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A semi-empirical cell voltage model for the direct methanol fuel cell: the methanol crossover effect

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Abstracts

A new semi-empirical model is established to describe the cell voltage of a direct methanol fuel cell (DMFC) as a function of current density. The model equation is validated experimental data for a small-scale fuel cell over a wide range of a methanol concentration and temperatures. A number of existing models are semi-empirical. They, however, have a serious mathematical defect. When the current density, j, becomes zero, the equation should reduce to the open circuit voltage, E_0. These models, however, do not meet the mathematical boundary condition. The proposed model focuses on very unfavorable conditions for the cell operation, i.e. low methanol solution concentrations and relatively low cell temperatures. A newly developed semi-empirical equation with reasonable boundary conditions, also includes the methanol crossover effect that plays a major role in determining the cell voltage of DMFC.

Keywords: DMFC; Cell voltage; Methanol crossover

1. Introduction

Characterization of the fuel cell (FC) frequently uses large and complex computer models, based on minute details of cell component design (physical dimensions, materials, etc.) along with chemical and physical considerations (transport phenomena, electrochemical kinetics, etc.). The codes, often proprietary, needed in the design and development of fuel cells are cumbersome and time-consuming for use in system analysis models. Simpler approaches are normally used for system studies. Another approach, which is not time and cost efficient, would be to conduct appropriate tests at every condition expected to be analyzed in the system. Alternatively, it is prudent to develop correlations based on the thermodynamic model, which describe cell performance according to operating conditions such as temperature and pressure [1].

In the development of model equations to describe the performance of polymer electrolyte fuel cells, a number of approaches using empirical models have been attempted [2–7]. In many cases a fairly good agreement between the model and experimental data is achieved by adjusting appropriate coefficient/parameters in the model equations. Srinvansan et al. [2] showed that it is possible to use a simple equation to describe the cell voltage vs. current density behavior for PEMFCs. This earliest approach tried to elucidate the behavior of such a complex system, and was solely based on the electro-chemical considerations, which formulated an empirical equation to describe the polarization curve. This empirical equation can replicate the polarization curve reasonably well at low and intermediate current density, but failed at high current density. Kim et al. [3] improved the empirical equation for better replication of the cell performance at high current density. Squadrito et al. [7] reformed the Kim's equation with addition of two extra terms to improve the prediction of the mass transfer related resistance. Argyropoulos et al. [8] corrected the equation that coefficients follow specific trends with fuel cell operating variables and allow any physically real interpretation of the model.

Methanol is an attractive fuel because its energy density is much higher than that of hydrogen, and it is an inexpensive liquid and easy to handle, store and transport. However, in practice, DMFC has a much lower open circuit voltage (OCV). One of the major reasons is that methanol

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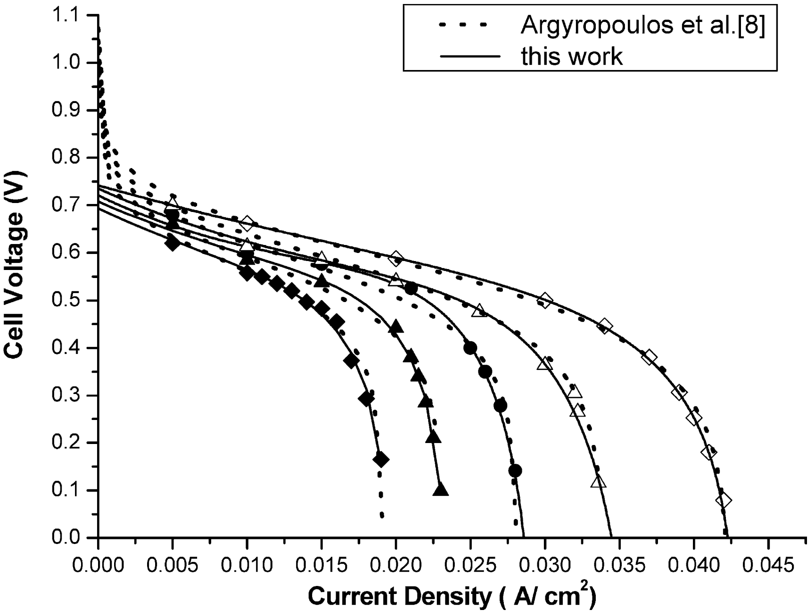

Fig. 1. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.125 M methanol solution. (Cell temperatures (◆) 343.15 K; (▲) 348.15 K; (○) 353.15 K; (△) 358.15 K; (◇) 363.15 K).

can cross through the proton exchange membrane (PEM), such as Nafion®, to reach the cathode side via physical diffusion and electro-osmotic drag (by protons). Such crossover not only results in a waste of fuel, but also lowers the cell performance. The effect of methanol crossover in the DMFC has attracted attention worldwide and its impact on cathode operation and system efficiency.

