

Swelling effect of a polymer electrolyte membrane on the development of a semi-empirical cell voltage model

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Abstract We developed a new cell voltage model which depends on the current density response of the proton exchange membrane fuel cell (PEMFC). The proposed model focuses on the conductivity of a PEMFC fuel cell. The model for conductivity of a polymer electrolyte membrane, Nafion, uses the thermodynamic function to represent water activity. We observed membrane conductivity by monitoring the chemical potential of the swelling of the hydrogel. The swelling equilibrium of the ionized hydrogel is governed by the free energy of mixing, the free energy of elasticity, and the concentration of counterions with fixed charges on the gel network. A cell voltage equation with reasonable boundary conditions, including the swelling effect, which plays a major role in determining the cell voltage of a PEMFC, was newly developed.

Keywords PEMFC · Cell voltage · Current density · Conductivity of Nafion · Swelling

1 Introduction

A number of approaches using empirical models have been attempted to develop model equations to describe the performance of polymer electrolyte fuel cells [1–5]. In many cases, fairly good agreement between the model and experimental data is achieved by adjusting appropriate coefficients/parameters in the model equations. Srinivasan et al. [1] developed an equation that describes the relation between the

cell potential and current density in the low and intermediate current density regions where electrode reactions are activation and ohmic controlled. Starting from this point, Kim et al. [2] introduced an additional term that allows fitting of experimental curves over the whole range of current density. However, they did not have evidence of a link between the introduced parameters and the experimental variables related to mass transport. An equation derived from a semi-empirical approach was also proposed by Squadrito et al. [5].

PEMFC employ perfluorosulfonate ionomers, such as Nafion, as their electrolytes. Nafion has significant ionic conductivity and can be used in fuel cells. Considerable research has been directed toward the development of polymer electrolytes with high ionic conductivity as well as mechanical, thermal, and chemical stability. One important factor that can affect the performance of fuel cells is the hydration of Nafion [6–9]. Adequate hydration of such membranes is critical to fuel cell operation. If the membrane is too dry, its conductivity falls, resulting in reduced cell performance. An excess of water in the fuel cell can lead to cathode flooding problems, also resulting in less-than-optimal performance.

Water is carried into the fuel cell via the humidified gas streams entering gas diffusion electrodes [1]. Some combination of water vapor and liquid water passes through each electrode to the electrode/membrane interface. Water is absorbed into the membrane and spreads throughout the membrane. Swelling occurs under these conditions. The sulfonic groups of Nafion easily dissociate into SO_3^- and H^+ in these membranes in the presence of water. Under these conditions, the proton can be considered a mobile charge that encounters low resistance when moving across a potential gradient [2–4].

Thermodynamically, the swelling equilibrium of the ionized hydrogel is governed by the free energy of mixing,

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the free energy of elasticity, and the concentration of counterions with fixed charges on the gel network. In the gel/water system, water diffuses into the network by forces determined by the difference in the osmotic pressure of water between the gel network and surroundings. Bounded electrolytes on the gel structure are dissociated in water and produce mobile ions. Because of the fixed charges, there is an unequal distribution of mobile ions between the inside of the gel and the external solution. This unequal distribution of solute induces an additional osmotic pressure that adds to the total osmotic pressure.

In this study, we consider Nafion to be a partially ionized hydrogel in water. In addition, we established a model of ion conductivity of Nafion based on the swelling effect of the hydrogel. The extent of conductivity depends largely on the water content of the membrane. We express membrane conductivity according to the thermodynamic activity of water, compared with the swelling ratio of Nafion. Moreover, we apply it to resistance in the fuel cell and define a new cell voltage model of the PEM fuel cell.

2 Model development

2.1 The swelling effect

At equilibrium, the chemical potential μ of every diffusible component i , including ions, is

$$\mu'_i = \mu''_i \quad (1)$$

where single prime and double prime represent the gel phase and the external phase of the gel, respectively. When i represents the solvent, Eq. 1 becomes

$$\Delta\Pi = \Delta\Pi_{\text{mix}} + \Delta\Pi_{\text{elas}} + \Delta\Pi_{\text{ion}} \quad (2)$$

where $\Delta\Pi$ is the osmotic pressure difference between the gel phase and external phase of the gel, and V_1 is the solvent molar volume. $\Delta\Pi$ consists of three contributions

$$\tilde{A}_{r,I} = \frac{\Delta A_I}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln\phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln\phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (3)$$

where $\Delta\Pi_{\text{mix}}$ is the mixing contribution of polymer/solvent, $\Delta\Pi_{\text{elas}}$ is the elastic contribution deforming the network of chains from their reference state, and $\Delta\Pi_{\text{ion}}$ is the contribution from an unequal distribution of mobile ions between the gel phase and the external phase and electrostatic forces.

