

Analytical method for determining the internal resistance and electrocatalyst utilization of fuel cells

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Abstract

Two analytical methods are developed that each allows one to determine: (i) the internal resistance of fuel cell electrodes, and (ii) the fraction of the electrocatalyst that is effectively used. To apply either method requires knowledge of the Tafel parameters for the electrocatalyst–electrolyte combination. In addition, one method — the maximum power method — requires that the potential and current of a fuel cell be measured when the cell is operating under steady-state conditions and at maximum power. Thus, its application is limited to fuel cells that are not damaged by operating at these conditions. The second method is approximate, but it does not require that the voltage and current be measured at the maximum power condition. To apply the second method — approximate maximum power method — requires the measurement of the fuel cell potential and slope of the potential–current relation of the fuel cell at a current that is less than the current corresponding to the maximum power condition. Using data available from the literature, the two techniques are used to evaluate these characteristics for a KOH fuel cell. They are also used to predict the voltage–current relation for the fuel cell. The results are found to be in close agreement with the reported measurements over a range of currents. The range is larger for the ‘maximum power method’ than for the ‘approximate maximum power method’.

Keywords: Fuel cells; Internal resistance; Electrocatalyst utilization

1. Introduction

An analytical method for predicting fuel cell performance can play an important role in assessing the effect of different parameters [1–5]. One of the difficulties that arises is that of establishing the values of certain ‘hybrid’ parameters. Such parameters depend on material properties, manufacturing techniques, and on the fuel cell design [6]. In general, the parameters describing fuel cell performance may be divided into three groups [7]: (i) those that depend on the properties of the materials chosen for fuel cell construction, such as the electrolyte–electrocatalyst combination, the resistivity of the electrolyte, and the resistivity of the current collector; (ii) those that depend on the fuel cell design decisions and manufacturing techniques (e.g., the electrode structure, and the amount of catalyst used in the electrodes), and (iii) the operating parameters (e.g., temperature, electrolyte concentration, pressures of the gases). If the value of a hybrid parameter is particularly important and the values of the material properties are known, then the design parameters of the fuel cell

would be chosen so as to give the hybrid parameter its optimum value.

An example of such a parameter is the internal resistance. This parameter is defined as the sum of the resistances between the poles of the load measured through the electrolyte. Thus, this resistance would include the resistance of the electrodes that arises from the transfer of charge from the electrocatalyst within the electrode to the poles of the external load. The value of the internal resistance depends on the resistivity of several of the materials that are chosen to construct the fuel cell and also on the design of the fuel cell and the methods by which the electrodes are manufactured. Since the fuel cell is inherently a low-voltage device, significant currents must be drawn to generate useful amounts of power. Therefore, significant losses can be present in a fuel cell due to its internal resistance.

Another hybrid parameter that is particularly important in determining fuel cell performance is the fraction of the electrocatalyst placed in the electrodes during the manufacturing process that is fully utilized during the operation of the fuel cell. When porous electrodes are manufactured for use with wet electrolytes, the electrocatalyst is usually dispersed as small crystallites on a carbon substrate, and the catalyzed

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carbon is placed in the interior of the electrode near the current collector. If once the fuel cell is assembled, the electrolyte penetrates the electrocatalyst layer of the electrode, the electrocatalyst can be effectively 'drowned' [8]: whereas, if the electrolyte does not reach the electrocatalyst layer within the electrode, the electrocatalyst is also ineffective. Thus, the effectiveness of the electrocatalyst depends on both the properties of the electrocatalyst–electrolyte combination and on the manufacturing of the electrodes. This parameter, like the internal resistance can only be assessed once the electrodes have been assembled into a fuel cell and operated to produce power.

Herein we propose a method to determine both the internal resistance of the electrodes and the fraction of the electrocatalyst that is used effectively in the operation of a fuel cell. The total capacity of an electrocatalyst can be characterized in terms of its Tafel parameters (i.e., its equilibrium exchange current and Tafel slope), and these material properties can be measured independently of the operation of the fuel cell, for example, with a rotating disk electrode. We find that if the Tafel parameters are known for the electrocatalyst, both the internal resistance and the fraction of the electrocatalyst being used effectively can be determined by measuring both the voltage and the current at which the fuel cell provides the maximum power to an external load.

