

Chapter 2

Cell Voltages, Polarisation and Performances

The fuel cell works under defined conditions such as gas variables, temperature, etc. The operating conditions determine the efficiency of fuel cells and hence require rigorous understanding. Behind the operation of every fuel cell, there are series of thermodynamic and chemical equations that should be well understood. In this chapter, we determine the performance, efficiency and then losses of the fuel cell. The open-circuit voltage (OCV) of a fuel cell is also taken into consideration along with various factors including pressure, temperature, fuel constituents and concentration, etc.

2.1 Electromotive Force of Fuel Cell

Before obtaining the EMF for the cell, we need to have a clear understanding of Gibbs free energy (ΔG). Gibbs free energy is defined as the energy available to do external work. Nowadays, a most common term ‘exergy’ is used, which is defined as the total external work extracted including that due to pressure and volume changes. We also use the term ‘zero-energy point’ for the elements in a normal state of standard pressure (0.1 MPa) and temperature (25°C).

Gibbs energy is basically free energy available for conversion into usable work. The change in Gibbs free energy is given by

$$\Delta G = \Delta H - T\Delta S \quad (2.1)$$

ΔH is the enthalpy change, which is the total thermal energy available, ΔS is the entropy change and $T\Delta S$ represents unavailable energy attributed to the entropy or disorder of the system. When the entropy change is positive, then the heat is extracted from the surroundings whereas for the negative entropy change, heat is given out to the surroundings.

The Gibbs free energy of formation G_f can also be expressed in terms of products and reactants as follows:

$$\Delta G_f = G_f(\text{products}) - G_f(\text{reactants}) \quad (2.2)$$

We can demonstrate the Gibbs energy of formation with the help of the following reaction:



$$\Delta G_f = (G_f)_{\text{H}_2\text{O}} - \left[(G_f)_{\text{H}_2} + \frac{1}{2}(G_f)_{\text{O}_2} \right] \quad (2.4)$$

However, for a fuel cell the reaction mechanism is not as simple as it appears to be. This can be addressed by considering the electrons moving in an external circuit. For each hydrogen molecule used, 2 electrons pass through the external circuit. Hence, for 1 mol of hydrogen used, $2N$ electrons will migrate through the external circuit [N – Avogadro's number or 6.023×10^{23} atoms]. Hence, the total charge flowing through the external circuit becomes $-2Ne$ or $-2F$ coulombs ($F = \text{Faraday's constant} = Ne = \text{charge on one mole of electrons}$).

The total electric work done in moving $-2F$ charge around the cell-circuit, for E voltage (ideal potential) of fuel cell is given by

$$\text{Work done} = -2FE \text{ J} \quad (2.5)$$

This work released Gibbs free energy (provided the system is reversible and has no losses).

$$\Rightarrow \Delta G_f = -2FE \quad (2.6)$$

$$\Rightarrow E = -\frac{\Delta G_f}{2F} \quad (2.7)$$

The more general form of Eq. (2.7) is given by

$$\boxed{E = -\frac{\Delta G_f}{nF}} \quad (2.8)$$

where n represents number of electrons participating in the cell reaction. Equation (2.8) is the fundamental electromotive force equation for the fuel cell. ' E ' also represents the OCV of cell.

For general cell reaction, the free energy is expressed as:



The free energy change is given by

$$\Delta G_f = \Delta G_f^\bullet + RT \ln \frac{[C]^x [D]^y}{[A]^u [B]^v} \quad (2.10)$$

R is the gas constant and $\Delta G_f^\bullet$ is the free energy change at standard temperature and pressure (STP) conditions. Substituting (2.8) in (2.10), we find

$$E = E^\circ + \frac{RT}{nF} \ln \frac{[A]^u [B]^v}{[C]^x [D]^y} \quad (2.11)$$

Equation (2.11) is the general form of the Nernst equation, where $[A]^u [B]^v$ is the reactant activity and $[C]^x [D]^y$ is the product activity. Hence, it is clear from Eq. (2.11), that the increase in concentration of reactants increases the cell potential. The potential can also be obtained by calculating the heat capacities, entropies and enthalpies. The heat capacity (C_p) can be given by

$$C_p = a + bT + cT^2 \quad (2.12)$$

where T is the temperature and a , b and c are empirical constants. Hence, the change in heat capacities of products and reactants can be obtained as

$$\Delta C_p = \Delta a + \Delta(bT) + \Delta(cT^2) \quad (2.13)$$

or

$$dC_p = da + d(bT) + d(cT^2) \quad (2.14)$$

The changes in enthalpy and entropy are expressed as:

$$\Delta S = \Delta S^\circ + \int_{298}^T \frac{\Delta C_p}{T} dT \quad (2.15)$$

and

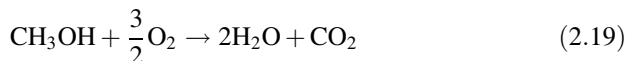
$$\Delta H = \Delta H^\circ + \int_{298}^T \Delta C_p dT \quad (2.16)$$

where ΔS° and ΔH° are the changes in entropies and enthalpies at standard temperature (298 K) and pressure. Using Eq. (2.14) in Eqs. (2.15) and (2.16) yields following results:

$$\Delta S = \Delta S^\circ + a \ln\left(\frac{T}{298}\right) + b(T - 298) + \frac{1}{2}C(T - 298)^2 \quad (2.17)$$

$$\Delta H = \Delta H^\circ + a(T - 298) + \frac{1}{2}(b - 298)^2 + \frac{1}{3}C(T - 298)^3 \quad (2.18)$$

We can obtain OCV for some fuel cells and batteries. For example, for DMFC [Chap. 1, Eq. (2.22)], the cell reaction is given by

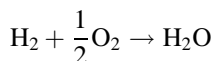


$6e^-$ are passing through the external circuit for each methanol molecule. The change in Gibbs free energy for Eq. (2.19) is -698 kJ/mol. By using Eq. (2.8), we obtain

$$E = \frac{698 \times 10^3}{6 \times 96,485} = 1.21 \text{ V} \quad (2.20)$$

(F = Faraday constant = $Ne = 6.023 \times 10^{23} \times 1.6 \times 10^{-19} \text{ C} = 96,485 \text{ C}$).

For a hydrogen fuel cell, the ΔG_f is 210.3 kJ/mol at temperature of 400°C. The basic reaction is given by:

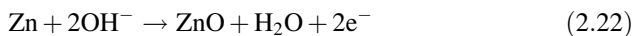


The OCV, ' E ' at 400°C is given by

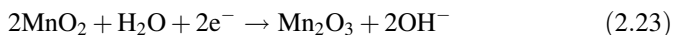
$$E = \frac{210.3 \times 10^3}{2 \times 96,485} = 1.09 \text{ V} \quad (2.21)$$

Similarly for batteries (here alkali battery), the anode and cathode reactions are given by:

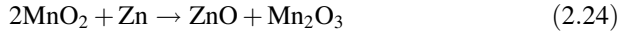
At Anode:



At Cathode:



The overall cell reaction is given by



The changes in Gibbs free energy for Eq. (2.24) is -277 kJ/mol, which yields OCV for transfer of $2e^-$ in the outer circuit follows.

$$E = \frac{277 \times 10^3}{2 \times 96,485} = 1.44 \text{ V}$$

2.2 Cell Efficiency

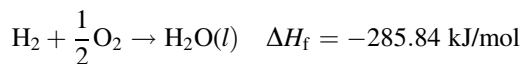
There are two processes which may take place inside a fuel cell, i.e., reversible or irreversible. If all energy is converted into electrical energy without any loss, then the process is considered to be reversible. On the other hand, if some of the energy is converted to heat which leads to losses in the system, then the process is considered to be irreversible. The efficiency of reversible system is considered to be 100 %, whereas for an irreversible system the efficiency is $<100\%$ attributed to the loss due to some thrown away or wasted energy. The efficiency of an energy conversion system (such as a fuel cell) is defined as electric energy produced per mol of fuel relative to the change in chemical energy of stored fuel; i.e.,

$$\eta = \frac{\Delta G_f}{\Delta H_f} \quad (2.25)$$

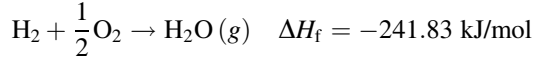
ΔH_f is the enthalpy of formation and is also considered to be the calorific value of fuel. The value of ΔH_f is positive when energy is required for the process whereas its negative value represents release of energy. The maximum possible efficiency is defined as:

$$\eta = \frac{\Delta G_f}{\Delta H_f} \times 100 \quad (2.26)$$

The efficiency of a fuel cell is determined by considering the standard free energy of the formation of water



or



The difference between the two heats of formation is 44.01 kJ/mol and gives the molar enthalpy of vaporisation of water (latent heat). The efficiency of an ideal fuel cell operation at standard conditions is $\left(\frac{237.30}{285.84}\right) = 0.83$ or 83% for the free energy of 237.3 kJ/mol.

The efficiency depends upon the temperature and pressure, etc., of the system, which is discussed later on in this chapter. The efficiency of a system can also be expressed in terms of the maximum EMF of a cell. Due to the losses in the fuel cells, the efficiency of systems decreases and actual cell voltage (V_{actual}) decreases as compared to the ideal cell voltage (V_{ideal}).

$$\begin{aligned} \eta &= \frac{\text{Useful energy}}{\Delta H_f} = \frac{V_{\text{actual}} \times \text{Current}}{V_{\text{ideal}} \times \frac{\text{Current}}{0.83}} \\ \eta &= \frac{0.83 V_{\text{actual}}}{V_{\text{ideal}}} \end{aligned} \quad (2.27)$$

For illustration, the efficiency of a hydrogen fuel cell operating at 25°C and after pressure is given by

$$\text{The open circuit voltage } E = -\frac{\Delta G_f}{nF}$$

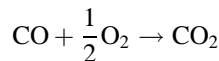
At 25 °C, $\Delta G_f = -237.3 \text{ kJ/mol}$

$$\Rightarrow E = \frac{237.3 \times 10^3}{2 \times 96,485} = 1.22 \text{ V}$$

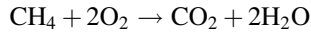
As the OCV is the ideal voltage, hence we can say, $V_{\text{ideal}} = 1.22 \text{ V}$. Using this value of V_{ideal} in Eq. (2.28), we get

$$\begin{aligned} \eta &= 0.83 \times \frac{V_{\text{actual}}}{1.22} = 0.675 V_{\text{actual}} \\ \Rightarrow \eta &= 0.675 V_{\text{actual}} \end{aligned} \quad (2.28)$$

The cell voltage will vary for different temperature and current densities, hence changing the efficiencies. For example, η changes from 8.27 at 100°C to 52% at 1000°C, when we use carbon monoxide, i.e.,



whereas, η does not change considerably for following reaction



This is due to the fact that the ΔG_f changes considerably with temperature for formation of carbon dioxide from the carbon monoxide. In contrast to this, the ΔG_f for formation of CO_2 from methane remains almost constant w.r.t. temperature.

