

ARTICLE

Expressions for Entropy Production Rate of Fuel Cells

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On the basis of a general model of fuel cells, the entropy production rates of a fuel cell system under different conditions are derived by using theories of electrochemistry and thermodynamics. In order to analyze the influence of the irreversible losses existing in an actual fuel cell, the equivalent circuit of the fuel cell is introduced, so that the irreversible factor of the fuel cell may be determined directly as a function of the internal, leak and load resistances. Moreover, the maximum power output and efficiency of the fuel cell are calculated, the optimal operation of the fuel cell is discussed, and the matching condition of the load resistance is determined.

Key words: Fuel cell, Irreversible loss, Entropy production rate, Optimal analysis, Matching condition

I. INTRODUCTION

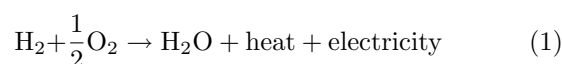
The fuel cell is a thermodynamic system which generates power by a direct conversion of the chemical energy in fuel into electrical power through electrochemical reactions. It is being developed for future power generating devices for transportation, portable electronic and local applications, on account of its very low negative effects and higher conversion efficiency [1,2]. Over the past few years, many researchers have devoted themselves to the parametric studies of the irreversible fuel cells through experiments [3-5], theoretical analysis [6-10] and numerical simulations [11-13]. For example, Yuan and Yan derived different expressions of the efficiency for the same fuel cell system [6-8]. Aloui *et al.* and Qi *et al.* simply analyzed the performance of the fuel cell, based on an assumption of no leakage resistance [14,15]. But some problems in fuel cells have not been solved, and consequently, they are worthy of further discussion.

The main aim of this work is not only to solve the problems in Refs.[6-8,14,15], but also to derive a concrete expression of the irreversible factor of the fuel cell by introducing the equivalent circuit of the fuel cell system. Moreover, the influence of the internal and leak resistances on the performance of the fuel cell is discussed. The maximum power output and efficiency of the fuel cell and the corresponding parameters are calculated. The optimally matching condition of the load resistance is determined.

II. THE GENERAL DESCRIPTION OF FUEL CELLS

Fuel cells are electrochemical devices that rely on the transport of reactants (such as oxygen from air in the

cathode and hydrogen from the fuel in the anode) and products (water vapor if pure hydrogen is used as the fuel) [1,2]. Figure 1 schematically shows a typical model of fuel cells, which consists of two electrodes with a thin layer of catalyst in contact with a membrane separating gas supply chambers. Hydrogen gas from any source such as biomass is fed through a channel from the anode. Similarly, oxygen enters the fuel cell from the cathode. Hydrogen and oxygen have a strong chemical affinity and because the membrane separating the two gases allows only hydrogen ions to pass through it, hydrogen will be divided into hydrogen ions and electrons. While hydrogen ions take the shortest path, i.e. through the membrane, electrons travel all the way round the external circuit creating useful current. The hydrogen ions combine with oxygen to produce water and heat as a by-product. The overall reaction is exothermic and can be written as



The fuel cell operates continuously producing useful current as long as the hydrogen and oxygen are sup-

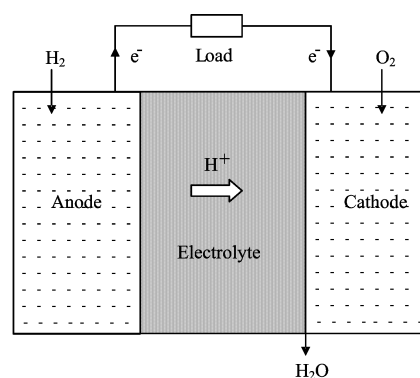


FIG. 1 The simple schematic diagram of a fuel cell.

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plied.

From the conservation equation of species in the chemical reaction, we have [6-8]

$$\frac{dn_i}{dt} = \frac{d_e n_i}{dt} \pm \nu_i v = 0 \quad (2)$$

where v is the velocity of the electrochemical reaction, n_i is the molar number of species i , $d_e n_i/dt$ is the exchange molar flow rate of species i between the fuel cell and the surrounding, and ν_i is the stoichiometric coefficient for species i in the reaction.

