

Fuel Cell Thermodynamics

Lindiwe Khotseng

Abstract

Thermodynamics is the study of energy change from one state to another. The predictions that can be made using thermodynamic equations are essential for understanding fuel cell performance, as a fuel cell is an electrochemical device that converts the chemical energy of a fuel and an oxidant gas into electrical energy. When a fuel cell is operating, some of the input is used to create electrical energy, but another portion is converted into thermal energy, depending on the type of fuel cell. Based on the first and second laws of thermodynamics, one can write down thermodynamic potentials to specify how energy can be transferred from one form to another. This chapter examines how electrical energy and thermal energy are transferred in the hydrogen fuel cell system. It also defines how reversible fuel cell voltages, which are the maximum fuel cell performances, are affected by departures from the standard state. Basic thermodynamic concepts allow one to predict states of the fuel cell system, including the potential, temperature, pressure, volume and moles of a fuel cell. The specific topics explored in this chapter include enthalpy, entropy, specific heat, Gibbs free energy, net output voltage irreversible losses in fuel cells and fuel cell efficiency.

Keywords: enthalpy, entropy, Gibbs free energy, specific heat, fuel cell efficiency, hydrogen fuel cell

1. Introduction

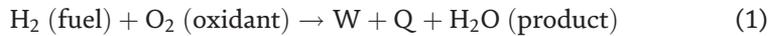
Fuel cells are electrochemical devices that convert chemical energy into work in the form of electric energy and heat. Any system producing energy obeys the laws of thermodynamics. The amount of work/heat produced depends on thermodynamic values for reversible reactions, while for irreversible reactions overpotential is required to complete the work. Hydrogen and oxygen are used to illustrate the simplest case. A general thermodynamic analysis of hydrogen fuel cells of the reversible work for the reversible reaction is performed. The concepts enthalpy, specific heat, entropy and Gibbs free energy are related to the reacting systems in fuel cells. Gibbs free energy is the thermodynamic potential that measures the reversible work by a thermodynamic system at constant pressure and temperature. Change in enthalpy and change in entropy are significant in particular to fuel cells; they indicate spontaneity of the adsorption process and increased randomness of adsorbate molecules on the solid surface, respectively. Specific heat is a measure of the amount of heat energy required to increase the temperature of a substance by 1°C. The fuel cell performance is examined through the reversible voltage, and the actual output voltage is after overpotential. The efficiency of a fuel cell is the useful

energy output which is the electrical energy produced, and the energy input is the enthalpy of hydrogen.

2. The thermodynamics of a fuel cell

A fuel cell, also known as a galvanic or voltaic cell, is a well-known example of a device that works by changing chemical energy into electrical energy, which is exhibited in terms of cell potential and electrical current output. The maximum possible electrical energy output and the corresponding electrical potential difference between the cathode and anode are achieved when the fuel cell is operated under thermodynamically reversible conditions, as shown in **Figure 1**, a fuel cell system to which fuel and oxidant streams enter and product stream exits. Unfortunately, it is inevitable that some of the energy will be dissipated as heat.

The overall electrochemical reactions occurring inside the fuel cell system boundary are described as follows:



where W is the rate of electrical work done by the system and Q is the rate of heat transferred into the system from the surroundings at constant pressure and temperature.

Electrical work is, in general, described by the relation:

$$W = EI\Delta t \quad (2)$$

where E is the cell voltage and I is the current. In a fuel cell reaction, electrons are transferred from the anode to the cathode, generating a current.

The amount of electricity ($I\Delta t$) transferred when the reaction occurs is given by nF , where n is the number of electrons transferred and F is Faraday's constant = 96,493 coulombs. The electrical work can hence be calculated as:

$$W = -nFE_{\text{cell}} \quad (3)$$

The Gibbs free energy is the maximum amount of work done on the system:

$$W_{\text{el}} = \Delta G \quad (4)$$

$$\Delta G = -nFE_{\text{cell}} \quad (5)$$

Hence the maximum cell potential or the reversible cell potential becomes:

$$E_{\text{rev}} = -\frac{\Delta G}{nF} \quad (6)$$

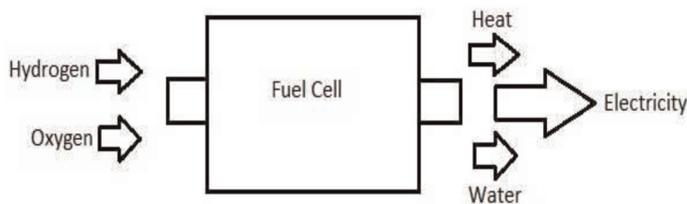


Figure 1.
Simple H_2/O_2 fuel cell diagram.

where E° is also called the reversible voltage, because it is the maximum possible voltage without any irreversible losses. This is the maximum possible voltage of an electrochemical cell, since it is attained assuming a reversible process. If we are looking at the redox reaction on a per-mole-of-fuel basis, the absolute Gibbs function is equivalent to the molar specific value. All fuel cell losses are associated with deviation from this maximum. Since F and n are constants for a particular global redox reaction, the functional dependence of the maximum possible voltage of an electrochemical cell is related strictly to the dependencies of the Gibbs free energy, namely, temperature and pressure of the reactants and products. If all the potential chemical energy for a reaction went into electrical work and there was no heat transfer, there would be no entropy change; $dG = dH$. In this case, we can show that:

$$E_{\text{rev}} = -\frac{\Delta H}{nF} \quad (7)$$

For a generic reaction:

For a general reaction or process of A and B giving products C and D:



$$\Delta G_f = \Delta G_f^\circ + RT \ln \left[\frac{aC^c aD^d}{aA^a aB^b} \right] \quad (9)$$

where a 's are the thermodynamic activity coefficients for the reacting species. To convert to voltage, we can divide it by nF :

$$E(T, P) = \underbrace{E^\circ}_I - \underbrace{\frac{RT}{nF} \ln \left[\frac{aC^c aD^d}{aA^a aB^b} \right]}_{II} \quad (10)$$

where I is the standard voltage evaluated at 1 atm pressure for all components and II accounts for the thermodynamic activity dependence on the Nernst voltage.