2.3 Polarisation and Cell Losses

In the previous section, we have obtained the open-circuit value (OCV) for a fuel cell as

$$E = -\frac{\Delta G_f}{nF}$$

This value is considered to be maximum for the ideal case. For example, at 200°C , the $\Delta G_f = -220$ kJ, which yields

$$E = \frac{220 \times 10^3}{2 \times 96,485} = 1.14 \text{ V}$$

Anyhow, the actual performance of a fuel cell is smaller than this voltage. Figure 2.1 demonstrates the ideal performance and actual performance of the cell.

Fig. 2.1 Graph depicting ‘no loss’ voltage and ‘actual voltage’

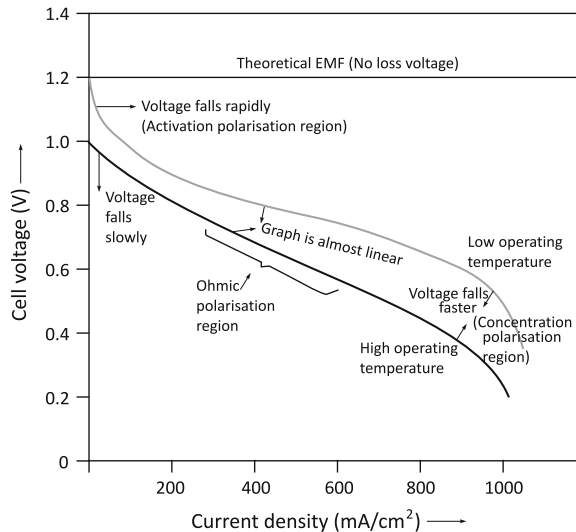


Figure 2.1 shows the variation of cell voltage with current density (current/area) for the cell operating at high and low temperatures. The initial fall in voltage is small for the cells operating at high temperatures, whereas the initial voltage fall is high for the cells operating at low temperatures. In addition to this, the cells operating at higher temperatures exhibit more linear behaviour. The reversible system is considered to be the ideal system because it is a ‘no loss’ system. The actual potential of a cell decreases from its ideal potential due to irreversible losses in the system. These fuel cell irreversibilities contribute to the voltage drop of the system. There are four major factors which contribute to the decrease in cell performance. The primary four sources of losses are fuel cross-over, activation polarisation, ohmic polarisation and concentration polarisation. We can summarise the total voltage as

$$\text{Total voltage } V = \text{Open circuit voltage } E - \text{Losses} \quad (2.29)$$

The fuel crossover losses are due to the wastage of fuel passing through the electrolyte. Fuel crossover losses are prominent in the fuel cell operation at low temperatures. The activation losses are due to the slow reaction kinetics on the surface of the electrodes. Ohmic losses are due to the resistance offered to the flow of electrons and ions through electrodes and electrolytes, respectively. The concentration losses are due to the change in concentration of the reactants at the surface of electrodes.

2.3.1 Activation Losses

Activation losses are the main cause of voltage drop (mainly at cathode) for the low- and medium-temperature fuel cells. In 1905, Tafel obtained a pattern for the verification of overvoltage against current density as shown in Fig. 2.2.

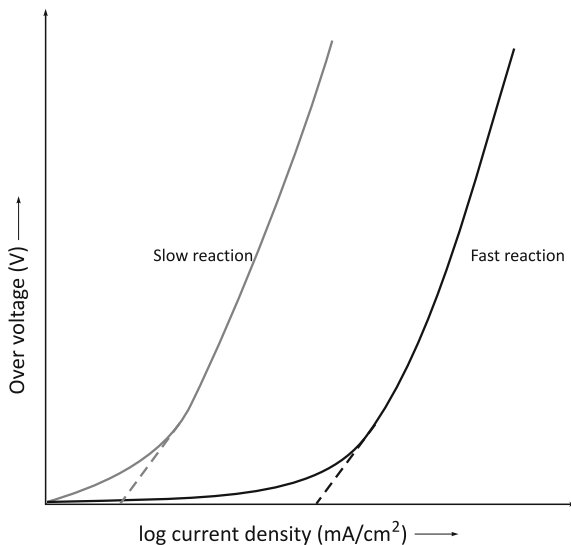
The voltage drop due to activation polarisation is represented by the Tafel equation as follows:

$$\eta_{\text{act}} = \frac{2.3 RT}{\alpha nF} \log \left(\frac{i}{i_0} \right) \quad (2.30)$$

where i_0 is the exchange current density.

$$\begin{aligned} \Rightarrow \eta_{\text{act}} &= \frac{2.3 RT}{\alpha nF} \log i - \frac{2.3 RT}{\alpha nF} \log i_0 \\ \Rightarrow \eta_{\text{act}} &= -\frac{2.3 RT}{\alpha nF} \log i_0 + \frac{2.3 RT}{\alpha nF} \log i \\ \Rightarrow \eta_{\text{act}} &= a + b \log i \end{aligned} \quad (2.31)$$

Fig. 2.2 Slow and fast electrochemical reactions represented as Tafel Plots



where

$$a = -\frac{2.3 RT}{\alpha nF} \log i_0 \quad (2.32)$$

and

$$b = \frac{2.3 RT}{\alpha nF} \quad (2.33)$$

α is the electron transfer coefficient and is proportional to the electrical energy, which changes the rate of the electrochemical reaction. The term ' b ' represents the Tafel slope. The factor $\frac{RT}{\alpha nF}$ is high for the slow electrochemical reaction, whereas it is small for the fast electrochemical reaction. The exchange current density i_0 is the current density at which overvoltage starts increasing from zero. For a slow electrochemical reaction, i_0 is small and vice versa. If we rearrange Eq. (2.30), then we obtain

$$i = i_0 \exp \left[\frac{\alpha nF \eta_{\text{act}}}{RT} \right] \quad (2.34)$$

Equation (2.34) is the Butler–Volmer equation and can be used as an alternative for the Tafel equation. It should be noted that the Tafel equation holds good only for $i > i_0$.

Basically, activation polarisation is dominant at low current density because the electronic barriers are to be overcome prior to ion and current flow. Activation polarisation is directly influenced by the rate of electrochemical reaction and is attributed to the sluggish electrode kinetics. When the exchange current density is

zero, then it indicates that the forward and reverse reactions are taking place at the same reaction rate; i.e., the flow of electrons takes place at same rate. When the exchange current density is high, then the reaction rate becomes higher in one direction and the electrode surface becomes more active. Current density influences the cell performance crucially; i.e., when i_0 is increased tenfold, the activation polarisation also increases by 100 mV [for slope of 100 mV/log (i_0)]. When the Tafel slope is 50 mV/log current density, then the tenfold increase in the current density yields 50 mV increase of the activation polarisation. If the Tafel slope gets lowered, then the activation polarisation also gets lowered down. Equation (2.30) also gives an impression that the rise in temperature might raise the η_{act} , whereas practically it is observed that the controlling factor for η_{act} is ' i_0 '. A smaller value of i_0 yields a greater voltage drop; usually the value of i_0 is smaller at cathode as compared to the anode for hydrogen fed fuel cells. But for the fuel cells, where methane is used as a fuel, the anode overvoltage cannot be neglected. The total voltage drop would be given by:

$$\text{Voltage drop} = b_{\text{anode}} \log \left(\frac{i}{i_{0a}} \right) + b_{\text{cathode}} \log \left(\frac{i}{i_{0c}} \right) \quad (2.35)$$

i_{0a} anode exchange current density
 i_{0c} cathode exchange current density
 $b_{\text{anode}}/b_{\text{cathode}}$ anode and cathode Tafel constants, respectively

Equation (2.35) is the same as Eq. (2.30). Hence, the activation polarisation may be due to one electrode or both electrodes. If the value of i_0 is increased then the activation polarisation is reduced, hence the focus should be on increasing the exchange current. The exchange current density can be increased by using catalysts. In addition to this, increasing the pressure and temperature (Fig. 2.1), would effectively increase the current density. Increasing the reactant concentration as well as electrode roughness would probably lead to an increase in current density due to occupancy of catalyst sites by the reactants.

2.3.2 Ohmic Losses (Resistive Losses)

The fuel cell consists of electrodes and electrolytes. Electrodes offer resistance to the flow of electrons whereas the electrolyte provides obstruction to the flow of ions. The ohmic losses occur due to the flow of electrons at cathodes and flow of ions through the electrolyte. The cell interconnects and bipolar plates also contribute to the ohmic losses. Usually, Ohm's law is given by

$$V = IR \quad (2.36)$$

where I is the current and R is the resistance. For a fuel cell, Eq. (2.36) can be written as

$$\eta_{\text{ohm}} = ir \quad (2.37)$$

where i is the current density in (mA/cm^2) and r is the area-specific resistance (ASR), i.e., the resistance corresponding to an area of 1 cm^2 of the cell. The ASR includes total cell resistance, i.e., ionic, electronic and contact resistance and the units of r are $\text{k}\Omega \text{ cm}^2$. The cell resistance remains constant; hence as the current increases, the ohmic polarisation also increases. The ohmic polarisation can be reduced by decreasing the electrode separation which decreases the resistance, thereby decreasing the ohmic polarisation. Second, if the electrodes are electrolyte supported, then the electrolyte must be made as thin as possible provided the two electrodes should not short circuit. Both the electrodes and electrolyte should exhibit high electronic and ionic conductivity, respectively.