In this study, we develop a new semi-empirical model for the cell voltage as a function of current density response of the DMFC, which is based on Tafel type kinetics for methanol oxidation, oxygen reduction and methanol crossover contribution which affects significantly the performance of DMFC at high current density region.

2. Model development

Srinivansan et al. [1] showed that it is possible to use a simple model equation to describe the cell voltage (E) vs. current density (j) behavior for PEMFCs in the activation and ohmic controlled current density region:

$$E = E_0 - b\log j - R_e j \tag{1}$$

with

$$E_0 = E_r + b\log j_0 \tag{2}$$

where E_r is the reversible cell potential, b is the Tafel slope for oxygen reduction and R is the ohmic resistance of the cell.

Using Eq. (1), with the appropriate coefficients, it was shown that as current density increased the predicted cell potential decreased much less rapidly than observed [2]. To increase the reliability of the aforementioned equation, Kim et al. [2] suggested

$$E = E_0 - b\log j - R_e j - m e^{nj} \tag{3}$$

where m and n are parameters that account for the ‘mass transport overpotential’ as a function of current density.

Squadrito [7] used Eq. (3) as a starting point to analyse the different contributions to the mass transport limitation and produced an equation in the form:

$$E = E_0 - b\log j - R_e j + a j^k \ln(1 - \beta j) \tag{4}$$

where a, k and β are parameters.

The term $\ln(1-\beta j)$ introduces a limit to the available current density. For $k=1$, a has the same dimension as R_e and can be interpreted as an additional resistance term due to the overall mass transport limitation.

Argyropoulos et al. [8] showed the applicability of Kim's and Squadrito's equation for predicting voltage response of the DMFC. This equation focuses on very unfavorable conditions for cell operation, i.e. low methanol solution concentrations and relatively low cell temperatures.

$$E_{\text{cell}} = E_0 - b\log j - R_e j + C_1 \ln(1 - C_2 j) \tag{5}$$

i.e. in the Squadrito equation $k=0$.

Number of models introduced here are semi-empirical. All models are based on Srinivansan et al.'s model, Eq. (1). It, however, has a serious mathematical defect. When the current density, j, becomes zero, the equation should reduce to the open circuit voltage, E_0. These models, however, do not meet the mathematical boundary condition. We propose a new semi-empirical cell voltage model based on Argyropoulos et al.'s model, Eq. (5) with the addition of one extra term to take into of the methanol crossover effect

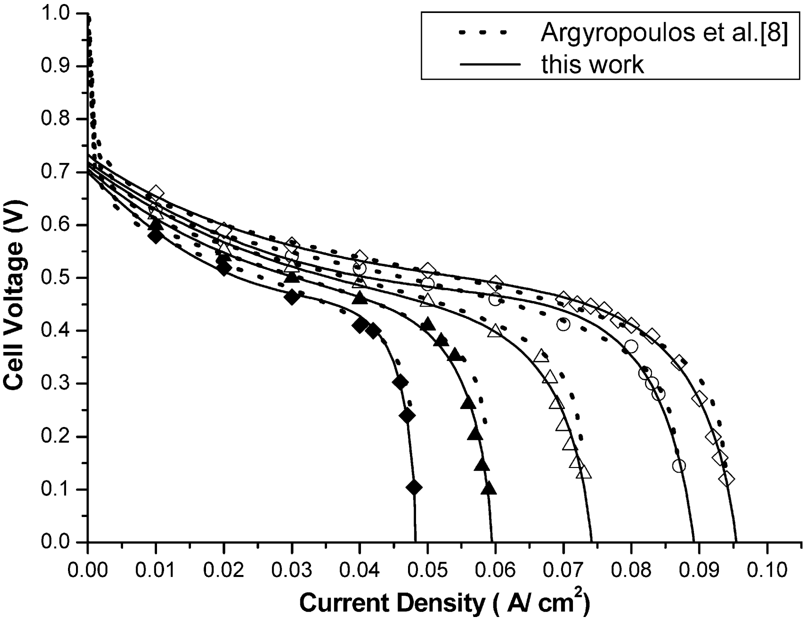

Fig. 2. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.25 M methanol solution. (Cell temperatures (♦) 343.15 K; (▲) 348.15 K; (○) 353.15 K; (△) 358.15 K; (◇) 363.15 K).

