ORIGINAL RESEARCH PAPER

Empirical Model Equations for the Direct Methanol Fuel Cell

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Abstract

Empirical model equations, proposed for polymer electrolyte fuel cells, are used to predict the cell voltage vs. current density response of a liquid feed direct methanol fuel cell. The model equations are validated against experimental data for a small-scale fuel cell over a wide range of methanol concentration and temperatures. A new empirical equation is presented which is able to predict the voltage response of liquid feed direct methanol fuel cells over a wide range of operating conditions and even in the case of very low current densities caused by, for example, the use of dilute methanol solutions or low cell temperatures.

Keywords: Direct Methanol Fuel Cell, Model, Performance, Empirical Equation

1 Introduction

In the development of model equations to predict the performance of polymer electrolyte fuel cells a number of approaches using empirical models have been attempted [1-6]. In many cases excellent agreement between the model and experimental data is achieved by adjusting appropriate coefficients/parameters in the model equations.

In this paper we examine the applicability of two widely accepted empirical equations for predicting voltage current density response of the DMFC. In addition a modification of one empirical model for the cell voltage, current density response is introduced, which is based on Tafel type kinetics for methanol oxidation and oxygen reduction and an effective mass transport term.

2 Empirical Equations For Modelling PEMFC Behaviour

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

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

with

$$E_o = E_r + b\log j_o \tag{2}$$

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] introduced a more complex equation:

$$E = E_o - b\log j - R_e j - me^{nj} \tag{3}$$

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

Parameter m affects both the slope of the linear region of the E *vs.* j plot and the current density at which there is a departure from the linearity. The value of n has a major effect in the mass transport limitation region. Kim et al reported that despite the excellent fit when applying Eq. (3) to experimental data they weren't able to find a theoretical explanation for the last term of Eq. (3) [2]. Lee proposed [3] a modified form of Kim's equation by adding the ratio of oxygen partial pressure to total pressure.

Squadrito [6] used Eq. (3) as a starting point to analyse the different contributions to the mass transport limitation and produced an equation in the form:

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

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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 dimensions as R_e and can be interpreted as an additional resistance term due to the overall mass transport limitation. The parameter k mainly influences the point at which there is a departure from linearity and a determines the shape of the curve at high current densities.

In this paper we investigate the applicability of Kim's and Squadrito's empirical equations for predicting voltage response of the DMFC. We focus on very unfavourable conditions for cell operation, i.e. low methanol solution concentrations and relatively low cell temperatures.

3 Experimental Equipment

Tests on the DMFC were performed with a cell with a cross-sectional area of 9 cm^2. The cell consisted of two non-porous graphite blocks with a series of parallel channels machined into the block for the flow of methanol and oxygen/air.

The cell was fitted with a membrane electrode assembly (MEA) sandwiched between the two graphite blocks. The cell was held together between two plastic insulation sheets and two stainless steel 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 to heat the cell to the desired operating temperature. The fuel cell was used in a simple flow rig, which consisted of a Watson Marlow peristaltic pump to supply aqueous methanol solution, from a reservoir, to a Eurotherm temperature controller to maintain the cell at a constant temperature. Air was supplied from cylinders, at ambient temperature, and the pressure regulated by needle valves.

The MEA studied in this work was made in the following manner: the anode consisted of a Teflonised (20%) carbon cloth support (E-Tek, type 'A'), of 0.3 mm thickness, upon which was spread a thin layer of uncatalysed (Ketjenblack 600) 10 wt.% Teflonised carbon (diffusion layer). The catalysed layer, unless otherwise specified consisted of 35 wt.% Pt-15 wt.%Ru (2 mg/cm^2 metal loading) dispersed on carbon (Ketjenblack) and bound with 10 wt.% Nafion® from a solution of 5 wt.% Nafion® dissolved in a mixture of water and lower aliphatic alcohol's (Aldrich), was spread on this diffusion backing layer. A thin layer of Nafion® solution was spread onto the surface of each electrode. The cathode was constructed using a similar method as for the anode, using a thin diffusion layer bound with 10 wt.% PTFE, and 1 mg/cm^2 Pt black with 10 wt.% Nafion® in the catalyst layer. The electrodes were placed on opposite side of a pre-treated Nafion® 117 membrane and hot pressed. Electrode preparation are described in detail elsewhere [7, 8].

Cell voltage vs. current density response was measured galvanostatically, by incrementally increasing the current from open circuit and measuring the cell potential and then reducing the current incrementally again measuring the cell voltage. The data reported were obtained with one MEA, which exhibited stable performance under continuous operation.