2.3.3 Concentration Losses (Mass Transport Losses)

The concentration losses are also known as gas transport losses. During an electrochemical process, the reactant is consumed at the electrode. This leads to the concentration gradient and loss of potential due to the inability of the surrounding material to maintain the initial bulk concentration. The losses due to the concentration gradient and depletion of reactants at the electrode are known as concentration losses. Hydrogen and oxygen are fed at the anode and cathode, respectively. During the working of the fuel cell, the concentration of oxygen and hydrogen will fall on the cathode and anode, respectively. The decrease in concentration depends on the circulation of air/hydrogen around the cathode/anode and the current being taken from the fuel cell. Hence, the partial pressure of oxygen and hydrogen changes the concentration; i.e., the decrease in concentration causes a decrease in partial pressure. This reduction in gas pressure causes a decrease in cell voltage. The main causes of concentration losses are solution of reactants into the electrolyte, dissolution of products out of the electrolyte, slow gas diffusion into electrode pores, diffusion of reactants through the electrolyte to the electrochemical reaction site and diffusion of products through the electrolyte from the electrochemical reaction site. The change in voltage caused by concentration polarisation can be explained with the help of Fick's law.

According to Fick's first law of diffusion, the current density is given by:

$$i = \frac{nFD(C_B - C_S)}{d} \quad (2.38)$$

where n is the number of electrons participating in the reaction, D is the diffusion coefficient of the reactants, C_B and C_S are bulk and surface concentration, respectively, and d is the diffusion layer thickness.

i_1 is postulated as the limited current density, i.e., the current density at which the rate of supply of fuel and rate of use of fuel equals. This occurs for the zero surface concentration. i.e., $C_S = 0$. Equation (2.38) becomes

$$i_1 = \frac{nFDC_B}{d} \quad (2.39)$$

Equation (2.38) can be rewritten as

$$\begin{aligned} i &= \frac{nFDC_B}{d} - \frac{nFDC_S}{d} \\ \Rightarrow i &= i_1 - \frac{nFDC_S}{d} \\ \Rightarrow \frac{i}{i_1} &= 1 - \frac{nFDC_S}{di_1} \\ \Rightarrow \frac{i}{i_1} &= 1 - \frac{C_S}{C_B} \end{aligned} \quad (2.40)$$

$$\Rightarrow \frac{C_S}{C_B} = 1 - \frac{i}{i_1} \quad (2.41)$$

There are two conditions, which may arise in the cell, i.e., zero current, which is the equilibrium condition and when the current is flowing (bulk concentration reduces). The Nernst equations for both conditions can be written as

$$(\text{for } i = 0) \quad E = E^\circ + \frac{RT}{nF} \ln C_B \quad (2.42)$$

$$E = E^\circ + \frac{RT}{nF} \ln C_S \quad (2.43)$$

The potential difference can be written as

$$\eta_{\text{conc.}} = \Delta E = \frac{RT}{nF} \ln \frac{C_B}{C_S} \quad (2.44)$$

$\eta_{\text{conc.}}$ is the concentration polarisation due to the concentration change at the electrode. Using Eq. (2.41) in Eq. (2.44) yields:

$$\eta_{\text{conc.}} = -\frac{RT}{nF} \ln \left(1 - \frac{i}{i_1} \right) \quad (2.45)$$

The concentration polarisation is predominant for high temperature fuel cells. When the hydrogen is supplied via reformer, then the rate of supply of hydrogen at the anode decreases as compared to its consumption rate; then the concentration polarisation dominates in the fuel cell. The removal of water can also be a prominent cause for the mass transport or concentration losses.

2.3.4 Fuel Crossover Losses

The fuel cell consists of an ion-conducting electrolyte through which the conduction process takes place. Sometimes, the fuel from the anode side may diffuse to the cathode side. It may react directly with the oxygen at the cathode due to the presence of catalyst. But this reaction yields no current, hence leading to the wastage of fuel, which migrates from cathode to anode through the electrolyte. This loss of fuel is known as the fuel crossover losses. The fuel crossover losses and internal currents are taken to be equivalent. When the cell is in open circuit, the cell current density would not be zero due to the internal current density. For example, if the internal current density is 0.5 mA/cm^2 , then the open circuit would yield 1.01 V , which is almost 19% less than the OCV. The gas usage is given by

$$\text{Charge} = 4F \times \text{amount of } \text{H}_2$$

By dividing it with time, we obtain

For single cell,

$$\text{H}_2 \text{ usage} = \frac{I}{4F} \text{ moles/s} \quad (2.46)$$

For stack of N cells,

$$\text{H}_2 \text{ usage} = \frac{IN}{4F} \text{ moles/s} \quad (2.47)$$

For a PEM cell with cell area 10 cm^2 , $0.034 \text{ cm}^2/\text{s}$ of H_2 is consumed. The gas usage becomes $1.4 \times 10^{-7} \text{ mol/s}$ corresponding to the volume of $2.43 \times 10^4 \text{ cm}^3$ for one mole of any gas. Hence, from Eq. (2.47), we find

$$\text{H}_2 \text{ usage} = 1.4 \times 10^{-7} \times 2 \times 96,485 = 27 \text{ mA}$$

For a cell area of 10 cm^2 , the current density becomes 2.7 mA/cm^2 . The fuel crossover losses can be summarised as

$$H_{\text{fuel}} = \frac{2.3 RT}{\alpha n F} \ln \left(\frac{i_n}{i_0} \right) \quad (2.48)$$

where i_n is the internal current density. For high-temperature fuel cells, the significance of the internal current decreases because exchange current density i_0 is quite high. Anyhow for the fuel cells operating at low temperatures, the fuel crossover and internal currents play a significant role.

2.3.5 Summation of Losses

The total effective cell voltage after the losses is given by

$$\begin{aligned} V &= E - (\text{Total losses}) \\ \Rightarrow V &= E - (\eta_{\text{act}} + \eta_{\text{ohm}} + \eta_{\text{conc.}} + \eta_{\text{fuel}}) \\ \Rightarrow V &= E - \left[\frac{2.3 RT}{\alpha n F} \log \left(\frac{i}{i_0} \right) + ir + \frac{RT}{n F} \ln \left(1 - \frac{i}{i_1} \right) + \frac{2.3 RT}{\alpha n F} \ln \left(\frac{i_n}{i_0} \right) \right] \\ \Rightarrow V &= E - ir - \frac{2.3 RT}{\alpha n F} \log \left(\frac{i}{i_0} \right) - \frac{2.3 RT}{\alpha n F} \log \left(\frac{i_n}{i_0} \right) + \frac{RT}{n F} \log \left(1 - \frac{i}{i_1} \right) \end{aligned} \quad (2.49)$$

It should be noted that the crossover current is very small for high-temperature fuel cells and then Eq. (2.49) is given by:

$$\Rightarrow V = E - ir - \frac{2.3 RT}{\alpha n F} \log \left(\frac{i}{i_0} \right) + \frac{2.3 RT}{n F} \log \left(1 - \frac{i}{i_1} \right) \quad (2.50)$$

There is an alternative approach to obtain the effective voltage. The total polarisation can also be summed up for the fuel cell. Usually, the total polarisation is predominantly due to concentration losses and activation losses; i.e.,

$$\eta_{\text{anode}} = (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{anode}} \quad (2.51)$$

and

$$\eta_{\text{cathode}} = (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{cathode}} \quad (2.52)$$

The general equation can be written can be written as

$$\eta_{\text{electrode}} = (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{electrode}} \quad (2.53)$$

The polarisation will lead to the change in electrode potential as follows

$$V_{\text{electrode}} = E_{\text{electrode}} \pm |\eta_{\text{electrode}}| \quad (2.54)$$

For the anode, the potential increases whereas the cathode potential shows a decrease. The cell voltage consists of anode and cathode potentials along with ohmic polarisation, i.e.,

$$\begin{aligned} V &= V_{\text{cathode}} - V_{\text{anode}} - ir \\ \Rightarrow V &= (E_{\text{cathode}} - E_{\text{anode}}) - \eta_{\text{cathode}} - \eta_{\text{anode}} - ir \\ \Rightarrow V &= E - (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{cathode}} - (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{anode}} - ir \end{aligned} \quad (2.55)$$

For low-temperature fuel cells, the i_n factor is also added; i.e.,

$$V = E - (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{cathode}} - (\eta_{\text{conc.}} + \eta_{\text{act}})_{\text{anode}} - ir - i_n \quad (2.56)$$

The major loss of fuel cell voltage is due to the ohmic and electrode polarisations. Efforts are made to reduce the polarisations, so that V approaches E and hence maximum efficiency is obtained. This can be done by improving the electrode structure, using highly conducting electrolyte and better electrocatalysts. Hence, the actual and ideal potentials for a fuel cell are different due to various losses.

