


Fig 3: Typical Nyquist Plot [7]



Re 0.33749 Im -0.00776

Fig 4: Nyquist plot generated for 0.25M methanol concentration [6].

As a typical example, the Nyquist plot that was generated for 0.25M methanol concentration was shown in Figure 4. The four lines in the figure represent impedance measurements at four different current values (55mA, 65mA, 80mA & 100mA). The limiting current for this fuel cell was found to be120mA. Similar plots were generated for the test cell running at 0.5M, 1M, 2M and 4M methanol concentrations and the resistances are shown in Table 2.

It can be observed in the table that, the mass transport losses were a magnitude higher than activation or ohmic losses as expected. And the activation losses were almost unchanged for various molar methanol concentrations employed, however the ohmic losses increased as the current increases, as expected. The highest mass transport losses were observed for 4M methanol concentration. The 4M methanol concentration produced about 31% higher average mass transport losses than for a 2M methanol concentration solution. There was a noticeable increase in mass transport losses when the methanol solution started to deviate from its stoichiometric concentration value of 1.78.

TABLE 2
OHMIC, ACTIVATION AND MASS TRANSPORT LOSSES FOR DIFFERENT METHANOL CONCENTRATIONS [6].

Methanol Concentra-tion	Ohmic Loss; Ohms	Activation Loss; Ohms	Mass transport loss; Ohms	Current; mA
0.25M	0.343	0.20	1.734	55
0.25M	0.368	0.20	1.839	65
0.25M	0.370	0.20	2.118	80
0.25M	0.372	0.20	2.283	100
0.5M	0.400	0.20	1.734	55
0.5M	0.404	0.20	1.752	65
0.5M	0.408	0.20	2.076	80
0.5M	0.411	0.20	2.118	100
1M	0.375	0.20	1.337	55
1M	0.390	0.20	1.492	65
1M	0.392	0.20	1.692	80
1M	0.400	0.20	1.734	100
2M	0.282	0.19	1.213	55
2M	0.304	0.19	1.372	65
2M	0.334	0.19	1.573	80
2M	0.339	0.19	1.714	100
4M	0.376	0.20	1.804	55
4M	0.378	0.20	1.949	65
4M	0.380	0.20	2.115	80
4M	0.384	0.20	2.374	100

4. MODELING OF DMFC

The electrochemical reactions in a fuel cell can be predicted by using the basic thermodynamic equations. The empirical constants can be determined using experimental data. Once the trends of the unknown parameters are known the model can be developed to predict the performance of the fuel cell at any operating conditions. The cell voltage can be predicted using an empirical approach by starting with the thermodynamically predicted voltage and then subtracting different voltage losses [8]. The model that was used to predict the polarization curve of the cell is shown below in Equation 4.

$$E_{cell} = E_{ocv} - (\eta_{activation} + \eta_{ohmic} + \eta_{masstransport}) \qquad (4)$$

Where, E_{cell} and E_{ocv} are the operating cell voltage, and thermodynamically predicted voltage of the fuel cell respectively. $\eta_{activation}$, η_{ohmic} and $\eta_{masstransport}$ are activation losses, ohmic losses, and mass transport losses of the cell. The equations for activation, ohmic and mass transport losses were shown below:

$$\eta_{activation} = A * \ln(i) + C2 \qquad (5)$$

$$\eta_{ohmic} = i * R + C1 \qquad (6)$$

$$\eta_{masstransport} = m * \exp(n * i) \qquad (7)$$

Where *A*, *R*, *m* and *n* are coefficients and *C1* and *C2* are constants. These were estimated using curve fits from experimental data. “*i*” is the current drawn out of the cell. The activation losses are estimated using the TAFEL equation, the simplified form of which is shown in equation 5. The linear relationship based on current was applied for

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the ohmic losses and finally the mass transport losses are assumed to follow an exponential pattern [9].