2. Internal resistance and electrocatalyst utilization obtained from maximum power method

Consider a fuel cell and suppose that it is operating in steady state. To describe its performance, we first separate the ohmic effects from the other polarizations. If the internal resistance is denoted as R_i , the resistance of the electrolyte as R_e , and the remainder of the internal resistance as R_c , then

$$R_i = R_c + R_e \quad (1)$$

Suppose V_e is the potential drop across the cell under open-circuit conditions and the sum of the kinetic and mass-transfer polarizations is denoted as V_p . Since the value of this polarization depends on the magnitude of the current, I , the potential drop across the external load, V , may be expressed as

$$V = V_e - V_p(I) - IR_i \quad (2)$$

It may also be written in terms of the electrical current and the resistance of the load

$$V = IR_l \quad (3)$$

After equating the two expressions for the potential drop across the external load and solving for the external load, one finds

$$R_l = \frac{V_e - V_p(I) - IR_i}{I} \quad (4)$$

The power provided to an external load by the cell, P , may be written as $I^2 R_l$ or

$$P = I(V_e - V_p(I) - IR_i) \quad (5)$$

Before the power can be optimized, it is necessary to determine the polarizations as a function of current. We shall make use of the Butler–Volmer approximation for this purpose and assume that the high-current approximation is valid, but that the design of the electrode is such that even in this current regime, there are no mass-transfer limitations. Under these conditions only the kinetic polarizations are important. The kinetic polarizations may be written in terms of the Tafel slope of the electrolyte–electrocatalyst combination for hydrogen oxidation, g_a and oxygen reduction, g_c , and the corresponding equilibrium exchange current densities i_{0a} and i_{0c} for the anode and cathode, respectively. If the total surface area of the electrocatalyst being used in the anode and in the cathode is denoted A , and if the fraction of this material that is used effectively is e_f , then the kinetic polarization may be written

$$V_p(I) = g_a \ln\left(\frac{I}{e_f A_i i_{0a}}\right) + g_c \ln\left(\frac{I}{e_f A_i i_{0c}}\right) \quad (6)$$

Eqs. (4)–(6) are the equations that govern the performance of the fuel cell. To determine the expression for the electrocatalyst utilization factor, e_f , and the internal resistance of the fuel cell, the conditions under which the fuel cell provides the maximum power are identified.

If I_m denotes the current at maximum power, then the differential of $P(I)$ must vanish for I equal I_m . After substituting Eq. (6) into Eq. (5) and differentiating with respect to I , one finds for I equal I_m

$$-g_a - g_c - 2I_m R_i + V_e - g_a \ln\left(\frac{I_m}{e_f A_i i_{0a}}\right) - g_c \ln\left(\frac{I_m}{e_f A_i i_{0c}}\right) = 0 \quad (7)$$

The latter relation may be solved to determine an expression for the internal resistance of the fuel cell

$$R_i = \frac{\left[-g_a - g_c + V_e - g_a \ln\left(\frac{I_m}{e_f A_i i_{0a}}\right) - g_c \ln\left(\frac{I_m}{e_f A_i i_{0c}}\right)\right]}{2I_m} \quad (8)$$

However, this expression still contains the unknown e_f .

The expression for the polarization at maximum power may be obtained from Eq. (6)

$$V_p(I_m) = g_a \ln\left(\frac{I_m}{e_f A_i i_{0a}}\right) + g_c \ln\left(\frac{I_m}{e_f A_i i_{0c}}\right) \quad (9)$$

and the expression for the load resistance at maximum power, R_{lm} , may be obtained by evaluating Eq. (4) at the maximum power condition and substituting Eqs. (8) and (9). After simplifying, one finds

$$R_{lm} = \frac{1}{2I_m} \left(g_a + g_c - g_a \ln\left(\frac{I_m}{e_f A_i i_{0a}}\right) - g_c \ln\left(\frac{I_m}{e_f A_i i_{0c}}\right) \right) \quad (10)$$