4 Empirical Model Evaluation

4.1 Kim's empirical equation

Figures 1 and 2 show the current voltage curves for the DMFC as predicted by Kim's originated equation at two methanol solution concentration and cell temperatures of 30 – 90 °C. In the case when a 0.75 M methanol solution was used lower cell temperatures were used (30 – 60 °C). The values of the various parameters that give the best (statistical) fit to the experimental data (Figures 1 and 2) are shown in Table 1.

In general the empirical equation gives unsatisfactory predictions for the lower methanol solution concentration and is better in the case of the more concentrated solution. The equation gives good predictions only for cases where the transition to the limiting current region is smooth and the cell

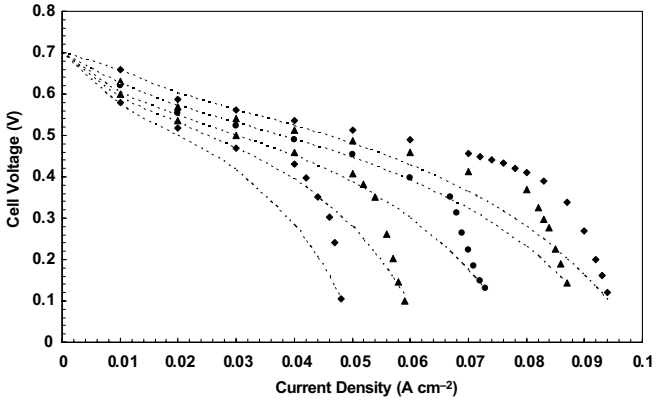

Fig. 1 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.25M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 343.15 ▲:348.15 K □: 353.15 K △:358.15 K ◇: 363.15 K).

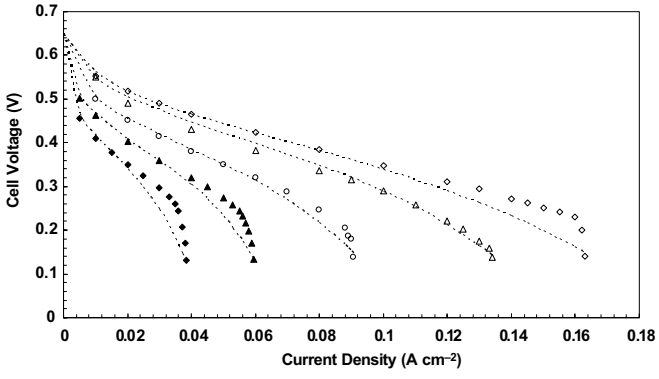

Fig. 2 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.75M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 303.15 ▲:313.151 K □: 323.15 K △: 333.15 K ◇: 343.15 K) .

Table 1 Calculated values for the Kim empirical equation coefficients for DMFCs operated with methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar.

MeOH solution concentration [M]	Cell temperature [K]	Calculated values for the Kim empirical equation coefficients				
		E_o [V]	B [V]	R [Ω cm^2]	m [V]	n
0.25	363.15	0.42	0.13	0.65	0.012	37
0.25	358.15	0.39	0.13	0.65	0.012	38
0.25	353.15	0.37	0.13	0.65	0.012	46
0.25	348.15	0.36	0.13	0.65	0.012	58
0.25	343.15	0.35	0.13	0.65	0.015	67.5
0.75	343.15	0.345	0.12	0.5	0.015	16.2
0.75	333.15	0.33	0.12	0.6	0.012	21.5
0.75	323.15	0.27	0.13	0.65	0.012	31
0.75	313.15	0.23	0.131	0.7	0.011	50
0.75	303.15	0.18	0.132	0.8	0.01	80

voltage falls in a similar way to that generally observed for hydrogen fuel cells [1].

In general with the use of Kim's empirical equations there is not a single optimum solution; different combinations of equation parameters can describe the experimental data with reasonable accuracy. Hence the predictions presented here are those that give fits with values of the parameters that are not changed radically form one condition to the other. For example, the term b, which represents the Tafel slopes, remains almost constant and the resistance term R increases with a decrease in temperature. The parameter n, increases with a decrease in temperature, as the influence of the mass transport limitation becomes more significant at lower temperature.

