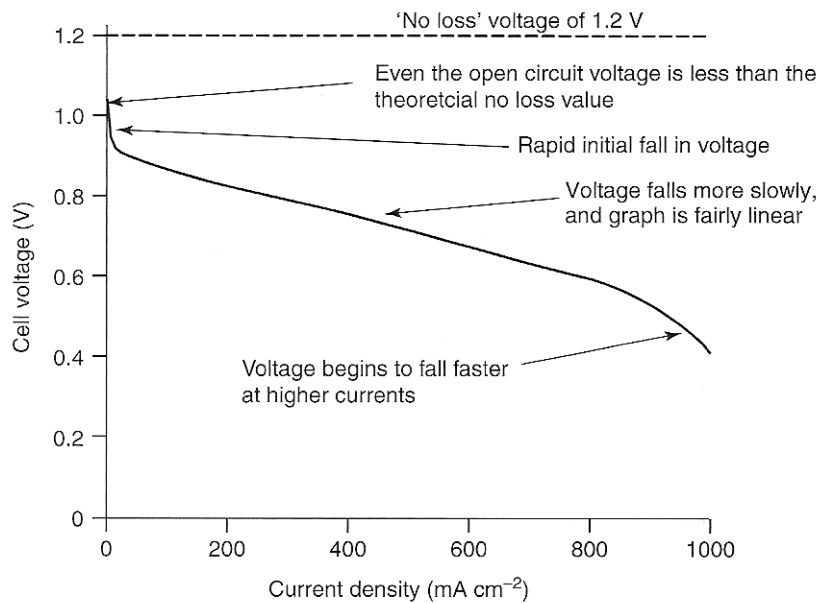# Operational Fuel Cell Voltage

Introduction

From Chapter 2, the reversible OCV of a hydrogen fuel cell is given by the equation,

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

When a fuel cell operates, the voltage is less than this. The figures show the performance of a typical single cell operating at about 70 °C, at normal air pressure.
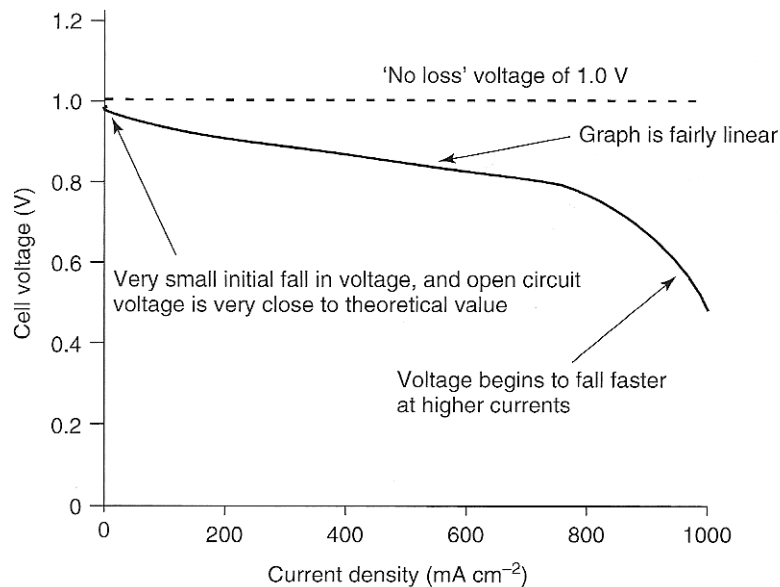

Graph showing the voltage for a typical low temperature, air pressure, fuel cell

The key point about the plot of the cell voltage against current density:
- The open circuit voltage is less than reversible OCV.
- There is a rapid initial fall in voltage.
- The voltage then falls less rapidly, and more linearly.
- There is sometimes a higher current density at which the voltage falls rapidly.

However, there are different behaviors in the V-I curve of the high temperature fuel cell. For a typical solid oxide fuel cell (SOFC) operates at about 800 °C, the V-I curve can be shown as following. The key points are:
- The open circuit voltage is equal to or only little less than the theoretical value.
- The initial fall in voltage is very small, and the graph is more linear.
- There may be a higher current density at which the voltage falls rapidly, as with lower-temperature cells.