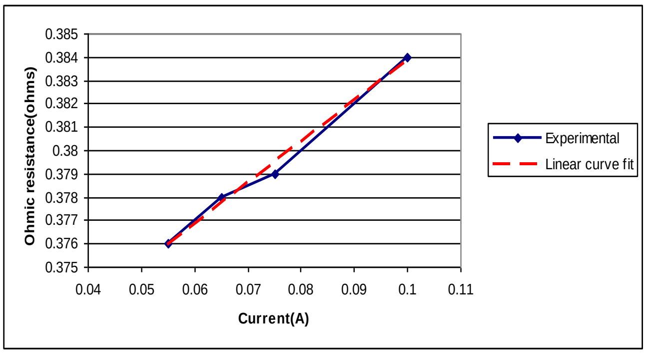

Fig 5: Ohmic losses vs. current for 4M methanol solution

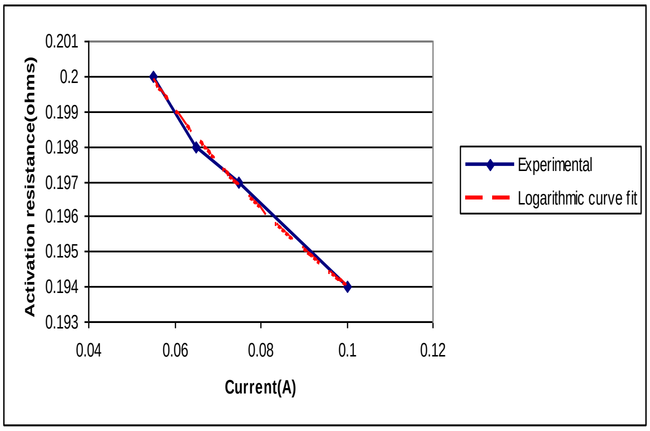

Fig 6: Activation losses vs. current for 4M methanol solution

The coefficients and constants of Equations 5, 6 and 7 were estimated using the experimental data furnished in Table 2 [6]. As examples, Figures 5, 6, and 7 show the change in ohmic, activation and mass transport losses with current for a 4M methanol concentration solution, respectively. A linear fit was used to predict the values of *R* and *C1* in equation 6 as shown in Figure 5. Similarly, Figure 6 shows a logarithmic fit used to simulate the TAFEL equation in order to predict the values of *A* and *C2* in equation 5 and Figure 7 shows the change in mass transport losses with current for a 4M methanol concentration solution. An exponential fit was used to predict the values of *m* and *n* in equation 7.

Similar technique was used to predict the values of the coefficients and constants for 0.25M, 0.5M, 1M and 2M methanol solutions. The values of the coefficients and constants of Equations 5, 6 and 7 for different methanol concentrations are shown in Tables 3, 4 and 5 respectively.

Once the coefficients and constants for the different losses were known, the variations of these coefficients and constants with the change in the methanol concentration were determined by curve fitting as a function of the methanol concentration.

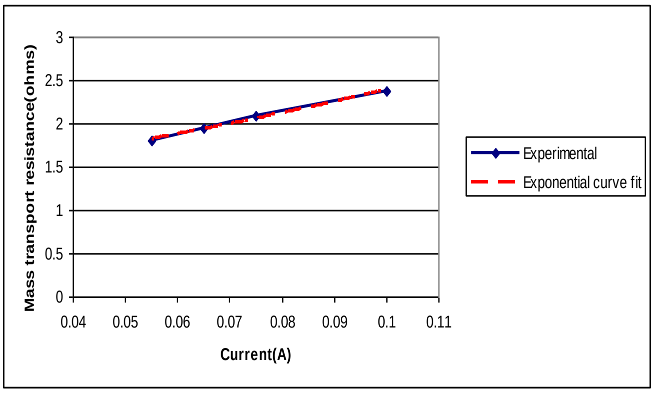

Fig 7: Mass transport losses vs. current for 4M methanol solution

TABLE 3
COEFFICIENTS FOR OHMIC LOSSES

Concentration	Coefficient, R	Constant, C1
0.25M	0.5151	0.3253
0.5M	0.2335	0.3880
1M	0.4883	0.3532
2M	1.2168	0.2235
4M	0.1754	0.3663

TABLE 4
COEFFICIENTS FOR ACTIVATION LOSSES

Concentration	Coefficient, A	Constant, C2
0.25M	-0.0059	0.1714
0.5M	-0.0070	0.1857
1M	-0.0056	0.1841
2M	-0.0036	0.1797
4M	-0.0098	0.1820

TABLE 5
COEFFICIENTS FOR MASS TRANSPORT LOSSES

Concentration	Coefficient-m	Coefficient-n
0.25M	1.2396	6.1474
0.5M	1.3197	4.7104
1M	1.0209	5.4057
2M	0.8283	7.3389
4M	1.3121	5.999

4.1 Polynomial Curve Fitting

Various regression curve fittings can be applied, however for simplicity, the coefficients and constants of Equation 5, 6 and 7 were fitted as a function of concentration using polynomial regression. Second through fourth order polynomial curve fits were tried for minimum error.