- i. For an ideal gas, $a = P_i/P^\circ$, where P_i is the partial pressure of the species of interest and P° is the reference pressure, 1 atm.
- ii. For water vapour, the partial pressure of the vapour cannot exceed the saturation pressure, P_{sat} , which is a function of temperature. Thus, the reference pressure is set to P_{sat} , and $a = P_v/P_{\text{sat}}$, which is the relative humidity, RH. This can normally be considered to be 1.0 in the immediate molecular region of the water-generating electrode. This is a reasonable assumption because water generation is always at the catalyst surface and the activity of water here is 1.0. Also, the reaction itself is not limited by the product water concentration at this surface:

$$E(T, P) = E^\circ - \frac{RT}{nF} \ln \left[\frac{\left(\frac{P_C}{P^\circ}\right)^c \left(\frac{P_D}{P^\circ}\right)^d}{\left(\frac{P_A}{P^\circ}\right)^a \left(\frac{P_B}{P^\circ}\right)^b} \right] \quad (11)$$

where the partial pressures are evaluated at the particular electrode where the reaction involving the species occurs. Using this expression, we can solve for the expected maximum (Nernst) voltage for a given fuel cell reaction. Two important points are as follows:

- i. The Nernst equation is a result of the equilibrium established at the electrode surfaces. A particular gradient can exist between the concentration of a species in the channel of a fuel cell and the electrode, especially under high-current-density conditions, which cannot be considered a true thermodynamic equilibrium situation anyway.
- ii. Only species directly involved in the electrochemical reaction of Eq. (8) are represented directly in the activity terms of Eq. (10). Species not participating in the electrochemical charge transfer reaction only indirectly alter the voltage through the species mole fractions of the participating species.

For the H₂/O₂ fuel cell potential, the open-circuit voltage is the maximum operating voltage (when no current is flowing) and is determined by the chemical thermodynamics of the overall cell reaction. The Nernst equation provides a relationship between the standard potential (E°) for the cell reaction and the open-circuit voltage, where it can be determined at the partial pressures of reactants and products at temperature (T):

$$E(T, P) = E^\circ - \frac{RT}{2F} \ln \left[\frac{\left(\frac{y_{H_2O} P_{cathode}}{P_{sat}} \right)}{\left(\frac{y_{H_2} P_{anode}}{P^\circ} \right) \left(\frac{y_{O_2} P_{cathode}}{P^\circ} \right)^{1/2}} \right] \quad (12)$$

To understand how the reversible voltage varies with temperature and pressure, respectively, we have previously shown that the Gibbs free energy is related to the reversible cell voltage by Eq. (5):

$$\Delta G = -nFE_{cell}$$

At constant pressure, the above relationship produces a Maxwell relation that links the change in open cell voltage with temperature T (a measurable quantity) to the change in entropy S [1]:

$$\left(\frac{\partial E}{\partial T} \right)_Q = \left(- \frac{\partial S}{\partial Q} \right)_T \quad (13)$$

$$\left(\frac{\partial E}{\partial T} \right)_P = \frac{\Delta S}{nF} \quad (14)$$

$$\Delta S = nF \left(\frac{\partial E}{\partial T} \right)_P \quad (15)$$

$$E_{rev} = E^\circ_{rev} + \frac{\Delta S}{nF} (T - T^\circ) \quad (16)$$

At constant temperature, Eq. (5) produces an equation that links voltage with pressure, p, to the change in volume:

$$\left(\frac{\partial E}{\partial P} \right)_T = - \frac{\partial v}{nF} \quad (17)$$

If the volume change of the reaction is negative (if fewer moles of gas are generated by the reaction than consumed, for instance), then the cell voltage will increase with increasing pressure.

Usually, only gas species produce an appreciable volume change. Assuming that the ideal gas law applies, we can write Eq. (17) as:

$$\left(\frac{\partial E}{\partial P}\right)_T = -\frac{\Delta n_g RT}{nFp} \quad (18)$$

where Δn_g represents the change in the total number of moles of gas upon reaction. Pressure, like temperature, turns out to have a minimal effect on reversible voltage:

$$E_{\text{rev}} = E_{\text{rev}}^{\circ} - \frac{(\Delta n)RT}{nF} \ln P \quad (19)$$

2.1 Enthalpy of reaction for a fuel cell

Enthalpy is the thermodynamic quantity that states the total heat content of the system, which is the sum of all internal process in a closed system [2]. For homogeneous systems, enthalpy is solely based on the size of the system as it is an extensive property. Enthalpy (H) is the sum of the internal energy of the system (U) and the product of pressure (P) and volume (V) of the system. The change in enthalpy in a system is equal to the heat gained or lost in the system:

$$H = U + PV \quad (20)$$

The enthalpy change (ΔH) for a reaction in a fuel cell indicates the full amount of heat released by the reaction at a constant pressure; hence, enthalpy is simply equal to the heat released:

$$H = Q_p \quad (21)$$

At constant pressure and volume, the thermodynamic properties of the cell are related to the behaviour of its potential and are defined from the Gibbs-Helmholtz equation [3]:

$$\Delta H = \Delta G - T \left(\frac{\partial \Delta G}{\partial T}\right)_p \quad (22)$$

