

# A Semi-Empirical Cell Voltage Model for Polymer Electrolyte/Methanol Systems: Applicability of the Group Contribution Method

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**ABSTRACT:** A new group contribution model is established to describe the cell voltage of a direct methanol fuel cell as a function of the current density. The model equation is validated with experimental data over a wide range of methanol concentrations and temperatures. The proposed model focuses on very unfavorable conditions for cell operation, that is, low methanol solution concentrations and relatively low cell temperatures. The proposed

group contribution method includes a methanol crossover effect that plays a major role in determining the cell voltage of a direct methanol fuel cell. © 2008 Wiley Periodicals, Inc. *J Appl Polym Sci* 110: 3186–3194, 2008

**Key words:** electrochemistry; lattice models; membranes; modeling; statistical thermodynamics

## INTRODUCTION

The characterization of a fuel cell 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 such as transport phenomena, electrochemical kinetics, and electrode kinetics. 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 would not be 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 describes cell performance according to operating conditions such as temperature and pressure.<sup>1</sup>

One important factor that can affect the performance of a fuel cell is the hydration of solid polymer electrolyte (SPEs).<sup>2,3</sup> Membranes can be neither too dry, in which case the proton conductivity decreases, nor too wet, in which case electrode flooding may

result. To solve the aforementioned problem of SPEs for fuel-cell applications, a general thermodynamic model able to reliably predict phase equilibria for these systems is required.

The most widely used and best known of the excess Gibbs energy group contribution models is the universal quasi-chemical activity coefficient functional group activity coefficient (UNIFAC).<sup>4</sup> It combines the concept of functional groups with analytical results of the universal quasi-chemical activity coefficient (UNIQUAC),<sup>5</sup> which is based on Guggenheim's quasi-chemical theory and contains a combinatorial part, which is due to differences in the sizes and shapes of the molecules in the mixture, and a residual part, which is due to energy interactions. It is accurate for semiquantitative predictions of vapor liquid equilibrium (VLE) for ordinary liquid mixtures and activity coefficients at infinite dilution.

Oishi and Prausnitz<sup>6</sup> modified the UNIFAC model by providing a free volume contribution suggested by the Prigogine–Flory–Patterson theory for polymer solutions to consider the compressibility and change in density upon isothermal mixing. Later, several variations of the UNIFAC model were reported by Voutsas and Tassios,<sup>7</sup> Mollmann and Gmengling,<sup>8</sup> Zhang et al.,<sup>9</sup> Magnussen et al.,<sup>10</sup> Gupta and Danner,<sup>11</sup> and Hooper et al.<sup>12</sup>

In the last few decades, numerous authors have discussed group contribution equation-of-state (EOS) models. Illustrative of their work is the work of Gmehling and coworkers.<sup>13–16</sup> These authors developed a group contribution EOS model based on the Soave–Redlich–Kwong equation for the prediction of

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gas solubilities and VLE at both low and high pressures. Another extension of UNIFAC to polymer solutions was given by Holten-Andersen et al.,<sup>17</sup> who obtained the free volume contribution from an EOS similar to that based on perturbed-hard-chain theory. In a similar investigation, High and Danner<sup>34</sup> also found that both models predict solvent activities reasonably well.

Li et al.<sup>16</sup> presented the LIQUAC model for the excess Gibbs energy to describe the influence of the electrolytes (salting-in or salting-out effects) on the VLE. The LIQUAC model consists of a Debye-Hückel term, the UNIQUAC term, and the osmotic virial equation for the middle range contribution to describe the phase behavior for both single- and mixed-solvent electrolyte systems.

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.<sup>18–26</sup> In many cases, a fairly good agreement between the model and experimental data has been achieved by the adjustment of appropriate coefficients/parameters in the model equations. Srinivasan et al.<sup>18</sup> showed that it is possible to use a simple equation to describe the cell voltage for proton-exchange membrane fuel cells. This earliest approach tried to elucidate the behavior of such a complex system and was based solely on electrochemical considerations, which led to an empirical equation describing the polarization curve. This empirical equation can replicate the polarization curve reasonably well at low and intermediate current densities but fails at a high current density. Kim et al.<sup>19</sup> improved the empirical equation for better replication of the cell performance at a high current density. Squadrito et al.<sup>23</sup> reformed Kim et al.'s equation with the addition of two extra terms to improve the prediction of the mass-transfer-related resistance. Argyropoulos et al.<sup>30</sup> corrected the equation so that the 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 that is easy to handle, store, and transport. However, in practice, a direct methanol fuel cell (DMFC) has a much lower open circuit voltage (OCV). One of the major reasons is that methanol can cross through a proton-exchange membrane, 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 a DMFC and its impact on cathode operation and system efficiency have attracted research attention worldwide.

In this study, we have developed a new semi-empirical model to describe cell voltage as a function of the current density for a DMFC. The proposed model takes into account methanol activity with a group contribution method, diffusion overpotential to represent the methanol crossover contribution, and the mass-transport limitation, which significantly affects the performance of DMFC.

