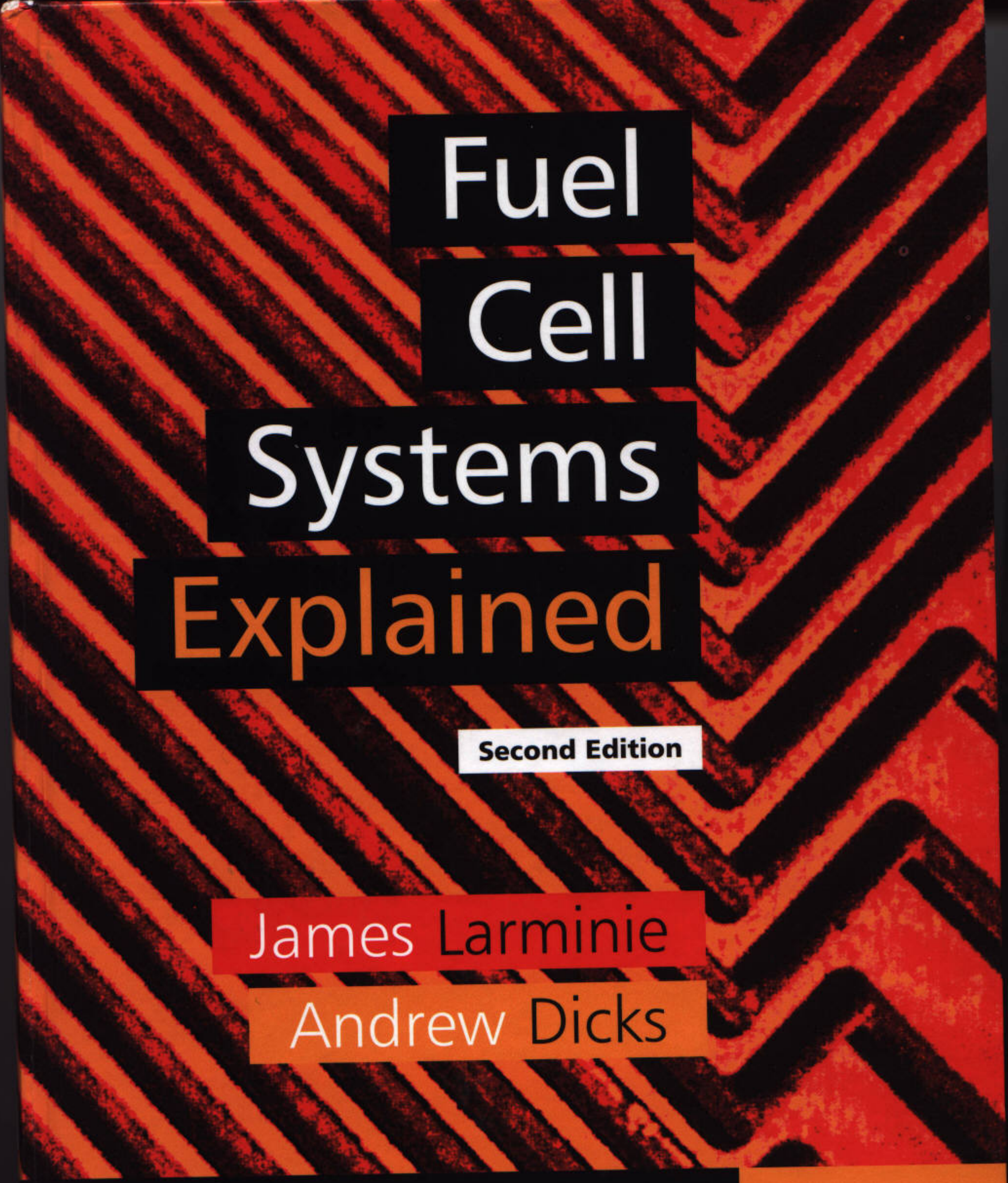

Fuel Cell Systems Explained

Second Edition

James Larminie
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WILEY

2

Efficiency and Open Circuit Voltage

In this chapter we consider the **efficiency of fuel cells** – how it is defined and calculated, and what the limits are. The energy considerations give us information about the open circuit voltage (OCV) of a fuel cell, and the formulas produced also give important information about how factors such as pressure, gas concentration, and temperature affect the voltage.

2.1 Energy and the EMF of the Hydrogen Fuel Cell

In some electrical power-generating devices, it is very clear what form of energy is being converted into electricity. A good example is a wind-driven generator, as in Figure 2.1. The energy source is clearly the kinetic energy of the air moving over the blades.

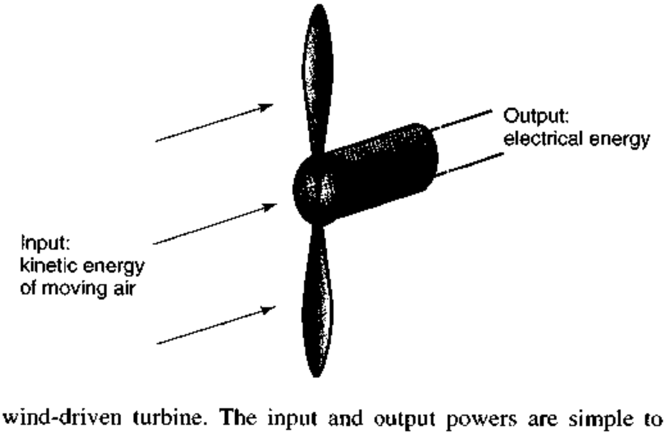

Figure 2.1 A wind-driven turbine. The input and output powers are simple to understand and calculate.