According to Faraday's law, the relationship between the velocity of the electrochemical reaction and the current can be described by the following equation [16,17]

$$v = \frac{I}{nF} = \frac{iA}{nF} \quad (3)$$

where n is the number of electrons participating in the reaction, F is Faraday's constant, i is the current density, and A is the surface area of electrode plate. Substituting Eq.(2) into Eq.(3), we have

$$\begin{aligned} \Delta \dot{H} &= \sum_j \left| \frac{d_e n_j}{dt} \right| h_j - \sum_i \left| \frac{d_e n_i}{dt} \right| h_i \\ &= \frac{iA}{nF} \Delta h \end{aligned} \quad (4)$$

where $\Delta h = \sum_j \nu_j h_j - \sum_i \nu_i h_i$, h is the molar enthalpy,

subscript j represents the j th product, and subscript i represents the i th reactant.

Since the Gibbs free energy change of an electrochemical reaction is a measure of the maximum electrical energy obtainable as work from the reaction [18], the maximum (reversible) power output generated by the reaction in the fuel cell can be determined by [1]

$$\begin{aligned} P_{\text{rev}} &= -\Delta \dot{G} \\ &= - \left(\sum_j \left| \frac{d_e n_j}{dt} \right| \mu_j - \sum_i \left| \frac{d_e n_i}{dt} \right| \mu_i \right) \\ &= - \frac{iA}{nF} \Delta g \end{aligned} \quad (5)$$

where $\Delta g = \sum_j \nu_j \mu_j - \sum_i \nu_i \mu_i$, and μ is the chemical potential.

III. EXPRESSIONS OF THE ENTROPY PRODUCTION RATE

Considering the electrochemical reaction of hydrogen and oxygen proceeding at temperature T in a fuel cell, the total energy released corresponds to the enthalpy change of the reaction, i.e., $-\Delta H$. When the fuel cell

system is completely irreversible, there is no power output and all the energy released by the electrochemical reaction will become heat and be released to the environment. In such a case, the total entropy production rate can be expressed as

$$\begin{aligned} \sigma_T &= -\frac{\Delta \dot{H}}{T} + (-\Delta \dot{H}) \left(\frac{1}{T_0} - \frac{1}{T} \right) \\ &= -\frac{\Delta \dot{H}}{T_0} \end{aligned} \quad (6)$$

where T_0 is the environment temperature. The basic thermodynamic relationship is

$$-\Delta H = -\Delta G - T\Delta S \quad (7)$$

It is seen that even in a reversible electrochemical reaction, the total energy, $-\Delta H$, is always divided into two parts: $-\Delta G$ and $-T\Delta S$, where $-T\Delta S$, which cannot be converted to electrical energy, is released as heat. When there is no load, i.e., the case of short or open circuit, the Gibbs free energy change, $-\Delta G$, will completely become heat and be released to the environment. In general, a part of the Gibbs free energy change, $-(1-\gamma)\Delta G$, is converted to electrical energy and transferred to the load, and the other part, $-\gamma\Delta G$, is released as heat, where γ indicates the irreversible factor in the fuel cell and its range is $0 \leq \gamma \leq 1$. Thus, in a practical fuel cell system, the total entropy production rate can be expressed as

$$\begin{aligned} \sigma_{T1} &= \sigma_1 + \sigma_2 \\ &= -\frac{\gamma \Delta \dot{G}}{T} - \Delta \dot{S} + (-\gamma \Delta \dot{G} - T\Delta \dot{S}) \left(\frac{1}{T_0} - \frac{1}{T} \right) \\ &= -\frac{\gamma \Delta \dot{G} + T\Delta \dot{S}}{T_0} \end{aligned} \quad (8)$$

when $\gamma=1$, Eq.(8) is identical with Eq.(6) and the fuel cell is completely irreversible. It is worthwhile to note that when $\gamma=0$, the total entropy production rate in the fuel cell system is not equal to zero even in the case of $T=T_0$. Using Eq.(8), one can easily derive the power output of the fuel cell as

$$\begin{aligned} P &= -\Delta \dot{H} - T_0 \sigma_{T1} \\ &= -(1-\gamma)\Delta \dot{G} \end{aligned} \quad (9)$$