The voltage drop across the load at maximum current V_m is given by the product $I_m R_{im}$ and from Eq. (10), one finds

$$V_m = \frac{1}{2} \left[g_a + g_c - g_a \ln \left(\frac{I_m}{e_f A_i i_{0a}} \right) - g_c \ln \left(\frac{I_m}{e_f A_i i_{0c}} \right) \right] \quad (11)$$

Since the voltage at maximum power can be measured directly, but the effective surface area of the electrocatalyst cannot, Eq. (11) will be used to determine the expression for e_f

$$e_f = \exp \left[\frac{2V_m - V_e - g_a - g_c + g_a \ln \left(\frac{I_m}{A_i i_{0a}} \right) + g_c \ln \left(\frac{I_m}{A_i i_{0c}} \right)}{(g_a + g_c)} \right] \quad (12)$$

If Eq. (12) is substituted into Eq. (8) and the result simplified, one finds

$$R_i = \frac{V_m - g_a - g_c}{I_m} \quad (13)$$

These latter two equations may be used to obtain the expression for the voltage and power provided by the cell in terms of directly measurable properties of the cell. By combining Eqs. (2), (6), (12) and (13), one finds that the voltage provided by a cell at a current I

$$V = (2V_m - g_a - g_c) + \left(\frac{I}{I_m} \right) (g_a + g_c - V_m) + g_a \ln \left(\frac{I_m}{I} \right) + g_c \ln \left(\frac{I_m}{I} \right) \quad (14)$$

The expression for the power provided to an external load can be obtained simply by multiplying Eq. (14) by I

$$P = I \left(2V_m - g_a - g_c + (g_a + g_c) \ln \left(\frac{I_m}{I} \right) \right) + \left(\frac{I^2}{I_m} \right) (g_a + g_c - V_m) \quad (15)$$

Eqs. (12) and (13) give the expressions for the fraction of the electrocatalyst that is fully utilized, e_f , and for the internal resistance, R_i , of the fuel cell in terms of: (i) the material properties of hydrogen and oxygen reaction and of the electrocatalyst–electrolyte interface (i.e., V_e and the Tafel parameters); (ii) the design parameter A_i , the area of the electrocatalyst that is placed in the electrodes, and (iii) the properties of the fuel cell that can be measured directly after the fuel cell has been manufactured and put under test, I_m and V_m . The determination of e_f and R_i from Eqs. (12) and (13) is referred to as the ‘maximum power method’.

3. Approximate maximum power method

As indicated in the previous section, the performance characteristic of a fuel cell can be completely determined from

material properties, design parameters and the measurement of the voltage and current at maximum power. The design parameters can be chosen and the material properties determined independently of the operation of the fuel cell, but the voltage and current at maximum power can only be determined by operating the fuel cell at maximum power. Operating at this condition until it comes into steady state can overheat or damage the fuel cell. However, a system of approximate equations can be developed to determine the characteristics of the fuel cell that do not require the current and voltage at maximum power to be measured. This method for determining the fuel cell parameter will be referred to as the ‘approximate maximum power method’.

For this purpose, we suppose the current, voltage and slope of the V – I relation to be measured at a condition where the current is less than that corresponding to the maximum power condition. These measurements will be denoted as I_0 , V_0 and σ_0 .

If $V(I)$ is expanded about I_m in a power series, one finds

$$V(I) = V_m + V_m \left(\frac{I_m - I}{I_m} \right) + \left(\frac{g_a + g_c}{2} \right) \left(\frac{I_m - I}{I_m} \right)^2 + O \left[\left(\frac{I_m - I}{I_m} \right)^3 \right] \quad (16)$$