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ISBN: 0-470-84857-X

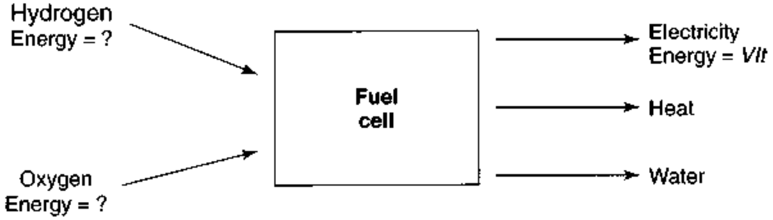

Figure 2.2 Fuel cell inputs and outputs.

With a fuel cell, such energy considerations are much more difficult to visualise. The basic operation has already been explained, and the input and outputs are shown in Figure 2.2.

The electrical power and energy output are easily calculated from the well-known formulas

$$\text{Power} = VI \qquad \text{and} \qquad \text{Energy} = VIt$$

However, the energy of the chemical input and output is not so easily defined. At a simple level we could say that it is the 'chemical energy' of the H_2, O_2, and H_2O that is in question. The problem is that 'chemical energy' is not simply defined – and terms such as enthalpy, Helmholtz function, and Gibbs free energy are used. In recent years the useful term 'exergy' has become quite widely used, and the concept is particularly useful in high-temperature fuel cells. There are also older (but still useful) terms such as calorific value.

In the case of fuel cells, it is the 'Gibbs free energy' that is important. This can be defined as the 'energy available to do external work, neglecting any work done by changes in pressure and/or volume' In a fuel cell, the 'external work' involves moving electrons round an external circuit – any work done by a change in volume between the input and output is not harnessed by the fuel cell.[1] Exergy is *all* the external work that can be extracted, including that due to volume and pressure changes. Enthalpy, simply put, is the Gibbs free energy plus the energy connected with the entropy (see Appendix 1).

All these forms of 'chemical energy' are rather like ordinary mechanical 'potential energy' in two important ways.

The **first** is that the *point of zero energy can be defined as almost anywhere*. When working with chemical reactions, the zero energy point is normally defined as pure elements, in the normal state, at standard temperature and pressure (25°C, 0.1 MPa). The term 'Gibbs free energy of formation', G_f, rather than the 'Gibbs free energy' is used when adopting this convention. Similarly, we also use 'enthalpy of formation' rather than just 'enthalpy'. For an ordinary hydrogen fuel cell operating at standard temperature and pressure (STP),[2] this means that the 'Gibbs free energy of formation' of the input is zero – a useful simplification.

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[1] Though it may be harnessed by some kind of turbine in a combined cycle system, as discussed in Chapter 6.

[2] Standard temperature and pressure, or standard reference state, that is, 100 kPa and 25°C or 298.15 K.

The **second** parallel with mechanical potential energy is that it is the *change* in energy that is important. In a fuel cell, it is the change in this Gibbs free energy of formation, ΔG_f, that gives us the energy released. This change is the difference between the Gibbs free energy of the products and the Gibbs free energy of the inputs or reactants.

$$\Delta G_f = G_f \text{ of products} - G_f \text{ of reactants}$$

To make comparisons easier, it is nearly always most convenient to consider these quantities in their 'per mole' form. These are indicated by ¯ over the lower case letter, for example, $(\overline{g}_f)_{H_2O}$ is the molar specific Gibbs free energy of formation for water.

Moles – g mole and kg mole

The *mole* is a measure of the 'amount' of a substance that takes into account its molar mass. The molar mass of H_2 is 2.0 amu, so one *gmole* is 2.0 g and one *kgmole* is 2.0 kg. Similarly, the molecular weight of H_2O is 18 amu, so 18 g is one *gmole*, or 18 kg is one *kgmole*. The *gmole*, despite the SI preference for kg, is still the most commonly used, and the 'unprefixed' *mole* means *gmole*.

A *mole* of any substance always has the same number of entities (e.g. molecules) – 6.022×10^{23} – called *Avogadro's number*. This is represented by the letter N or N_a.

A 'mole of electrons' is 6.022×10^{23} electrons. The charge is $N \cdot e$, where e is 1.602×10^{-19} C – the charge on one electron. This quantity is called the *Faraday constant*, and is designated by the letter F.

$$F = N \cdot e = 96485\,\mathrm{C}$$

Consider the basic reaction for the hydrogen/oxygen fuel cell:

$$2H_2 + O_2 \rightarrow 2H_2O$$

which is equivalent to

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

The 'product' is one mole of H_2O and the 'reactants' are one mole of H_2 and half a mole of O_2. Thus,

$$\Delta\overline{g_f} = \overline{g_f} \text{ of products} - \overline{g_f} \text{ of reactants}$$

So we have

$$\Delta\overline{g}_f = (\overline{g}_f)_{H_2O} - (\overline{g}_f)_{H_2} - \tfrac{1}{2}(\overline{g}_f)_{O_2}$$

This equation seems straightforward and simple enough. However, the Gibbs free energy of formation is *not constant*; it changes with temperature and state (liquid or gas). Table 2.1 below shows $\Delta\overline{g}_f$ for the basic hydrogen fuel cell reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

Table 2.1 $\Delta\bar{g}_f$ for the reaction $H_2 + \frac{1}{2}O_2 \rightarrow H_2O$ at various temperatures

Form of water product	Temperature (°C)	$\Delta\bar{g}_f$ (kJ mol^{-1})
Liquid	25	−237.2
Liquid	80	−228.2
Gas	80	−226.1
Gas	100	−225.2
Gas	200	−220.4
Gas	400	−210.3
Gas	600	−199.6
Gas	800	−188.6
Gas	1000	−177.4

for a number of different conditions. The method for calculating these values is given in Appendix 1. Note that the values are negative, which means that energy is released.