It is very significant to note that Eq.(9) may be directly derived from the concept of availability [19] for finite-time processes [20,21]. The availability A provides a general expression for the maximum extractable work when a prepared system is allowed to undergo a transformation from its initial state to a designated final state. In a finite time process, it may be defined as [19]

$$-\Delta A = A(t_i) - A(t_f) - T_0 \int_{t_i}^{t_f} \sigma dt \quad (10)$$

where the change of availability $-\Delta A$ is taken between the initial time t_i and the final time t_f and σ is the entropy production rate of the fuel cell system and environment together. When $\sigma=0$ [6-8],

$$A(t_i) - A(t_f) = W_{\text{rev}} = -\Delta G \quad (11)$$

When the Gibbs free energy change, $-\Delta G$, completely becomes heat and is released to the environment, we have $\sigma = -\Delta\dot{G}/T_0$ and $\Delta A=0$. This shows clearly that in such a description, the entropy production rate does not include that produced by the electrochemical reaction, i.e., $\left[-\Delta\dot{S} - T\Delta\dot{S}\left(\frac{1}{T_0} - \frac{1}{T}\right)\right]$. In general, the entropy production rate and power output of the fuel cell system may be, respectively, expressed as

$$\begin{aligned} \sigma &= -\frac{\gamma\Delta\dot{G}}{T} + (-\gamma\Delta\dot{G})\left(\frac{1}{T_0} - \frac{1}{T}\right) \\ &= -\frac{\gamma\Delta\dot{G}}{T_0} \end{aligned} \quad (12)$$

$$\begin{aligned} P &= -\Delta\dot{G} - T_0\sigma \\ &= -(1-\gamma)\Delta\dot{G} \end{aligned} \quad (13)$$

Obviously, in the two different descriptions mentioned above, expressions of the entropy production rate of the fuel cell are different from each other, but the same power output is obtained. However, the authors in Refs.[6-8] confused the two different descriptions, and consequently, could not derive the correct results.

Using Eq.(9) or Eq.(13), one can derive the efficiency of the fuel cell as

$$\begin{aligned} \eta &= \frac{P}{-\Delta\dot{H}} \\ &= \frac{-(1-\gamma)\Delta\dot{G}}{-\Delta\dot{H}} \\ &= \frac{(1-\gamma)\Delta g}{\Delta h} \\ &= (1-\gamma)\eta_r \end{aligned} \quad (14)$$

where $\eta_r = \Delta g/\Delta h$ is the efficiency of a reversible fuel cell [22]. It is clearly seen from Eq.(14) that one may obtain the efficiency of a reversible fuel cell only when $\gamma=0$

IV. THE EQUIVALENT CIRCUIT OF THE FUEL CELL AND THE CONCRETE EXPRESSION OF γ

In order to further investigate the influence of irreversibility of the fuel cell, one may introduce an equivalent circuit of the fuel cell, as shown in Fig.2, where E is the open circuit potential without considering the leak resistance, V is the terminal voltage, R_I is the internal resistance, R_L is the leak resistance, R is the load resistance, and I_T , I_L , and I are the total, leak, and

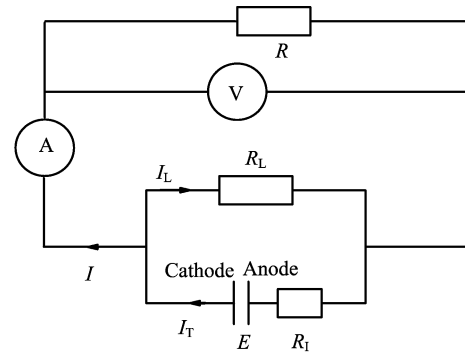


FIG. 2 The equivalent circuit of the fuel cell.

load electric currents, respectively. In general, when the leak resistance is not considered, the fuel cell achieves its maximum reversible voltage in the case of no current required by the external load. The reversible cell voltage is also the equilibrium cell potential obtained at thermodynamic reversible condition, which is given by the following equation

$$E = -\frac{\Delta g}{nF} \quad (15)$$

When the fuel cell begins to supply the electric current to an external load, its output voltage is always less than the reversible cell voltage because of some voltage drops across the cell caused by irreversible losses. Multiple phenomena contribute to irreversible losses in an actual fuel cell. The losses include three main sources: activation overpotential, V_{act} , ohmic overpotential, V_{ohm} , and concentration overpotential, V_{conc} [23-26], and consequently, it is reasonable to consider the equivalent activation resistance, R_{act} , equivalent ohmic resistance, R_{ohm} , and equivalent concentration resistance, R_{conc} , which are related with the three overpotentials, respectively [27-30]. Thus, the total equivalent internal resistance of the fuel cell R_I consists of these resistances, i.e.,

$$R_I = R_{\text{act}} + R_{\text{conc}} + R_{\text{ohm}} \quad (16)$$

According to Fig.2, one can obtain the following relations:

$$\frac{RR_L/(R+R_L)}{R_I+RR_L/(R+R_L)} = \frac{V}{E} \quad (17)$$

$$\begin{aligned} P &= \frac{V^2}{R} \\ &= \frac{1}{R} \left[\frac{RR_L/(R+R_L)}{R_I+RR_L/(R+R_L)} E \right]^2 \\ &= \frac{RE^2}{(R_I+R+RR_L/R_L)^2} \end{aligned} \quad (18)$$