Graph showing the voltage of a typical air pressure fuel cell operating at about 800°C

Comparing these two figures, the reversible voltage is lower for the higher temperature, the operating voltage is generally higher, because the voltage drop or ireversibilities are smaller.

Fuel Cell Irreversibilities – Causes of Voltage Drop

The terms can be used to described the voltage different from the reversible OCV are:

- Overvoltage or overpotntial （過電位）
- Polarisation （極化）
- Irreversibilty （不可逆）
- Losses （損失）
- Voltage（壓降）

The voltage difference is caused by four major ireversibilities of a fuel cell. They are listed as following:

- Activation losses:
  These are caused by the slowness of the reactions taking place on the surface of the electrode.

- Fuel crossover and internal current:
  From the concept of fuel cell, the electrolyte should only transports ion through the cell. However, a certain fuel diffusion and electron flow will always be possible. It results the voltage losses of the fuel cell.

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- Ohmic losses:
  The voltage losses are caused by the resistance to the flow of electrons through the material of the electrodes and various interconnections. This voltage drop is essentially proportional to current density.

- Mass transport or concentration losses:
  These losses are resulted from the change in concentration of the reactants at the surface of the electrodes.

Activation losses

The Tafel Equation

The overvoltage at the surface of an electrode followed a similar pattern in a great variety of electrochemical reaction. When a graph of overvoltage against log of current density is plotted, the graph approximates to a straight line (See the below figure).
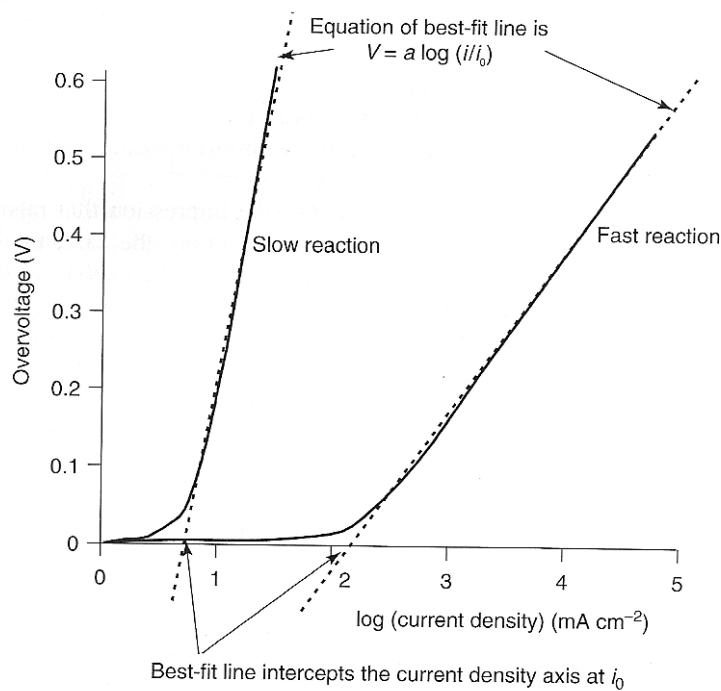
Tafel Plot for slow and fast electrochemical reactions

Such behaviors are observed and reported by Tafel. So, the equation that describes the overvoltage of the electrochemical reaction is called Tafel equation.

$$\Delta V_{act} = A \ln\left(\frac{i}{i_o}\right)$$

It is important to remember that the Tafel equation only holds true when $i > i_o$. The constants A and exchange current density i_o are discussed as following:

A
A constant is higher for an electrochemical reaction that is slow. It can be shown that for a fuel cell with **z** electron transferred per mole, the constant A is given by:

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$$A = \frac{RT}{z\alpha F}$$

The constant α is called **charge transfer coefficient** and is proportion of the electrical energy applied that is harnessed in charging the rate of an electrochemical reaction. In the other words, α depends on the symmetry of the activation barrier and expresses how the change in the electrical potential across the reaction interface changes the sizes of the forward versus reverse activation barrier. The value of α which depends on the reaction involved and the material the electrode made from is always between 0 and 1. For "symmetric" reactions, $\alpha=0.5$. For most electrochemical reaction, α ranges from about 0.2 to 0.5.

