Analytical Modeling of the Polarization Curves of a 40-W Fuel Cell Stack

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Abstract
In this study, the performance of a bench scale fuel cell stack, run on hydrogen/air, is measured experimentally. The experimental data, obtained from the 40-watt proton exchange membrane fuel cell (PEMFC), are used in estimating the parameters of a completely analytical model that describes the polarization curve. The analytical model consists of the three fundamental losses experienced by a fuel cell, namely: activation, ohmic, and concentration losses. The current loss is also considered in the model. While the Tafel constants, ohmic resistance, and the concentration loss constant are estimated through multiple linear regression analysis, the limiting current density and the current loss are obtained through measurements. The model and its estimated parameters are used to demonstrate the proportions of the three fundamental losses and to predict the fuel cell delivered power density as a function of the current density. The theoretical equations derived in the literature, which model fuel cell performance, are found to reasonably fit the obtained experimental data.

Keywords: PEMFC, Performance Modeling, Polarization Curve, *i-V* curve, Fuel Cell Losses.

1. Introduction
Fuel cell is an electrochemical device which converts fuel (e.g. hydrogen) directly to electricity without undergoing combustion. Fuel cell technology is suitably integrated into the renewable energy scheme. When fueled with hydrogen that is obtained via renewable energy resources, fuel cell is characterized as zero-emission energy conversion technology. Even when fed by other fuels, the fuel cell system releases low emission since no combustion reactions take place and less fuel is consumed – for a desired power output – due to the high fuel cell efficiency. The performance of a fuel cell is shown by a graph of its output voltage (V) versus the drawn current density (i). This graph, which is also referred to as the *i-V* or polarization curve, is the most important characteristic of a fuel cell. It is a convenient tool for the design and optimization of fuel cells.

For a given temperature (T), pressure (P), and set of species' concentrations, thermodynamics can determine the maximum possible (ideal) voltage that a fuel cell can theoretically produce from a specific electrochemical reaction. However, the actual voltage output is always less than the ideal voltage due to irreversible losses. These losses increase as more current is drawn from the fuel cell. These irreversible losses (also called overpotentials) are caused by the following factors: kinetics of the electrochemical reactions on the electrodes (activation losses), internal charge transport resistance (ohmic losses), and mass transport limitations in the electrodes (concentration losses). In addition, a forth type of losses known as current loss can also affect the fuel cell performance. Therefore, the fuel cell voltage output can be described by the following equation:

$$V = E_{\text{thermo}} - (\eta_{\text{act,a}} + \eta_{\text{act,c}}) - \eta_{\text{ohmic}} - (\eta_{\text{conc,a}} + \eta_{\text{conc,c}}) \quad (1)$$

where V is the real output voltage; E_{thermo} is the thermodynamically predicted voltage; $\eta_{\text{act,a}}$ and $\eta_{\text{act,c}}$ are the activation losses on the anode and cathode, respectively, due to reaction kinetics; η_{ohmic} is the ohmic losses due to ionic and electrical resistances; and $\eta_{\text{conc,a}}$ and $\eta_{\text{conc,c}}$ are the concentration losses on the anode and cathode, respectively, due to mass transport.

For a hydrogen/air fuel cell where $\eta_{act,a}$ and $\eta_{conc,a}$ are negligible compared to $\eta_{act,c}$ and $\eta_{conc,c}$, respectively, Eq. 1 can be rewritten as follows [1]:

$$V = E_{thermo} - [a_c + b_c \cdot \ln(i + i_{loss})] - R_{ohmic} \cdot i - c_c \cdot \ln\left(\frac{i_{L,c}}{i_{L,c} - (i + i_{loss})}\right) \quad (2)$$

where the third, forth, and fifth terms represent $\eta_{act,c}$, η_{ohmic}, $\eta_{conc,c}$, respectively. The equation's parameters are defined as follows: a_c and b_c are Tafel constant and slope, respectively, i_{loss} is the current density loss, R_{ohmic} is the area specific internal resistance of the cell, c_c is the concentration loss constant, and $i_{L,c}$ is the limiting current density. The parameters a_c, b_c, c_c, and $i_{L,c}$ correspond to the cathode electrode.