From Eq.(5), Eq.(9), and Eq.(15) and Fig.2, one can

obtain

$$P = (1 - \gamma)I_T E = \frac{(1 - \gamma)E^2}{R_I + RR_L/(R + R_L)} \quad (19)$$

Comparing Eq.(19) with Eq.(18) yields

$$\gamma = 1 - \frac{1}{(1/R + 1/R_L)[R_I + R(1 + R_I/R_L)]} \leq 1 \quad (20)$$

and consequently, Eq.(12) may be expressed as

$$\sigma = \left\{ 1 - \frac{1}{(1/R + 1/R_L)[R_I + R(1 + R_I/R_L)]} \right\} \cdot \frac{E^2/T_0}{R_I + RR_L/(R + R_L)} \quad (21)$$

It is seen from Eq.(20) that when $R_L \rightarrow \infty$ and $R_I = 0$, one gets $\gamma = 0$, which is an ideal case. The full cell is identical with a voltage resource with the voltage E and its power output attains its reversible value, E^2/R . In a real fuel cell system, internal and leak resistances inevitably exist, and consequently, the power output of the fuel cell is always less than E^2/R .

It is also seen from Eq.(20) that when $R = 0$ or ∞ , one gets $\gamma = 1$ and the Gibbs free energy change is completely dissipated. This corresponds to the short or open circuit case, and consequently, the power output of the fuel cell is equal to zero.

V. MAXIMUM POWER OUTPUT AND EFFICIENCY

The power output and efficiency are two important parameters of the fuel cell. Using Eq.(14), Eq.(19), and Eq.(20), we can further optimize the performance of the fuel cell.

It is easily proved from Eq.(19) and its extremal condition that when the load resistance

$$R = \frac{R_I R_L}{R_I + R_L} \equiv R_P \quad (22)$$

the power output of the fuel cell attains its maximum, i.e.,

$$P_{\max} = \frac{1}{4} \frac{E^2}{(R_I + R_L)R_I/R_L} \quad (23)$$

In such a case, Eq.(14), Eq.(20), and Eq.(21) may be, respectively, simplified as

$$\eta = \frac{1}{2(1 + 2R_I/R_L)} \eta_r \equiv \eta_P \leq 0.5\eta_r \quad (24)$$

$$\gamma = 1 - \frac{1}{2(1 + 2R_I/R_L)} \equiv \gamma_P \geq 0.5 \quad (25)$$

$$\sigma = \frac{1}{4} \frac{(1 + 4R_I/R_L)E^2/T_0}{(R_I + R_L)R_I/R_L} \equiv \sigma_P \quad (26)$$

Using Eq.(26), one can derive the power dissipated by the internal and leak resistances at the maximum power output as

$$P_{D,m} = \frac{1}{4} \frac{(1 + 4R_I/R_L)E^2}{(R_I + R_L)R_I/R_L} \quad (27)$$

Comparing Eq.(27) with Eq.(23), one can find

$$P_{D,m} \geq P_{\max} \quad (28)$$

where the equal sign holds only when $R_L \rightarrow \infty$. This analysis shows clearly that for a real fuel cell system operating at the maximum power output, the internal and leak resistances will dissipate at least half of the total power.

From Eq.(14) and Eq.(20), we can obtain the efficiency of the fuel cell as

$$\eta = \frac{\eta_r}{(1/R + 1/R_L)[R_I + R(1 + R_I/R_L)]} \quad (29)$$

Using Eq.(29) and its extremal condition, one can prove that when the load resistance,

$$R = R_L \sqrt{R_I/(R_I + R_L)} = R_\eta \quad (30)$$

the efficiency of the fuel cell attains its maximum, i.e.,

$$\eta_{\max} = \frac{\eta_r}{\left(\sqrt{R_I/R_L} + \sqrt{1 + R_I/R_L}\right)^2} \quad (31)$$