2.4 Performance of Fuel Cells

For low-temperature fuel cells, electrocatalysts are required to achieve desirable reaction rates at the anode and cathode, whereas the high-temperature fuel cells do not require any electrocatalyst. The most common type of electrode reactions and their corresponding Nernst potential are as follows:

Reaction	Nernst potential
$\text{H}_2 + \frac{1}{2} \text{O}_2 \longrightarrow \text{H}_2\text{O}$	$E = E^\circ + \frac{RT}{2F} \left[\ln \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}}} \right) + \ln \left[p_{\text{O}_2}^{1/2} \right] \right] \quad (2.57)$
$\text{CO} + \frac{1}{2} \text{O}_2 \longrightarrow \text{CO}_2$	$E = E^\circ + \frac{RT}{2F} \left[\ln \left(\frac{p_{\text{CO}}}{p_{\text{CO}_2}} \right) + \ln \left[p_{\text{O}_2}^{1/2} \right] \right] \quad (2.58)$
$\text{H}_2 + \frac{1}{2} \text{O}_2 + \text{CO}_{2(\text{c})} \longrightarrow \text{H}_2\text{O} + \text{CO}_{2(\text{a})}$	$E = E^\circ + \frac{RT}{2F} \left[\ln \left(\frac{p_{\text{H}_2}}{p_{\text{H}_2\text{O}} (p_{\text{CO}_2})_{(\text{a})}} \right) + \ln \left[p_{\text{O}_2}^{1/2} (p_{\text{CO}_2})_{(\text{c})} \right] \right] \quad (2.59)$
$\text{CH}_4 + 2\text{O}_2 \longrightarrow 2\text{H}_2\text{O} + \text{CO}_2$	$E = E^\circ + \frac{RT}{8F} \left[\ln \left(\frac{p_{\text{CH}_4}}{p_{\text{H}_2\text{O}}^2 p_{\text{CO}_2}} \right) + \ln \left[p_{\text{O}_2}^2 \right] \right] \quad (2.60)$

There is a simple way to obtain the Nernst equations. For example, consider a reaction



which indicates that a moles of A react with b moles of B to form c moles of C. The two reactants A, B and product C are designated different activities, i.e., a_A , a_B and a_C . For an ideal gas, the activity is defined as

$$a = \frac{p}{p^\circ} \quad (2.62)$$

where p° is the standard pressure at 0.1 MPa and p is the partial pressure of gas. For example, the activity of oxygen is given by

$$a = \frac{p_{O_2}}{p_{O_2}^\circ} \quad (2.63)$$

The Gibbs free energy gets modified and can be written as

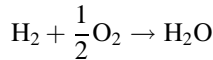
$$\Delta G_f = G_f^\circ - RT \ln \left[\frac{a_A^a a_B^b}{a_C^c} \right] \quad (2.64)$$

or

$$-\frac{\Delta G_f}{2F} = -\frac{\Delta G_f^\circ}{2F} + \frac{RT}{2F} \ln \left[\frac{a_A^a a_B^b}{a_C^c} \right] \quad (2.65)$$

$$\Rightarrow E = E^\circ + \frac{RT}{2F} \ln \left[\frac{a_A^a a_B^b}{a_C^c} \right] \quad (2.66)$$

Equation (2.66) infers the increase in the potential with increase in the activity of reactants. Equation (2.66) is also referred to as a Nernst equation and can also be written in terms of E.M.F. Let us demonstrate it with the help of the following reaction inside fuel cell (operating at high temperature).



The activities for reactants and products can be given as

$$a_{H_2} = \frac{p_{H_2}}{p_{H_2}^\circ}, \quad a_{O_2} = \frac{p_{O_2}}{p_{O_2}^\circ}, \quad a_{H_2O} = \frac{p_{H_2O}}{p_{H_2O}^\circ}$$

At high temperatures, the steam behaves as an ideal gas and $p^\circ = p_{O_2}^\circ = p_{H_2O}^\circ = 1$ bar.

The E.M.F. is simplified as

$$E = E^\circ + \frac{RT}{2F} \ln \left(\frac{p_{\text{H}_2} p_{\text{O}_2}^{1/2}}{p_{\text{H}_2\text{O}}} \right) \quad (2.67)$$

Equation (2.67) can be written as

$$E = E^\circ + \frac{RT}{2F} \ln \left(\frac{p_{\text{O}_2}^{1/2}}{p_{\text{H}_2\text{O}}} \right) + \frac{RT}{2F} \ln(p_{\text{H}_2}) \quad (2.68)$$

If p_{O_2} and $p_{\text{H}_2\text{O}}$ are unchanged and the partial pressure of hydrogen increases from p_1 to p_2 , then the change in voltage will be given by

$$\begin{aligned} \Delta V &= \frac{RT}{2F} \ln p_2 - \frac{RT}{2F} \ln p_1 \\ \Rightarrow \Delta V &= \frac{RT}{2F} \ln \left(\frac{p_2}{p_1} \right) \end{aligned} \quad (2.69)$$

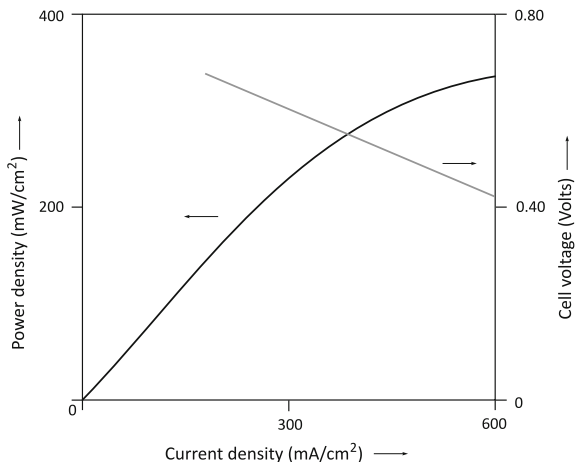
The Nernst equation can also be expressed in another form; let us suppose that the pressure on the anode and cathode are essentially the same and the system pressure can be taken p . Then the p_{H_2} , p_{O_2} and $p_{\text{H}_2\text{O}}$ are expressed as $n_1 p$, $n_2 p$ and $n_3 p$ where n_1 , n_2 and n_3 are constants that depend on concentration and molar mass of hydrogen, oxygen and water, respectively. Equation (2.67) then becomes

$$\begin{aligned} E &= E^\circ + \frac{RT}{2F} \ln \left(\frac{n_1 n_2^{1/2} p^{1/2}}{n_3} \right) \\ E &= E^\circ + \frac{\frac{RT}{2F} \ln \left(\frac{n_1 n_2^{1/2}}{n_3} \right)}{\text{Ist term}} + \frac{\frac{RT}{4F} \ln(p)}{\text{IInd term}} \end{aligned} \quad (2.70)$$

The first term contributes to the fall in E.M.F. due to the concentration change of reactants and products. During the operation of a fuel cell, the concentration of products will increase at the cost of reactant concentration, which will make the first term smaller. The current density and fuel concentration are lower at the outlet; hence, the E.M.F. is small near the exit. The term 'RT' indicates high Nernst voltage at high temperatures. The second term indicates the increase in system pressure which would eventually lead to an increase of cell E.M.F. If pressure gets increased from p_1 to p_2 , then the second term increases. The increase in pressure is more significant for the low-temperature fuel cells because high pressure helps in reducing the losses especially for the cathode.

The fuel cell performance is affected by a number of variables including current density, gas composition, fuel utilisation, pressure and temperature. When the operating conditions for a fuel cell are changed; then the system cost may increase.

Fig. 2.3 The relation between current density, power density and cell voltage of fuel cell



Ideally, the fuel cell system must possess low cost, high power density, portability and less system weight. When the cell stack size is reduced, the cell cost may also get reduced and the efficiency of cell may decrease. For stationary power applications, higher voltages and hence higher efficiency are required. In contrast to this, high current density or lower cell voltages are apt for mobile applications. Figure 2.3 gives the voltage–power relationship for a fuel cell.

It is clear from Fig. 2.3, that the higher current density and power density usually occur for low cell voltage. Hence, for getting maximum efficiency, the operating conditions should be balanced to get a good compromise between current density, voltage and operating cost. The effect of temperature and pressure on the ideal potential of fuel cell can be described on the basis of Gibbs free energy with pressure and temperature. As we know

$$\begin{aligned}
 \Delta G_f &= \Delta H - T\Delta S \\
 \Rightarrow -nFE &= \Delta H - T\Delta S \\
 \boxed{\left(\frac{\partial E}{\partial p}\right)_T &= \frac{\Delta S}{nF}}
 \end{aligned} \tag{2.71}$$

and

$$\left(\frac{\partial E}{\partial T}\right)_p = \frac{\Delta V}{nF} \tag{2.72}$$

For the reaction $\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$, the entropy change is negative due to which the reversible potential decreases with increase in the temperature. In contrast to this, the volume change is negative for this reaction which leads to an increase in reversible cell voltage with an increase in pressure. The pressure increase also increases the gas solubility; mass transfer reacts and reactant partial pressures. Hence, the fuel cell efficiency increases and the electrolyte evaporation rate

decreases at elevated pressures in the fuel cell system. Another major factor that determines fuel cell efficiencies is gas composition and utilisation of reactants. The fuel utilisation is given by

$$U_{\text{fuel}} = \frac{\text{Fuel}_{\text{in}} - \text{Fuel}_{\text{out}}}{\text{Fuel}_{\text{in}}} \quad (2.73)$$

It is apparent, if the fuel and oxygen gas have a higher concentration, then the fuel cell will possess higher efficiencies and hence high cell voltages. The difference between fuel provided at the inlet and fuel flow rate at the outlet of the fuel cell represents the fuel consumed. Certain other factors such as fuel leakage and chemical reaction may lead to more consumption of fuel, which increases the apparent utilisation of the fuel. From inlet to outlet, the gas composition keeps on changing, hence leading to reduced cell voltages. The voltage reduction is attributed to the lowest electrode potential (from the Nernst equation) because the electrodes are good ionic conductors and the cell voltage values cannot be greater than the minimum Nernst potential.

The current density and impurities also affect the fuel cell performance. In the initial stages, activation polarisation decreases the cell voltage. When current densities increase, then the concentration losses are predominant and a sharp decrease in cell performance is observed. During normal fuel cell application, ohmic losses are observed due to internal resistances of the fuel cell. This section deals with the effect of different variables on fuel cell performance and efficiency. The different fuel cells and their performances are discussed one by one.

2.4.1 Performance of PAFC

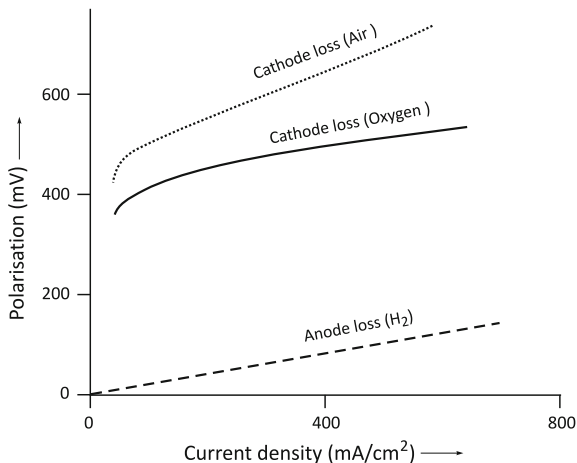
For PAFC, the polarisation contribution of the two half cells is shown in Fig. 2.4. Hydrogen is taken to be the reference point/zero polarisation.