If there are no losses in the fuel cell, or as we should more properly say, if the process is 'reversible', then **all** this Gibbs free energy is converted into electrical energy. (In practice, some is also released as heat.) We will use this to find the reversible OCV of a fuel cell.

The basic operation of a fuel cell was explained in Chapter 1. A review of this chapter will remind you that, for the hydrogen fuel cell, **two** electrons pass round the external circuit for each water molecule produced and each molecule of hydrogen used. So, for one *mole* of hydrogen used, $2N$ electrons pass round the external circuit – where N is Avogadro's number. If $-e$ is the charge on one electron, then the charge that flows is

$$-2Ne = -2F \quad \text{coulombs}$$

F being the Faraday constant, or the charge on one mole of electrons.

If E is the voltage of the fuel cell, then the electrical work done moving this charge round the circuit is

$$\text{Electrical work done} = \text{charge} \times \text{voltage} = -2FE \quad \text{joules}$$

If the system is reversible (or has no losses), then this electrical work done will be equal to the Gibbs free energy released $\Delta\bar{g}_f$. So

$$\Delta\bar{g}_f = -2F \cdot E$$

Thus

$$E = \frac{-\Delta\bar{g}_f}{2F} \qquad [2.1]$$

This fundamental equation gives the electromotive force (EMF) or reversible open circuit voltage of the hydrogen fuel cell.

For example, a hydrogen fuel cell operating at 200°C has $\Delta \overline{g}_f = -220\,\text{kJ}$, so

$$E = \frac{220{,}000}{2 \times 96{,}485} = 1.14\,\text{V}$$

Note that this figure assumes no 'irreversibilities', and as we shall see later, assumes pure hydrogen and oxygen at standard pressure (0.1 MPa). In practice the voltage would be lower than this because of the voltage drops discussed in Chapter 3. Some of these irreversibilities apply a little even when no current is drawn, so even the OCV of a fuel cell will usually be lower than the figure given by equation 2.1.

Reversible processes, irreversibilities, and losses – an explanation of terms

An example of a simple reversible process is that shown in Figure 2.3. In position **A**, the ball has no kinetic energy, but potential energy *mgh*. In position **B**, this PE has been converted into kinetic energy. If there is no rolling resistance or wind resistance the process is *reversible*, in that the ball can roll up the other side and recover its potential energy.

In practice, some of the potential energy will be converted into heat because of friction and wind resistance. This is an *irreversible* process, as the heat cannot be converted back into kinetic or potential energy. We might be tempted to describe this as a 'loss' of energy, but that would not be very precise. In a sense, the potential energy is no more 'lost' to heat than it is 'lost' to kinetic energy. The difference is that in one you can get it back – it's reversible, and in the other you cannot – it's irreversible. So, the term 'irreversible energy loss' or 'irreversibility' is a rather more precise description of situations that many would describe as simply 'a loss'.

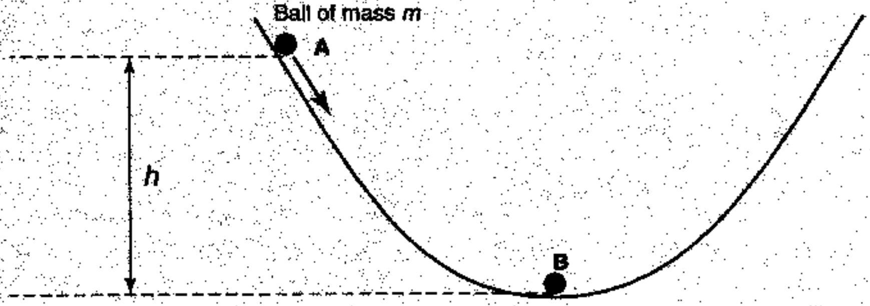

Figure 2.3 Simple reversible process.

2.2 The Open Circuit Voltage of Other Fuel Cells and Batteries

The equation that we have derived for the OCV of the hydrogen fuel cell

$$E = \frac{-\Delta \overline{g}_f}{2F}$$

can be applied to other reactions too. The only step in the derivation that was specific to the hydrogen fuel cell was the '2' electrons for each molecule of fuel, which led to the 2 in the equation. If we generalise it to any number of electrons per molecule, we have the formula

$$E = \frac{-\Delta \overline{g}_f}{zF} \qquad [2.2]$$

where z is the number of electrons transferred for each molecule of fuel.