We used the Helmholtz energy of mixing [10] as the form for the Flory–Huggins theory. This expression is given by

$$\tilde{A}_{r,I} = \frac{\Delta A_I}{N_r kT} = \left(\frac{\phi_1}{r_1}\right) \ln\phi_1 + \left(\frac{\phi_2}{r_2}\right) \ln\phi_2 + \chi_{OB} \phi_1 \phi_2 \quad (4)$$

where r_2 is the segment number of the polymer molecule relative to $r_1 = 1$ for the solvent. χ_{OB} is an interaction parameter defined by

$$\chi_{OB} = C_\beta \left(\frac{1}{r_2} - \frac{1}{r_1}\right)^2 + \left(2 + \frac{1}{r_2}\right) \tilde{\varepsilon} - \left(\frac{1}{r_2} - \frac{1}{r_1} + C_r \tilde{\varepsilon}\right) \tilde{\varepsilon} \phi_2 + C_\gamma \tilde{\varepsilon}^2 \phi_2^2 \quad (5)$$

where C_β and C_γ are universal constants. These constants are not adjustable parameters and are determined by comparison with Madden et al.'s [11] Monte Carlo simulation data. The given values of C_β and C_γ are 0.141 and 1.798, respectively. $\tilde{\varepsilon}$ is a reduced interaction-energy parameter given by

$$\tilde{\varepsilon} = \frac{\varepsilon}{kT} = \frac{\varepsilon_{11} + \varepsilon_{22} - 2\varepsilon_{12}}{kT} \quad (6)$$

where ε_{11} , ε_{22} , and ε_{12} are the corresponding nearest-neighbor segment–segment parameters. To obtain an analytical expression for the secondary lattice, Oh et al. [12] defined a new Helmholtz energy of mixing with a fractional form to improve the mathematical approximation defect and to reduce the number of parameters. The expression is given by

$$\tilde{A}_{r,II} = \frac{\Delta A_{II}}{N_r kT} = \tilde{T} \left[\tilde{\rho}^{-1} (1 - \tilde{\rho}) \ln(1 - \tilde{\rho}) + \left(\frac{1}{r_a}\right) \ln\tilde{\rho} + \chi_{OB}^0 (1 - \tilde{\rho}) \right] \quad (7)$$

where \tilde{T} is reduced temperature, \tilde{P} is reduced pressure, and $\tilde{\rho}$ is reduced average chain length density. r_a and interaction parameter χ_{OB}^0 are estimates for the pseudo-pure substance mixed solution.

$$\chi_{OB}^0 = C_\beta \left(\frac{1}{r_a} - 1\right)^2 + \left(2 + \frac{1}{r_a}\right) \tilde{\varepsilon}_{II} - \left(\frac{1}{r_a} - 1 + C_r \tilde{\varepsilon}_{II}\right) \tilde{\varepsilon}_{II} \tilde{\rho} + C_\gamma \tilde{\varepsilon}_{II}^2 \tilde{\rho}^2 \quad (8)$$

$$\frac{1}{r_a} = \frac{\phi_1}{r_1} + \frac{\phi_2}{r_2} \quad (9)$$

$$\tilde{T} = \tilde{\varepsilon}_{II}^{-1} = kT/\varepsilon_{aa} \quad (10)$$

$$\tilde{\rho} = N_r v^0 / V \quad (11)$$

where v^0 is the hard-core volume of one site or one segment and $\tilde{\varepsilon}_{II}$ is reduced energy.

$$v^0 = \sum_i \phi_i v_i^0 = \phi_1 v_1^0 + \phi_2 v_2^0 \quad (12)$$

$$\tilde{\varepsilon}_{II} = \varepsilon_{aa} / kT \quad (13)$$

$$\varepsilon_{aa} = \phi_1^2 \varepsilon_{11} + 2\phi_1 \phi_2 \varepsilon_{12} + \phi_2^2 \varepsilon_{22}. \quad (14)$$