Figure 2.4 indicates the polarisation losses for PAFC with anode and cathode loading of 0.5 mg Pt/cm², pressure 1 atm, 100% phosphoric acid and operating temperature of 180°C. The anode losses are very small on pure H₂, whereas the cathode polarisation is greater with air and comparatively small for pure oxygen. As discussed, it is known that an increase in cell pressure enhances the performance of the cell (Eq. 2.72).

$$\Delta V = \frac{RT}{2F} \ln \left(\frac{p_2}{p_1} \right) \quad (2.74)$$

The above equation holds well for the pressure range of 1 atm ≤ *p* ≤ 10 atm and temperature range of 180°C < *T* < 220°C. Figure 2.5 demonstrates that the increase in pressure from 3 to 8 atm increases the cell voltage for H₂ fuel fuel/Air PAFC.

Fig. 2.4 Polarisation of anode and cathode for PAFC



At higher pressure and current density, the diffusion polarisation at the cathode decreases and reversible cell potential increases. At the cathode, increased oxygen and water pressures decrease activation polarisation. As shown in Fig. 2.5, an increase of 44 mV is observed when pressure and temperature are increased by 2.9 atm and 15°C, respectively. An increase in temperature exhibits a beneficial effect on cell performance because the polarisation losses diminish with increased temperature. The relationship between voltage gain and temperature change is given by:

$$\Delta V(\text{mV}) = A\Delta T(^{\circ}\text{C}) \quad (2.75)$$

Fig. 2.5 The increase in PAFC cell performance with pressure increase

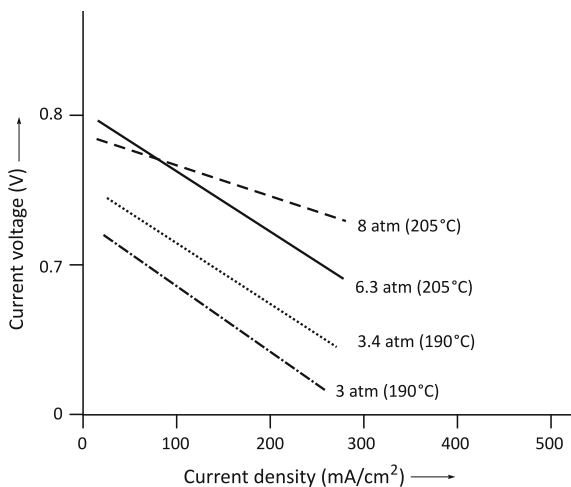
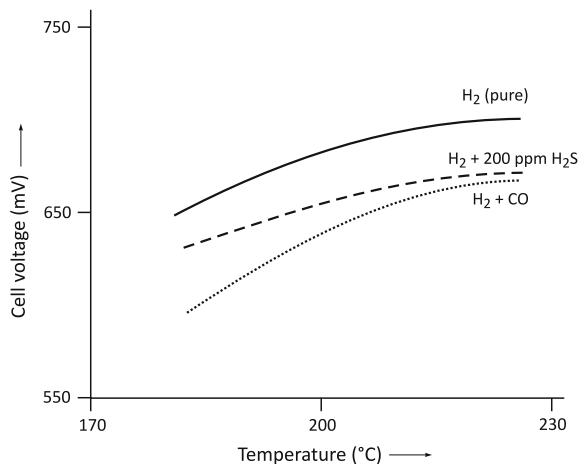


Fig. 2.6 Effect of temperature and impurities on the cell voltage of PAFC



The validity of Eq. (2.75) holds good within a temperature range of $180^{\circ}\text{C} < T < 250^{\circ}\text{C}$. The value of A has been given between 0.55 and 0.75. For 250 mA/cm^2 current density, the value of A is given to be 1.15 which means that the voltage increases by 1.15 mV per degree rise in temperature. Increasing the temperature also increases the relative tolerance of the anode for CO poisoning due to reduced adsorption. The impurities such as carbon monoxide and hydrogen sulphide originate while the fuel enters the fuel processor and reformer chamber. The CO in the fuel affects the anode performance because CO poisons the electrocatalytic activity of Pt. electrodes. As discussed in Chap. 1, two carbon monoxide molecules replace 1 H_2 molecule, hence affecting the reaction kinetics of the cell. The effect of temperature and impurity (H_2S and CO) on cell voltage is shown in Fig. 2.6. As evident from Fig. 2.6, cell performance increases with temperature, but problems such as evaporation, electrolyte degradation, corrosion and catalyst sintering also elevate it. The CO poisoning decreases cell performance considerably as compared to the fuel contaminated with sulphide compounds. The fuel processors and coal gasifiers in PAFC power plants usually incorporate hydrogen sulphide and carbonyl sulphide as impurities in the hydrogen fuel. The platinum anodes can tolerate $<20 \text{ ppm}$ of H_2S and $<50 \text{ ppm}$ of (H_2S + carbonyl sulphide) concentration within a temperature range of $190\text{--}210^{\circ}\text{C}$ and 9.2 atm. A CO level of up to 1% is acceptable at working temperature above 190°C . If temperature is increased, then the CO absorbed on the anode gets desorbed. Similarly, the sulphur-poisoned anodes can also be reactivated by increasing the temperature or by increasing the cathode potentials.

The cathode performance is also affected by the utilisation and composition oxidant. The use of 21% O_2 instead of pure O_2 decreases the current density. As the oxygen is utilised, the cathode polarisation also increases. The voltage loss due to change in oxidant utilisation at cathode is given by

$$(\Delta V)_{\text{cathode}} = A_c \ln \left(\frac{p_2}{p_1} \right)_{\text{O}_2} \left[\begin{array}{l} A_c = 148 \text{ for } 0.04 \leq \frac{p_2}{p_1} \leq 0.2 \\ A_c = 96 \text{ for } 0.2 < \frac{p_2}{p_1} < 1 \end{array} \right] \quad (2.76)$$

Similarly, the voltage loss due to change in hydrogen partial pressure at the anode is given by

$$(\Delta V)_{\text{anode}} = A_a \ln \left(\frac{p_2}{p_1} \right)_{\text{H}_2} [A_a = 55] \quad (2.77)$$

The anode reaction is reversible; hence hydrogen utilisation does not have much significance on cell performance. Hydrogen is derived from coal gases/liquids petroleum products and hydrocarbons such as methane. The reformed fuel may contain CO and CO₂ as traces. CO₂ and unreacted hydrocarbons act as diluents because they are electrochemically inert. Low utilisations cause poor fuel use but yield high performance. The current density also influences the cell performance and the voltage losses can be given by:

$$(\Delta V)_{\text{CD}} = A_{\text{CD}} \Delta J \left[\begin{array}{l} A_{\text{CD}} = -0.53 \text{ for } 100 < J < 200 \text{ mA/cm}^2 \\ A_{\text{CD}} = -0.39 \text{ for } 200 < J < 650 \text{ mA/cm}^2 \end{array} \right] \quad (2.78)$$

The value of A_{CD} are obtained at 207°C, 8.2 atm and oxidant/fuel utilisation of 70 /85%, respectively. At atmospheric conditions of 1 atm, operating temperature 204°C, and oxidant/fuel utilisation of 60 /80%, respectively, Eq. (2.78) becomes

$$(\Delta V)_{\text{atm}} = A_{\text{atm}} \Delta J \left[\begin{array}{l} A_{\text{atm}} = -0.74 \text{ for } 50 < J < 120 \text{ mA/cm}^2 \\ A_{\text{atm}} = -0.45 \text{ for } 120 < J < 215 \text{ mA/cm}^2 \end{array} \right] \quad (2.79)$$

The PAFC technology is considered to be the only commercial available fuel cell. The PAFC plants rely heavily on the quality of power produced from the stacks. The largest power of 11 MW has been achieved using the PAFC plant built by international fuel cells and Toshiba for Tokyo Electric Power. The major industrial developers of PAFC are Fuji Electric, Toshiba and Mitsubishi Electric Company (Japan) and UTC fuel cells (ONSI Corporation, United States). Mitsubishi Electric Company has demonstrated cell performance of 0.65 mV at 300 mA/cm². In 1991, Tokyo Electric Company demonstrated cell performance of 0.71 V at 431 mA/cm². Bharat Heavy Electrical Ltd. of India and Caltex Oil Corporation of South Korea are new entrants for the PAFC technology.

2.4.2 Performance of AFC

Till now, we have been familiar with the concept that the activation overvoltage on the cathode is reduced upon increase in pressure and temperature. Upon increasing the pressure, the change in OCV is given by the second term of Eq. (2.74), i.e.,

$$\Delta V = \frac{RT}{4F} \ln \left(\frac{p_2}{p_1} \right) \quad (2.80)$$

Temperature pressure and electrolyte concentration should be balanced to achieve maximum efficiency. For example, to obtain high performance for the Bacon cell, the pressure has to be reduced and temperature should be increased. Moreover, the electrolyte concentration of KOH should be increased by 75%, so that the electrolyte does not boil. Figure 2.7 depicts the variation of KOH electrolyte concentration with temperature and pressure.