account. The first term of Eq. (6), E_0 has the same meaning as mentioned above. In this study, we therefore replace the second term of Eq. (6), $b \log j$, by $b \log(1-\kappa_b j)$. When the current density becomes zero, all terms should be zero except E_0 term. The term, $\log j$, however, goes to infinity. It is not possible to have infinity at $j=0$. The third term, $R_e j$ presents the ohmic resistance of the cell. To take into the methanol crossover contribution account, we employ Arrenius type of equation, the last term in the above Eq.

$$E_{\mathrm{cell}} = E_0 - b \log(1-\kappa_b j) - R_e j - E^0_{\mathrm{MC}}\left(1 - \mathrm{e}^{-\alpha j/T}\right) \tag{6}$$

It term describes the methanol cross over contribution and mass transfer limitation region. In general, the methanol crossover effect plays a major role in determining the cell voltage of DMFC. E^0_{MC} and α represent the methanol crossover effect and mass transport overpotential, respectively. E^0_{MC} affects both the slope of the linear region of the E

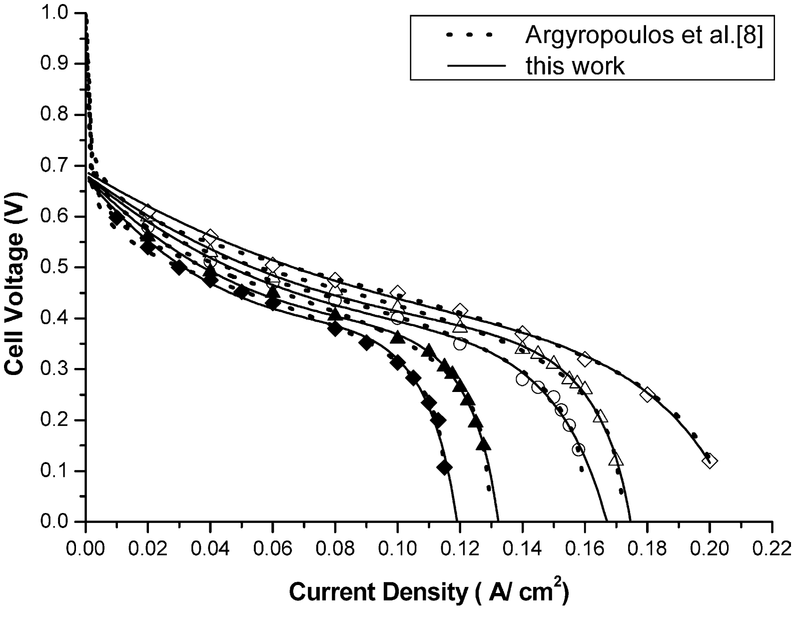

Fig. 3. Comparison between experimental data [8] and empirical equation based prediction for a cell operated with 0.5 M methanol solution. (Cell temperatures (♦) 303.15 K; (▲) 318.15 K; (○) 323.15 K; (△) 338.15 K; (◇) 343.15 K).

Table 1
Calculated values for this empirical equation coefficients for DMFCs operated with methanol solution

Cell temperature (K)	MeOH solution concentration (M)	Calculated values					
		E_0 (V)	R_e (Ω/cm^2)	B (V)	κ_b (j/cm2)-1	E^0_{MC} (V)	$\alpha \times 10^3$ (K cm^2/j)
363.15	0.125	0.7419	3.3587	0.2390	22.9693	26.4902	−2.1155
358.15	0.125	0.7352	0.6013	0.5045	27.0293	10.7593	−17.7265
353.15	0.125	0.7210	0.4402	0.4473	33.1061	15.3641	−17.4602
348.15	0.125	0.7081	5.1479	0.2058	42.5061	7.7599	−23.6987
343.15	0.125	0.6936	4.7548	0.1972	50.7664	52.0001	−3.8307
363.15	0.25	0.7334	4.0383	0.3830	10.0522	16.7081	−2.0918
358.15	0.25	0.7189	4.3825	0.3693	10.8035	14.3243	−2.7831
353.15	0.25	0.7133	2.9661	0.6235	12.5491	23.4663	−2.9815
348.15	0.25	0.7055	4.1504	0.5626	15.6690	28.4851	−3.7203
343.15	0.25	0.6998	2.5476	0.7973	18.5831	24.8149	−7.8302
343.15	0.5	0.6887	0.8810	0.6696	4.1893	16.4817	−0.4176
333.15	0.5	0.6821	2.8169	0.2872	5.5202	9.8046	−0.8185
323.15	0.5	0.6809	1.7434	0.6169	5.4013	15.9043	−0.7369
313.15	0.5	0.6798	3.6108	0.3621	7.2109	12.4608	−4.0232
303.15	0.5	0.6771	3.5390	0.4854	7.8440	16.0587	−4.4514

vs. j plot and the current density at which there is a departure from the linearity. The value of α has a major effect in the mass transport limitation region.