## MODEL DEVELOPMENT

### Modified double-lattice model

The framework of the lattice model starts with a simple cubic lattice (coordination number  $z = 6$ ) containing  $N_r$  sites. For the systems (two different polymer chains, polymer/solvent systems, etc.) that interact strongly, they must be in the correct orientation to each other (i.e., a specific interaction). Ordinary polymer solutions are described by the primary lattice, whereas a secondary lattice is introduced as a perturbation to account for oriented interactions.

#### Primary lattice

Oh and Bae<sup>28</sup> defined a new Helmholtz energy of mixing as a form of the Flory-Huggins theory. The expression is given by

$$\frac{\Delta A}{N_r k T} = \left(\frac{\phi_1}{r_1}\right) \ln \phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln \phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (1)$$

where  $\Delta A$  is Helmholtz energy of mixing,  $N_r$  is the total number of lattice sites (coordination number  $z = 6$ ),  $k$  is the Boltzmann constant,  $r_i$  is the chain length,  $\phi_i$  is the volume fraction of component  $i$ , and  $\chi_{OB}$  is a new interaction parameter defined later in eq. (3). The subscripts 1 and 2 refer to the solvent and polymer, respectively:

$$r_i = \frac{V_{mi}(\text{vdw})}{15.17 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}} \quad (2)$$

$V_{mi}$  is a Van der Waals molar volumes of a group  $i$  component.

The constant  $15.17 \times 10^{-6} \text{ m}^3 \text{ mol}^{-1}$  is the molar hard-core volumes of a  $\text{CH}_2$  group. In our model, the group contribution concept is considered to calculate the chain length contrary to that of the existing modified double-lattice model.

$\chi_{OB}$  is defined as follows:

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\epsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\epsilon}\right) \tilde{\epsilon} \phi_2 + C_\gamma \tilde{\epsilon}^2 \phi_2^2 \quad (3)$$

where  $C_\beta$  and  $C_\gamma$  are universal constants. These constants are determined by comparison with Madden

et al.'s<sup>29</sup> Monte Carlo simulation data. The best-fit values of  $C_\beta$  and  $C_\gamma$  are 0.1415 and 1.7986, respectively.  $\tilde{\varepsilon}$  is a reduced interaction energy parameter given by

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}}{kT} \quad (4)$$

where  $\varepsilon_{11}$ ,  $\varepsilon_{22}$ , and  $\varepsilon_{12}$  refer to the corresponding nearest neighbor segment–segment interactions.

### Secondary lattice

To improve the mathematical approximation defect and to reduce the number of parameters, a new Helmholtz energy of mixing as a fractional form is defined. The expression is given by

$$\frac{\Delta A_{\text{sec},ij}}{N_{ij}kT} = \frac{2}{z} \left[ \eta \ln \eta + (1 - \eta) \ln(1 - \eta) + \frac{zC_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta}{1 + C_\alpha \delta \tilde{\varepsilon}_{ij} (1 - \eta) \eta} \right] \quad (5)$$

where  $\Delta A_{\text{sec},ij}$  is the Helmholtz energy of mixing of the secondary lattice for the  $i$ - $j$  segment–segment pair and  $N_{ij}$  is the number of  $i$ - $j$  pairs.  $\delta \tilde{\varepsilon}$  is the reduced energy parameter contributed by the oriented interactions, and  $\eta$  is the surface fraction permitting oriented interactions. For simplicity, we arbitrarily set  $\eta$  to 0.3, as suggested by Hu et al.<sup>30</sup>  $C_\alpha$  is a universal constant that is determined by comparison with Panagiotopolus et al.'s<sup>33</sup> Gibbs ensemble Monte Carlo simulation data of the Ising lattice. The best-fit value of  $C_\alpha$  is 0.4881.

### Incorporation of the secondary lattice into the primary lattice

To incorporate a secondary lattice, we replace  $\varepsilon_{ij}$  with  $\varepsilon_{ij} - \frac{\Delta A_{\text{sec},ij}}{N_{ij}}$  in eq. (4). If an oriented interaction occurs in the  $i$ - $j$  segment–segment pairs, we replace  $\tilde{\varepsilon}$  with  $\frac{\varepsilon}{kT} + 2 \frac{\Delta A_{\text{sec},ij}}{N_{ij}kT}$  in eq. (4). If an oriented interaction occurs in the  $i$ - $i$  segment–segment pairs, we replace  $\tilde{\varepsilon}$  with  $\frac{\varepsilon}{kT} - \frac{\Delta A_{\text{sec},ii}}{N_{ii}kT}$ . In this study, we assume that the oriented interaction occurs in the  $i$ - $i$ ,  $j$ - $j$ , and  $i$ - $j$  segment–segment pairs. That is, the oriented interaction occurs in all the SPE and water group segment pairs.