Temperature

The temperature in the Tafel equation seems to imply raising the temperature increases the voltage.

$$\Delta V_{act} = \frac{RT}{z\alpha F} \ln\left(\frac{i}{i_o}\right)$$

In fact, the effect of increases in i_o with **temperature** far outweigh any increase in A. The key to make the activation overvoltage as low as possible is i_o. It is affected by several parameters other than the material used for electrode.

i_o

Exchange current density is considered as the current density at which the overvoltage begins to move from zero ($i_o = i @ \Delta V_{act}=0$). i_o is higher when the reaction is faster.

Consider the reaction at the cathode of PEMFC,

$$O_2 + 4e^- + 4H^+ \rightarrow 2H_2O$$
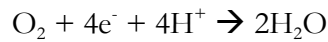
At the zero current density, there is no activity at the electrode and no reaction take place. Actually, the reaction is taking place all the time, but the reverse reaction is also taking place at the same rate. The equilibrium can be expresses as

$$O_2 + 4e^- + 4H^+ \leftrightarrow 2H_2O$$

The reaction equation shows there is a backwards and forwards flow of electrons from and to the electrode. This difference of backwards/forwards current density is i_o, the 'exchange' current density. It shows that if this current density is high, then the surface of electrode is more active. This current density is in controlling the performance of a fuel cell electrode. It is vital to make its value as high as possible.

Tafel equation can be rearranged to give,

$$i = i_o \exp\left(\frac{z\alpha F\Delta V_{act}}{RT}\right)$$

The equation called the Butler-Vollmer equation and is quite often used as an equivalent alternative to Tafel equation.

Consider a fuel cell with activation overvoltage, the voltage of fuel cell can be expressed by the equation,

$$V = E - A \ln\left(\frac{i}{i_o}\right)$$

Where E is reversible OCV. When plot the V-I curve using value of i_o = 0.01, 1.0 and 100 mAcm^{-2} and A = 0.06V, the figure can be seen below.
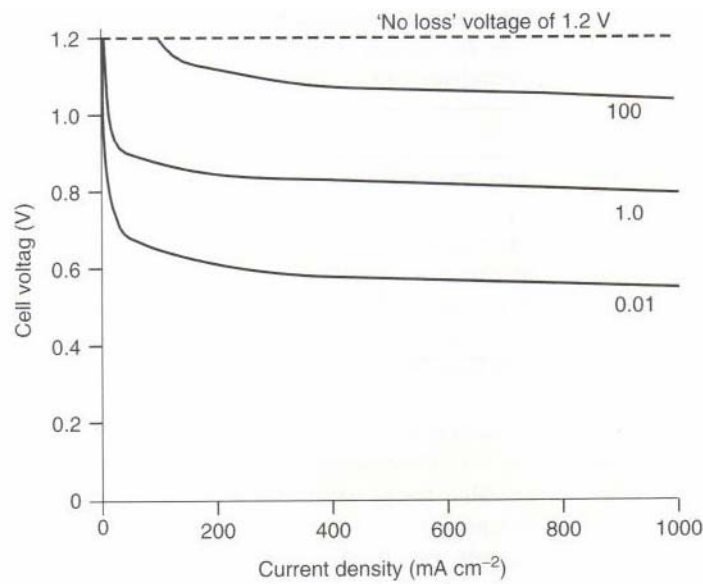
Graph of cell voltage against current density, assuming losses are due only to the activation overvoltage at one electrode, for exhange current density value of 0.01, 1.0, and 100 mAcm^{-2}

The importance of i_o can be easily seen. The voltage drops greatly with the smallest i_o. Note that, when i_o is 100 mAcm^{-2}, there is no voltage drops until the current density is greater than 100 mAcm^{-2}.