Confirmed in Eq. (6), as the value of the current density approaches zero, the cell voltage becomes the open circuit voltage (OCV), E_0.

3. Result and discussion

In Figs. 1–3, calculated cell voltages are presented for three different aqueous methanol solution concentrations (0.125, 0.25 and 0.5 M) and for a range of cell operating temperatures. Solid lines are calculated from this work (Eq. (6)). Dotted lines are from Eq. (5) [8]. Our results show that both models fit fairly well to experimental data. The proposed model, however, gives slightly better results compared to the other model in the low current density region. Model parameters are listed in Table 1.

The advantage of the model equation proposed in this study is the ability to follow the voltage profile in the limiting current density region. The existing models do not satisfy the boundary condition. As the current density goes to zero, their open circuit voltages (OCV) diverse to the infinity. Our calculated E_0 values, however, are reasonable and increase with temperature as shown in Table 1.

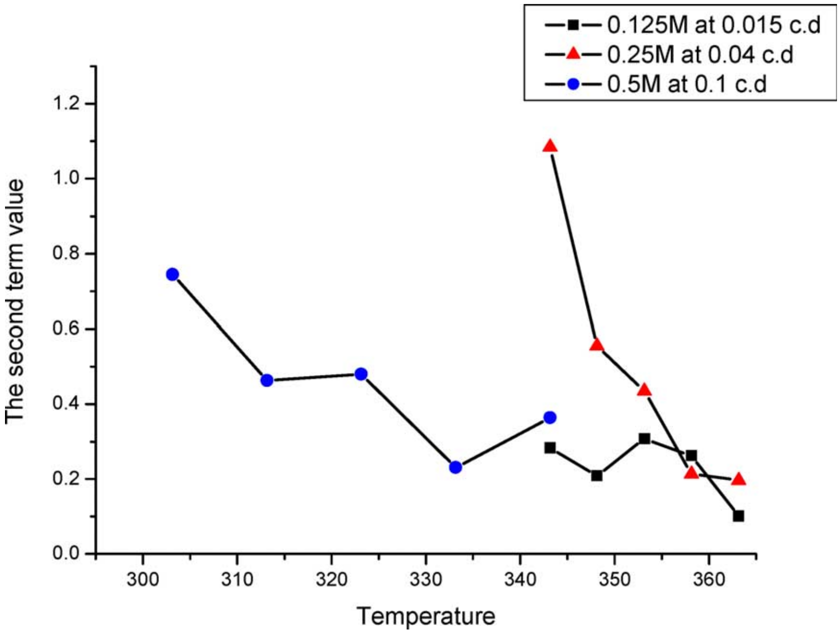

Fig. 4. The calculated voltage value of the second term of Eq. (6) at various temperatures. (Methanol concentration (■) 0.125 M; (▲) 0.25 M; (●) 0.5 M).