The derivation was also not specific to fuel cells and applies just as well to other electrochemical power sources, particularly primary and secondary batteries. For example, the reaction in the familiar alkali battery used in radios and other portable appliances can be expressed (Bockris, 1981) by the equation

$$2MnO_2 + Zn \rightarrow ZnO + Mn_2O_3$$

for which $\Delta \overline{g}_f$ is $-277\,\text{kJ mol}^{-1}$. At the anode the reaction is

$$Zn + 2OH^- \rightarrow ZnO + H_2O + 2e^-$$

And at the cathode we have

Electrons flow from anode to cathode

$$2MnO_2 + H_2O + 2e^- \rightarrow Mn_2O_3 + 2OH^-$$

Thus, two electrons are passed round the circuit, and so the equation for the OCV is exactly the same as equation 2.1. This gives

$$E = \frac{2.77 \times 10^5}{2 \times 96485} = 1.44\,\text{V}$$

Another useful example is the methanol fuel cell, which we will look at later in Chapter 5. The overall reaction is

$$2CH_3OH + 3O_2 \rightarrow 4H_2O + 2CO_2$$

with 12 electrons passing from anode to cathode, that is, 6 electrons for each molecule of methanol. For the methanol reaction, $\Delta \overline{g}_f$ is $-698.2\,\text{kJ mol}^{-1}$. Substituting these numbers into equation 2.2 gives

$$E = \frac{6.98 \times 10^5}{6 \times 96485} = 1.21\,\text{V}$$

We note that this is similar to the open circuit reversible voltage for the hydrogen fuel cell.

2.3 Efficiency and Efficiency Limits

It is not straightforward to define the efficiency of a fuel cell, and efficiency claims cannot usually be taken at face value. In addition, the question of the maximum possible efficiency of a fuel cell is not without its complications.

The wind-driven generator of Figure 2.1 is an example of a system where the efficiency is fairly simple to define, and it is also clear that there must be some limit to the efficiency. Clearly, the air passing through the circle defined by the turbine blades cannot lose all its kinetic energy. If it did, it would stop dead and there would be an accumulation of air behind the turbine blades. As is explained in books on wind power, it can be shown, using fluid flow theory, that

Maximum energy from generator = 0.58 × kinetic energy of the wind

The figure of 0.58 is known as the 'Betz Coefficient'.

A more well-known example of an efficiency limit is that for heat engines – such as steam and gas turbines. If the maximum temperature of the heat engine is T_1, and the heated fluid is released at temperature T_2, then Carnot showed that the maximum efficiency possible is

$$\text{Carnot limit} = \frac{T_1 - T_2}{T_1}$$

The temperatures are in Kelvin, where 'room temperature' is about 290 K, and so T_2 is never likely to be small. As an example, for a steam turbine operating at 400°C (675 K), with the water exhausted through a condenser at 50°C (325 K), the Carnot efficiency limit is

$$\frac{675 - 325}{675} = 0.52 = 52\%$$

The reason for this efficiency limit for heat engines is not particularly mysterious. Essentially there must be some heat energy, proportional to the lower temperature T_2, which is always 'thrown away' or wasted. This is similar to the kinetic energy that must be retained by the air that passes the blades of the wind-driven generator.

With the fuel cell the situation is not so clear. It is quite well known that fuel cells are not subject to the Carnot efficiency limit. Indeed, it is commonly supposed that if there were no 'irreversibilities' then the efficiency could be 100%, and if we define efficiency in a particular (not very helpful) way, then this is true.

In Section 2.1 we saw that it was the 'Gibbs free energy' that is converted into electrical energy. If it were not for the irreversibilities to be discussed in Chapter 3, all this energy would be converted into electrical energy, and the efficiency could be said to be 100%. However, this is the result of choosing one among several types of 'chemical energy'. We have also noted, in Table 2.1, that the Gibbs free energy changes with temperature, and we will see in the section following that it also changes with pressure and other factors. All in all, to define efficiency as

$$\frac{\text{electrical energy produced}}{\text{Gibbs free energy change}}$$

is not very useful, and is rarely done, as whatever conditions are used the efficiency limit is always 100%.

Since a fuel cell uses materials that are usually burnt to release their energy, it would make sense to compare the electrical energy produced with the heat that would be produced by burning the fuel. This is sometimes called the *calorific value*, though a more precise description is the change in ‘ enthalpy of formation’. Its symbol is $\Delta\overline{h}_f$. As with the Gibbs free energy, the convention is that $\Delta\overline{h}_f$ is negative when energy is released. So to get a good comparison with other fuel-using technologies, the efficiency of the fuel cell is usually defined as

$$\frac{\text{electrical energy produced per mole of fuel}}{-\Delta\overline{h}_f} \qquad [2.3]$$

However, even this is not without its ambiguities, as there are two different values that we can use for $\Delta\overline{h}_f$. For the ‘burning’ of hydrogen

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \text{ (steam)}$$

$$\Delta\overline{h}_f = -241.83\,\text{kJ mol}^{-1}$$

whereas if the product water is condensed back to liquid, the reaction is

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \text{ (liquid)}$$

$$\Delta\overline{h}_f = -285.84\,\text{kJ mol}^{-1}$$

The difference between these two values for $\Delta\overline{h}_f$ ($44.01\,\text{kJ mol}^{-1}$) is the molar enthalpy of vaporisation[3] of water. The higher figure is called the *higher heating value* (HHV), and the lower, quite logically, the ‘lower heating value’ (LHV). Any statement of efficiency should say whether it relates to the higher or lower heating value. If this information is not given, the LHV has probably been used, since this will give a higher efficiency figure.