We replace  $\tilde{\varepsilon}$  with

$$\varepsilon_{12} = \left( \varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^* \right) + \left( -\frac{\Delta A_{\text{sec},11}}{N_{11}} - \frac{\Delta A_{\text{sec},22}}{N_{22}} + \frac{2\Delta A_{\text{sec},12}}{N_{12}} \right) \quad (6)$$

where  $\varepsilon_{11}^*$ ,  $\varepsilon_{22}^*$ , and  $\varepsilon_{12}^*$  are van der Waals energy interaction parameters.  $\Delta A_{\text{sec},11}$ ,  $\Delta A_{\text{sec},22}$ , and  $\Delta A_{\text{sec},12}$

are the additional Helmholtz functions for the corresponding secondary lattice. Equation (6) then becomes

$$\tilde{\varepsilon} = \frac{\varepsilon_{11}^* + \varepsilon_{22}^* - 2\varepsilon_{12}^*}{kT} - 2C_\alpha(1 - \eta)\eta \times \left[ \frac{\frac{\delta \varepsilon_{11}}{kT}}{1 + C_\alpha \frac{\delta \varepsilon_{11}}{kT} (1 - \eta)\eta} + \frac{\frac{\delta \varepsilon_{22}}{kT}}{1 + C_\alpha \frac{\delta \varepsilon_{22}}{kT} (1 - \eta)\eta} - \frac{2 \frac{\delta \varepsilon_{12}}{kT}}{1 + C_\alpha \frac{\delta \varepsilon_{12}}{kT} (1 - \eta)\eta} \right] \quad (7)$$

In a binary mixture, the activity of solvent 1 in polymer 2 is

$$\ln a_1 = \ln \phi_1 - r_1 \left( \frac{1}{r_2} - \frac{1}{r_1} \right) \phi_2 + r_1 \left[ C_\beta \left( \frac{1}{r_2} - \frac{1}{r_1} \right)^2 + \left( \frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + \left( 2 + \frac{1}{r_2} \right) \tilde{\varepsilon} \right] \phi_2^2 - 2r_1 \left[ \left( \frac{1}{r_2} - \frac{1}{r_1} + C_\gamma \tilde{\varepsilon} \right) \tilde{\varepsilon} + C_\gamma \tilde{\varepsilon}^2 \right] \phi_2^3 + 3r_1 C_\gamma \tilde{\varepsilon}^2 \phi_2^4 \quad (8)$$

### Cell voltage model

Srinivansan et al.<sup>18</sup> showed that it is possible to use a simple model equation to describe the behavior of the cell voltage ( $E$ ) versus the current density ( $j$ ) for proton-exchange membrane fuel cells in the activation and ohmic controlled current density region:

$$E = E_0 - b \log j - R_e j \quad (9)$$

with

$$E_0 = E_r + b \log j_0 \quad (10)$$

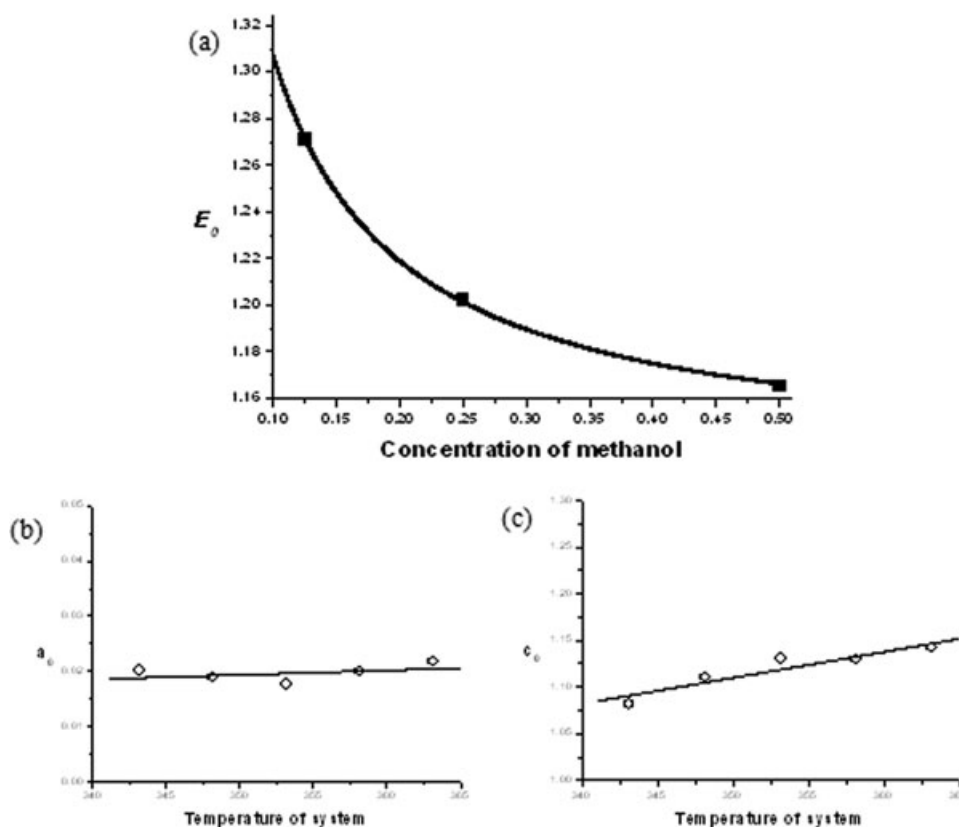
where  $E_r$  is the reversible cell potential,  $b$  is the Tafel slope for oxygen reduction, and  $R_e$  is the ohmic resistance of the cell.