Chemical potential for the gel systems is calculated by

$$\mu_1 - \mu_1^0 = \left(\frac{\partial \Delta_{\text{mix}} A}{\partial N_1} \right)_{T,V,N_2} = r_1 \left(\Delta f_E + \phi_2 \frac{d\Delta f_E}{d\phi_1} \right) \quad (15)$$

where

$$\Delta f_E = \Delta A_{(I+II)} / N_r \quad (16)$$

$$\frac{d\Delta f_E}{d\phi_1} = \frac{\partial \Delta f_E}{\partial \phi_1} + \frac{\partial \Delta f_E}{\partial \tilde{\rho}} \frac{\partial \tilde{\rho}}{\partial \phi_1} + \frac{\partial \Delta f_E}{\partial \tilde{\epsilon}_{II}} \frac{\partial \tilde{\epsilon}_{II}}{\partial \phi_1} + \frac{\partial \Delta f_E}{\partial r_a} \frac{\partial r_a}{\partial \phi_1} \quad (17)$$

For a perfect network polymer, Flory and Erman obtain the chemical potential as a result of elastic forces [13]

$$\frac{\Delta \mu_{1,\text{elas}}}{kT} = \left(\frac{\phi_g^0}{2x_c} \right) \lambda^{-1} \left\{ 1 + B \left[\dot{B} (1 + B)^{-1} + (\lambda/g)^2 (B + \lambda^2 \dot{B}) (1 + \lambda^2 B/g)^{-1} \right] \right\} \quad (18)$$

where

$$\dot{B} = \partial B / \partial \lambda^2 = B \left[(\lambda^2 - 1)^{-1} - 2(\lambda^2 + g)^{-1} \right] \quad (19)$$

with

$$B = \frac{\lambda^2 - 1}{(1 + \lambda^2/g)^2} \quad (20)$$

and λ is the linear swelling ratio

$$\lambda = \left(\frac{V}{V^0} \right)^{1/3} = \left(\frac{\phi_g^0}{\phi_g} \right)^{1/3} \quad (21)$$

where V and V^0 are the volume of the gel network and the volume in the reference state, respectively; and ϕ_g and ϕ_g^0 are the corresponding volume fractions of the gel. The network parameter g relates x_c and ϕ_g^0 as follows:

$$g = \frac{1}{4} P \phi_g^0 x_c^{1/2} \quad (22)$$

where the parameter g represents the constraints on fluctuations of junctions from the surrounding chains in which they are embedded. If fluctuations can be suppressed due to their embedment in the surrounding randomly configured chains, $g = 0$, and a real network approaches a “phantom network” in the limit of a high degree of swelling. If fluctuations are suppressed completely by the constraints, $g \rightarrow \infty$, the network is called an “affine network.” The dimensionless parameter P depends on the characteristics of the generic type of polymer and the molar volume of solvent. We set P to unity, and x_c is the average chain length between crosslinking points. Fixed charges on a gel network result in an unequal distribution of mobile ions between the gel and the surrounding solution and an osmotic pressure difference between the two phases. This osmotic pressure difference contributes to the total osmotic

pressure. To describe the effect of ions on gel-swelling behaviors, ion–ion, ion–solvent, and ion–polymer interactions are required. These interactions, however, are neglected in the ideal Donnan theory

$$\Delta \Pi_{\text{ion}} = RT \sum_j \left(C_j^{\text{gel}} - C_j^{\text{ext}} \right) \quad (23)$$

where C_j^{gel} and C_j^{ext} are concentrations of mobile ions within the gel and in the surrounding solution. When salt is not present in the external solution, all C_j^{ext} are zero and C_j^{gel} is given by the concentration of counterions within the gel.