In accordance with Eq. (5), in terms of electrochemical processes, change in enthalpy can be written as:

$$\Delta H = nF \left[T \left(\frac{\partial E_{\text{cell}}}{\partial T}\right)_p - E_{\text{cell}} \right] \quad (23)$$

The overall reaction in Eq. (1) is the same as the reaction of hydrogen combustion. Combustion is an exothermic process, which means that there is energy released in the process [4, 5]:



From the table of enthalpies of formation (h_f°) and absolute entropies of formation (s_f°) obtained from the basic thermodynamic data (see **Table 1**), the heat of formation of both liquid and vapour water can be calculated using the equation above to form:

The heat (or enthalpy) of a chemical reaction is the difference between the heat of formation of products and reactants. This means [6]:

$$\begin{aligned} \Delta H_f &= \sum \text{products} - \sum \text{reactants} \\ &= (h_f)_{\text{H}_2\text{O}} - \left[(h_f)_{\text{H}_2} + 1/2 (h_f)_{\text{O}_2} \right] \end{aligned} \quad (25)$$

$$\Delta H_{f, \text{H}_2\text{O}(l)} = \text{HHV} = -285.8 \text{ kJ/mol} \text{ and } \Delta H_{f, \text{H}_2\text{O}(g)} = \text{LHV} = -241.8 \text{ kJ/mol.}$$

The enthalpy of the hydrogen combustion reaction (Eq. (25)) is also called hydrogen's heating value. The 285.83 kJ/mol is known as hydrogen's higher heating value (HHV), which means that 1 mol of hydrogen is fully combusted with 1/2 mol of oxygen and cooled down to 25°C. If hydrogen is combusted with sufficient excess oxygen and cooled down to 25°C, the value will become 241.82 kJ/mol, which is known as hydrogen's lower heating value (LHV) [7]. The difference between the LHV and HHV of 44.01 kJ/mol is equal to the molar latent heat of water vaporisation at 25°C.

In the heating value for reactions involving water as a product, there is a choice in the calculation of thermodynamic voltages between a high heating value (HHV) and a low heating value (LHV), defined as follows for a given reaction:

- High heating value: It is assumed all the product water is in the liquid phase.
- Low heating value: It is assumed all the product water is in the gas phase.

Note that all calculations are based on HHV or LHV and do not necessarily correspond to the actual physical state of the product water at the fuel cell electrode. The terms HHV and LHV are used in combustion calculations as well, where the product water is nearly always in the gas phase. The difference between the two values is proportional to the latent heat of vaporisation of the liquid. The use of the LHV (gas-phase vapour product) will result in a lower calculated thermal voltage, since some energy is used for the latent heat of vaporisation of the liquid. In practice, the LHV is completely appropriate for high-temperature fuel cells, but the HHV is also commonly used. An important point regarding low-temperature fuel cells that is often confusing is that the choice of HHV or LHV is arbitrary and 100°C is not a point of demarcation between the two. Often 100°C is thought of as a natural boundary between the HHV and LHV because it is the phase change temperature of water at 1 atm pressure. The delineation between liquid and gas, however, is more complex and is related to the local vapour pressure and total pressure.

2.2 Entropy (S)

The concept of entropy is one of the thermodynamic parameters that are important to the science of fuel cells to understand. Entropy is defined as the

	h°_f (kJ/mol)	s°_f (kJ/mol.K)	ΔG°_f (kJ/mol)
Hydrogen, H ₂	0	0.131	0
Oxygen, O ₂	0	0.205	0
Water (liquid), H ₂ O (l)	-285.8	0.070	-237.2
Water (vapour), H ₂ O (g)	-241.8	0.189	-228.6

Table 1. Enthalpies of formation and absolute entropies of formation of fuel cell reactants and products (at 25°C and 1 atm).

measure of the unavailable energy in a closed thermodynamic system that is usually considered to be a measure of the system's disorder, known as the second law of thermodynamics. The total entropy of a system increases over time, as the molecular disorder increases. Therefore, if the system is in equilibrium, the change between the initial state and the final state, the system is going through a reversible change. Since entropy represents the unavailable energy used in the system, a system of zero entropy optimises the work output of the system. The fuel cell generates the amount of electricity and rejects an amount of thermal energy Q to its environment. As there is heat transfer, and it is a real system, there must be an increase in entropy. The amount of heat rejected and the maximum amount of electrical power that a fuel cell will generate can be determined by formulating the entropy changes occurring in the cell:



The entropy of H_2 and O_2 will disappear, but the new entropy of H_2O and heat formation will appear. As long as the process is reversible, which is the assumption for the fuel cell, the entropy appearing in the rejected heat can be written as [8]:

$$\Delta S = \frac{\Delta Q_{\text{rev}}}{T} \quad (27)$$

The equation for the change of entropy (ΔS) is equal to the change in enthalpy (ΔQ) divided by the temperature (T) of the system.