In such a case, Eq.(19)-Eq.(21) may be, respectively, simplified as

$$P = \frac{1}{\left(\sqrt{R_I/R_L} + \sqrt{1 + R_I/R_L}\right)^2} \cdot \frac{E^2/R_L}{R_I/R_L + \frac{\sqrt{R_I/(R_I + R_L)}}{1 + \sqrt{R_I/(R_I + R_L)}}} \equiv P_\eta \quad (32)$$

$$\gamma = 1 - \frac{1}{\left(\sqrt{R_I/R_L} + \sqrt{1 + R_I/R_L}\right)^2} = \gamma_\eta \quad (33)$$

$$\sigma = \left[1 - \frac{1}{\left(\sqrt{R_I/R_L} + \sqrt{1 + R_I/R_L}\right)^2} \right] \cdot \frac{E^2/(R_L T_0)}{R_I/R_L + \frac{\sqrt{R_I/(R_I + R_L)}}{1 + \sqrt{R_I/(R_I + R_L)}}} \equiv \sigma_\eta \quad (34)$$

In order to further expound the important significance of the four parameters P_{\max} , η_P , η_{\max} , and P_η ,

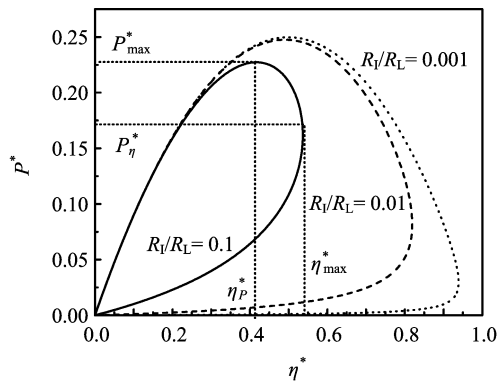


FIG. 3 The curves of the fuel cell. The solid, dashed, and dash-dot curves correspond to the cases of 0.1, 0.01, and 0.001, respectively.

we plot the P^* - η^* curve by using Eq.(18) and Eq.(29), as shown in Fig.3, where $P^*=P/(E^2/R_l)$ and $\eta^*=\eta/\eta_r$ are two dimensionless parameters which relate to the power output and efficiency, respectively. It is clearly seen from the curves in Fig.3 that when the fuel cell is operated in the part of the P^* - η^* curve which have a positive slope, the power output will decrease as the efficiency is decreased. For a fuel cell, one always hopes to obtain the power output and efficiency as large as possible, which leads to the fact that the parts of the curves with a positive slope are not the optimal operating regions of the fuel cell. Obviously, the optimal operating region of the fuel cell should be situated in the part of the P^* - η^* curve which has a negative slope. When the fuel cell is operated in this region, the power output will increase as the efficiency is decreased, and vice versa. This indicates clearly that P_{\max} and η_{\max} determine the upper bounds of the power output and efficiency, while P_η and η_P determine the allowable optimized values of the lower bounds of the power output and efficiency. It is thus clear that the optimal ranges of the power output and efficiency should be

$$P_{\max} \geq P \geq P_\eta \quad (35)$$

$$\eta_P \leq \eta \leq \eta_{\max} \quad (36)$$

respectively. According to Eq.(35) or Eq.(36), we can further determine that when the fuel cell is operated in the optimal region mentioned above, the range of the entropy production rate is

$$\sigma_P \geq \sigma \geq \sigma_\eta \quad (37)$$

and the optimally matching condition of the load resistance is

$$R_P \leq R \leq R_\eta \quad (38)$$

It is seen from Eq.(18) and Eq.(29) that in the region of $R < R_P$, both the power output and efficiency will decrease as the load resistance is decreased, while in the

region of $R > R_\eta$, both the power output and efficiency will decrease as the load resistance is increased. It is obvious that the regions of $R < R_P$ and $R > R_\eta$ are not optimal although the fuel cell can be operated in these regions. This observation means that both R_η and R_P are also two important parameters of the fuel cell, which determine, respectively, the allowable optimized values of the upper and lower bounds of the load resistance. Thus, in the design and operation of the fuel cell, engineers should choose a reasonable load resistance according to Eq.(38), so that the fuel cell can be operated in the optimal region.

VI. CONCLUSION

With the help of a general model of fuel cells, we have derived the correct expressions for the entropy production rate of a fuel cell system from different points of view, so that the problems in Refs. [6-8,14,15] have been solved. It is important that the concrete expression of the irreversible factor, γ , has been obtained by introducing the equivalent circuit of the fuel cell. It is more important that the influence of the internal and leak resistances on the performance of the fuel cell has been conveniently discussed, and the maximum power output and efficiency of the fuel cell and the optimally matching condition of the load resistance have been directly determined. The results obtained here will be helpful for the further understanding of the performance of fuel cells.

VII. ACKNOWLEDGMENT

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