In this paper, the experimentally obtained *i-V* data of a 40-W fuel cell are modeled by estimating the parameters in the theoretical equation that describes the voltage output versus the current drawn, namely Eq. (2). The fitted parameters are a_c, b_c, R_{ohmic}, and c_c. Both i_{loss} and $i_{L,c}$ are measured experimentally. In addition, the exchange current density ($i_{0,c}$) and the transfer coefficient (α_c) for the oxygen reduction reaction are determined.

2. Methodology

The system used in this study is a Heliocentris hy-Expert™ Instructor fuel cell system. The system is based on a fuel cell stack with rated and maximum power outputs of 40 W and 50 W, respectively. The stack consists of 10 cells connected in series with a cell active surface area (A) of 25 cm^2. The membrane has a thickness of 27 μm and the electrodes are platinum loaded with 0.3 mg Pt/cm^2. The fuel cell stack is operated on pure hydrogen (99.999 vol%) and air without prior humidification. Hydrogen is supplied to the stack at around 1.6 bar and the flow rate is measured by a digital hydrogen flow meter. The hydrogen is supplied in a dead-end mode. Air is blown into the cells, in parallel, at atmospheric pressure by two fans attached to the cell stack. For each cell, the air is passed through parallel channels with individual inlets and outlets. The fans provide air for both the electrochemical reaction and for cooling. The two fans are either controlled by the user or by an internal controller. At full fan speed, the flow rate from both fans, is around 478 slm (standard liter per minute; STP). However, the fan can be run at selected percentages of the maximum fan speed. When the fan is controlled by the internal controller, the fan speed is set automatically according to the stack power output so that adequate cooling is ensured. Therefore, the more the current is drawn from the fuel cell stack, the more air is provided to the stack. In addition, during the automated fan operation, enough air is provided to the cells to minimize any concentration polarization between the flow channels and the electrode in the cathode side. It should be noticed that at any given current, increasing the fan speed – above the automatically set speed – does not increase the output fuel cell voltage. Therefore, it is concluded that the fuel cell does not experience noticeable concentration losses when the air flow rate is controlled by the internal controller. All the experiments are carried out at 40±1.5°C.

The value of the current loss, i_{loss}, is assumed to be related only to the hydrogen consumption/flow rate measured at open circuit. Therefore, i_{loss} is calculated by multiplying the hydrogen flow rate at open circuit by $2 \cdot F/A$. Furthermore, i_{loss} is assumed to be constant over the whole range of the drawn current density. The apparent limiting current density is obtained experimentally. The current at which the voltage drops rapidly, approaching zero, is designated to be the apparent limiting current density. The fuel cell efficiency is measure by the following equation: $\text{Efficiency} = (i \cdot V \cdot A)/(\dot{m} \cdot \text{HHV})_{H_2}$ (3), where $\dot{m}$ and HHV are the mass flow rate and the higher heating value of hydrogen, respectively. The exchange current density is calculated from Tafel equation parameters where $b = RT/\alpha nF$ and $a = -b \ln(i_0)$ (n is the number of electrons transferred in the reaction, F is Faraday constant, and R is the universal gas constant).

"Microsoft Office Excel 2007" is used for multiple linear regression. The Regression Analysis tool in Excel performs linear regression analysis by using the least squares method to fit a line through a set of data.