As there is no heat transfer in electrical work, the entropy is zero. The entropy in an H_2/O_2 fuel cell can be calculated using the absolute entropy values given in **Table 1**. The second law of thermodynamics requires that in a fuel cell, there will be a net increase in entropy. Therefore, the entropy that shows up in the rejected heat and the product water (liquid water) must be greater than the entropy contained in the reactants (H_2 and O_2) [9, 10]:

Entropy gain \geq entropy loss

$$\frac{Q}{T} + \sum \text{products} \geq \sum \text{reactants} \quad (28)$$

$$Q \geq T [\text{products} - \text{reactants}] \quad (29)$$

To calculate the amount of heat rejected per mole of H_2 :

$$\begin{aligned} \sum S_{\text{reactants}} &= 0.131 \frac{\text{kJ}}{\text{mol.k}} \times 1 \text{ mol H}_2 + 0.205 \frac{\text{kJ}}{\text{mol.k}} \times \frac{1}{2} \text{ mol O}_2 \\ &= 0.2335 \text{ kJ/mol.K} \end{aligned}$$

$$\begin{aligned} \sum S_{\text{products}} &= 0.070 \frac{\text{kJ}}{\text{mol.k}} \times 1 \text{ mol H}_2\text{O} (l) \\ &= 0.070 \text{ kJ/mol.K} \end{aligned}$$

The minimum of heat released during the reaction:

$$\begin{aligned} Q_{\text{min}} &= T \left(\sum S_{\text{reactants}} - \sum S_{\text{products}} \right) = 298 \text{ k} (0.0134 - 0.070) \\ &= 48.72 \text{ kJ per mole of H}_2 \end{aligned}$$

As heat capacity effects are generally minor, ΔH and ΔS values are usually assumed to be independent of temperature. A simplified entropy calculation can be with entropy values obtained from **Table 1**:

$$\Delta S_f = (s^\circ)_{\text{H}_2\text{O}} - \left[(s^\circ)_{\text{H}_2} + 1/2 (s^\circ)_{\text{O}_2} \right] \quad (30)$$

$$\Delta S_{f, \text{H}_2\text{O} (l)} = \text{HHV} = -0.163 \text{ kJ/mol.K} \text{ and } \Delta S_{f, \text{H}_2\text{O} (g)} = \text{LHV} = -0.045 \text{ kJ/mol.K.}$$

2.3 Gibbs free energy

From the second law of thermodynamics, the change in free energy, or maximum useful work, can be obtained when a ‘perfect’ fuel cell operating irreversibly is dependent upon temperature. Therefore, W_{el} , the electrical power output, is [11]:

$$\Delta G = \Delta H - T \Delta S \quad (31)$$

where H is the total energy of the system, S is the ‘unavailable’ energy and G is the ‘free’ energy, or the energy available to do useful work.

The change in Gibbs free energy varies with both temperature and pressure. It can be shown that for a H_2/O_2 fuel cell:

$$\Delta G_f = \Delta G_f^\circ + RT \ln \left[\frac{p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{O}_2}^{1/2}} \right] \quad (32)$$

where ΔG_f° is the change in Gibbs free energy at standard pressure, which varies with the temperature T of the fuel cell, in Kelvin; p_{H_2} , p_{O_2} and $p_{\text{H}_2\text{O}}$ are the partial pressure of the hydrogen, oxygen and vapour, respectively; and R is the universal gas constant (8.314 J/(kg.K)). The fact that the value of ΔG_f° is negative means that the energy is released from the reaction [12–14].

For the H_2/O_2 fuel cell reaction, the change in Gibbs free energy is:

$$\Delta G_f = G_{f,\text{products}} - G_{f,\text{reactants}} = G_{f,\text{H}_2\text{O}} - [G_{f,\text{H}_2} + G_{f,\text{O}_2}] \quad (33)$$

The maximum possible electrical energy output and the corresponding electrical potential difference between the cathode and anode are achieved when the fuel cell is operated under the thermodynamically reversible condition. This maximum possible cell potential is called ‘reversible cell potential’, one of the significantly important parameters for FC.

From Eq. (23) we calculated ΔH to be 285.830 kJ/mol for hydrogen’s HHV and 241.98 kJ/mol for hydrogen’s LHV, while for ΔS in Eq. (28), the entropy of reaction is 0.163 kJ/mol for HHV and for LHV 0.044 kJ/mol.

To calculate Gibbs free energy for H_2/O_2 fuel cell reaction:

$$\Delta G_f (l) = \text{HHV} = -285.8 \text{ kJ/mol} - (273.15 \text{ K}) (-0.1633 \text{ kJ/mol}) = -237.1 \text{ kJ/mol}$$

$$\Delta G_f (g) = \text{LHV} = -241.8 \text{ kJ/mol} - (273.15 \text{ K}) (-0.045 \text{ kJ/mol}) = -228.6 \text{ kJ/mol}$$

The fact that the value of ΔG_f° is negative means that the energy is released from the reaction. From Eq. (6), the potential or reversible open cell voltage E° of any electrochemical device is defined as:

$$E^\circ = -\frac{\Delta G}{nF}$$

where n is the amount of exchanged electrons and F is Faraday's constant. For the hydrogen oxidation or water formation, $n = 2$. The free enthalpies ΔG of water formation are either:

$$\Delta G_{f, H_2O(l)} = -237.13 \text{ kJ/mol or } \Delta G_{f, H_2O(g)} = -228.57 \text{ kJ/mol}$$

The corresponding potential is therefore (Table 2):

$$E_1^\circ = \frac{-\Delta G_{f, H_2O(l)}}{2F} = -1.23 \text{ V and } E_g^\circ = \frac{-\Delta G_{f, H_2O(g)}}{2F} = -1.18 \text{ kJ/mol}$$

2.4 Specific heat capacity

Another property that is important in thermodynamics and the study of fuel cells is the specific heat. The specific heat of a solid or liquid is usually defined as the heat required to raise unit mass through 1 degree temperature rise. For a gas there are an infinite number of ways in which heat may be added between any two temperatures, and hence a gas could have an infinite number of specific heats. However, only two specific heats for gases are defined, as specific heat at constant volume, c_v , and specific heat at constant pressure, c_p .