When the concentration of KOH is increased, the vapour pressure is reduced. For AFC, the reactant gas pressure and electrolyte pressure differ from each other. For example, both the reactant gases in the Apollo system were about 0.7 bar above the electrolyte pressure. For the Orbitor fuel cell, the oxygen pressure was 0.35 below the hydrogen pressure. The crucial problem in AFC is the carbonation of electrodes when air is used instead of pure oxygen. There are many groups which are actively engaged in the production and development of AFC. EFFCELL GmbH, a Swiss company, has developed AFC for mobile applications. Hydrocell (Finland) developed portable AFC with an integrated CO₂ scrubber system. Scottish Fuel Cell Consortium (SFEC) of Scotland has been focused on the development of fuel cell hybrid battery electric drive trains. Gaskatel GmbH (Germany) is focusing on the electrochemical processes within AFC, particularly gas diffusion electrode kinetics. Astris Energi Inc. (Canada) has developed 1–10 kW systems for AFC. Cenergie Corporation (Atlanta, USA) has

Fig. 2.7 Variation of KOH concentration with different pressure and temperature

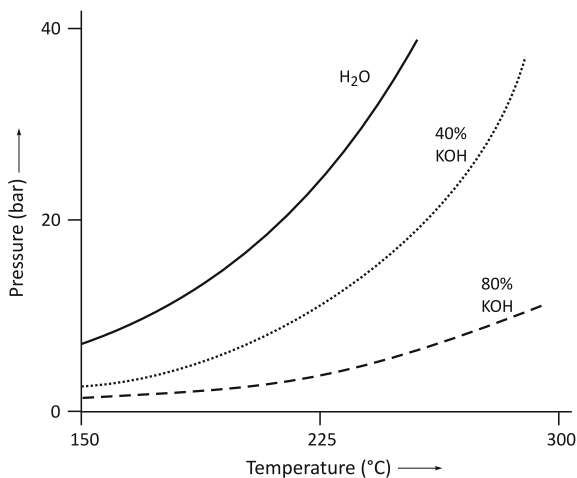
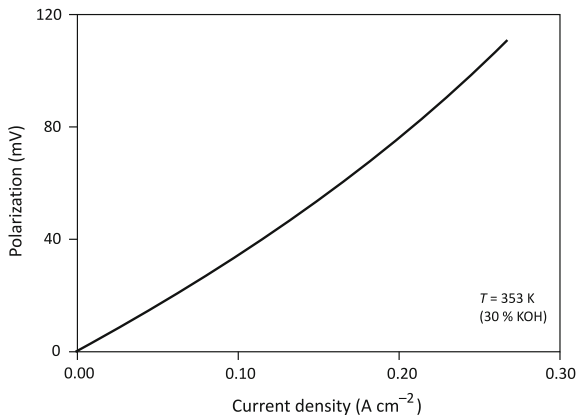


Fig. 2.8 Polarisation versus current density characteristics for the AFC



been focused on developing novel designs for SOFC. Apollo Energy Systems (Pampona Beach, USA) is developing the AFC for mobile and portable applications. Independent Power Technologies Ltd. (Moscow) are developing AFC for stationary applications. Fuel Cell Control Ltd. (UK) develops system integrators for AFC engines, which find applications in remote base transmitters and cellular communications. DLR German Aerospace Center (Stuttgart) focuses on the degradation mechanics and production of gas diffusion electrodes. The typical polarisation characteristics for AFC (Ni anode) are shown in Fig. 2.8.

2.4.3 Performance of PEMFC

The research is focused on lowering the cost of PEMFC and improving its performance. Usually, increasing the power for a system makes it more efficient. Additionally, it will also increase the cost and weight of the fuel cell system. The pressure increase raises the exchange current density and hence the OCV also increases lowering the cathode overpotential. The rate in OCV is given by

$$\Delta V = \frac{RT}{4F} \ln \left(\frac{p_2}{p_1} \right)$$

Let current I Amperes in flowing through n stacks of PEMFC; then the power gain will be given by

$$P_{\text{gain}} = \frac{RT}{4F} \ln \left(\frac{p_2}{p_1} \right) nI \quad (2.81)$$

We derive the voltage loss and hence power loss in a more detailed way as follows:

Whenever a gas expands, work is done by gas, or in other words, the work is done on the gas for compressing it. In an adiabatic reversible process (no heat loss), the pressure change from p_1 to p_2 will lead to temperature change of T_1 to T'_1 ; i.e.,

$$\frac{T'_1}{T_1} = \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} \quad (2.82)$$

where $\gamma = \frac{C_p}{C_v}$ or ratio of specific heat at constant pressure to specific heat at constant volume. T'_1 is the isentropic temperature, anyhow practically the temperature change is higher than T'_1 and is given by T_2 . The work done can be given by the change in enthalpy of gas as

$$\text{Actual work} = W = C_p(T_2 - T_1)m \quad (2.83)$$

where m is the mass of gas compressed. For Eq. (2.83), the heat flow and kinetic energy of gas has been considered to be negligible. The gas is taken to be perfect gas and hence C_p is taken to be constant. For the isentropic system, the work done can be written as

$$\text{Isentropic work} = W' = C_p(T'_1 - T_1)m \quad (2.84)$$

To obtain the efficiency, we have to divide Eq. (2.83) and (2.84) as follows:

$$\begin{aligned} \eta &= \frac{\text{Isentropic work}}{\text{Actual work}} \\ \Rightarrow \eta &= \frac{C_p(T'_1 - T_1)m}{C_p(T_2 - T_1)m} = \frac{T'_1 - T_1}{T_2 - T_1} \end{aligned} \quad (2.85)$$

Substituting Eq. (2.82) in (2.85) we get,

$$\begin{aligned} \eta &= \frac{\left(T_1 \left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - T_1 \right)}{T_2 - T_1} \\ \Rightarrow \eta &= \frac{T_1}{T_2 - T_1} \left(\left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \end{aligned} \quad (2.86)$$

$$\Rightarrow \Delta T = \frac{T_1}{\eta} \left(\left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \quad (2.87)$$

Equation (2.87) provides the temperature change, which will be used to obtain the power lost (P_{lost}) for unit time; i.e.,

$$\text{Power lost} = W = C_p \Delta T \dot{m} \quad (2.88)$$

$\dot{m}$ indicates the rate of flow of gas in kg/s; we get

$$\text{Power lost} = C_p \frac{T_1}{\eta} \left(\left(\frac{p_2}{p_1} \right)^{\frac{\gamma-1}{\gamma}} - 1 \right) \dot{m} \quad (2.89)$$

Hence, we can make the net assessment of the system on the basis of Eqs. (2.81) and (2.89). Two models are usually considered to obtain the voltage gains: the optimistic and realistic models. The optimistic model always yields gains at high pressure, whereas the realistic model gives the net loss when pressure is increased. Figure 2.9 shows the boundary conditions for both models.

An increase in oxygen pressure also affects the performance of PEMFC as shown in Fig. 2.10. In increase in oxygen pressure from 3 to 10.2 atmospheres, and current density 215 mA/cm², produces an increase of 42 mV in the cell voltage (at 93°C). The current density and operating temperature value play a crucial role in determining the cell gain. For instance, the PEMFC at 80°C (431 mA/cm²) yielded a voltage gains of 22 mV for pressure increase of 2.4 to 3.4 atm, whereas for a PEMFC at 50°C (500 mA/cm²) demonstrates an increase of 83 mV in voltage upon pressure change from 1 to 5 atmospheres.

An increase in operating temperature lowers the internal resistance (mainly ohmic resistance) of the cell. The experimental data suggest an increase of voltage

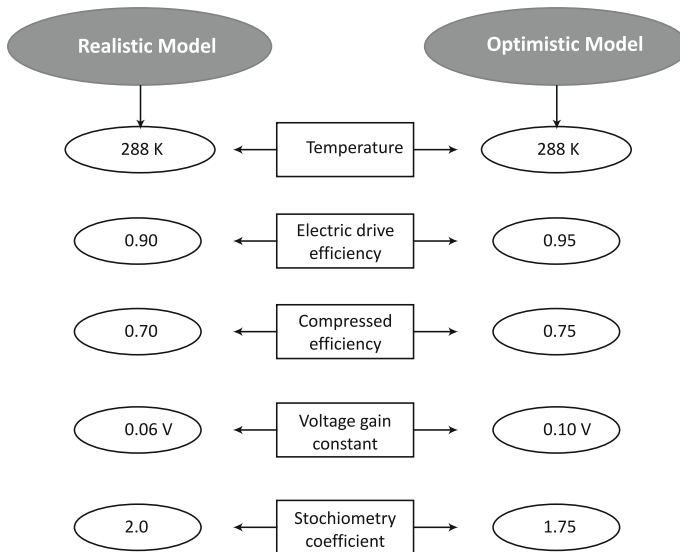


Fig. 2.9 The values of different constants used in realistic and optimistic models

Fig. 2.10 The effect of O_2 pressure on the PEMFC performance for operating temperature 93°C (H_2 at 3 atm)

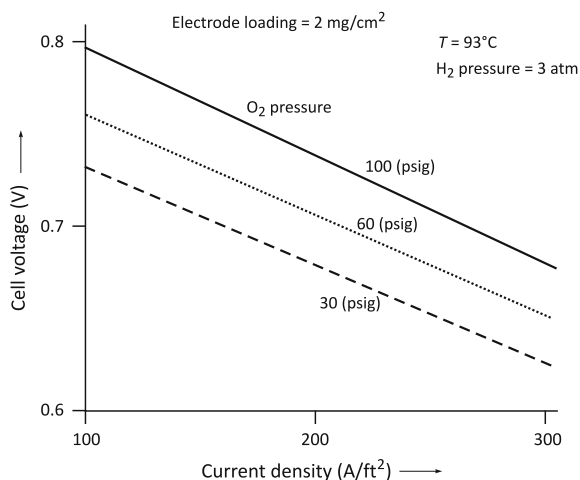
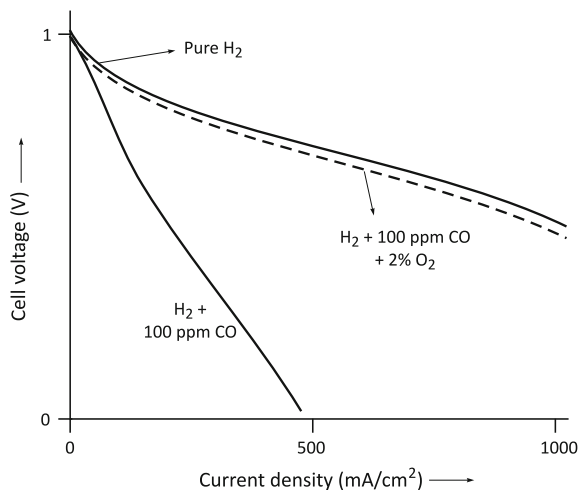


Fig. 2.11 PEMFC performance of bleeding oxygen into anode compartment



within 1.1 mV to 2.5 mV range per $^\circ\text{C}$ rise in operating temperature. At higher temperatures, the CO chemisorptions also decrease, hence increase the voltage gain. The stack operation has considerably affected the fuel cell performance: the CO content in methanol reformed gas can be reduced from 1% to 10 ppm using a selective oxidation process. Los Alamos National Laboratory (LANL) has addressed this problem by bleeding a small amount of oxygen into the anode chamber. Figure 2.11 shows the PEMFC performance of bleeding oxygen in the anode compartment.