3. Results and Discussion

Fig. 1 shows the polarization curves of the fuel cell stack when operated at 40±1.5°C with two different air flow rates. The data are recorded for positive and negative load increments, and also for random load values. In the first set of experiments shown in Fig. 1, where the air flow rate is maintained constant at 2.87 slm, the fuel cell is deliberately operated under low air flow rate in order to study the concentration losses effect and to obtain the related parameters. The effects of the activation, ohmic, and concentration losses along with that of the current loss are apparent in the first set of experiments as shown in Fig. 1. In the second set of experiments, the air flow rate is manipulated by a controller that increases the flow rate as more current is drawn. This action insures that the fuel cell is operated in a region where the concentration losses are negligible. In other words, the stack is run under current densities much smaller than the limiting current density.

At low current densities (i.e. i < 0.02 A/cm^2), where the ohmic and concentration losses are insignificant, the fuel cell exhibits nearly similar performance, despite the difference in the air flow rates. This observation is expected since both sets of experiments are carried out at the same temperature. Operating the fuel cell at constant temperature results in similar reaction kinetics and, therefore, comparable rate of reactions, which in turn leads to similar activation losses. At larger current densities (i.e. i > 0.2 A/cm^2), however, the fuel cell performs better in case of the higher air flow rate, where the concentration losses are not pronounced.

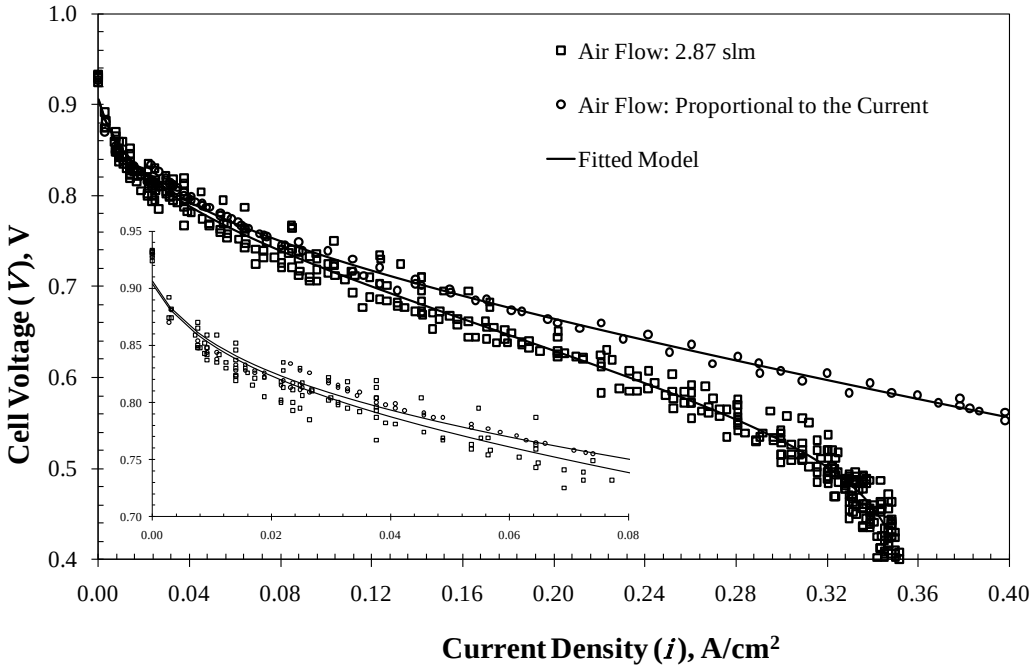

Figure 1 – The fuel cell polarization curves obtained for two different air flow rates at 40±1.5°C along with the fitted curves.

Nonlinear regression attempts to fit the data to Eq. 2 result in parameters with unrealistic values (e.g. R_{ohmic} = 0.01 Ω·cm^2). Therefore, it is decided to fit the data to the model (i.e. Eq. 2) using multiple linear regression analysis. In order to find the model parameters using multiple linear regression analysis, the value of the limiting current density has to be obtained first. This introduces a limitation to this data fitting method. Since the limiting current density is obtained by restricting the air flow to the cathode (in the first set of experiments only), the measured limiting current density is, therefore, related to the oxygen reduction reaction on the cathode and, hence, given the symbol $i_{L,c}$. The value of $i_{L,c}$ is found experimentally. The current at which the voltage drops rapidly – approaching zero – is designated to be the apparent limiting current density. Since the limiting current density is reduced by the current loss [1], the actual limiting current density ($i_{L,c}$ = 0.35947 A/cm^2) is obtained by adding

the current loss (i_{loss} = 0.00473 A/cm^2) to the apparent limiting current density (0.35474 A/cm^2) obtained from Fig. 1. The actual limiting current density is the maximum current density that can be drawn from the fuel cell in the absence of current losses.