The empirical expressions of ionic conductivity presented by Springer et al. [14] are used. At all temperatures, the ionic conductivity is

$$\sigma = (0.00514w - 0.00326) \exp \left[1268 \left(\frac{1}{303.15} - \frac{1}{T} \right) \right] \quad (24)$$

The membrane water content is given by

$$w = 0.043 + 17.81a - 39.85a^2 + 36.0a^3. \quad (25)$$

Below one water molecule per charge site, the membrane conductivity is assumed to be constant. The membrane resistance is integrated over the membrane thickness, t_m , as

$$R_e = \int_0^{t_m} \frac{dz}{\sigma} \quad (26)$$

2.2 Cell voltage model

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

$$E = E_0 - b \log j - R_e j \quad (27)$$

with

$$E_0 = E_r + b \log j_0 \quad (28)$$

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

Using Eq. 17, with the appropriate coefficients, it was shown that as the current density increases, the predicted cell potential decreases much less rapidly than that observed in [1]. To increase the reliability of the aforementioned equation, Kim et al. [2] suggested

$$E = E_0 - b \log j - R_e j - m e^{nj} \quad (29)$$

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

Squadrito et al. [5] used Eq. 19 as a starting point to analyze the different contributions to the mass transport limitation and produced an equation in the form:

$$E = E_0 - b \log j - R_e j + a j^k \ln(1 - \beta j) \quad (30)$$

where a , k , and β 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.

Numbers in models introduced here are semi-empirical and are based on Srinivasan et al.'s model in Eq. 27. However, there is 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 total cell voltage is given as

$$E_{\text{cell}} = E_0 - R_e j - D_e \frac{j/j_0}{1 - \kappa_{CB} \frac{j}{j_0}} - D_e \ln\left(1 + \frac{j}{j_{\text{lim}}}\right) \quad (31)$$

where R_e represents the ohmic resistance and the electrode–electrolyte overpotential of the cell. We also add the diffusion overpotential term to take into account the rapid voltage drop in the high current density region. D_e represents the effective coefficient for diffusion overpotential with mass transport limitation and j_{lim} is the current limit density.

As the value of the current density approaches zero, the cell voltage becomes the appropriate open circuit voltage (OCV) as confirmed in Eq. 31.

3 Results and discussion

The polymer chain of Nafion does not have chemical crosslinking, but physical crosslinking. Gierke et al. [15] proposed a cluster network model to predict the fundamental features of unique equilibrium ionic selectivities, as

well as the ionic transport properties of perfluorinated ionomer membranes. As a result of electrostatic interactions, these ionic groups tend to aggregate to form tightly packed regions referred to as clusters. The presence of these electrostatic interactions between the ions and the ion pairs enhances the intermolecular forces and thereby exerts a significant effect on the properties of the parent polymer.

Figure 1 is a cluster-network model for Nafion membranes. The polymeric ions and absorbed electrolyte phase separate from the fluorocarbon backbone into approximately spherical clusters connected by short narrow channels. The polymeric charges are most likely embedded in the solution near the interface between the electrolyte and fluorocarbon backbone. This configuration minimizes both the hydrophobic interaction of water with the backbone and the electrostatic repulsion of proximate sulfonate groups. The dimensions shown were deduced from experiments. The shaded areas around the interface and inside the channel are the double layer regions from which the hydroxyl ions are excluded electrostatically.

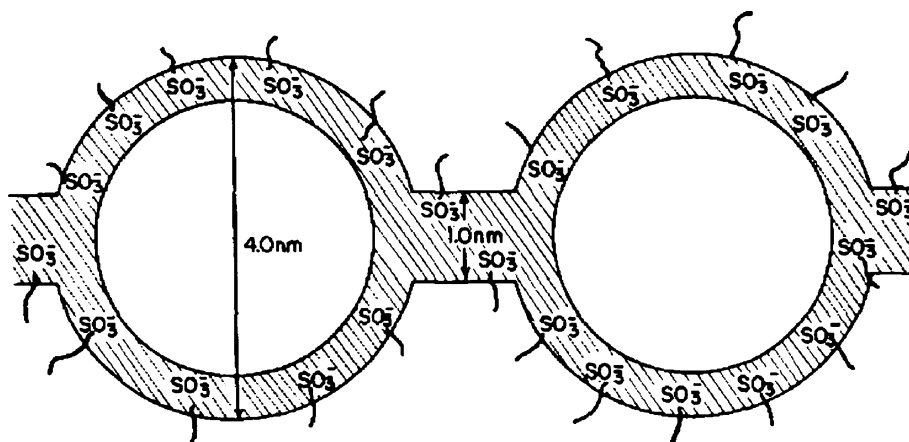
As a result of these findings, we propose that Nafion has crosslinking between polymer chains. We propose swelling in the network as a mechanism.