For a reversible ideal gas, a non-flow process at constant pressure and at constant volume is given as, respectively:

$$dQ = C_p dT \quad (34)$$

and

$$dQ = C_v dT \quad (35)$$

For a substance that is modelled as incompressible, the specific heats are assumed to be equal, $C_p = C_v$ [15]:

$$C_p = C_v = \frac{dQ}{dT} \quad (36)$$

For an ideal gas in which a fuel cell is assumed to be, the specific enthalpy depends only on temperature:

$$h_f = dQ = C_p dT \quad (37)$$

$$h_T = h_{298.15} + \int_{298.15}^T C_p dT \quad (38)$$

where $h_{298.15}$ is the enthalpy at a reference temperature.

The specific heat can also be related to specific entropy at temperature T :

	ΔH (kJ/mol)	ΔG (kJ/mol)	ΔS (kJ/mol.K)	E (V)
$H_2 + 1/2O_2 \rightarrow H_2O(l)$	-285.8	-237.1	-0.163	1.23
$H_2 + 1/2O_2 \rightarrow H_2O(g)$	-241.8	-228.6	-0.045	1.18

Table 2.
 Enthalpies, entropies and Gibbs free energy of H_2/O_2 fuel cell reaction in (kJ/mol.K) and the resulting theoretical cell potential at 25°C.

$$dS = \frac{dQ}{T} = C_p \frac{dT}{T} \quad (39)$$

$$s_T = s_{298.15} + \int_{298.15}^T \frac{1}{T} C_p dT \quad (40)$$

The specific enthalpy and entropy for H₂/O₂ fuel cell are given by [16]:

$$\Delta H = [h^\circ_{f,H_2O} + C_{p, H_2O} (T - 298.15)]_{H_2O} - \frac{1}{2} [h^\circ_{f,O_2} + C_{p, O_2} (T - 298.15)]_{O_2} - [h^\circ_{f,H_2} + C_{p, H_2} (T - 298.15)]_{H_2} \quad (41)$$

$$\Delta S = \left[h^\circ_{f,H_2O} + C_{p, H_2O} \ln \frac{T}{298.15} \right]_{H_2O} - \frac{1}{2} \left[h^\circ_{f,O_2} + C_{p, O_2} \ln \frac{T}{298.15} \right]_{O_2} - \left[h^\circ_{f,H_2} + C_{p, H_2} \ln \frac{T}{298.15} \right]_{H_2} \quad (42)$$

The values of molar entropy and enthalpy of formation at 298.15 K are given in **Table 1** [17]. Eqs. (38) and (40) can be used to determine the specific heat capacity, C_p, at constant pressure. Specific heat relationships are generally modelled with a high-order polynomial, such as those listed below for hydrogen fuel cell gases, valid in the range of 300–1000 K [18]. It is reported that over a range of temperatures, C_p is not constant, while over the range of 300–350 K, the obtained C_p values are 0.6% accurate [4].

Hydrogen, H₂:

$$C_p (T) = 3.057 + 2.677 \times 10^{-3} (T) - 5.810 \times 10^{-6} (T)^2 + 5.521 \times 10^{-9} (T)^3 - 1.812 \times 10^{-12} (T)^4$$

Oxygen, O₂:

$$C_p (T) = 3.626 - 1.878 \times 10^{-3} (T) + 7.055 \times 10^{-6} (T)^2 - 6.764 \times 10^{-9} (T)^3 + 2.156 \times 10^{-12} (T)^4$$

For H₂O:

$$C_p (T) = 4.070 - 1.808 \times 10^{-3} (T) + 4.152 \times 10^{-6} (T)^2 - 2.964 \times 10^{-9} (T)^3 + 0.807 \times 10^{-12} (T)^4$$

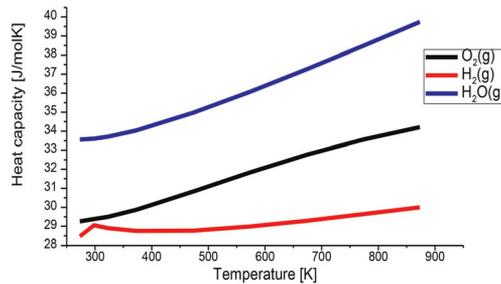


Figure 2. Specific heat values for hydrogen, oxygen and water as a function of temperature.

The heat capacity values for hydrogen, oxygen and water as a function of temperature are shown in **Figure 2**. The data were obtained from Kabza [4].