4.2 Squadrito equation

The Squadrito equation [6] was essentially developed from Kim's equation with the addition of two extra terms to improve prediction of the mass transfer related resistance. As expected the equation provides an improved fit of the experimental data under the operating conditions of the DMFC cell investigated, as can be seen in Figures 3 to 5. Good agreement is achieved even at a low concentration of (0.125 M) methanol (Figure 3)

In general the Squadrito equation shows mathematical stability, i.e. it normally converges and produces meaningful solutions with commercial curve fitting software programs (e.g. DataFit, Curve Expert etc.) A major drawback is the number of fitting coefficients required (6 in total); that poses computational burden in order to achieve optimal fit of data. The coefficients obtained for the three sets of data are shown in Table 2. Trends in the coefficient of the model equation are apparent. The coefficients 'a' and β, increase with a decrease in temperature, which reflect poorer mass transport conditions at lower temperatures. Overall the equation is attractive for representing the DMFC operation over a wide range of operating conditions.

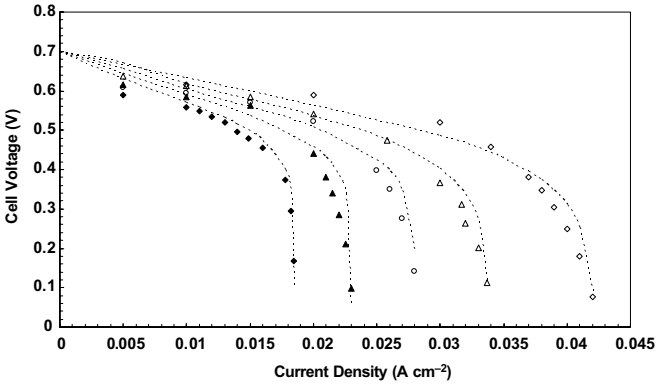

Fig. 3 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.125M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 343.15 ▲:348.15 K ●: 353.15 K △:358.15 K ◇: 363.15 K).

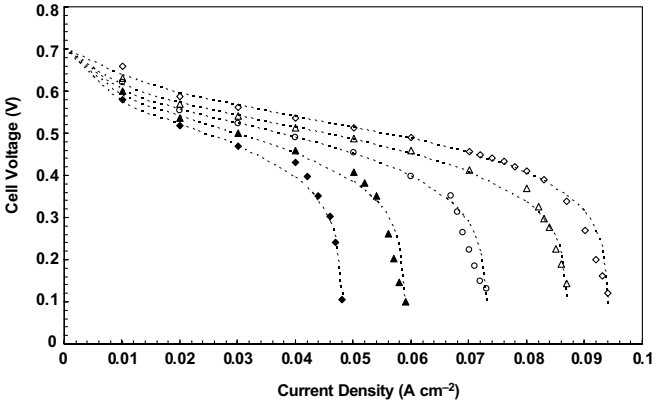

Fig. 4 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.25M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 343.15 ▲:348.15 K ○: 353.15 K △:358.15 K ◇: 363.15 K).

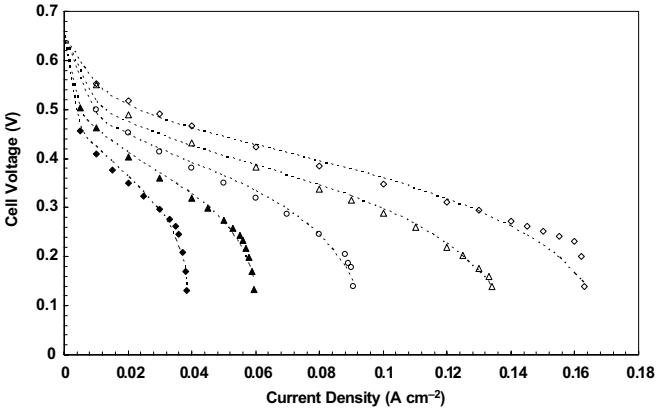

Fig. 5 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.75M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 303.15 ▲:313.151 K ○: 323.15 K △:343.15 K ◇: 353.15 K).

Table 2 Calculated values for the Squadrito empirical equation coefficients for DMFCs operated with methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar.

MeOH solution concentration [M]	Cell temperature [K]	Calculated values for the Squadrito empirical equation coefficients					
		Eo [V]	*b* [V]	*R* [Ω cm^2]	*a* [V] $(cm^{-2}A^{-1})^k$	*k*	*β*
0.125	363.15	0.38	0.134	.05	0.274	0.36	23.7
0.125	358.15	0.37	0.133	.05	0.28	0.37	29.6
0.125	353.15	0.36	0.132	.04	0.29	0.4	35.54
0.125	348.15	0.35	0.131	.03	0.3	0.43	43.47
0.125	343.15	0.34	0.13	.02	0.3	0.440	54.16
0.25	363.15	0.39	0.126	.12	0.27	0.6	10.62
0.25	358.15	0.37	0.125	.13	0.28	0.58	11.45
0.25	353.15	0.36	0.124	.14	0.29	0.55	13.65
0.25	348.15	0.35	0.123	.15	0.3	0.52	16.9
0.25	343.15	0.34	0.122	.16	0.31	0.5	20.75
0.75	343.15	0.29	0.129	0.1	0.27	0.62	5.73
0.75	333.15	0.27	0.125	0.2	0.28	0.58	6.9
0.75	323.15	0.25	0.124	0.4	0.29	0.55	10.4
0.75	313.15	0.22	0.123	.15	0.3	0.52	16
0.75	303.15	0.19	0.122	.16	0.31	0.5	25.3