Swelling occurs when the solvent mixes spontaneously with an analogous linear polymer to form an ordinary polymer solution; the swollen gel is actually a solution. Thus an opportunity for an increase in entropy is afforded by the added volume of the polymer throughout which the solvent may spread.

If the polymer chains making up the network contain ionizable groups, the swelling forces may increase greatly as a result of the localization of charges on the polymer chains. Ion exchange resins are of this type, but we are mainly concerned with ionic networks in which the density of crosslinking is much lower than what is common for ion exchange resins.

The exchange of ions and solvent between a swollen ionic network and the surrounding electrolyte is described

Fig. 1 Cluster-network model for Nafion membranes



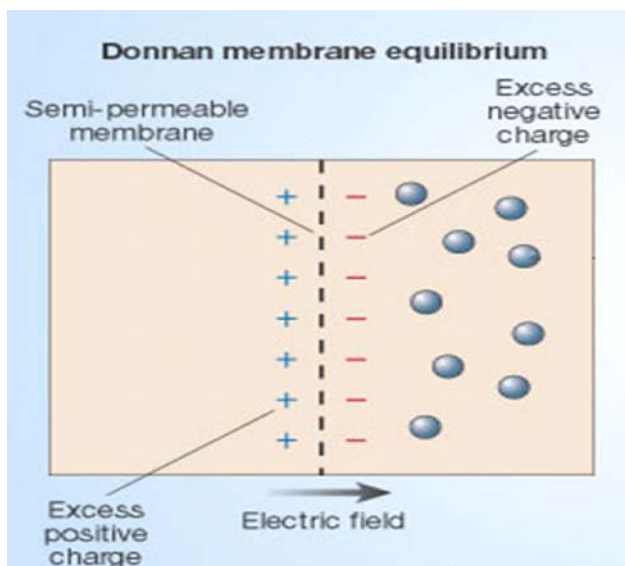


Fig. 2 Diagram of Donnan membrane equilibrium

in Fig. 2. It is apparent that the equilibrium between the swollen ionic gel and its surroundings is close to a Donnan membrane equilibrium. The polymer acts as its own membrane, preventing the charged substituents, which are distributed essentially at random through the gel, from diffusing into the outer solution. The swelling force resulting from the presence of these fixed charges may be identified with the swelling pressure, or net osmotic pressure, across the semipermeable membrane in a typical Donnan equilibrium. The concentration of mobile ions will always be greater in the gel than outside because of the attracting power of the fixed charges. Consequently, the osmotic pressure of the solution inside will exceed that of the external solution. The expansive force may be equated to this difference in osmotic pressures for the two solutions.

We proposed a semi-empirical model to describe the conductivity as a function of thermodynamic activity for a PEM fuel cell. This model describes the cell voltages as a function of current density for a PEM fuel cell. The performance of the PEMFC at higher current densities has been shown to be limited by a mass transport process, which occurs mainly by diffusion.

Figures 3 and 4 show cell voltages for two different gas pressures. In Fig. 3, anode and cathode pressure is 1 bar. In Fig. 4, anode pressure is 2.5 bar and cathode pressure is 3 bar. These figures show that the proposed model agrees very well with experimental data.

Figure 5 shows a comparison of this model and Squadrito et al.'s model. A solid line is calculated in our model and a dotted line fits Squadrito et al.'s model. Our model appears to be more accurate than Squadrito's model. Furthermore, Squadrito's model cannot predict the open circuit voltage. The voltage is unlimited when current density is zero.

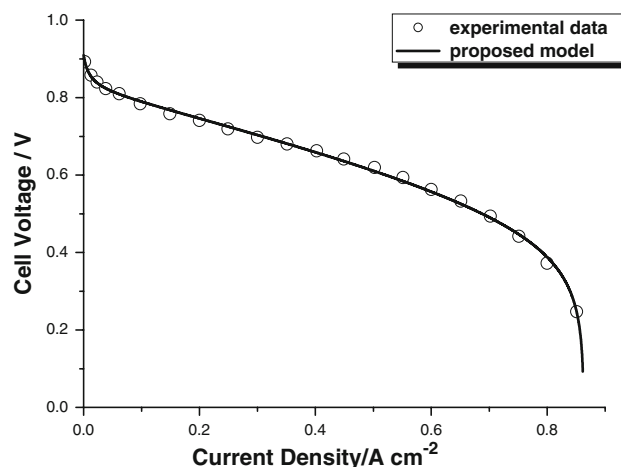


Fig. 3 Comparison between experimental data [5] and empirical equation-based prediction. The cell operated with Nafion 117 at 1 bar/H₂ gas and 1 bar/air gas