4.2 Second Order Polynomial

Figure 8 shows the second order polynomial fit for constant *C1* as a function of concentration. The value of *C1* changes with concentration given by equation 8.

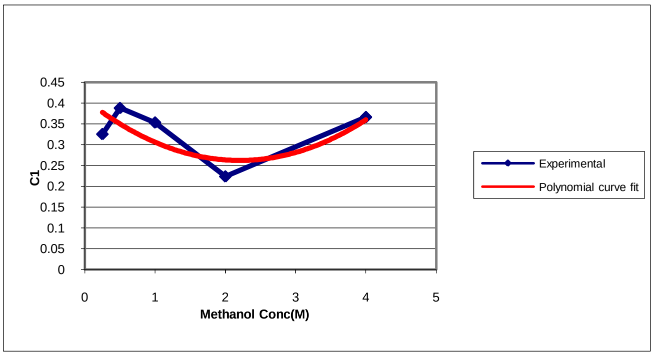

Fig 8: Constant C1 vs. Methanol concentration

$$C1 = 0.0302M^2 - 0.1331M + 0.4088 \qquad (8)$$

Similarly equations for coefficients or constants *R*, *A*, *C2*, *m* and *n* as a function of concentration were derived and are shown in equations 9 through 13

$$R = -0.223M^2 + 0.9393M + 0.0202 \qquad (9)$$

$$A = -0.0011M^2 + 0.0041M - 0.0079 \qquad (10)$$

$$C2 = -0.0026M^2 + 0.0085M + 0.1782 \qquad (11)$$

$$m = 0.1325M^2 - 0.5682M + 1.4602 \qquad (12)$$

$$n = -0.3108M^2 + 1.5651M + 4.8193 \qquad (13)$$

Equations 8 through 13 are substituted in equation 5, 6 and 7 to get the activation, ohmic and mass transport losses as a function of concentration and current which are shown below.

$$\eta_{ohmic} = (-0.223M^2 + 0.939M + 0.0202)*(i) + (0.0302M^2 - 0.1331M + 0.4088) \qquad (14)$$

$$\eta_{activation} = (-0.0011M^2 + 0.0031M - 0.0079)* \ln(i) + (-0.0026M^2 + 0.0085M + 0.1782) \qquad (15)$$

$$\eta_{masstransport} = (0.1325M^2 - 0.5682M + 1.4602)* e^{(-0.3108M^2 + 1.5651M + 4.8193)*(i)} \qquad (16)$$

4.3 Third order Polynomial

Similar to the second order polynomial curve fit, a third order polynomial fit yields the equation for ohmic, activation and mass transport losses shown in equations 17 through 19

$$\eta_{ohmic} = (-0.2475M^3 + 1.2884M^2 - 1.3285M + 0.7135)*(i) + (0.0471M^3 - 0.2575M^2 + 0.2986M + 0.2769) \qquad (17)$$

$$\eta_{activation} = (-0.0008M^3 + 0.0038M^2 - 0.0033M - 0.0056)*\ln(i) + (-0.0009M^3 + 0.0032M^2 - 0.00004M + 0.1809) \qquad (18)$$

$$\eta_{masstransport} = (0.0413M^3 - 0.1196M^2 - 0.1889M + 1.3455) *e^{(-0.774M^3 + 4.416M^2 - 5.5277M + 6.9877)*(i)} \qquad (19)$$