3. Fuel cell thermodynamic efficiency

In the process of energy conversion in a fuel cell, the initial chemical energy between the enthalpy of the products and reactants is converted into electrical energy and thermal energy, as stated in the first law of thermodynamics. The efficiency of any energy conversion device is defined as the ratio between useful energy output and energy input [19–22]:

$$\eta = \frac{\text{actual electrical work}}{\text{maximum available work}}$$

$$\eta = \frac{\Delta G}{\Delta H} = \frac{\Delta H - T\Delta S}{\Delta H} \quad (43)$$

The maximum possible thermodynamic efficiency of a fuel cell can be written as [9]:

$$\eta = 1 - \frac{T\Delta S}{\Delta H} \quad (44)$$

In the case of a fuel cell, the useful energy output is the electrical energy produced, and the energy input is the enthalpy of hydrogen, that is, hydrogen's HHV. Assuming that all of the Gibbs free energy can be converted into electrical energy (the reaction is reversible), the maximum theoretical efficiency of a fuel cell is [23, 24] (**Figure 3**):

$$\eta = \frac{\Delta G}{\Delta H} = \frac{237.34}{286.02} \times 100\% = 83\%$$

For hydrogen's LHV, the fuel cell efficiency would be [26]:

$$\eta = \frac{\Delta G}{\Delta H} = \frac{228.74}{241.98} \times 100\% = 94.5\%$$

The LHV has higher efficiency compared to HHV, because the reversible efficiency of the fuel cell decreases as the operating temperature increases [27].

The expected fuel cell efficiency is not always achieved due to thermodynamic and electrochemical irreversible losses [28].

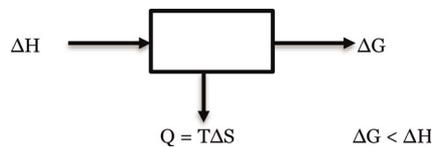


Figure 3. Energy inputs and outputs for a fuel cell as an energy conversion device [25].

4. Irreversible losses

Other than calculating energy quantities during the conversion of chemical energy to electrical energy, there is also the matter of electron flow through

materials in the fuel cell process. The single fuel cell provides a voltage dependent on operating conditions such as temperature, applied load and fuel/oxidant flow rates [29, 30]. If a fuel cell is supplied with reactant gases, but the electric current is not closed, it will not generate any current, and one would expect the cell potential to be at the theoretical cell potential for the given conditions (temperature, pressure and concentration of reactants). In reversible conditions, the energy loss is the heat lost towards the environment, $T\Delta s$, due to negative entropy [12].

However, in practice, the thermodynamic cell potential is decreased from its ideal potential, usually less than 1 V, due to irreversible losses known as overpotential or polarisation [17]. The fuel cell performance overpotential is due to [14, 31]:

- i. Activation overpotential: The activation polarisation is related to the charge transfer processes occurring during the electrochemical reactions on electrode surfaces. The losses are caused by the slowness of the reactions taking place on the surface of the electrodes [32]. Activation polarisation depends on the nature of type of electrode, ionic interactions, ion-solvent interactions and the electrode-electrolyte interface [33].
- ii. Ohmic overpotential: In most fuel cells, the most important contribution to this resistance is the electrolyte, due to the ionic nature of its conductivity, resistance to the flow of electrons through the electrodes and the contact resistance at the cell terminals.
- iii. Mass transport (concentration) overpotential: Concentration polarisation occurs due to a decrease in the concentration of the reactants at the electrode-electrolyte interface. Due to diffusion or convection problems in the electrolyte, the concentration of the reactants is not maintained at the initial level. Reaction product accumulation can also cause a dilution of reactants. The concentration gradient thereby formed causes a drop in electrode activity, and the terminal voltage is reduced.
- iv. Fuel crossover overpotential: ‘Crossover’ is one of the common effects occurring in alcohol fuel cells [22]. Although the electrolyte, a polymer membrane, is not electrically conductive and practically impermeable to reactant gases, some amount of fuel will diffuse from anode to cathode to react with oxygen, resulting in fewer electrons in the generated current of electrons that travel through an external circuit [34]. With this transit the cathode potential decreases, thus reducing the overall efficiency of a fuel cell. It occurs when the intermediates generated by fuel oxidation have higher concentration than oxygen at the cathode. The increase of temperature escalates the crossover effect [35].

The standard measure of performance is the polarisation curve, which represents the cell voltage behaviour against operating current density (**Figure 4**). From the figure, the voltage loss caused by mixed potential and crossover, activation polarisation, ohmic polarisation and mass transport losses is the most significant in the tail of the I-V curve. The maximum fuel cell is then examined through the reversible voltage of the system, which is calculated using thermodynamics and the actual voltage of the system [36]. The final voltage is lower than the thermodynamic voltage and is usually between 0.5 and 1.0 V. Although polarisations cannot be eliminated, material choice and electrode designs can contribute to their minimisation [37]:

$$E = E_{\text{therm}} - \eta_{\text{act}} - \eta_{\text{ohm}} - \eta_{\text{conc}} \quad (45)$$

where E is the cell potential, E_{therm} is the thermodynamic potential, η_{act} is the voltage loss due to activation polarisation, η_{ohm} is the voltage loss due to ohmic polarisation and η_{conc} is the voltage loss due to mass transport polarisation and the entropy generation results [38–41]:

$$S = \frac{E}{nFT} \quad (46)$$

In addition, the related heat lost for irreversibility can be calculated as (Figure 4):

$$q = T\Delta s - nFE = \Delta H - \Delta G - nFE \quad (47)$$

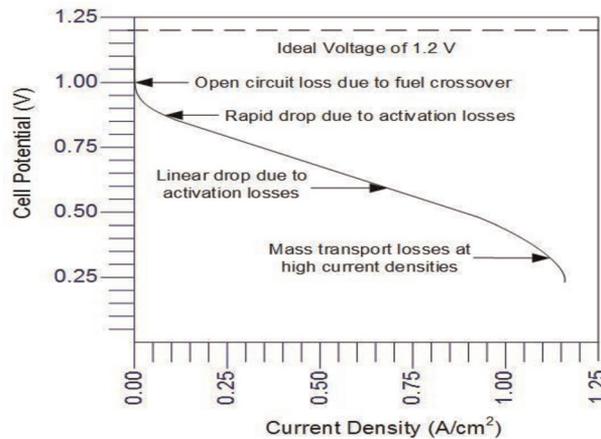


Figure 4. H_2/O_2 polarisation curve at equilibrium and voltage losses in fuel cell [30].