The air and hydrogen partial pressures are 5 atm and 3 atm, respectively (Nafion—117 μm thick). Using the bleeding oxygen concept, the performance of PEMFC with fuel H_2 becomes equivalent to the performance of PEMFC with fuel $\text{H}_2 + 100 \text{ ppm CO} + 2\% \text{ O}_2$. But the main drawback of this approach is the loss of fuel, which could be overcome using platinum|ruthenium anodes. LANL also obtained voltage gain of 0.78 V at 200 mA/cm^2 current density (operating temperature 80°C), Nafion membrane and platinum loading of 0.4 mg/cm^2 . Currently, the major focus is to develop a fuel cell with low cost and high system efficiency for terrestrial applications.

2.4.4 Performance of MFC

For MFC, the performance can be analysed using half-cell reactions. If acetate is oxidised by bacteria at the anode, the half cell reaction is given by



The Nernst equation for oxidation of acetate is given by

$$E_a = E_a^\circ - \frac{RT}{8F} \left(\frac{[\text{CH}_3\text{COO}^-]}{[\text{HCO}_3^-]^2 [\text{H}^+]^9} \right) \quad (2.91)$$

The reaction and Nernst potential at cathode is given by

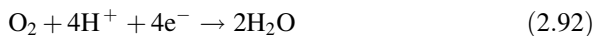
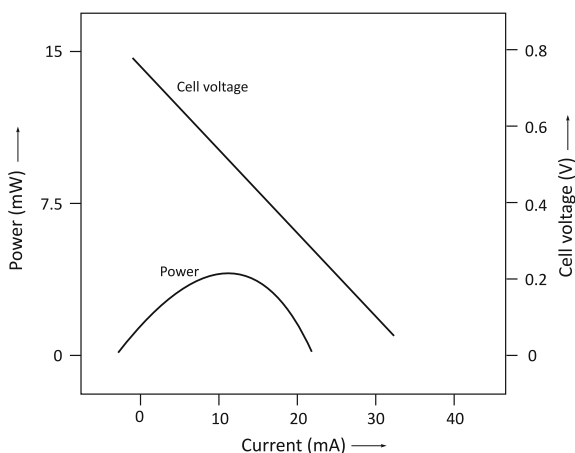


Fig. 2.12 The polarisation and power curve of MFC operating on starch



$$E_c = E_c^\circ - \frac{RT}{4F} \left(\frac{1}{p_{O_2} [H^+]^4} \right) \quad (2.93)$$

For MFC, ferricyanides and manganese oxides have been used as alternatives for oxygen. The main application of MFC is to treat the wastewater. The ohmic resistance plays dominant role in the polarisation curves. The polarisation and power curves for MFC are shown in Fig. 2.12 for starch substrate. The polarisation curves for MFC are usually linear in nature and hence the internal resistance value can be easily obtained from their slope. The performance of MFC depends upon the electrochemical reactions occurring between the electron acceptor with high potential and organic substrate with low potential. In MFC, it becomes uncertain to have an idea of the cell voltage because the electron transfer takes place via the organic substrate and complex chain which varies from microbe to microbe.

For MFC, pH buffer, electrolyte, electrode material, anodic chamber and cathode chamber conditions play a crucial role in determining the cell voltage. Oxygen is the most commonly used electron acceptor in MFC. When ferricyanide is used as an electron acceptor, then the power output increase (i.e., power output of 4310 and 3600 mW/m²) can be obtained due to the higher mass transfer rate and low activation energy required for cathodic reaction while using ferricyanide. The current and power densities are also boosted when hydrogen peroxide is used as an electron acceptor. In the anodic chamber, high fuel concentrations yield a higher output in a wide range of concentrations. When *S. putrefaciens* was used in MFC, high power density could be obtained for lactate fuel concentration up to 200 mM.

The pH difference occurs between the anodic and cathodic chambers if no buffer solution is used in the MFC. This pH difference causes an increase in the proton diffusion from the anode to the cathode chamber until equilibrium is achieved. Using an HCl solution to the cathode, the current density increases and if NaCl is added to the MFC, then the power density increases due to enhanced conductivity of the catholyte and analyte. Several research groups investigated electrode materials with less activation polarisation. As compared to the graphite electrode, Pt./Pt. black yields less activation polarisation due to its higher catalytic activity. A 100-fold increase in current could be obtained using a woven graphite/Mn(IV) graphite anode as compared to the graphite anode only because Mn(IV) served as the mediator for MFC. A fourfold increase in the current could be observed when a Fe(III+) graphite cathode and Mn(IV) graphite anode combination was used instead of plain graphite electrodes. The Pt./Pt. black electrode activity gets reduced by the PtO layer on their surface. Anyhow, the current density is observed to increase from 0.84 to 1.445 mA/cm² when polyaniline is coated on the Pt. black anode. Cobalt tetramethoxyphenylporphyrin (CoTMPP) and Iron (III) phthalocyanine (FePc)-based cathodes are also used as an alternative MFC cathodes because they deliver almost similar performance and are relatively cheap.

Nafion membranes (Du Pont, Delaware) are the most commonly used membrane in the MFC system for the selective permeability of protons, in spite of the cost issues. The surface area of the polymer exchange membrane influences the power

output because the increase in PEM surface area decreases the internal resistance. The power output of 2.2 mW/m² was observed when the salt bridge was used in MFC inoculated with *G. metallireducens*. When graphite electrodes with a surface area of 17 cm² for both anode and cathode were used, then the voltage of 67 mV could be achieved for MFC inoculated with *Escherichia coli*. Though many efforts are being made to improve the cell performance, the slow metabolism of the microbes limits the performance.

2.4.5 Performance of DCFC

Scientific Applications and Research Associate (SARA) Inc. started an R&D program on DCFC (molten hydroxide) in the 1990s. SARA built prototypes for demonstrating the molten hydroxide DCFC technology and the latest prototypes include MARK II-D and MARK III-A. Figure 2.13 demonstrates the power and

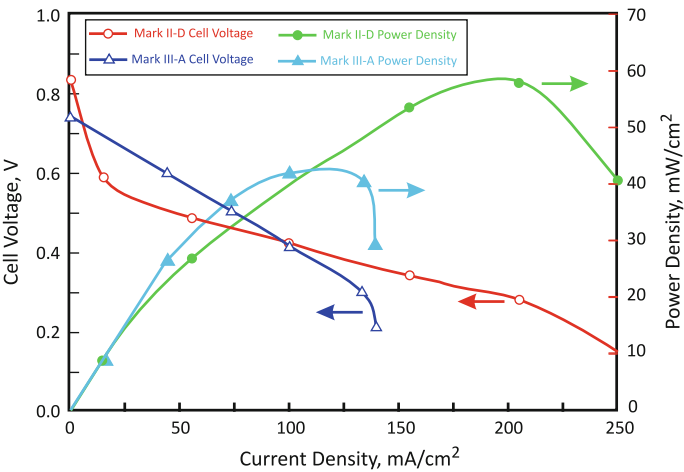


Fig. 2.13 The characteristics of MARK II-D and MARK III-A at an operating temperature of 630°C (Photo courtesy by SARA)

Table 2.1 Materials and design parameters of prototype cells

Prototype cell	Anode	Cathode	Cathode container	Electrode spacing (cm)	Anode surface area (cm ²)
MARK III-A	7.6 cm dia, 12.6 cm long graphite	Fe2Ti	Prismatic	2	300
MARK II-A	2 cm dia, 4.1 cm long graphite	Ni foam-lined C-1018 steel	Cylindrical	1.3	26

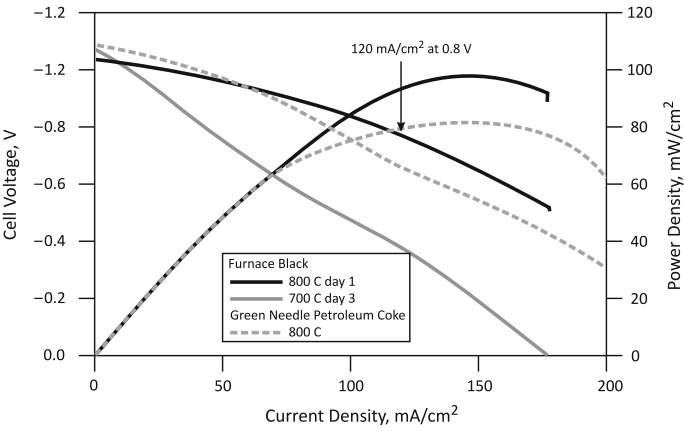


Fig. 2.14 Cell potential and power density versus current density for the DCFC (Photocourtesy by LLNL, California)

voltage density characteristics for MARK II-D and MARK III-A at the operating temperature of 630°C.

The maximum efficiency for the MARK III-A prototype was 60% at a current density of 50 mA/cm², whereas the peak power densities achieved by MARK III-A and MARK II-D are 42 and 58 mW/cm², respectively. The major losses in DCFC occurred due to ohmic losses, which are attributed to the large spacing between anode and cathode. High performance could be achieved by increasing the cathode surface area, coal derived anode, optimisation of air flow and improved current collector–anode contact. Table 2.1 demonstrate the design parameter for MARK III-A and MARK II-D.