We can now see that there is a limit to the efficiency, if we define it as in equation 2.3. The maximum electrical energy available is equal to the change in Gibbs free energy, so

$$\text{Maximum efficiency possible} = \frac{\Delta\overline{g}_f}{\Delta\overline{h}_f} \times 100\% \qquad [2.4]$$

This maximum efficiency limit is sometimes known as the ’thermodynamic efficiency’. Table 2.2 gives the values of the efficiency limit, relative to the HHV, for a hydrogen fuel cell. The maximum voltage, from equation 2.1, is also given.

---

[3] This used to be known as the molar ‘latent heat’.

Table 2.2 $\Delta\overline{g}_f$, maximum EMF (or reversible open circuit voltage), and efficiency limit (HHV basis) for hydrogen fuel cells

Form of water product	Temp °C	$\Delta\overline{g}_f$, kJ mol^{-1}	Max EMF V	Efficiency limit %
Liquid	25	−237.2	1.23	83
Liquid	80	−228.2	1.18	80
Gas	100	−225.2	1.17	79
Gas	200	−220.4	1.14	77
Gas	400	−210.3	1.09	74
Gas	600	−199.6	1.04	70
Gas	800	−188.6	0.98	66
Gas	1000	−177.4	0.92	62

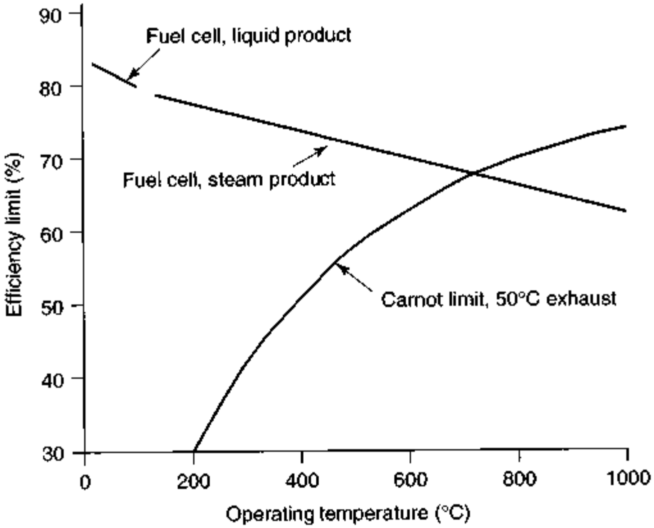

Figure 2.4 Maximum H_2 fuel cell efficiency at standard pressure, with reference to higher heating value. The Carnot limit is shown for comparison, with a 50°C exhaust temperature.

The graphs in Figure 2.4 show how these values vary with temperature, and how they compare with the 'Carnot limit'. Three important points should be noted:

- Although the graph and table would suggest that lower temperatures are better, the voltage losses discussed in Chapter 3 are nearly always less at higher temperatures. So *in practice* fuel cell voltages are usually *higher* at higher temperatures.
- The waste heat from the higher-temperature cells is more useful than that from lower-temperature cells.

- Contrary to statements often made by their supporters, fuel cells do NOT always have a higher efficiency limit than heat engines.[4]

This decline in maximum possible efficiency with temperature associated with the hydrogen fuel cell does not occur in exactly the same way with other types of fuel cells. For example, when using carbon monoxide we get

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2$$

$\Delta \overline{g}_f$ changes even more quickly with temperature, and the maximum possible efficiency falls from about 82% at 100°C to 52% at 1000°C. On the other hand, for the reaction

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O$$

$\Delta \overline{g}_f$ is fairly constant with temperature, and the maximum possible efficiency hardly changes.

2.4 Efficiency and the Fuel Cell Voltage

It is clear from Table 2.2 that there is a connection between the maximum EMF of a cell and its maximum efficiency. The *operating* voltage of a fuel cell can also be very easily related to its efficiency. This can be shown by adapting equation 2.1. If all the energy from the hydrogen fuel, its 'calorific value', heating value, or enthalpy of formation, were transformed into electrical energy, then the EMF would be given by

$$\begin{aligned} E &= \frac{-\Delta \overline{h}_f}{2F} \\ &= 1.48\,\text{V if using the HHV} \\ \text{or } &= 1.25\,\text{V if using the LHV} \end{aligned}$$

These are the voltages that would be obtained from a 100% efficient system, with reference to the HHV or LHV. The actual efficiency of the cell is then the actual voltage divided by these values, or

$$\text{Cell efficiency} = \frac{V_c}{1.48} 100\% \text{ (with reference to HHV)}$$

However, in practice it is found that not all the fuel that is fed to a fuel cell can be used, for reasons discussed later. Some fuel usually has to pass through unreacted. A *fuel utilisation coefficient* can be defined as

$$\mu_f = \frac{\text{mass of fuel reacted in cell}}{\text{mass of fuel input to cell}}$$

---

[4] In Chapter 7 we see how a heat engine and a high-temperature fuel cell can be combined into a particularly efficient system.

This is equivalent to the ratio of fuel cell current and the current that would be obtained if all the fuel were reacted. The fuel cell efficiency is therefore given by

$$\text{Efficiency, } \eta = \mu_f \frac{V_c}{1.48} 100\% \qquad [2.5]$$

If a figure relative to the LHV is required, use 1.25 instead of 1.48. A good estimate for μ_f is 0.95, which allows the efficiency of a fuel cell to be accurately estimated from the very simple measurement of its voltage. However, it can be a great deal less in some circumstances, as is discussed in Section 2.5.3, and in Chapter 6.