5. Conclusion

Thermodynamics is used to understand the process of energy conversion in fuel cells. The determination of a fuel cell's performance depends on thermodynamic evaluation. The heat potential of a fuel is given by the enthalpy of the reaction. Not all heat potential of a fuel can be used to perform useful work; the reversible work of a fuel is defined by Gibbs free energy, which is the electrical work. The study of the electrical effects shows that the molar flow of the fuel used is proportional to the electric current and the reversible work is proportional to the reversible voltage. The cell voltage varies with temperature, pressure and reactant/product activities. Irreversible losses cause a difference in the efficiency of reversible and real processes, with efficiency of real processes always less than reversible processes. The losses are due to two major reasons, namely, irreversible kinetic losses and fuel utilisation losses.

Acknowledgements

We greatly appreciate the National Research Foundation and the Tertiary Education Support Programme for financial support as well as the Chemistry Department at the University of the Western Cape.

Author details

Lindiwe Khotseng
Department of Chemistry, University of the Western Cape, Cape Town,
South Africa

*Address all correspondence to: lkhotseng@uwc.ac.za

IntechOpen

© 2019 The Author(s). Licensee IntechOpen. This chapter is distributed under the terms of the Creative Commons Attribution License (<http://creativecommons.org/licenses/by/3.0>), which permits unrestricted use, distribution, and reproduction in any medium, provided the original work is properly cited. 

References

- [1] Yong-Qiang X, Chun-Hui L, Jin-Chuan F. The electrochemical thermodynamics for chemical reactions in dispersed cells. *Journal of Colloid and Interface Science*. 1999;217:107-110. DOI: 10.1006/jcis.1999.6221
- [2] Tran D, Tanner G, Yang K, Woodley R. Thermodynamic effects of nanotechnological augmentation of hydrogen fuel cells. *PAM Review*. 2017: 76-86. DOI: 10.5130/pamr.v4i0.1443
- [3] Spiegel C. PEM Fuel Cell Modeling and Simulation Using Matlab. New York, NY: Elsevier; 2008. 443 p
- [4] Kabza A. Fundamentals. In: Fuel Cell Formulary [Internet]. 2015. pp. 30–34. Available from: http://www.pemfc.de/FCF_A4.pdf [Accessed: 2019-09-11]
- [5] Winter M, Brodd J. What are batteries, fuel cells, and supercapacitors. *Chemical Reviews*. 2004;104(10): 4245-4270. DOI: 10.1021/cr02030k. Available from: <https://doi.org/10.1021/cr02030k>
- [6] Filho LP. Thermodynamic studies and applications of polymeric membranes to fuel cells and microcapsules [thesis]. Tarragona: Universitat Rovira i Virgili; 2007
- [7] Blomen LJM, Mugerwa MN. Fuel cell systems. In: Srinivasan S, Dave BB, Murugesamoorthi KA, Parthasarathy A, Appleby AJ, editors. *Overview of Fuel Cell Technology*. New York, NY: Plenum Press; 1993. pp. 37-72
- [8] Bejan A. *Advanced Engineering Thermodynamics*. Hoboken, NJ: Wiley; 2016. 741 p
- [9] Larminie J, Dicks A. *Fuel cell systems explained*. West Sussex: Wiley; 2003. 401 p
- [10] Sieniutycz S. Thermodynamic aspects of power generation in imperfect fuel cells: Part I. *International Journal of Ambient Energy*. 2010;31(4): 195-202. DOI: 10.1080/01430750.2010.9675812
- [11] Kakaç S, Pramuanjaroenkij LA, Vasiliev A. Mini-Micro Fuel Cells. In: Barbir F, editor. *Fuel Cell Basic Chemistry and Thermodynamics*. New York, NY: Academic Press; 2012. pp. 13-26. DOI: 10.1007/978-1-4020-8295-5_2
- [12] Offer GJ, Mermelstein J, Brightman E, Nigel PB. Thermodynamics and kinetics of the interaction of carbon and Sulphur with solid oxide fuel cell anodes. *Journal of the American Ceramic Society*. 2009; 92(4):763-780. DOI: 10.1111/j.1551-2916.2009.02980.x
- [13] Kee RJ, Zhu H, Goodwin DG. Solid oxide fuel cells with hydrocarbon. *Proceedings of the Combustion Institute*. 2005;30(2):2379-2404. DOI: 10.1016/j.proci.2004.08.277
- [14] Nether P. Two-dimensional transient model of a cascaded micro-tubular solid oxide fuel cell fed with methane. *Journal of Power Sources*. 2006;157(1):325-334. DOI: 10.1016/j.jpowsour.2005.07.077
- [15] Moran MJ, Shapiro HN. *Fundamentals of Engineering Thermodynamics*. 5th ed. New York, NY: Wiley; 2006. 831 p
- [16] EG & G Technical Services Inc. *Fuel Cells: A Handbook*. 7th ed. Morgantown; 2004. 427 p
- [17] Kotz JC, Treichel PM, Townsend JR, Treichel DA. Principles of chemical reactivity: Energy and chemical reactions. In: *Chemistry and Chemical Reactivity*. 10th ed. Stamford: Cengage Learning; 2015. pp. 180-217