For the given experimental condition, the thermodynamic voltage is estimated – using Nernst equation – to be 1.2121 V. In the multiple linear regression analysis, $V–E_{thermo}$ is considered the dependent variable whereas ln ($i+i_{loss}$), i, and ln [$i_{L,c}$/($i_{L,c}–(i+i_{loss})$)] are considered the independent variables. The analytical model (Eq. 2) is fitted to the data to obtain the model parameters. The regression results are listed in Table 1. For the case in which the air flow rate is proportional to the current generated and the concentration losses are not pronounced, the last term in Eq. 2 is cancelled and, therefore, only 3 parameters are fitted.

Table 1 – The measured, fitted, and the calculated polarization curve model parameters at 40±1.5°C for the two studied air flow rates.

Flow Rate	Measured Parameter	Fitted Parameters*					Calculated Parameters	
$\dot{V}_{air}$ (slm)	$i_{L,c}$ (A/cm^2)	a_c (V)	b_c (V)	R_{ohmic} (Ω.cm^2)	c_c (V)	R^2	α_c	$i_{0,c}$ (A/cm^2)
2.87	0.3595	0.534 ±0.017	0.0423 ±0.0044	0.4140 ±0.0631	0.0394 ±0.0037	0.988	0.1594	3.289×10^{-6}
i-dependent		0.536 ±0.011	0.0428 ±0.0029	0.3956 ±0.0269		0.994	0.1596	3.222×10^{-6}

*The numbers below the parameter values are the 95% confidence intervals. The Tafel constants are based on Tafel equation written in the natural logarithmic form.

By inspecting the values of the fitted parameters the following are observed. For the two cases, close values of the Tafel intercepts (a_c), Tafel slopes (b_c), and exchange current densities ($i_{0,c}$) are obtained confirming that the cathode kinetics are similar in the two cases. This is expected since the two sets of experiments are conducted at the same temperature. The kinetics related parameters, a_c, b_c, and $i_{0,c}$ are found to be around 0.5 V, 0.04 V, and 3×10^{-6}, respectively. The estimated exchange current densities are two orders of magnitude lower than what is considered a typical value by Larminie and Dicks [2] for a low temperature and ambient pressure H_2/air fuel cell. Nevertheless, a value of 1.0764×10^{-6} A/cm^2 at T = 25°C is reported in the literature [3]. The transfer coefficient (α_c), calculated from b_c, is also found to be almost the same in both cases – around 0.16. This is also to be expected since the obtained values of α_c are for the same reaction, i.e. the oxygen reduction reaction. Larminie and Dicks [2] consider the value of α_c to range from 0.1 to 0.5 in most circumstances. Furthermore, the fitted values of R_{ohmic} are also found to be similar – around 0.4 Ω·cm^2. A well-designed fuel cell would have R_{ohmic} in the range of 0.05–0.10 Ω.cm^2 [1], while values between 0.10–0.20 Ω.cm^2 are considered typical [4]. However, values as high as 0.24 Ω.cm^2 at 70°C [5] and even 0.363 Ω.cm^2 at 50°C [6] are reported for Nafion 115. Moreover, values between 0.26567 and 0.45108 Ω.cm^2 – obtained through nonlinear regression analysis – are reported for different types of gas diffusion layers of a single cell operated at 80°C and 1.5 bar using humidified H_2/air as reactants [7]. In our study, the membrane thickness is only 27 μm and, therefore, R_{ohmic} is supposed to be at the lower range. But, since neither the anode nor the cathode gasses are humidified, higher values of R_{ohmic} are obtained. The fitted value of c_c is found to be around 0.04 V in the case where mass transfer limitation is pronounced. The estimated value is found to be close to the value of c calculated from an equation derived theoretically by O'Hayre et al [1] that is: $c=(RT/nF)(1+1/\alpha)$ (4). In effect, the estimated value of c_c is expected to be even higher than the value calculated by Eq. 4, since the theoretically derived equation does not account for the accumulation of the products and inert gases, which are water and nitrogen, respectively, in our case.