2.5 The Effect of Pressure and Gas Concentration

2.5.1 The Nernst equation

In Section 2.1 we noted that the Gibbs free energy changes in a chemical reaction vary with temperature. Equally important, though more complex, are the changes in Gibbs free energy with reactant pressure and concentration.

Consider a general reaction such as

$$j\text{J} + k\text{K} \rightarrow m\text{M} \qquad [2.6]$$

where j moles of J react with k moles of K to produce m moles of M. Each of the reactants, and the products, has an associated 'activity'. This 'activity' is designated by a, a_J, and a_K being the activity of the reactants, and a_M the activity of the product. It is beyond the scope of this book to give a thorough description of 'activity'. However, in the case of gases behaving as 'ideal gases', it can be shown that

$$\text{activity } a = \frac{P}{P^0}$$

where P is the pressure or partial pressure of the gas and P^0 is standard pressure, 0.1 MPa. Since fuel cells are generally gas reactors, this simple equation is very useful. We can say that activity is proportional to partial pressure. In the case of dissolved chemicals, the activity is linked to the molarity (strength) of the solution. The case of the water produced in fuel cells is somewhat difficult, since this can be either as steam or as liquid. For steam, we can say that

$$a_{\text{H}_2\text{O}} = \frac{\text{P}_{\text{H}_2\text{O}}}{\text{P}^0_{\text{H}_2\text{O}}}$$

where $P^0_{\text{H}_2\text{O}}$ is the vapour pressure of the steam at the temperature concerned. This has to be found from steam tables. In the case of liquid water product, it is a reasonable approximation to assume that $a_{\text{H}_2\text{O}} = 1$.

The activities of the reactants and products modify the Gibbs free energy change of a reaction. Using thermodynamic arguments (Balmer, 1990), it can be shown that in a chemical reaction such as that given in equation 2.6

$$\Delta \overline{g}_f = \Delta \overline{g}_f{}^0 - RT \ln \left(\frac{a_J^j \cdot a_K^k}{a_M^m} \right)$$

where $\Delta \overline{g}_f{}^0$ is the change in molar Gibbs free energy of formation at standard pressure.

Despite not looking very 'friendly', this equation is useful, and not very difficult. In the case of the hydrogen fuel cell reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O$$

the equation becomes

$$\Delta \overline{g}_f = \Delta \overline{g}_f{}^0 - RT \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right)$$

$\Delta \overline{g}_f{}^0$ is the quantity given in Tables 2.1 and 2.2. We can see that if the activity of the reactants increases, $\Delta \overline{g}_f$ becomes more negative, that is, more energy is released. On the other hand, if the activity of the product increases, $\Delta \overline{g}_f$ increases, so becomes less negative, and less energy is released. To see how this equation affects voltage, we can substitute it into equation 2.1 and obtain

$$E = \frac{-\Delta \overline{g}_f{}^0}{2F} + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right)$$

$$= E^0 + \frac{RT}{2F} \ln \left(\frac{a_{H_2} \cdot a_{O_2}^{\frac{1}{2}}}{a_{H_2O}} \right) \qquad [2.7]$$

where E^0 is the EMF at standard pressure and is the number given in column 4 of Table 2.2. The equation shows precisely how raising the activity of the reactants increases the voltage.

Equation 2.7, and its variants below, which give an EMF in terms of product and/or reactant activity, are called *Nernst equations*. The EMF calculated from such equations is known as the 'Nernst voltage' and is the reversible cell voltage that would exist at a given temperature and pressure. The logarithmic function involving the reactants allows us to use the regular rules of the logarithmic functions such as

$$\ln\left(\frac{a}{b}\right) = \ln(a) - \ln(b) \qquad \text{and} \qquad \ln\left(\frac{c^2}{d^{\frac{1}{2}}}\right) = 2\ln(c) - \frac{1}{2}\ln(d)$$

This makes it straightforward to manipulate equation 2.7 to get at the effect of different parameters. For example, in the reaction

$$H_2 + \tfrac{1}{2}O_2 \rightarrow H_2O \quad \text{(steam)}$$

at high temperature (e.g. in a solid oxide fuel cell (SOFC) at 1000°C) we can assume that the steam behaves as an ideal gas, and so

$$a_{H_2} = \frac{P_{H_2}}{P^0}, \qquad a_{O_2} = \frac{P_{O_2}}{P^0}, \qquad a_{H_2O} = \frac{P_{H_2O}}{P^0}$$

Then equation 2.7 will become

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{\frac{P_{H_2}}{P^o} \cdot \left(\frac{P_{O_2}}{P^o} \right)^{\frac{1}{2}}}{\frac{P_{H_2O}}{P^o}} \right)$$

If all the pressures are given in bar, then $P^0 = 1$ and the equation simplifies to

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) \qquad [2.8]$$

In nearly all cases the pressures in equation 2.8 will be partial pressures, that is, the gases will be part of a mixture. For example, the hydrogen gas might be part of a mixture of H_2 and CO_2 from a fuel reformer, together with product steam. The oxygen will nearly always be part of air. It is also often the case that the pressure on both the cathode and the anode is approximately the same – this simplifies the design. If this system pressure is P, then we can say that

$$P_{H_2} = \alpha P$$

$$P_{O_2} = \beta P$$

$$\text{and} \quad P_{H_2O} = \delta P$$

where α, β, and δ are constants depending on the molar masses and concentrations of H_2, O_2, and H_2O. Equation 2.8 then becomes

$$\begin{aligned} E &= E^0 + \frac{RT}{2F} \ln \left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta} \cdot P^{\frac{1}{2}} \right) \\ &= E^0 + \frac{RT}{2F} \ln \left(\frac{\alpha \cdot \beta^{\frac{1}{2}}}{\delta} \right) + \frac{RT}{4F} \ln(P) \qquad [2.9] \end{aligned}$$

The two equations 2.8 and 2.9 are forms of the Nernst equation. They provide a theoretical basis and a quantitative indication for a large number of variables in fuel cell design and operation. Some of these are discussed in later chapters, but some points are considered briefly here.