4.3 An alternative empirical equation

The Squadrito equation contains 3 parameters that are used primarily to predict the behaviour of the fuel cell voltage response when mass transport limitations arise. We propose that a simpler equation may be more suitable that involves only two parameters to represent the mass transport limitation and which only has one function of current density. The equation is of the form

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

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

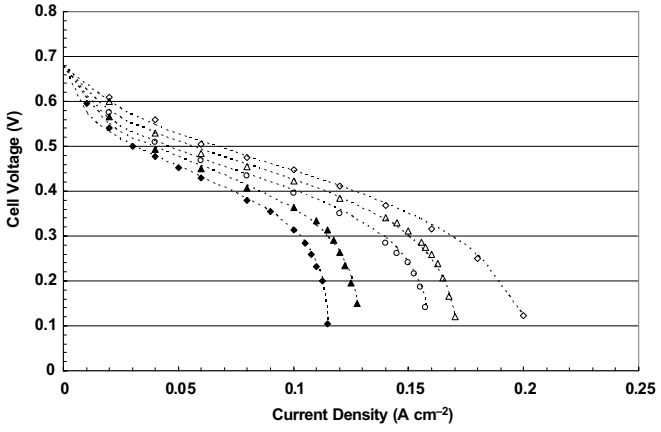

Fig. 6 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.5 M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 343.15 ▲:348.15 K ○: 353.15 K △:358.15 K ◇: 363.15 K).

The equation above was used to model the cell voltage response of a small-scale single DMFC cell. Model predictions are presented, for four different aqueous methanol solution concentrations (0.125, 0.25, 0.5 and 0.75 M) and for a range of cell operating temperatures, in Figures 6 – 9. It can be seen that the predictions are in good agreement with experimental data, over the wide range of experimental conditions. The advantage of the model equation is the ability to follow the voltage profile in the limiting current region. This behaviour would make the use of the more complex Squadrito equation redundant. The parameter values used to obtain the model predictions are given in Table 3. The values of the resistance term R decrease with an increase in temperature. The values of the terms C_1 and C_2 increase and decrease with an increase in temperature respectively which is generally consistent with the expected effect of temperature on the cell polarisation behaviour around the limiting current region.

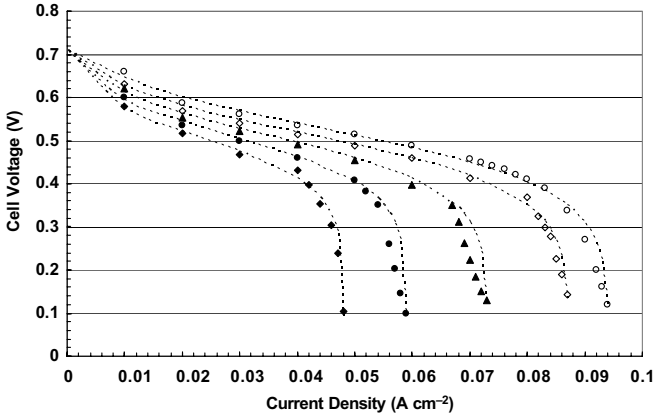

Fig. 7 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.25 M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 343.15 ●:348.15 K ▲: 353.15 K ◇: 358.15 K ○: 363.15 K).

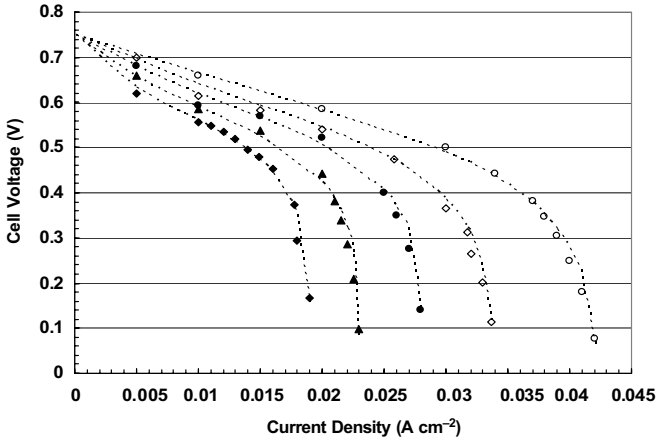

Fig. 8 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.125 M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures◆: 343.15 ▲:348.15 K ●: 353.15 K ◇: 358.15 K ○: 363.15 K)