The work presented here is been extended to cover more polarization curves in different air flow rates, more detailed work on the current loss, and the effect of temperature on fuel cell performance and the exchange current density. The extension of this work is to be published in the near future [8].

Since all the parameters in Eq. 2 are estimated, the voltage at any drawn current density can be readily predicted. Furthermore, the contribution of each of activation, ohmic, and concentration losses towards the total losses can be calculated individually. Fig. 2 shows the thermodynamic (ideal) cell voltage, the predicted cell voltage, and the voltage losses due to activation, ohmic, and concentration overpotentials for the 2.87 slm-air flow case.

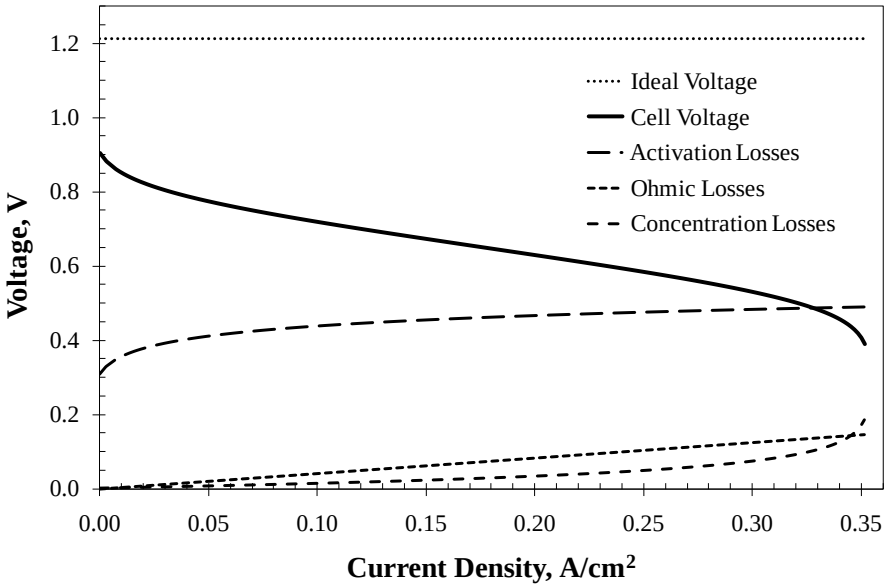

Figure 2 – The ideal cell voltage, the predicted cell voltage, and the voltage losses in the fuel cell when operated at 40±1.5°C with an air flow rate of 2.87 slm.

Fig. 2 shows that the activation losses are by far the largest losses experienced by the fuel cell at any current density. In the presented case, the concentration losses are the smallest losses experienced by the fuel cell except at current densities close to the limiting current density. It is also clear from Fig. 2 that at low current densities (i.e. $i < 0.02$ A/cm^2) the ohmic and concentration losses are indeed insignificant.

Furthermore, the analytical fitted model (Eq. 2) is used to predict the power density curve. The experimental and predicted power densities as a function of the current density is shown in Fig. 3 for the 2.87 slm-air flow rate case. Fig. 3 shows that the fuel cell power density increases with increasing current density until it reaches a maximum value after which it falls. The maximum power density is measured to be 0.17 W/cm^2 at 0.325 A/cm^2. The efficiency of the fuel cell is also depicted in the same figure which shows that the fuel cell efficiency reaches its maximum value at low loads. The maximum fuel cell stack efficiency, at the operated condition, is found to be 50% at 0.038 A/cm^2 or 0.031 W/cm^2.