Partial Pressures

In a mixture of gases, the *total* pressure is the sum of all the 'partial pressures' of the components of the mixture. For example, in air at 0.1 MPa, the partial pressures are as shown in Table 2.3

Table 2.3 Partial pressures of atmospheric gases

Gas	Partial pressure MPa
Nitrogen	0.07809
Oxygen	0.02095
Argon	0.00093
Others (including CO_2)	0.00003
Total	0.10000

In fuel cells, the partial pressure of oxygen is important. On the fuel side the partial pressure of hydrogen and/or carbon dioxide is important if a hydrocarbon (e.g. CH_4) is used as the fuel source. In such cases the partial pressure will vary according to the reformation method used – see Chapter 7.

However, if the mixture of the gases is known, the partial pressures can be easily found. It can be readily shown, using the gas law equation $PV = NRT$, that the volume fraction, molar fraction, and pressure fraction of a gas mixture are all equal. For example, consider the reaction

$$CH_4 + H_2O \rightarrow 3H_2 + CO_2$$

The product gas stream contains three parts H_2 and one part CO_2 by moles and volume. So, if the reaction takes place at 0.10 MPa

$$P_{H_2} = \frac{3}{4} \times 0.1 = 0.075\,\text{MPa} \quad \text{and} \quad P_{CO_2} = \frac{1}{4} \times 0.1 = 0.025\,\text{MPa}$$

2.5.2 Hydrogen partial pressure

Hydrogen can either be supplied pure or as part of a mixture. If we isolate the pressure of hydrogen term in equation 2.8, we have

$$E = E^0 + \frac{RT}{2F} \ln\left(\frac{P_{O_2}^{\frac{1}{2}}}{P_{H_2O}}\right) + \frac{RT}{2F} \ln(P_{H_2})$$

So, if the hydrogen partial pressure changes, say, from P_1 to P_2 bar, with P_{O_2} and P_{H_2O} unchanged, then the voltage will change by

$$\begin{aligned}\Delta V &= \frac{RT}{2F}\ln(P_2) - \frac{RT}{2F}\ln(P_1) \\ &= \frac{RT}{2F}\ln\left(\frac{P_2}{P_1}\right) \qquad [2.10]\end{aligned}$$

The use of H_2 mixed with CO_2 occurs particularly in phosphoric acid fuel cells, operating at about 200°C. Substituting the values for R, T, and F gives

$$\Delta V = 0.02\ln\left(\frac{P_2}{P_1}\right)\,\mathrm{V}$$

This agrees well with experimental results, which correlate best with a factor of 0.024 instead of 0.020 (Parsons Inc., 2000).[5] As an example, changing from pure hydrogen to 50% hydrogen/carbon dioxide mixture will reduce the voltage by 0.015 V per cell.

2.5.3 *Fuel and oxidant utilisation*

As air passes through a fuel cell, the oxygen is used, and so the partial pressure will reduce. Similarly, the fuel partial pressure will often decline, as the proportion of fuel reduces and reaction products increase. Referring to equation 2.9 we can see that α and β decrease, whereas δ increases. All these changes make the term

$$\frac{RT}{2F}\ln\left(\frac{\alpha\cdot\beta^{\frac{1}{2}}}{\delta}\right)$$

from equation 2.9 smaller, and so the EMF will fall. This will vary within the cell – it will be worst near the fuel outlet as the fuel is used. Because of the low-resistance bipolar plates on the electrode, it is not actually possible for different parts of one cell to have different voltages, so the current varies. The current density will be lower nearer the exit where the fuel concentration is lower. The RT term in the equation also shows us that this drop in Nernst voltage due to fuel utilisation will be greater in high-temperature fuel cells.

We have seen in Section 2.4 above that for a high system efficiency the fuel utilisation should be as high as possible. However, this equation shows us that cell voltage, and hence the cell efficiency, will *fall* with higher utilisation. So we see fuel and oxygen utilisation need careful optimising, especially in higher-temperature cells. The selection of utilisation is an important aspect of system design and is especially important when reformed fuels are used. It is given further consideration in Chapter 7.

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[5] Parsons Inc (2000) uses base 10 logarithms, and so the coefficient given there is 0.055.