By the use of eq. (9), with the appropriate coefficients, it has been shown that as the current density increases, the predicted cell potential decreases much less rapidly than observed.<sup>18</sup> To increase the reliability of the aforementioned equation, Kim et al.<sup>19</sup> suggested

$$E = E_0 - b \log j - R_e j - m e^{nj} \quad (11)$$

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

Squadrito et al.<sup>23</sup> used eq. (11) as a starting point to analyze the different contributions to the mass-



**Figure 1** Dependence of parameter  $E_0$  on the methanol concentration and dependence of parameters  $a_0$  and  $b_0$  on the temperature.

transport limitation and produced an equation in the following form:

$$E = E_0 - b \log j - R_e j + a j^k \ln(1 - \beta j) \quad (12)$$

where  $a$ ,  $k$ , and  $\beta$  are adjustable model 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.<sup>27</sup> showed the applicability of Kim et al.'s and Squadrito et al.'s equations to predicting the voltage response of a DMFC:

$$E_{\text{cell}} = E_0 - b \log j - R_e j + C_1 \ln(1 - C_2 j) \quad (13)$$

That is,  $k = 0$  for Squadrito et al.'s equation.

The numbers of the models introduced here are semi-empirical and are based on Srinivansan et al.'s model [eq. (9)]. However, it shows a serious mathematical defect. When  $j$  becomes zero, the equation should reduce to voltage  $E_0$ . These

models, however, do not meet the mathematical boundary condition.

To improve this mathematical defect, we suggest a new semi-empirical cell voltage model as follows:

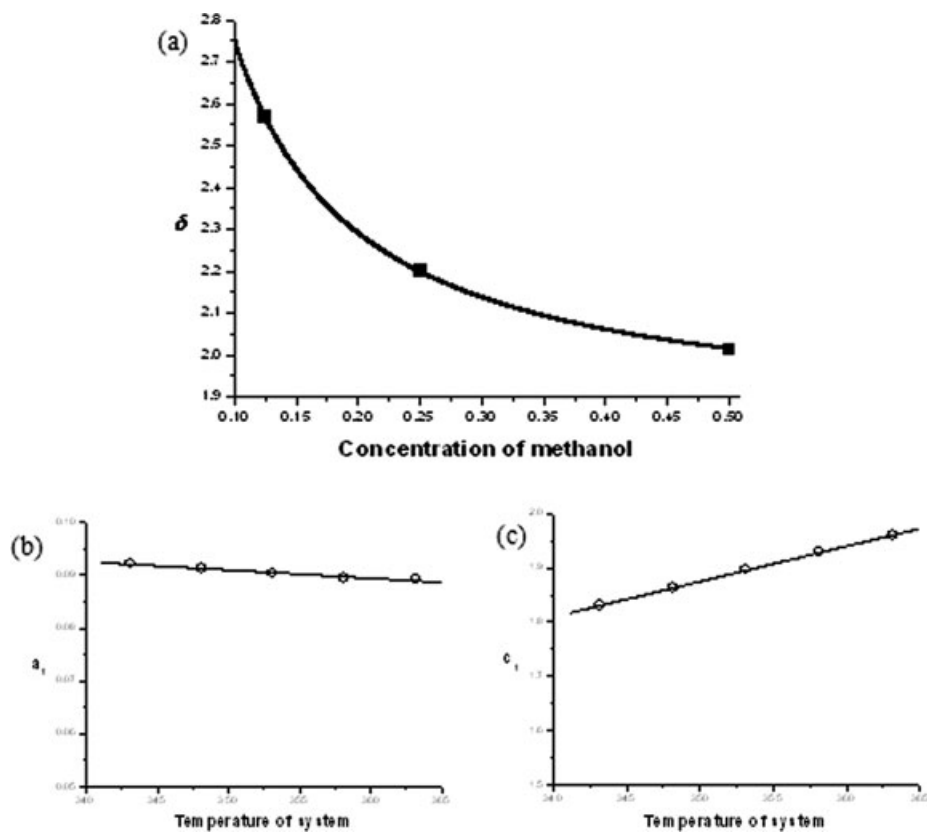
$$E_{\text{cell}} = E_0^* - \kappa_R j + \lambda_d \ln(1 - j/j_{\text{lim}}) \quad (14)$$