A pure graphite rod acts as the anode and fuel which is immersed into a molten sodium hydroxide solution. The electrolyte is contained within the prismatic or cylindrical container, which also acts as the cathode. The cell operates between 400° and 650° and humidified air is fed into the cell via a gas distributor.

Fig. 2.15 Peak power density characteristics obtained for the DCFC. (Photocourtesy by SRI)

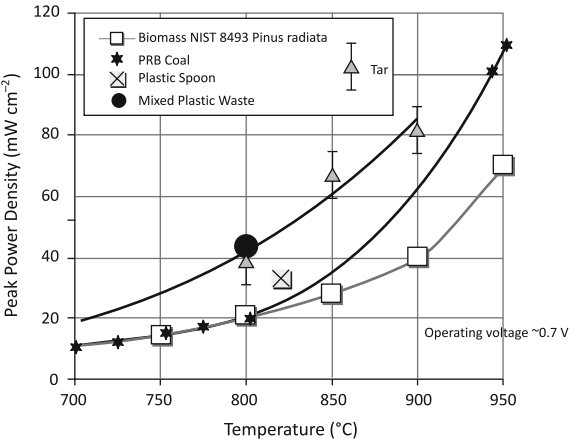
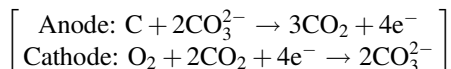


Figure 2.14 demonstrates the potential and power density characteristic obtained for molten carbonate electrolyte DCFC obtained by Lawrence Livermore National Laboratory (LLNL, California). LLNL used 32% Li_2CO_3 –68% K_2CO_3 melt as an electrolyte and the Nernst potential is given by:

$$E = E^\circ - \frac{RT}{4F} \ln[\text{CO}_2]_a^3 + \frac{RT}{4F} \ln\left([\text{O}_2][\text{CO}_2]_c^2\right) \quad (2.94)$$

The anode and cathode cell reactions are



LLNL obtained current densities from 58 to 124 mA/cm^2 for a cell voltage of 0.8 V. The performance of solid electrolyte based DCFC obtained by SRI is shown in Fig. 2.15. At 950°C, power densities of 100 mW/cm^2 could be obtained.

CellTech Power LLC obtained power obtained of 10 mW/cm^2 at 0.248 V and 50 mW/cm^2 at 0.507 V for temperatures of 800 and 1000°C, respectively. $(\text{ZrO}_2)(\text{HfO}_2)_{0.02}(\text{Y}_2\text{O}_3)_{0.08}$ was used as an electrolyte, carbon black as an anode and 0.6 mm thick $\text{La}_{0.84}\text{Sr}_{0.16}\text{MnO}_3$ as cathode for the CellTech fuel cell. The DCFC cell performance depends upon the carbon source surface area and oxygen surface groups, which increases the active sites on the carbon source.

2.4.6 Performance of MCFC

Significant polarisation losses occur in MCFC and its operating conditions are almost same as those of PAFC. For an MCFC, the anode and cathode compartments are at the same pressure, and the change in reversible voltage can be given by

$$\Delta V = \frac{RT}{4F} \ln \frac{p_2}{p_1}$$

If $T = 650^\circ\text{C}$, then the above equation becomes

$$\Delta V = 20 \ln \frac{p_2}{p_1} \quad (2.95)$$

Equation (2.95) infers that for a tenfold increase in pressure, an increase of 46 mV in reversible cell potential is observed. As the pressure is increased, the mass transport rates and gas solubilities also increase. Anyhow, the increased pressure may promote some reactions: decomposition of methane to carbon/hydrogen, methanation (methane formation) and carbon deposition and methane formation are favoured. The carbon deposition may lead to the plugging of gas passages in the anode. The steam reformation also gets inhibited due to higher pressure, which is a

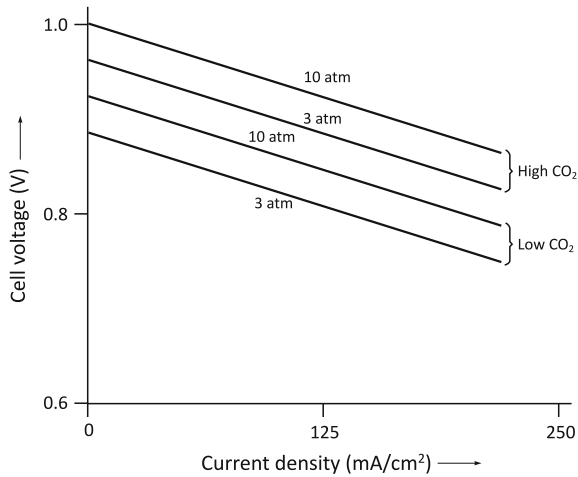


Fig. 2.16 MCFC performance with pressure and CO₂

demerit for the system using an internal reformer. If methane forms during the operation of MCFC, then 3 mol of H₂ are consumed, which is detrimental for the fuel cell because fuel loss and hence power wastage occurs. The pressure difference between the anode and cathode compartments must be kept as minimum as possible. The MCFC electrolyte is contained in the ceramic matrix, which is susceptible to cracking under stresses. For overcoming these things, the partial pressure of H₂O in gas stream is increased to avoid carbon deposition. In addition to this, water and CO₂ are added to the fuel to modify the equilibrium such that methane formation is minimised. The performance of MCFC is affected by the gas composition, i.e., the increase in CO₂ and oxygen content (Fig. 2.16). As the CO₂ content increases, the cell performance also increases. The stack size and design also affect the performance of MCFC. Figure 2.17 shows that the stack networking helps in increasing the overall performance as well as simplifying the system design.

The stack design concept was given by the ECN project and this stack is known as SMARTERTM (used both for MCFC and SOFC stacking). This geometry contains two different geometries of cells stacked together: single pass operation is applied to one cell and anode recycle to other. These systems require no preheating and glass flow rates are larger increasing the heat capacity of the system. In addition to this, the SMARTERTM stack system exhibits less pressure on the internal reformation catalyst because the fuel entering the stack has already been partially reformed.

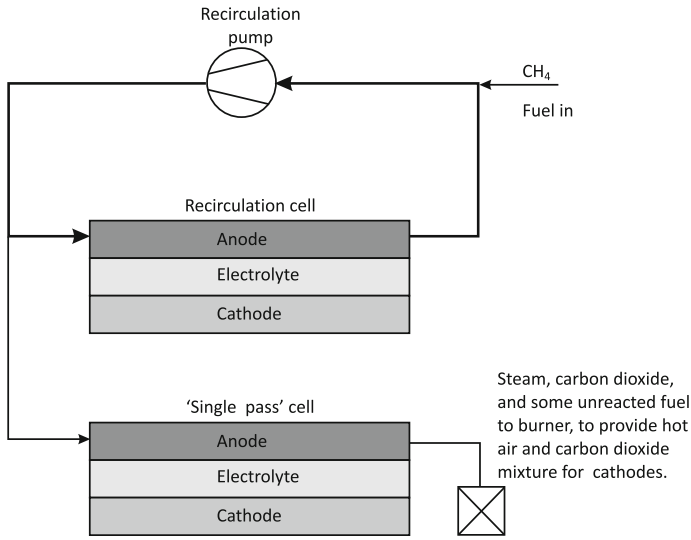


Fig. 2.17 The SMARTER stack concept for enhancing the power output (Larminie and Dicks 2003)

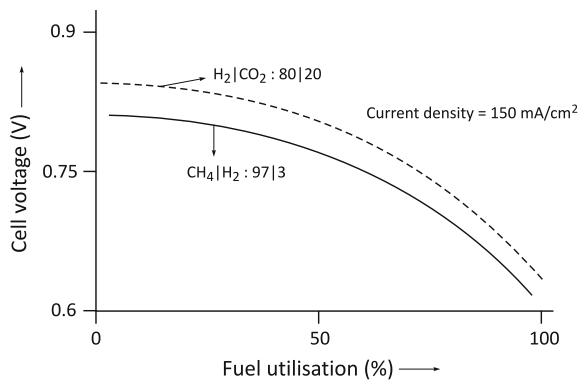
The increase in temperature increases the equilibrium constant (K) as the equilibrium composition increases for the product:

$$K = \frac{p_{\text{CO}} p_{\text{H}_2\text{O}}}{p_{\text{H}_2} p_{\text{CO}_2}} \quad (2.96)$$

The polarisation is also small at higher temperatures. The results obtained for the effect of temperature on the performance of 8.5 cm^2 MCFC cell are as follows:

$$\Delta V(\text{mV}) = A(T_2 - T_1) \quad \left[\begin{array}{ll} A = 2.16 & 575^\circ\text{C} \leq T \leq 600^\circ\text{C} \\ A = 1.40 & 600^\circ\text{C} \leq T \leq 650^\circ\text{C} \\ A = 0.25 & 650^\circ\text{C} \leq T \leq 700^\circ\text{C} \end{array} \right] \quad (2.97)$$

Fig. 2.18 MCFC cell voltage dependence on fuel utilisation



The carbonates usually melt above 500°C and cell performance is enhanced on increasing the temperature. Beyond 650°C, the gains decrease along with the electrolyte loss due to evaporation and high corrosion rates. As the reactants are consumed, the activation and concentration polarisation increase, hence decreasing the MCFC performance. The average cell voltage at 172 mA/cm² is found to decrease by about 30 mV for 20–50% utilisation of oxidant. Figure 2.18 depicts the cell performance for 30–60% fuel utilisation.

The major loss in MCFC occurs due to ohmic polarisation and the magnitude of ohmic losses can be given as

$$\Delta V_{CD}(\text{mV}) = A_{CD} \Delta J \quad \left[\begin{array}{ll} A_{CD} = -1.21 & 50 \leq J \leq 100 \\ A_{CD} = -1.78 & 150 \leq J \leq 200 \end{array} \right]$$

where J is the current density in mA/cm².

We have discussed the current density, performance and ideal behaviour of different fuel cells. The SOFC, its working, design principles and performance variables are studied in Chap. 3. Hence, we do not discuss it in the current chapter.

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