2.5.4 System pressure

The Nernst equation in the form of equation 2.9 shows us that the EMF of a fuel cell is increased by the system pressure according to the term

$$\frac{RT}{4F}\ln(P)$$

So, if the pressure changes from P_1 to P_2 there will be a change of voltage

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{P_2}{P_1}\right)$$

For an SOFC operating at 1000°C, this would give

$$\Delta V = 0.027\ln\left(\frac{P_2}{P_1}\right)$$

This agrees well with reported results (Bevc, 1997 and Parsons Inc., 2000) for high-temperature cells. However, for other fuel cells, working at lower temperatures, the agreement is not as good. For example, a phosphoric acid fuel cell working at 200°C should be affected by system pressure by the equation

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{P_2}{P_1}\right) = 0.010\ln\left(\frac{P_2}{P_1}\right)$$

whereas reported results (Parsons, 2000) give a correlation to the equation

$$\Delta V = 0.063\ln\left(\frac{P_2}{P_1}\right)$$

In other words, at lower temperatures, the benefits of raising system pressure are much greater than the Nernst equation predicts. This is because, except for very high temperature cells, increasing the pressure also reduces the losses at the electrodes, especially the cathode. (This is considered further in Chapter 3.)

A similar effect occurs when studying the change from air to oxygen. This effectively changes β in equation 2.9 from 0.21 to 1.0. Isolating β in equation 2.9 gives

$$E = E^0 + \frac{RT}{4F}\ln(\beta) + \frac{RT}{2F}\ln\left(\frac{\alpha}{\delta}\right) + \frac{RT}{4F}\ln(P)$$

For the change in β from 0.21 to 1.0, with all other factors remaining constant, we have

$$\Delta V = \frac{RT}{4F}\ln\left(\frac{1.0}{0.21}\right)$$

For a proton exchange membrane (PEM) fuel cell at 80°C this would give

$$\Delta V = 0.012\,\text{V}$$

In fact, reported results (Prater, 1990) give a much larger change, 0.05 V being a typical result. This is also due to the improved performance of the cathode when using oxygen, reducing the voltage losses there.

2.5.5 An application – blood alcohol measurement

In addition to generating electrical power, fuel cells are also the basis of some types of sensors. One of the most successful is the fuel cell–based alcohol sensor – the 'breathalyser' (Figure 2.5). This measures the concentration of alcohol in the air that someone breathes out of his or her lungs. It has been shown that this is directly proportional to the concentration of alcohol in the blood. The basic chemistry is that the alcohol (ethanol) reacts in a simple fuel cell to give a (very small) voltage. In theory the ethanol could be fully oxidised to CO_2 and water. However, the ethanol is probably not fully reacted and is only partially oxidised to ethanal.

The anode and cathode reactions are probably

$$C_2H_5OH \text{ (ethanol)} \rightarrow CH_3CHO \text{ (ethanal)} + 2H^+ + 2e^-$$

and

Electrons flow round external circuit

$$\tfrac{1}{2}O_2 + 2H^+ + 2e^- \rightarrow H_2O$$

Figure 2.5 Fuel cell–based breathalyser as used by police forces in the USA. (Reproduced by kind permission of Lion Laboratories Ltd.)

We have seen that the voltage is affected by the concentration of the reactants, and so the voltage of the cell will be affected by the concentration of the alcohol in the gas blown into the cell. Thus, we can get a measure of the alcohol concentration in the blood. This type of fuel cell is the basis of the majority of roadside blood alcohol measurement instruments used by police forces throughout the world.

2.6 Summary

The reversible OCV for a hydrogen fuel cell is given by the equation

$$E = \frac{-\Delta \overline{g}_f}{2F} \qquad [2.1]$$

In general, for a reaction where z electrons are transferred for each molecule of fuel the reversible OCV is

$$E = \frac{-\Delta \overline{g}_f}{zF} \qquad [2.2]$$

However, $\Delta \overline{g}_f$ changes with temperature and other factors. The maximum efficiency is given by the expression

$$\eta_{\max} = \frac{\Delta \overline{g}_f}{\Delta \overline{h}_f} \times 100\% \qquad [2.4]$$

The efficiency of a working hydrogen fuel cell can be found from the simple formula

$$\text{Efficiency, } \eta = \mu_f \frac{V}{1.48} 100\% \qquad [2.5]$$

where μ_f is the fuel utilisation (typically about 0.95) and V is the voltage of a single cell within the fuel cell stack. This gives the efficiency relative to the HHV of hydrogen.

The pressure and concentration of the reactants affects the Gibbs free energy, and thus the voltage. This is expressed in the Nernst equation, which can be given in many forms. For example, if the pressures of the reactants and products are given in bar and the water product is in the form of steam, then

$$E = E^0 + \frac{RT}{2F} \ln \left(\frac{P_{H_2} \cdot P_{O_2}^{\frac{1}{2}}}{P_{H_2O}} \right) \qquad [2.8]$$

where E^0 is the cell EMF at standard pressure.

Now, in most parts of this chapter we have referred to or given equations for the EMF of a cell or its reversible open circuit voltage. In practice the operating voltage is less than these equations give, and in some cases much less. This is the result of losses or irreversibilities, to which we give careful consideration in the following chapter.

References

Balmer R. (1990) *Thermodynamics*, West, St Paul, Minnesota.

Bevc F. (1997) "Advances in solid oxide fuel cells and integrated power plants", *Proceedings of the Institution of Mechanical Engineers*, **211**(Part A), 359–366.

Bockris J.O'M., Conway B.E., Yeager E. and White R.E. (eds) (1981) *A Comprehensive Treatment of Electrochemistry*, Vol. 3, Plenum Press, New York, p. 220.

Parsons Inc., EG&G Services (2000) *Fuel Cells: A Handbook*, 5th ed., US Department of Energy, p. 5-19 and p. 8-22.

Prater K. (1990) "The renaissance of the solid polymer fuel cell", *Journal of Power Sources*, **29**, 239–250.