4. Conclusions

In this paper, the *i-V* data obtained from a 40-watt fuel cell stack operated at 40°C with pure hydrogen and air are fitted to an analytical model, where the voltage output is a function of the thermodynamic voltage and activation, ohmic, and concentration losses. Although nonlinear regression analysis could provide mathematically acceptable fitted parameters, the obtained parameters' values are not reasonable in fuel cell operating terms. In contrast, linear regression results in better fit in terms of the

reasonability of the fitted parameters; however, i_L has to be estimated first, which introduces a limitation to this approach. Therefore, it's very important to refer to the typical values of the polarization curve parameters when performing regression. The thermodynamic voltage in the model is calculated based on Nernst equation. The Tafel intercept (a_c) and slope (b_c), the exchange current density ($i_{0,c}$), the cell resistance (R_{ohmic}), and the concentration loss constant (c_c) are found by multiple linear regression analysis and are estimated to be around 0.5 V, 40 mV, 3×10^{-6} A/cm^2, 0.4 Ω.cm^2, and 40 mV, respectively. The transfer coefficient of the oxygen reduction reaction, α_c, is found to be very small – around 0.16. Using the fitted parameters of the model, the proportions of the three fundamental types of losses are illustrated where it is shown that the activation losses are by far the largest losses experienced by the fuel cell at any current density. When operated at 40±1.5°C with an air flow rate of 2.87 slm, the maximum fuel cell efficiency and power density are measured to be 50% at 0.038 A/cm^2 and 0.17 W/cm^2 at 0.325 A/cm^2, respectively.

In conclusion, it is demonstrated in this study that a theoretically derived equation can reasonably model the polarization curve of a PEM fuel cell operating under steady-state.

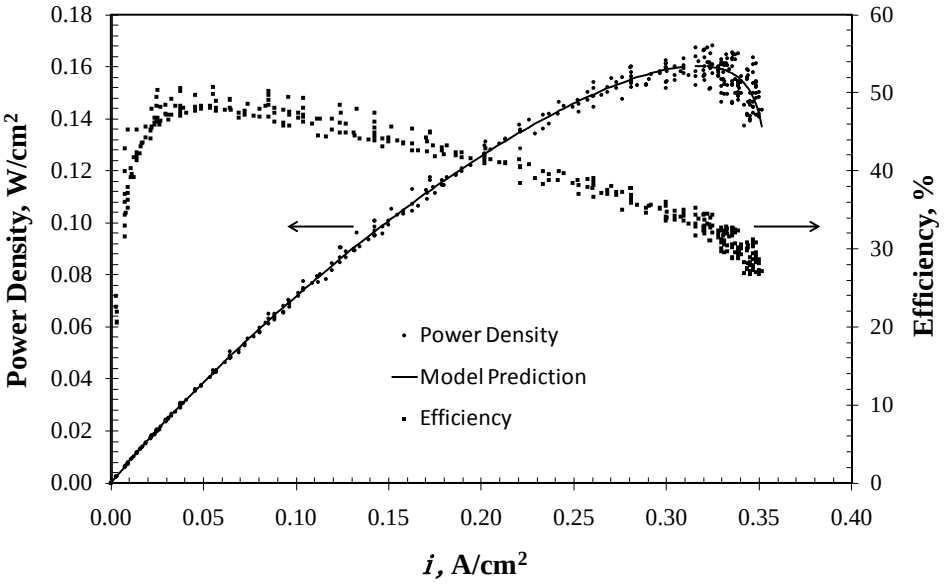

Figure 3 – Combined fuel cell power density and efficiency curves at 40±1.5°C with an air flow rate of 2.87 slm.

5. References

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