with

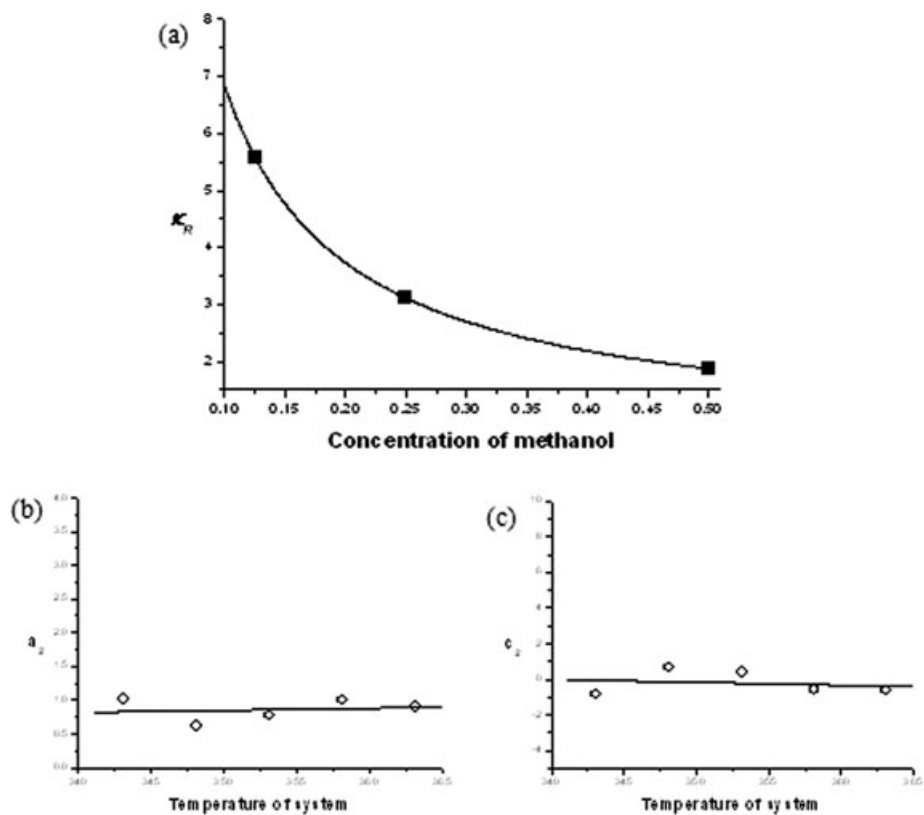
$$E_0^* = E_0 - \delta a_{\text{MeOH}} \quad (15)$$

We employ a methanol activity term ( $\delta a_{\text{MeOH}}$ ) to take into account the methanol crossover effect,<sup>31</sup> and  $\delta$  is an effective coefficient. To describe the methanol activity of DMFC, we employ a group contribution method [eqs. (6)–(8)].

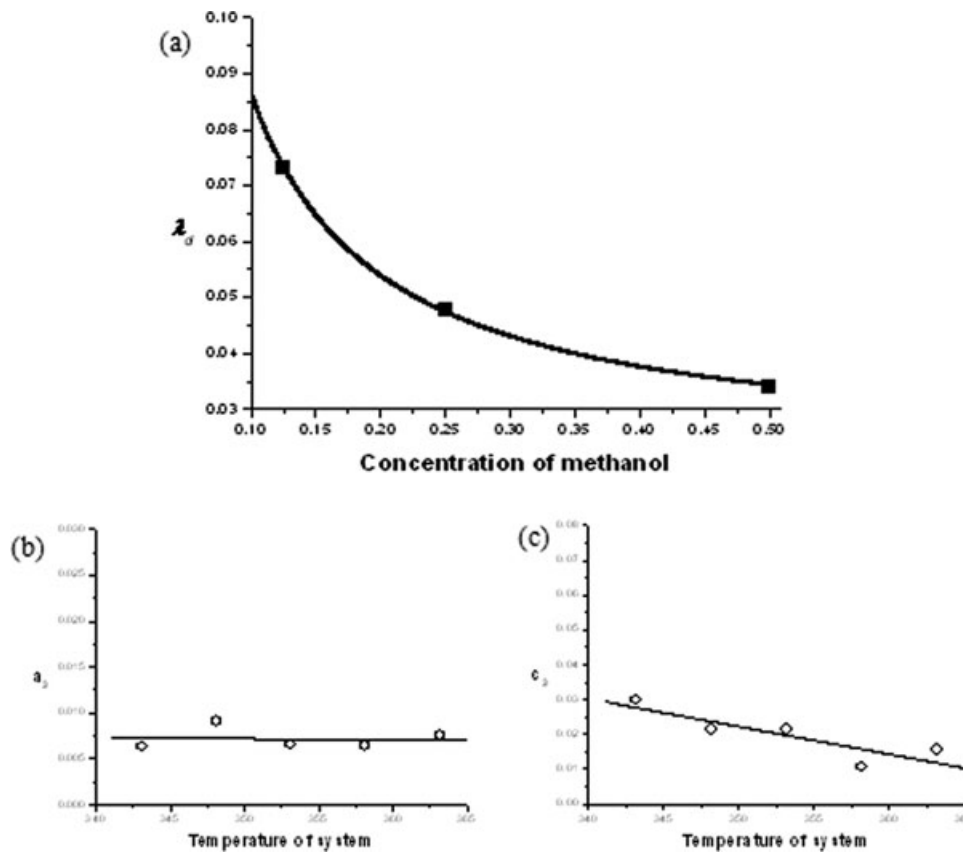
The first term of eq. (14),  $E_0^*$  is the voltage when no methanol crossover occurs. In eq. (15),  $E_0^*$  is defined as an appropriate OCV. The second term,  $\kappa_R j$ , presents the ohmic resistance and electrode–electrolyte overpotential of the cell. We also add the diffusion overpotential to take into account the rapid voltage drop at a high current density.