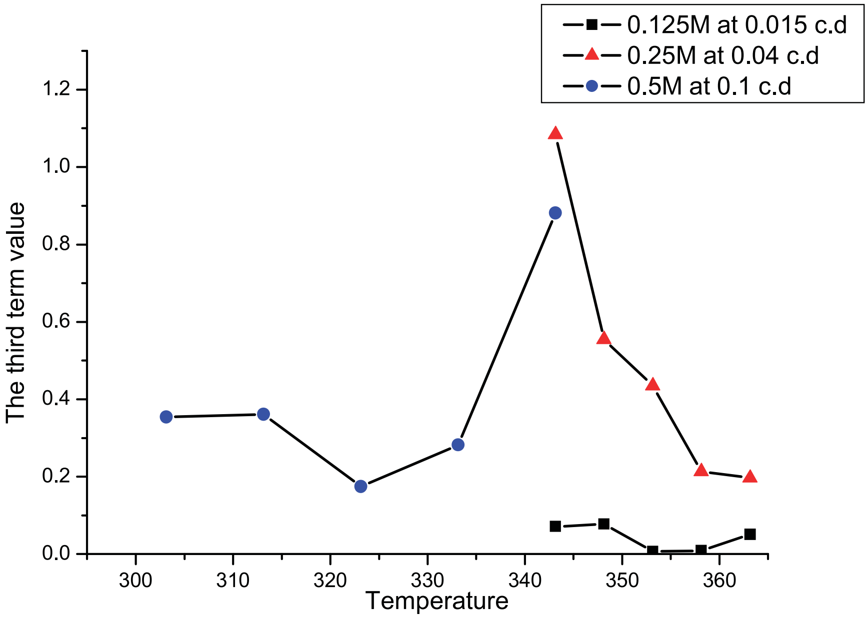

Fig. 5. The calculated voltage value of the third term of Eq. (6) at various temperatures. (Methanol concentration (■) 0.125 M; (▲) 0.25 M; (●) 0.5 M).

Figs. 4–6 show calculated values of each term in the proposed model (Eq. (6)) at the fixed current density. These curves are calculated with each of characteristic parameters. Fig. 4 represents calculated values of $b\ \log(1-\kappa_b j)$ at the given current density, the second term of Eq. (6). Results show that this term decreases with increasing temperature. Fig. 5 shows calculated values of the third term, $R_e j$ of Eq. (6). Fig. 6 gives the calculated values of $E^0_{\mathrm{MC}}\left(1-\mathrm{e}^{-\alpha j/T}\right)$ term. This last term of Eq. (6) takes into account the methanol crossover effect and mass transport overpotential as a function of current density. It also decreases with increasing temperature.

Undoubtedly, the methanol crossover is not the only issue in DMFC. One must also consider aspects such as the pressure effect and fuel flow rate. In fuel cells, membranes operate under the significant mechanical pressure that acts in opposition to the osmotic pressure and fuel flow rate is also involved in a methanol crossover.

4. Conclusion

We propose the new semi-empirical model to predict the cell voltage response of a small-scale single DMFC cell. The advantage of this model follows from its simplicity and accuracy. The ultimate goal of the semi-empirical model

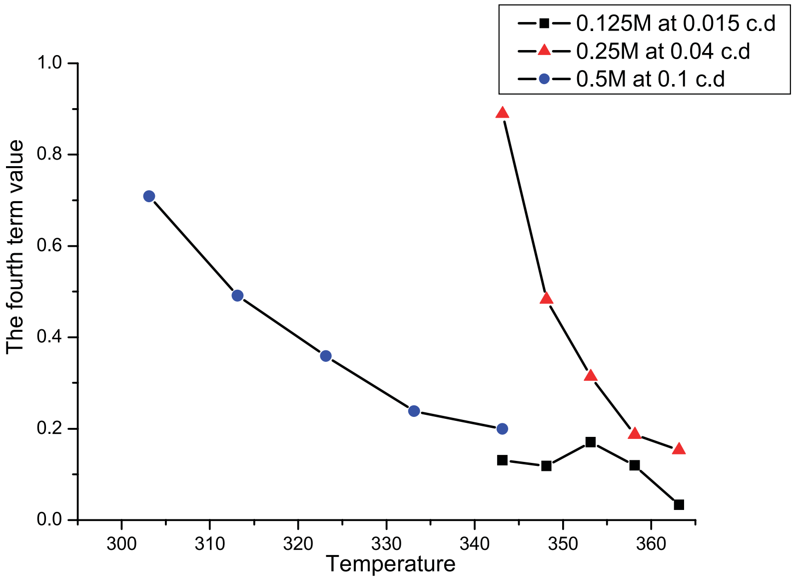

Fig. 6. The calculated voltage value of the fourth term of Eq. (6) at various temperatures. (Methanol concentration (■) 0.125 M; (▲) 0.25 M; (●) 0.5 M).

lies in its ability to predict the cell voltage response for fuel cell systems which are not included in the experimental data, that is the set of data uses to determine the parameters.

In general the present investigation has showed the applicability of Argyropoulos' equation, originally derived to model the voltage vs. current density behavior of DMFC operated under diverse operating conditions. We modified Argyropoulos's model to correct mathematical defect at the current density $=0$ and also considered the methanol crossover effect. A new empirical equation has also been used to predict the voltage response of liquid feed DMFCs over a wide range of operating conditions. Further work will follow to explain the physicochemical significance of the equation and the influence of solid polymer electrolyte in order to obtain a more general and accurate empirical model.

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