For a low temperature, hydrogen-fed fuel cell running on air at ambient pressure, a typical value for i_o would be 0.1 mAcm^{-2} at the cathode and about 200 mAcm^{-2} at the anode. In the case, the anode overvoltage is negligible.

For some fuel cell, for instant DMFC, the anode overvoltage is by no means negligible. The total overvoltage should combine the overvoltages at both anode and cathode.

$$\text{Activation Voltage Drop} = A_a \ln\left(\frac{i}{i_{oa}}\right) + A_c \ln\left(\frac{i}{i_{oc}}\right)$$

In the form of

$$\Delta V_{act} = A \ln\left(\frac{i}{b}\right)$$

where

$$A = A_a + A_c \quad \text{and} \quad b = i_{oa}^{\frac{A_a}{A}} \cdot i_{oc}^{\frac{A_c}{A}}$$

Furthermore, in all cases, the item in the equation that shows the most variation is the exchange current density rather than A.

Reducing the Activation Overvoltage

Form the Tefel equation, it can be seen which to increase the value of i_o (especially at the cathode) will improve the performance of fuel cell. The ways to increase the value can be done as following:

1. Rising the cell temperature
   From the V-I curves of low- and high-temperature fuel cells, the overvoltages are totally different. At low temperature cell, i_o at the cathode will be about 0.1 mA/cm^2, and high-temperature cell, it will be about 100 mA/cm^2. There is 10 times improvement.

2. Using more effective catalysts
   Using the different metals as catalysts results different i_o which are shown below table. The effect is very significant.

Metal	i_o (A/cm^2)
Pb	2.5×10^{-13}
Zn	3×10^{-11}
Ag	4×10^{-7}
Ni	6×10^{-6}
Pt	5×10^{-4}
Pd	4×10^{-3}

3. Increasing the roughness of the electrodes
   This increases the real reaction surface area of each nominal 1 cm^2, and this increases i_o.

4. Increasing reactant concentration
   The catalyst sites are more effectively occupied by reactant. (This also increases the reversible OCV.)

5. Increasing pressure
   This is also presumed to work by increasing catalyst site occupancy. (This also increases the reversible OCV.)

Summary
- Activation overvoltage is the most important irreversibility and cause of voltage drop, and occurs mainly at the cathode.

- Activation overvoltage at both electrodes is important in cells using fuels other than hydrogen, such as methanol.
- At higher temperature and pressure the activation overvoltage becomes less important.

Fuel Crossover and Internal Currents

In a practical fuel cell, some fuel will diffuse from the anode through the electrolyte to the cathode. Also, very small amounts of electron can conduct even the electrolyte of a fuel cell would have been chosen for its ion conducting properties. Both phenomena are producing no current since the fuel/electron will react with oxygen directly because of catalyst. This small amount of waste fuel is known as **fuel crossover**.

For PEMFC, the overvoltage of one mole hydrogen cross through the electrolyte is equal to the overvoltage of two electrons crossing from anode to cathode internally. Thus, the fuel crossover as "equivalent to" an internal current is assumed.

From last section, when the PEMFC operates at normal pressure, 30°C, and use air as cathode fuel, the activation overvoltage is

$$V = E - A \ln\left(\frac{i}{i_o}\right)$$

where E = 1.2 V; A = 0.06 V; and i_0 = 0.04 mA/cm². The cell voltage can be calculated related to current density as following.

Current density (mA/cm²)	Voltage (V)
0	1.2
0.5	1.05
1.0	1.01
2.0	0.97
4.0	0.92
6.0	0.90
8.0	0.88
10.0	0.87
12.0	0.86
14.0	0.85
16.0	0.84
18.0	0.83

For a fuel cell with internal current, the internal current density is not zero, even if the cell is open circuit. So, from the above Table, the voltage will be 0.97 V at 2.0 mA/cm², over 0.2 V (or 20%) less than the reversible OCV. This large deviation from the reversible OCV is caused by the very steep initial fall in voltage.