**Figure 2** Dependence of parameter  $\delta$  on the methanol concentration and dependence of parameters  $a_1$  and  $b_1$  on the temperature.



**Figure 3** Dependence of parameter  $\kappa_R$  on the methanol concentration and dependence of parameters  $a_2$  and  $b_2$  on the temperature.



**Figure 4** Dependence of parameter  $\lambda_d$  on the methanol concentration and dependence of parameters  $a_3$  and  $b_3$  on the temperature.

In general, the methanol crossover effect plays a major role in determining the OCV of a DMFC. The proposed model describes the methanol crossover contribution and diffusion contribution for the mass-transfer limitation.  $\delta$  represents the methanol cross-

over effect, and  $\lambda_d$  represents the coefficient and effective coefficient in the diffusion overpotential for the mass-transport limitation.

As confirmed in eq. (14), when the value of the current density approaches zero, the cell voltage

**TABLE I**  
Parameter Functions That Are Dependent on the Concentration at Each Temperature

Temperature (K)	Function ( $c$ is a variable concentration)	
	$E_0$ (V) = $b_0 + \frac{1}{a_0c}$	$\delta$ (V) = $b_1 + \frac{1}{a_1c}$
343.15	$1.0817 + \frac{1}{0.0202c}$	$1.8297 + \frac{1}{0.0922c}$
348.15	$1.1101 + \frac{1}{0.0188c}$	$1.8622 + \frac{1}{0.0913c}$
353.15	$1.1307 + \frac{1}{0.0175c}$	$1.8963 + \frac{1}{0.0903c}$
358.15	$1.1292 + \frac{1}{0.0199c}$	$1.9293 + \frac{1}{0.0895c}$
363.15	$1.1418 + \frac{1}{0.0217c}$	$1.9591 + \frac{1}{0.0892c}$
Temperature (K)	Function ( $c$ is a variable concentration)	
	$\kappa_R$ (V/j) = $b_2 + \frac{1}{a_2c}$	$\lambda_d$ (V) = $b_3 + \frac{1}{a_3c}$
343.15	$-0.8602 + \frac{1}{1.0102c}$	$0.0299 + \frac{1}{0.0063c}$
348.15	$0.6379 + \frac{1}{0.6170c}$	$0.0214 + \frac{1}{0.0091c}$
353.15	$0.3679 + \frac{1}{0.7678c}$	$0.0212 + \frac{1}{0.0065c}$
358.15	$-0.5922 + \frac{1}{1.0031c}$	$0.0105 + \frac{1}{0.0064c}$
363.15	$-0.6451 + \frac{1}{0.8959c}$	$0.0155 + \frac{1}{0.0075c}$

**TABLE II**  
**Functions That Are Dependent on the Temperature**  
**at Each Concentration for the Parameter**  
**Functions of Table I**

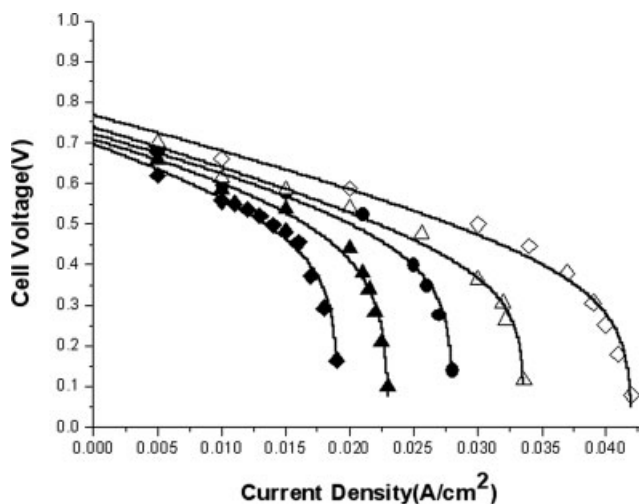
Parameter	Function ( $T$ is a variable temperature)
$a_0$ (1/V · M)	$-0.00934 + 8.21 \times 10^{-5}T$
$b_0$ (V)	$0.13515 + 2.78 \times 10^{-3}T$
$a_1$ (1/V · M)	$0.14559 - 1.56 \times 10^{-4}T$
$b_1$ (V)	$-0.40518 + 6.51 \times 10^{-3}T$
$a_2$ (j/V · M)	$-0.25362 + 3.15 \times 10^{-3}T$
$b_2$ (V/j)	$5.42961 - 1.60 \times 10^{-2}T$
$a_3$ (1/V · M)	$0.00928 - 6.01 \times 10^{-6}T$
$b_3$ (V)	$0.30051 - 7.95 \times 10^{-4}T$

becomes the appropriate OCV ( $E_0^*$ ) containing methanol crossover.