From Eq. (16), one finds that if

$$\left(\frac{I_m - I}{I_m V_m} \right) \ll \left(\frac{2}{g_a + g_c} \right) \quad (17)$$

then the third term in Eq. (16) is small compared with the second. Thus, we suppose the condition listed in Eq. (17) is met and adopt as an approximate expression for the cell voltage the first two terms of Eq. (16)

$$V_a = V_m \left(1 + \frac{I_m - I}{I_m} \right) \quad (18)$$

If the approximate voltage V_a and (dV_a/dI) are now required to have the same values as those measured at I_0 , one finds two linear Eqs. from Eq. (18). These may be solved simultaneously to obtain the expressions for I_m and V_m in terms of the measured values of I_0 , V_0 and σ_0

$$I_m = \frac{I_0 \sigma_0 - V_0}{2 \sigma_0} \quad (19)$$

$$V_m = \frac{V_0 - I_0 \sigma_0}{2} \quad (20)$$

These expressions for I_m and V_m may be substituted into Eqs. (12)–(15) to obtain the approximate expressions for the fraction of the electrocatalyst that is fully utilized, for the internal resistance of the fuel cell, for cell potential V_a and for the approximate power

$$e_{ra} = \exp \left[\frac{V_0 - V_c - I_0 \sigma_0 - g_a - g_c + g_a \ln \left[\frac{\sigma_0 I_0 - V_0}{2 \sigma_0 A_i i_{0a}} \right] + g_c \ln \left[\frac{\sigma_0 I_0 - V_0}{2 \sigma_0 A_i i_{0c}} \right]}{g_a + g_c} \right] \quad (21)$$

$$R_{ia} = \frac{\sigma_0 (2g_a + 2g_c + I_0 \sigma_0 - V_0)}{V_0 - I_0 \sigma_0} \quad (22)$$

$$V_a = V_0 + \sigma_0 (I - I_0) \quad (23)$$

$$P_a = I^2 \sigma_0 + \frac{I^2 (2g_a \sigma_0 + 2g_c \sigma_0)}{(I_0 \sigma_0 - V_0)} + I \left(-g_a - g_c + \frac{(-I_0 \sigma_0 + V_0)^2}{I_0 \sigma_0 - V_0} \right) + (I g_a + I g_c) \ln \left[\frac{I_0 \sigma_0 - V_0}{2 I \sigma_0} \right] \quad (24)$$

Although the criterion given in Eq. (17) cannot be applied without knowing the voltage and current at maximum power, Eqs. (21) and (22) can be applied at a series of successively higher currents until the change from one current to the next higher current gives rise to a negligible calculated change in e_f and in R_i . This method of determining the values of e_f and R_i from Eqs. (21) and (22) is referred to as the 'approximate maximum power method'.

4. Application of the maximum power and approximate maximum power methods

The values of the Tafel parameters for O_2 -Pt-KOH and H_2 -Pt-KOH have been reported in Refs. [9,10], respectively. The values are listed in Table 1. Also in Ref. [10], the measured performance of KOH fuel cells using Pt as the electrocatalyst is presented. For one of the fuel cells that they studied, the measurements of the voltage as a function of current were presented. Their data are shown as the solid dots in Fig. 1, and the measurements of cell voltage and current at maximum power are listed in Table 2.

The values of the parameters necessary to apply the 'maximum power method' are listed in Table 1. From Eq. (14) and the values of the parameters listed there, one may calculate the voltage as a function of current. The result is shown as the solid curve in Fig. 1 (a) where the calculations may be

Table 1
Tafel parameters for H_2 -Pt-KOH and O_2 -Pt-KOH

Temperature °C	KOH (N)	g_{0a} (V)	i_{0a} (mA/cm ²)	g_{0c} (V)	i_{0c} (nA/cm ²)
45	6	0.043	0.259	0.027	2.15

compared with the measurements. As may be seen there, very close agreement is obtained except at the smaller currents. Under open-circuit conditions, the fuel cell did not reach the theoretical value of 1.23 V for the H_2 - O_2 reaction. Although it is a common observation that the measured open-circuit potential of a fuel cell does not reach the theoretical value, the reason is not understood. It is often attributed to 'parasitic' currents.