The fuel crossover and internal current are obviously not easy to measure. (An ammeter cannot be inserted in the circuit.) Measuring the consumption of reactant gas is a way to measure it.

For example, a PEMFC with are 10 cm^2 has an open circuit hydrogen consumption of 0.0034 cm^3/s at STP. From Avogadro's Law, the volume of one mole of any gas is 2.43×10^4 cm^3. So, the gas usage is 1.4×10^{-7} mole/s. From Appendix 2, the fuel usage is related to current by the formula,

$$\text{Gas usage} = \frac{nI}{zF} \quad \text{(mole/s)}$$

Where n: numbers of cell; z: numbers of transferred electrons per mole of fuel.

Therefore, for a single cell PEMFC (n = 1; z = 2) with area 10 cm^2,

$$I = \text{gas usage} \times zF = 1.4 \times 10^{-7} \times 2 \times 96485 = 27 \text{ mA}$$

$$\text{Current density} = i_n = 2.7 \text{ mA/cm}^2$$

i_n gives the total of current density equivalent of fuel lost because if fuel crossover and the actual internal current density. Combine the crossover losses with activation overvoltage, the equation of cell voltage can be rewritten as,

$$V = E - A \ln\left(\frac{i + i_n}{i_o}\right)$$

For a low-temperature cell, A = 0.06 V; i_o = 0.04 mA/cm^2; i_n = 3 mA/cm^2.
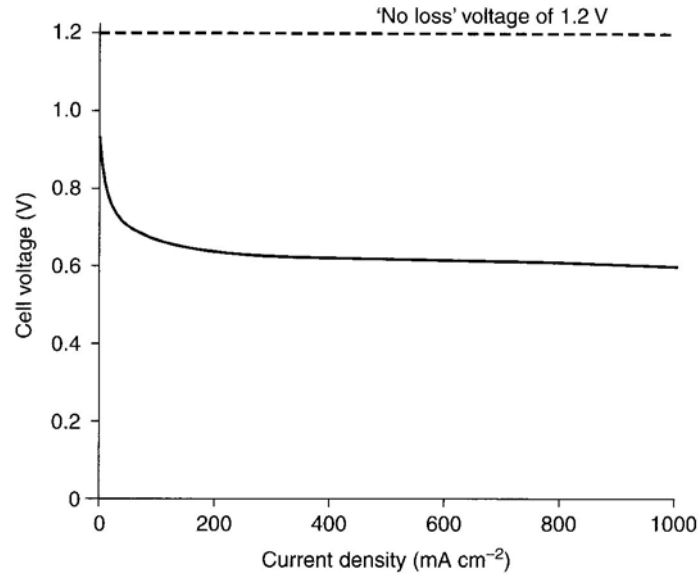
Graph showing the fuel cell voltage modeled using activation and fuel crossover/internal current losses only

Ohmic Losses

The losses due to the electrical resistance of the electrodes, and the resistance to the flow of ions in the electrolyte, are defined as Ohmic losses whose voltage drop is simply proportional to the current.

$$V = IR$$

However, the equation should be expresses in terms of current instead of current. Thus, the area-specific resistance, **r**, is used rather than resistance, **R**.

$$\Delta V_{ohm} = ir$$

where i: the current density (mA/cm²); r: the area-specific resistance (kΩcm²).

There are three ways to reduce the internal resistance of the cell:
- The use of electrodes with the highest possible conductivity.
- Good design and use appropriate materials for the biopolar plates or cell interconnects.
- Making the electrolyte is as thin as possible. (This is often difficult. 維持機械強度、減少燃料穿透現象。)

Mass Transport or Concentration Losses

When the oxygen at the cathode of a fuel cell is supplied in the form of air (there will be slight reduction in the concentration of the oxygen), the change in concentration will cause a reduction in the partial pressure of oxygen. At the anode, the similar situation happens when the hydrogen used and consumed will result the slight pressure drop.
In both cases, the reduction in gas pressure will result in a reduction in voltage. The approach that yield an equation has some value and use to see the effect of this reduction in pressure (or partial pressure) by revisiting the following equations,

$$E = E^o + \frac{RT}{zF} \ln\left(\frac{P_J^j \cdot P_K^k}{P_M^m}\right)$$

It gives the change in OCV caused by a change in pressure of the reactants. For a hydrogen-feed fuel cell, the change in voltage caused by a change in hydrogen pressure only is