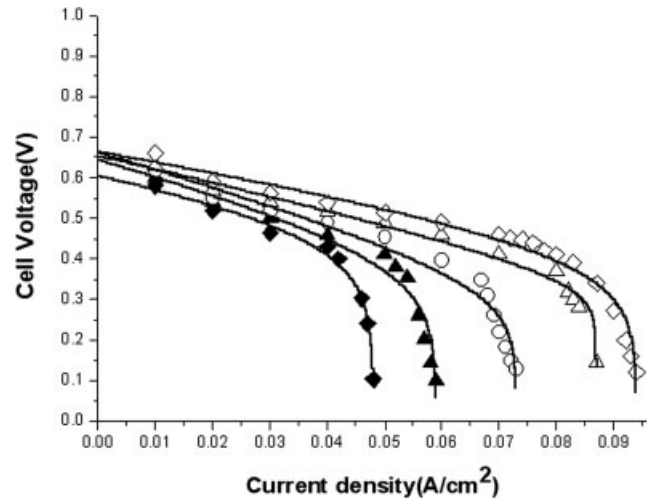
## RESULTS AND DISCUSSION

We propose a new semi-empirical group contribution model to predict the cell voltage as a function of the current density for a liquid-fed DMFC. Model predictions are presented for three different aqueous methanol solution concentrations, that is, for cell operating temperatures of various ranges. The performance of a DMFC at higher current densities has been shown to be limited by a mass-transport process, which mainly occurs by diffusion.

In this study, we assume that the model parameters ( $E_0$ ,  $\delta$ ,  $\kappa_R$ , and  $\lambda_d$ ) are dependent on the methanol concentration to generalize cell voltage parameters obtained from experimental data. To



**Figure 5** Comparison of the experimental data from ref. 27 with calculated values for a cell operated with a 0.125M methanol solution at cell temperatures of (◆) 343.15, (▲) 348.15, (○) 353.15, (△) 358.15, and (◇) 363.15 K.



**Figure 6** Comparison of the experimental data from ref. 27 with calculated values for a cell operated with a 0.25M methanol solution at cell temperatures of (◆) 343.15, (▲) 348.15, (○) 353.15, (△) 358.15, and (◇) 363.15 K.

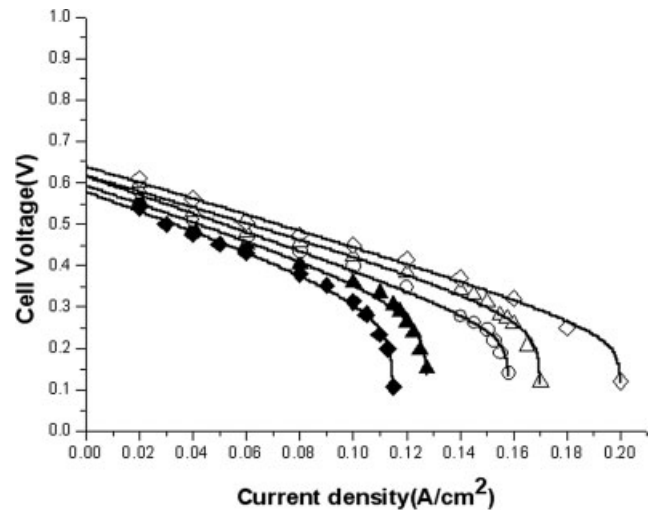
simply correlate with experimental data, we suggest each parameter as follows:

$$E_0 = b_0 + \frac{1}{a_0c}$$

$$\delta = b_1 + \frac{1}{a_1c}$$

$$\kappa_R = b_2 + \frac{1}{a_2c}$$

$$\lambda_d = b_3 + \frac{1}{a_3c}$$



**Figure 7** Comparison of the experimental data from ref. 27 with calculated values for a cell operated with a 0.5M methanol solution at cell temperatures of (◆) 343.15, (▲) 348.15, (○) 353.15, (△) 358.15, and (◇) 363.15 K.

TABLE III  
Calculated Group Interaction Parameters for the  
Methanol Concentration (0.125M)/Temperature  
(343.15–363.15 K) System (K)

Solvent	Polymer					
	CF	CF <sub>2</sub>	CF <sub>3</sub>	O	SO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>
CH <sub>3</sub> OH	29.51	5685.37	118.76	-755.34	-170.69	228.67
	33.28	5701.45	120.91	-749.81	-162.43	234.26
	36.84	5729.15	123.17	-741.73	-155.82	241.53
	41.13	5742.68	126.08	-734.74	-146.38	249.77
	45.55	5770.12	129.54	-728.06	-137.15	259.09

where  $c$  is the methanol concentration. These parameters are described in Figures 1–4. We set these coefficients ( $a_0$ – $a_3$  and  $b_0$ – $b_3$ ) to be linearly dependent on the temperature. The determined values of the parameters are listed in Tables I and II.