Since the high-current approximation was used to obtain the expression for the kinetic polarization, V_p , the theoretical expression for the voltage as a function of current is not

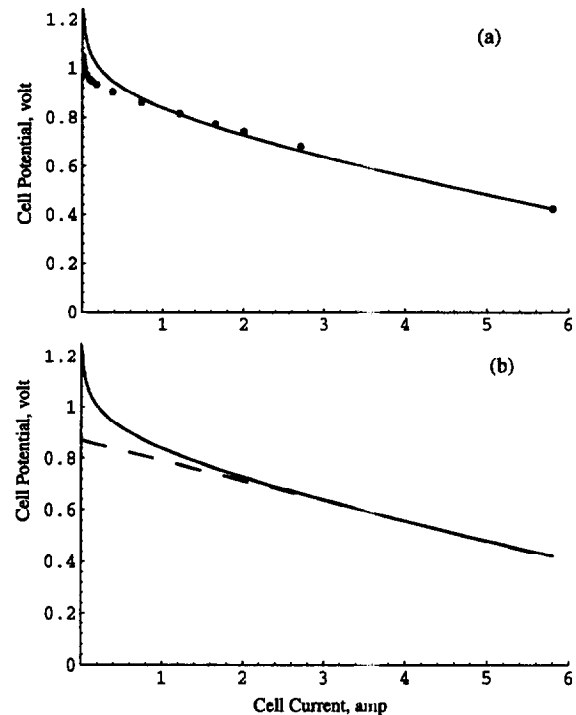


Fig. 1. (a) Comparison of measured and predicted fuel cell potential as a function of current. The solid dots are measurements presented in Ref. [10] and the solid line is that predicted from the 'maximum power method'. (b) Comparison of the predicted voltage-current relation (solid line) obtained from the 'maximum power method' with that obtained from the 'approximate maximum power method' (dashed line). The measurements are listed in Tables 1 and 2 on which the two calculations are based.

Table 2
Measured characteristics of a fuel cell reported in Ref. [10]

Temperature (°C)	45
Cross-sectional area of electrodes (cm ²)	64
Electrode separation (cm)	0.18
Total area of Pt in each electrode, A_i (cm ²)	1.7×10^4
Cell voltage at maximum power, V_m (V)	0.421
Cell current at maximum power, I_m (A)	5.8
Cell voltage at current of 4 A, V_0 (V)	0.556
Measured slope of V - I curve at current of 4 A σ_0 (V/A)	-0.0782
Total internal resistance, R_i , predicted from V_m , I_m Ω	0.060
Total internal resistance, R_{ia} , predicted from I_0 , V_0 , σ_0 Ω	0.065
Percentage electrocatalyst used, predicted from V_m , I_m (%)	15.4
Percentage electrocatalyst used, predicted from I_0 , V_0 , σ_0 (%)	21.4

accurate at small currents. Since the complete expression for the voltage as a function of current is available, this limit may be explored. One finds that at a current of 0.01 A, the predicted potential is 1.23 V and the potential is predicted to be larger at smaller currents. Since the theoretical maximum of the cell potential is also 1.23 V, one would expect that the cell potential predicted from Eq. (14) would only be valid at cell currents that were large compared to 0.01 A. As may be seen in Fig. 1(a), the predicted cell potential approaches the measurements as the current increases and coincides with the measurements for currents greater than approximately 0.8 A.

The values of the parameters needed to apply the 'approximate maximum power method' are also listed in Table 2. The value of the current at which the slope was measured was 4 A. The slope at this current coincides with that obtained from the 'maximum power method' and, as may be seen from Fig. 1(a) and (b), they both coincide with the data. In Fig. 1(b), the potential predicted from the 'maximum power method' (Eq. (14)) may be compared with the calculation obtained from the 'approximate maximum power method' (V_a , Eq. (18)). The value of V_a is shown in Fig. 1(b) as a dashed line.