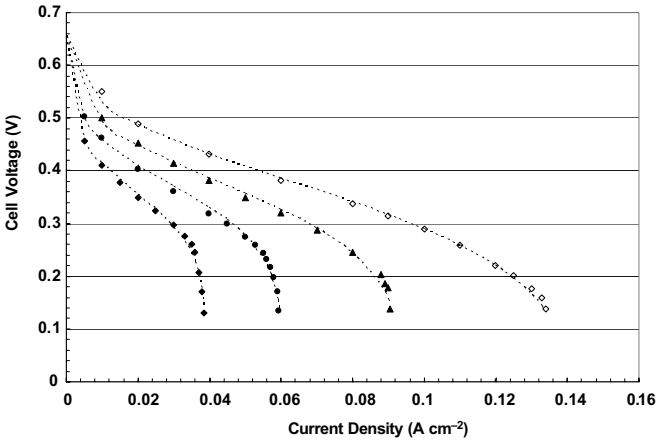

Fig. 9 Comparison between experimental data and empirical equation based prediction for a cell operated with 0.75 M methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar. (Cell temperatures ◆: 303.15 ●:313.151 K ▲: 323.15 K ◇: 343.15 K)

Table 3 Calculated values of coefficients for the Argyropoulos, et al. empirical equation for DMFCs operated with methanol solution supplied at a rate of 1.12 cm^3/min with air fed cathodes pressurised at 2 bar.

Cell temperature [K]	MeOH solution concentration [M]	Calculated values for the Argyropoulos, Scott et al. empirical equation coefficients				
		Eo [V]	*B* [V]	*R* [Ω cm^2]	C_1 [V]	C_2 [cm^{-2}A^{-1}]
343.15	0.125	0.39	0.1176	0.126645	0.085	52.3
348.15	0.125	0.4043	0.119	0.094513	0.09	43.34
353.15	0.125	0.42	0.121	0.0649	0.095	35.45
358.15	0.125	0.432	0.123	0.041364	0.108	29.4
363.15	0.125	0.448	0.125	0.0225	0.12	23.57
343.15	0.25	0.36	0.11766	0.126645	0.057	20.82
348.15	0.25	0.37	0.119	0.094513	0.061	16.93
353.15	0.25	0.38	0.121	0.0649	0.065	13.665
358.15	0.25	0.3912	0.12297	0.041364	0.069	11.45
363.15	0.25	0.4058	0.125	0.0225	0.073	10.6
343.15	0.5	0.347	0.11766	0.126645	0.07	8.62
348.15	0.5	0.3636	0.119	0.094513	0.077	7.69
353.15	0.5	0.368	0.121	0.0649	0.082	6.2
358.15	0.5	0.382	0.123	0.04136	0.088	5.77
363.15	0.5	0.4	0.125	0.0225	0.12	4.75
303.15	0.75	0.215	0.109	0.346	0.053	25.5
313.15	0.75	0.25	0.111	0.29451	0.059	16.5
323.15	0.75	0.28	0.113	0.248	0.078	10.43
333.15	0.75	0.32	0.115	0.192	0.102	6.6

5 Conclusions

The main drawback in the use of empirical equations to predict cell voltage, current density behaviour is the inability to establish specific trends that can be explained on a theoretical basis. In addition the equation are typically solved with non-linear regression algorithms which use least square methods. Unfortunately these equations have rarely a unique solution and instead have a number of potential solutions with large variations in the fitted coefficients. Also the convergence of the empirical equations is sensitive to the selection of initial values, with some requiring prior knowledge of the potential results in order to remain numerically stable.

In general the present investigation has showed the applicability of Squadrito's equation, originally derived to model the voltage, current density behaviour of hydrogen PEMFC, for the case of the DMFC operated under diverse operating conditions. A new simpler empirical equation has also been used which is able to predict the voltage response of liquid feed direct methanol fuel cells over a wide range of operating conditions. The proposed equation is valid even in the case of very low current densities caused by, for example, the use of dilute methanol solutions or low cell temperatures. Further work will follow to explain the physicochemical significance of the equation and the influence of parameters to try to obtain a more general and accurate empirical model.

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