- [18] Mench M. *Fuel Cell Engines*. Hoboken, NJ: Wiley; 2008 515 p
- [19] Singhal SC, Kendall K, editors. *High-Temperature Solid Oxide Fuel Cells: Fundamentals, Design and Applications*. Amsterdam: Elsevier; 2003. 406 p
- [20] Li X. Thermodynamic performance of fuel cells and comparison with heat engines. In: Zhao TS, Kreuer K-D, Van Nguyen T, editors. *Advances in Fuel Cells*. Oxford: Elsevier; 2007, p. 1-46
- [21] Haynes C. Clarifying reversible efficiency misconceptions of high temperature fuel cells in relation to reversible heat engines. *Journal of Power Sources*. 2001;**92**:199-203. DOI: 10.1016/S0378-7753 (00)00541-3
- [22] Dos Santos MC, Parreira LS, De Moura Souza F, Camargo Junior J, Gentil T. *Fuel Cells: Hydrogen and Ethanol Technologies*. In: Hashmi S, editor. *Reference Module in Materials Science and Materials Engineering*. Oxford: Elsevier; 2017. p. 1-21. DOI: 10.1016/8978-0-12-803581-8.09263-8
- [23] Pavelka M, Marski F. Detailed thermodynamic analysis of polymer electrolyte membrane fuel cells efficiency. *International Journal of Hydrogen Energy*. 2013;**38**(17): 7102-7113. DOI: 10.1016/j.ijhydene.2013.03.149
- [24] Barbir F. *Fuel cell basics*. In: Kakaç S, Pramuanjaroenkij A, Vasilie L, editors. *Mini-Micro Fuel Cells: Fundamentals and Applications*. Amsterdam: Springer; 2007. pp. 13-26
- [25] Barbir F. *PEM Fuel Cells: Theory and Practice*. Waltham: Elsevier; 2013. 509 p
- [26] Lutz AE, Larson RS, Keller JO. Thermodynamic comparison of fuel cells to the Carnot cycle. *International Journal of Hydrogen Energy*. 2002; **27**(10):1103-1111. DOI: 10.1016/S0360-3199(02)00016-2
- [27] Reimer U, Lehnert W, Holade Y, Kokoh B. Irreversible losses in fuel cells. In: Hacker V, Mitsushima S, editors. *Fuel Cells and Hydrogen: From Fundamentals to Applied Research*. Amsterdam: Elsevier; 2018. pp. 15-38
- [28] Sieniutycz S. Thermodynamic basis of fuel cell systems. *Cybernetics and Physics*. 2012;**1**(1):67-72
- [29] Harned HS, Owen BB. *The Physical Chemistry of Electrolytic Solutions*. 3rd ed. New York: Reinhold; 1958
- [30] Explanation of the thermodynamics behind fuel cell and electrolyser design [Internet]. 2018. Available from: www.fuelcellstore.com/blog-section/explanation-of-the-thermodynamics-behind-fuel-cell-and-electrolyser-design [Accessed: 2019-08-27]
- [31] Pilatowsky I, Romero RJ, Isaza CA, Gamboa SA, Sebastian PJ, Rivera W. *Thermodynamics of Fuel Cells*. London: Springer; 2011. pp. 25-36. DOI: 10.1007/978-1-84996-028-1
- [32] Acharya PR. *An advanced fuel cell simulator [thesis]*. Houston-Dallas-Austin, TX: Texas A&M University; 2004
- [33] Zhang J, Tang Y, Song C, Zhang J. Polybenzimidazole-membrane-based PEM fuel cell in the temperature range of 120–200°C. *Journal of Power Sources*. 2007;**172**(1):163-171. DOI: 10.1016/j.jpowsour.2007.07.047. Available from: <https://doi.org/10.1016/j.jpowsour.2007.07.047>
- [34] Corre GPG, Irvine JTS. High temperature fuel cell technology. In: Stolten D, editor. *Hydrogen and Fuel Cells: Fundamentals, Technologies and Applications*. Wenham: Wiley-VCH Verlag; 2010. pp. 61-88

- [35] Rajput RK. Engineering Thermodynamics. 3rd ed. Laxmi: New Delhi; 2007. 922 p
- [36] Srikar VT, Turner KT, Yung TIA, Spearing SM. Structural design considerations for micro-machined solid-oxide fuel cells. *Journal of Power Sources*. 2004;**125**(1):62-69. DOI: 10.1016/j.jpowsour.2003.07.002
- [37] Umberto L. Overview on fuel cells. *Renewable and Sustainable Energy Reviews*. 2014;**30**:164-169. DOI: 10.1016/j.rser.2013.09.025
- [38] Moran MJ, Shapiro HN. Fundamentals of Engineering Thermodynamics. 5th ed. New York, NY: Wiley; 2006. 831 p
- [39] Wark K Jr. Advanced Thermodynamics for Engineers. New York, NY: McGraw-Hill; 1995 622 p
- [40] Bejan A. Advanced Engineering Thermodynamics. Hoboken, NJ: Wiley; 2016. 741 p
- [41] Fuel Cell Technology. Hydrogen Fuel Cell Engines and Related Technologies. 2001. Available from: <https://energy.gov/sites/prod/files/2014/03/f9/fcm00r0.pdf> [Accessed: 09-09-2019]