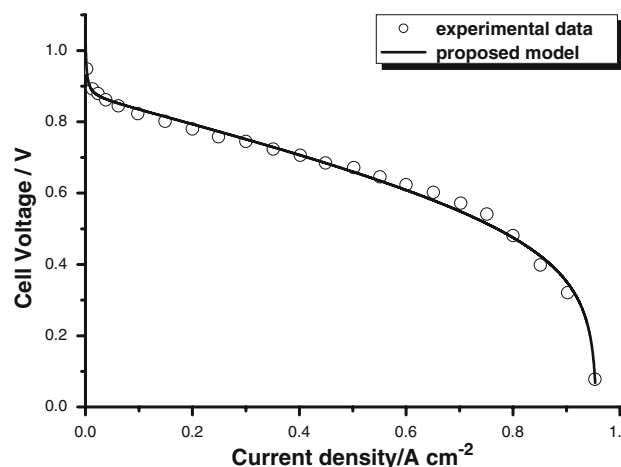


Fig. 4 Comparison between experimental data [5] and empirical equation-based prediction. The cell operated with Nafion 117 at 2.5 bar/H₂ gas and 3 bar/air gas

The model equation proposed in this study is able to express the cell voltages for the given systems over the entire current density region. The existing models, however, do not satisfy the mathematical boundary condition. That is, when the current density goes to zero, the open circuit voltage (OCV) diverges to infinity. As shown in Figs. 1 and 2, the cell voltage decreases with increasing current density. In the high current density region, the cell voltage decreases radically. This is because diffusion affects the performance of the total cell voltage. In this study, we consider both of these contributions.

4 Conclusion

The major purpose of this work was to develop a new cell voltage model for PEMFCs incorporating the activity of a

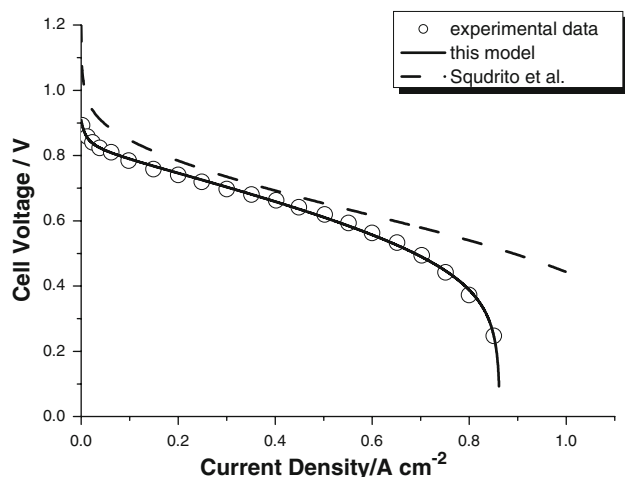


Fig. 5 Comparison of the Squadrito et al. model [5] and our equation-based prediction. The cell operated with Nafion 117 at 1.5 bar/H₂ gas and 1.5 bar/air gas pressure

Nafion membrane with a swelling effect. This activity model incorporates the mixing contribution of polymer/solvent based on a modified double lattice with hole model, the elastic contribution from deforming the network of chains from their reference state, and the contribution of an unequal distribution of mobile ions between the gel phase and the external phase by electrostatic forces (Donnan equilibrium).

We compared the calculated cell voltage of PEMFC at several anode and cathode pressures with experimental cell voltage data. The proposed model is in good agreement with experimental data. A common weakness of many PEMFC models is that they have a serious mathematical defect; when the current density becomes zero, the equation should reduce to the open circuit voltage. However, these models do not meet this mathematical boundary

condition. This drawback is overcome in our model, which can predict the open circuit voltage accurately. The proposed model is valid for the full range of current densities from zero to the limiting current density.

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