In Figures 5–7, the calculated cell voltages are presented for three different aqueous methanol solution concentrations (0.125, 0.25, and 0.5M) at cell operating temperatures of various ranges. Obtained group interaction energy parameters are listed in Tables III–V. The advantage of the proposed model lies in the ability to follow well the voltage profile in the limiting current region.

A few comments are necessary regarding the limiting current operating region of a DMFC. As can be seen from the figures, there are two types of variations in the voltage with the current density, depending on the cell operating conditions. One is a steep fall in the voltage with the current density shown to be limited by a mass-transport process, which mainly occurs by diffusion. The other pattern is a more gradual fall in the voltage and is similar to that commonly seen for hydrogen fuel cells. A common weakness of many semi-empirical models for a DMFC is that they are valid only for narrow operating conditions. The current equation should be applicable over a wide range of operating conditions.

The model equation proposed in this study is able to express the cell voltage in the entire current den-

TABLE IV  
Calculated Group Interaction Parameters for the  
Methanol Concentration (0.25M)/Temperature  
(343.15–363.15 K) System (K)

Solvent	Polymer					
	CF	CF <sub>2</sub>	CF <sub>3</sub>	O	SO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>
CH <sub>3</sub> OH	31.16	5702.15	121.67	-751.18	-168.56	231.51
	35.36	5726.74	124.66	-745.24	-160.74	237.94
	38.54	5748.39	126.94	-737.59	-153.69	244.62
	43.02	5769.52	129.35	-731.61	-144.44	252.83
	47.66	5791.05	132.27	-724.12	-135.21	262.12

TABLE V  
Calculated Group Interaction Parameters for the  
Methanol Concentration (0.5M)/Temperature  
(343.15–363.15 K) System (K)

Solvent	Polymer					
	CF	CF <sub>2</sub>	CF <sub>3</sub>	O	SO <sub>3</sub> <sup>-</sup>	H <sup>+</sup>
CH <sub>3</sub> OH	34.05	5729.62	126.03	-745.06	-165.97	236.84
	38.17	5754.45	129.64	-739.48	-157.16	242.68
	41.37	5776.51	131.76	-731.34	-150.83	249.13
	46.98	5797.28	134.57	-725.78	-141.55	257.49
	50.84	5819.42	137.35	-718.29	-132.07	267.08

sity region. Also, our calculated  $E_0^*$  values are fairly reasonable at the given temperatures. In practice, the OCV value decreases with the methanol concentration increasing.<sup>31</sup> As shown in these figures, the cell voltage decreases with increasing current density. Especially in the high current density region, the cell voltage decreases radically. This decrease is due to the diffusion affecting the performance of the total cell voltage.

Figure 8 presents a plot of the cell voltage versus the current density with Flemion as an electrolyte. The solid line was calculated with previously obtained group interaction parameters with no additional adjustable model parameters. Open squares represent experimental data from Hommura et al.<sup>32</sup> As can be seen in this figure, the calculated curve for different polymer electrolytes such as Flemion shows a trend similar to that of Nafion, in which the cell voltage decreases with increasing current density. This is expected because most commercially available polymer electrolytes developed for fuel-cell applications have a similar chemical structure.

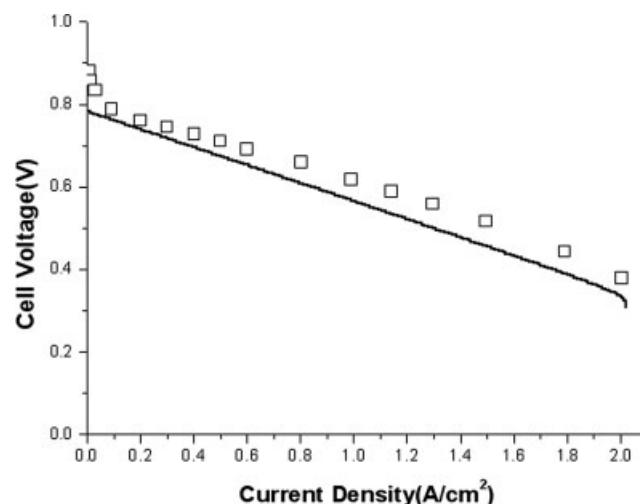


Figure 8 Comparison of the experimental data from ref. 32 with calculated values for a cell operated with Flemion.



## CONCLUSIONS

We have established a new semi-empirical group contribution model to describe the cell voltage of a DMFC as a function of the current density. The proposed model is valid even in the case of low current densities caused by, for example, the use of dilute methanol solutions of low cell temperatures. The ultimate goal of the semi-empirical group contribution model lies in its ability to predict the cell voltage response for fuel-cell systems that are not included in the experimental data, that is, the set of data used to determine the parameters.

Further work will follow to consider the pressure effect and the influence of the SPE structure to obtain a more general and accurate group contribution model for DMFCs.

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