4.4 Fourth order Polynomial

The equations for ohmic, activation and mass transport losses with a fourth order polynomial fit are shown in equation 20 through 22

$$\eta_{ohmic} = (0.2673M^4 - 2.1655M^3 + 5.3862M^2 - 4.2813M + 1.2816)*(i) + (-0.0508M^4 + 0.4118M^3 - 1.0367M^2 + 0.8601M + 0.1688) \qquad (20)$$

$$\eta_{activation} = (0.0015M^4 - 0.0112M^3 + 0.0261M^2 - 0.0194M - 0.0025)*\ln(i) + (0.0045M^4 - 0.0335M^3 + 0.0726M^2 - 0.0501M + 0.1905) \qquad (21)$$

$$\eta_{masstransport} = (-0.2372M^4 + 1.7432M^3 - 3.7557M^2 + 2.4302M + 0.8405) *e^{(1.3016M^4 - 10.113M^3 + 24.369M^2 - 19.905M + 9.7536)*(i)} \qquad (22)$$

4.5 Simulated Results

Figure 9, as a typical case, shows the polarization curve that was generated by using the proposed second, third and fourth order polynomial model with the corresponding experimental data for 2M methanol concentration. It is evident from the graph that the accuracy of the results does not considerably increase with the increase in the order of the polynomial function. A second order polynomial curve fit model yielded a maximum error of 11.4%, a third order polynomial curve fit model yielded a maximum error of 10.73% and a fourth order polynomial curve fit model yielded a maximum error of 11.07%. Considering the complexity of the third and fourth order polynomial model, a second order polynomial curve fit model can be effectively used to predict the performance of the cell.

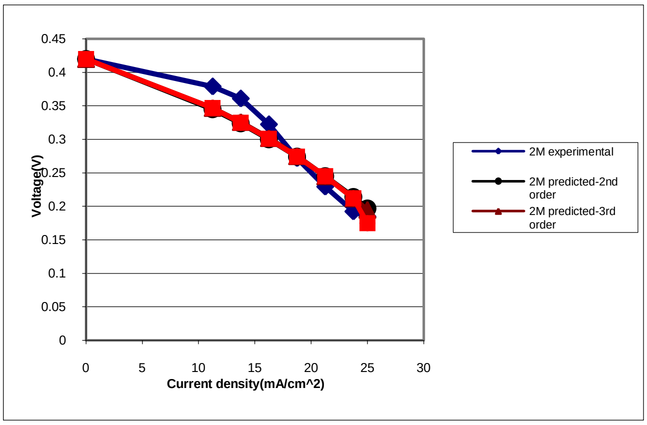

Fig 9: Experimental vs. Predicted polarization curve for 2M methanol solution

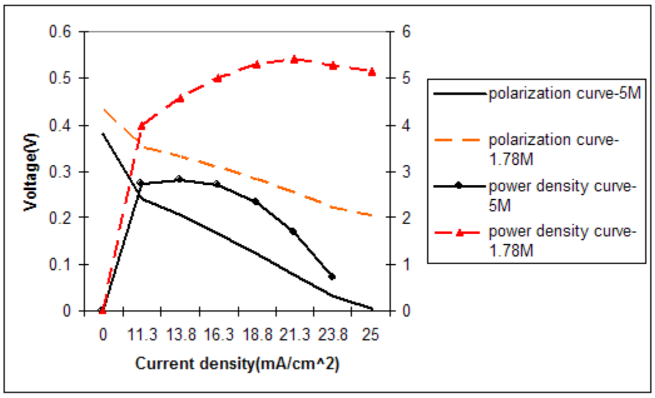

Fig 10: Simulated polarization and power density curve for 5M & 1.78M methanol solution

Once, the trends of variation of the coefficients and constants of Equations 5, 6 and 7 with the methanol concentration change have been established, the described models could be used to predict the performance of the fuel cell at any other operating conditions of interest, substantially reducing the experimental requirement and efforts. As a typical example, Figure 10 shows the polarization curves and power density curves for a 5M & 1.78M methanol solution that was simulated using the second order polynomial fit approach.

5. CONCLUSION

The performance of a direct methanol fuel cell was investigated under varying concentrations of methanol. The improved performance was observed whenever the molar concentrations of methanol in the solutions were closer to the corresponding stoichiometric value. Impedance spectroscopy revealed that the mass transport losses dominate, generally, by a magnitude higher than other losses. A simulation model was developed to predict the performance of the direct methanol fuel cell. The results predicted by the models were then compared to the corresponding experimental data. The average errors between the predicted values and the corresponding experimental data were found to be between 10.73 and 11.4% for the second, third and fourth order polynomial and under the operating conditions employed.

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