The current used in the 'approximate maximum power method' was approximately 70% of I_m (see Table 2). The 'approximate power method' insures that V_a has the same

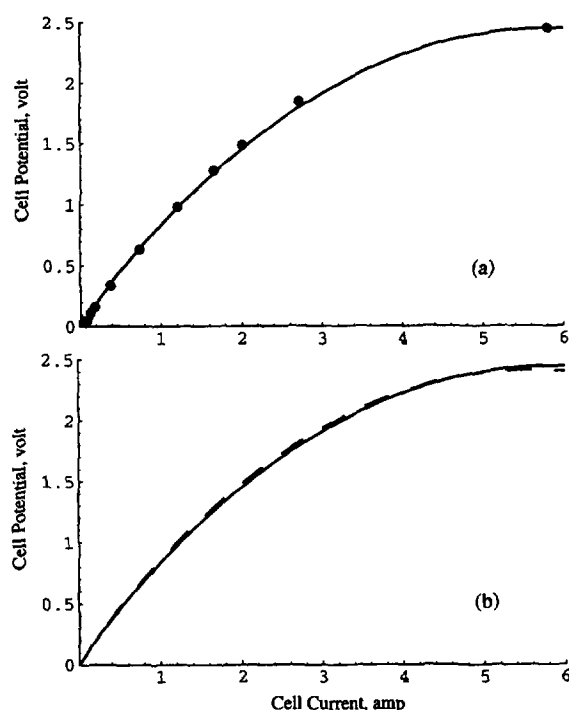


Fig. 2. (a) Comparison of the measured and predicted power provided by a fuel cell. The solid dots are the measurements reported in Ref. [10]. The solid line is the predicted fuel cell power that is obtained from the 'maximum power method'. (b) Comparison of the predicted power-current relation obtained from the 'maximum power method' (solid line) with that obtained from the 'approximate maximum power method' (dashed line). The measurements of the voltage and slope of the V - I relation at a current of 4 A are listed in Tables 1 and 2.

value as V when I is equal I_m . As seen in Fig. 1(b), the values of the cell potential that is obtained from the 'approximate maximum power method' coincides with the values obtained from the 'maximum power method' down to currents of approximately 3 A, or 34% of the current at maximum power, and at currents above 3 A both methods give predictions that correspond with the data.

The 'maximum power method' may be used in Eq. (15) to predict the cell power as a function of cell current. The results obtained are shown in Fig. 2(a) where it can be compared with measurements reported in Ref. [10]. As seen in this figure, the predictions are in close agreement with the measurements.

Using the values of the parameters listed in Tables 1 and 2, the 'approximate maximum power method' (Eq. (24)) may be used to calculate the power as a function of current. The result is shown in Fig. 2(b) as the dashed line. The solid line in this figure was calculated from the 'maximum power method'. As may be seen there, the two procedures almost completely coincide. Since the cell power calculated from Eq. (15) is shown in Fig. 2(a) to be in agreement with the measured power, the 'approximate maximum power method' is seen to lead to an accurate calculation of the power as a function of current.

The calculated power from the 'approximate maximum power method' is actually more accurate at low currents than might be expected from the approximate calculation of the cell potential at low currents. However, it should be recalled that in order to calculate the cell power, the cell potential was multiplied by the cell current (see Eq. (5)), and even though the expression for the cell potential contains a term $\ln I$ which is not defined in the limit of I going to zero, the expression for the power contains the term $I \ln I$ and in the limit I going to zero, the term $I \ln I$ goes to zero. Thus, as the current approaches zero, the expression for the power obtained from the 'approximate maximum power method' approaches the correct limit of zero.

The internal resistance of the fuel cell reported in Ref. [10], may be calculated from both methods, (i.e. from Eqs. (13) and (22)). The data required for both calculations are listed in Tables 1 and 2. The values of R_i and R_{ia} for the fuel cell reported in Ref. [10] are listed in Table 2. As may be seen there, both calculation procedures give approximately the same value. They differ by 8%.

The two calculation procedures may also be used to calculate the fraction of the electrocatalyst used. The values for both e_f and e_{fa} obtained from Eqs. (12) and (21) are listed in Table 2. They differ by 6%.

In Ref. [10], the calculated value of R_i is compared with the value measured by the current interrupt method, and as discussed there close agreement is found. The value of e_f obtained by the procedure described herein is more important that it cannot be measured directly by another technique. Thus, the basis for the accuracy of its calculation must be the accuracy with which the equations used to calculate e_f can be used to calculate the quantities such as the cell potential and

cell power. For the fuel cell constructed and tested by the methods described in Ref. [10], this accuracy appears from the results shown in Figs. 1 and 2 to be at least 'good'.

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