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

Assume limiting current density i_1 at which the fuel is used up at a rate equal to its maximum supply speed. The current density cannot rise above this value, because the fuel gas cannot be supplied at a greater rate. If P_1 is the pressure when current density is zero, then the current density losses is (i_1-0). If P_2 is the pressure when current density is i, then the current density losses is (i_1-i). The relationship between P and current density can be expressed as

$$P_2 = P_1\left(1 - \frac{i}{i_1}\right)$$

And, the equation can be had by combining the above two equations.

$$\Delta V = \frac{RT}{zF} \ln\left(1 - \frac{i}{i_1}\right)$$

The equation gives us the voltage change due to the mass transport losses related to the current density. However, the above equations are written in term of a voltage gain, an the term $(1 - i/i_1)$ is always less than 1. So, for voltage drop,

$$\Delta V_{trans} = -\frac{RT}{zF} \ln\left(1 - \frac{i}{i_1}\right)$$

In general, the concentration or mass transport losses can be shown as,

$$\Delta V_{trans} = -B \ln\left(1 - \frac{i}{i_1}\right)$$

B is a constant that depends on the fuel cell and its operating state.

However, the theoretical approach has many weaknesses, especially in the case of fuel cells supplied with air rather then pure oxygen. There are also problems with lower-temperature cells, and those supplied with hydrogen mixed with other gases such as carbon dioxide for the fuel. **No account is taken for the production and removal of reaction products, such as water, and neither is any account taken of the build-up of nitrogen in the air system.**
Another approach is entirely empirical and yields an equation that fits the results very well.

$$\Delta V_{trans} = m \exp(ni)$$

The value of m will typically be about 3×10^{-5} V, and n about 8×10^{-3} cm^2/mA. The equation can be used to give a better fit to measured results, and so this will be quite widely used in the fuel cell community.

Operational Voltage (Combing the Irreversibilities)

To construct an equation that brings together all the ireversibilities.

$$V = E - \Delta V_{act} - \Delta V_{ohm} - \Delta V_{tran}$$

$$V = E - A \ln\left(\frac{i + i_n}{i_o}\right) - ir + m \exp(ni)$$

E: the reversible OCV.
i_n: the internal and fuel crossover equivalent current density.
A: the slope of the Tafel line.
i_o: the exchange current density.
m and n: the constant in the mass-transfer overvoltage equation.
r: the area-specific resistance.

The crossover current i_n is usually very small, and although useful for explaining the initial fall in voltage, it has little impact on the operating losses of fuel cells at working current. The equation for the activation overvoltage is rearranged to

$$\Delta V_{act} = A \ln\left(\frac{i}{i_o}\right) = A \ln(i) - A \ln(i_o)$$

Since the second term of the equation is a constant, it can be combined with the OCV term of voltage equation.

$$E_{oc} = E + A \ln(i_o)$$

Note that E_{oc} will always be less than E because i_0, being small, will generate negative logarithms. Substitute into the voltage equation, the new equation is obtained,

$$V = E_{oc} - A \ln(i) - ir + m \exp(ni)$$

However, it must be borne in mind that the logarithmic model does not work at very low current, especially at zero. It is best to start the plots with a current of 1.0 mA/cm².

Equation constants

Constant	Ballard Mark V PEMFC at 70°C	High temperature, e.g. SOFC
E_{oc} (V)	1.031	1.01
r (kΩ cm^2)	2.45×10^{-4}	2.0×10^{-3}
A (V)	0.03	0.002
m (V)	2.11×10^{-5}	1.0×10^{-4}
n (cm^2 mA^{-1})	8×10^{-3}	8×10^{-3}